

Pesticide residues in food 2013

Joint FAO/WHO Meeting
on Pesticide Residues

EVALUATIONS 2013

PART I - RESIDUES



World Health
Organization



Food and Agriculture
Organization of
the United Nations

Pesticide residues in food 2013

Evaluations

Part I - Residues

FAO
PLANT
PRODUCTION
AND PROTECTION
PAPER

220

Sponsored jointly by FAO and WHO

Joint meeting of the
FAO Panel of Experts on Pesticide Residues
in food and the Environment
and the
WHO Core Assessment Group
Geneva, Switzerland 17-26 September 2013

Monographs containing summaries or residue data and toxicological data considered at the 2013 JMPR, together with recommendations, are available upon request from FAO or WHO under the title:

Pesticide residues in food 2013
Evaluations
Part I: Residues
FAO Plant Production and Protection Paper No. 220

INTERNATIONAL PROGRAMME ON CHEMICAL SAFETY

The preparatory work for the toxicological evaluation of pesticide residues carried out by the WHO Expert Group on Pesticide Residues for consideration by the FAO/WHO Joint Meeting on Pesticide Residues in Food and the Environment is actively supported by the International Programme on Chemical Safety (IPCS).
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E-ISBN 978-92-5-108245-4 (PDF)

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^{1/} Evaluated for the Periodic Review Programme of the Codex Committee on Pesticide Residues.

^{2/} New compound

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GENEVA, 17–26 SEPTEMBER 2013

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Abbreviations

(Well-known abbreviations in general use are not included. Specific abbreviations for pesticide degradation products, etc., may be used in the monographs and these are either identified where first used or in a table within the monograph. Two-letter codes for pesticide formulations are given in the Manual on development and use of FAO and WHO specifications for pesticides, 1st Ed., FAO Plant Production and Protection Paper 173, FAO, Rome, 2002.)

ACN	Acetonitrile
ADI	acceptable daily intake
ai	active ingredient
AR	applied radioactivity
ARfD	acute reference dose
asp gr fn	aspirated grain fraction
AU	Australia
BBCH	B iologischen Bundesanstalt, B undessortenamt und C hemische Industrie
bw	body weight
CAC	Codex Alimentarius Commission
CAS	Chemical Abstracts Service
CCN	Codex classification number (for compounds or commodities)
CCPR	Codex Committee on Pesticide Residues
CIPAC	Collaborative International Pesticides Analytical Council
$C_{\max}$	maximum concentration
CXL	Codex MRL
DALA	Days after last application
DAP	days after planting
DAT	days after treatment
DM	dry matter
DT ₅₀	time required for 50% dissipation of the initial concentration
dw	dry weight
ECD	electron capture detector
EHC	Environmental Health Criteria monograph
EHE	ethylhexyl ester
EPO	early post-emergence
ERR	Extracted radioactive residues
EU	European Union
FAO	Food and Agriculture Organization of the United Nations
fw	fresh weight
GAP	good agricultural practice
GC	gas chromatography
GC-ECD	gas chromatography with electron capture detection
GC-FPD	gas chromatography with flame photometric detection
GC/MS	gas chromatography/mass spectrometry
GC/MSD	gas chromatography/mass selective detector
GC-NPD	gas chromatography coupled with nitrogen-phosphorus detector
GEMS/Food	Global Environment Monitoring System – Food Contamination Monitoring and Assessment Programme
GLC	gas liquid chromatography
GLP	good laboratory practice
GPC	gel permeation chromatography
HPLC	high performance liquid chromatography
HR	highest residue in the edible portion of a commodity found in trials used to estimate a maximum residue level in the commodity

HR-P	highest residue in a processed commodity calculated by multiplying the HR of the raw commodity by the corresponding processing factor
IEDI	international estimated daily intake
IESTI	international estimate of short-term dietary intake
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
JP	Japan
LC	liquid chromatography
LOD	limit of detection
LOQ	limit of quantification
MOA	mode of action
MRL	maximum residue limit
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MWHC	Maximum water holding capacity
ND	non-detect - below limit of detection
NMR	Nuclear Magnetic Resonance
NOAEC	no-observed-adverse-effect concentration
NOAEL	no-observed-adverse-effect level
OECD	Organisation for Economic Co-operation and Development
PAG3	2-(2-hydroxymethylphenyl)-2-oxoacetic acid
PBI	plant back interval
PES	Post-extraction solids
Pf	processing factor
PH	pre-harvest
PHI	pre-harvest interval
ppm	parts per million
PRE	pre-emergence
RAC	raw agricultural commodity
ROI	Region of Interest
RSD	relative standard deviation
RTI	re-treatment interval
SC	suspension concentrate
SL	soluble liquid
SPE	solid phase extraction
STMR	supervised trials median residue
STMR-P	supervised trials median residue in a processed commodity calculated by multiplying the STMR of the raw commodity by the corresponding processing factor
TAR	total administered radioactivity
TF	transfer factor
TLC	thin-layer chromatography
TMPA	2,2,3,3-tetramethylcyclopropane carboxylic acid
TRR	total radioactive residues
UK	United Kingdom
USA	United States of America
US/CAN	United States of America and Canada
USEPA	United States Environmental Protection Agency
US-FDA	USA – Food and Drug Administration
UV/VIS	Ultraviolet-visible spectroscopy
WG	wettable granule
WHO	World Health Organization
WP	wettable powder

Use of JMPR Reports and Evaluations by registration authorities

Most of the summaries and evaluations contained in this report are based on unpublished proprietary data submitted for use by JMPR in making its assessments. A registration authority should not grant a registration on the basis of an evaluation unless it has first received authorization for such use from the owner of the data submitted for the JMPR review or has received the data on which the summaries are based, either from the owner of the data or from a second party that has obtained permission from the owner of the data for this purpose.

1. INTRODUCTION

A Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group on Pesticide Residues (JMPR) was held at World Health Organization (WHO) Headquarters, Geneva (Switzerland), from 17 to 26 September 2013. The Panel Members of the Food and Agriculture Organization of the United Nations (FAO) met in preparatory sessions on 12–16 September.

The Meeting was opened by Dr Kazuaki Miyagishima, Director, Department of Food Safety and Zoonoses, WHO. On behalf of FAO and WHO, Dr Miyagishima welcomed and thanked the participants for providing their expertise and for the significant time and effort put into such an important activity. He also expressed gratitude to the respective national authorities, institutes and organizations that have allowed their experts to contribute to this important work on pesticide residues. Dr Miyagishima said that whereas the assessment of new compounds is very important and represents the major part of the work of JMPR, it is also crucial to continue our efforts on the periodic re-evaluation of old pesticides still in use. This should allow developing countries to use old, inexpensive pesticides so that they can access international markets for their food commodities; it also should allow the removal of those compounds that are most persistent in the environment and pose the greatest risk to public health. Dr Miyagishima also noted that in order to continue using the best available science in a transparent manner, the WHO Core Assessment Group will meet during an additional day this year to update the guidance documents for experts and sponsors. Finally, JMPR is celebrating in 2013 the 50th anniversary of the first joint FAO/WHO evaluation of pesticide residues in food, and Dr Miyagishima addressed his best wishes to the Meeting on behalf of the two parent organizations.

During the meeting, the FAO Panel of Experts was responsible for reviewing residue and analytical aspects of the pesticides under consideration, including data on their metabolism, fate in the environment and use patterns, and for estimating the maximum levels of residues that might occur as a result of use of the pesticides according to good agricultural practice (GAP). Maximum residue levels and supervised trials median residue (STMR) values were estimated for commodities of animal origin. The WHO Core Assessment Group was responsible for reviewing toxicological and related data in order to establish acceptable daily intakes (ADIs) and acute reference doses (ARfDs), where necessary.

The Meeting evaluated 36 pesticides, including 11 new compounds and 3 compounds that were re-evaluated within the periodic review programme of the Codex Committee on Pesticide Residues (CCPR), for toxicity or residues, or both.

The Meeting allocated ADIs and ARfDs, estimated maximum residue levels and recommended them for use by CCPR, and estimated STMR and highest residue (HR) levels as a basis for estimating dietary intake.

The Meeting also estimated the dietary intakes (both short-term and long-term) of the pesticides reviewed and, on this basis, performed dietary risk assessments in relation to their ADIs or ARfDs. Cases in which ADIs or ARfDs may be exceeded were clearly indicated in order to facilitate the decision-making process of CCPR. The rationale for methodologies for long- and short-term dietary risk assessment are described in detail in the FAO manual on the submission and evaluation of pesticide residue data for the estimation of maximum residue levels in food and feed (2009).

The Meeting considered a number of current issues related to the risk assessment of chemicals, the evaluation of pesticide residues and the procedures used to recommend maximum residue levels.

AZOXYSTROBIN (229)

First draft was prepared by Dr Ursula Banasiak, Delegate of the Federal Institute for Risk Assessment, Berlin, Germany

EXPLANATION

Azoxystrobin (methyl (E)-2-[2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate) was first evaluated for toxicology and residues by the JMPR in 2008. The Meeting derived an ADI of 0.2 mg/kg bw per day and decided that an ARfD is unnecessary. The 2008 JMPR concluded that the residue definition for plant commodities for compliance with MRL values and for consumer risk assessments was parent azoxystrobin. Maximum residue levels, STMRs and STMR-Ps for 82 commodities or commodity groups were estimated. The compound was re-evaluated for residues by the JMPR in 2011 and 2012.

Azoxystrobin was listed by the Forty-fourth Session of the CCPR (2012) for the review of additional MRLs. The 2013 JMPR received GAP information and residue data in coffee beans, pulses, potatoes, barley, oats and sorghum.

RESIDUE ANALYSIS*Analytical methods*

The Meeting received information on analytical methods for azoxystrobin residues in coffee beans (POPIT Met.029, PLARA 082 v.07), potatoes (RAM 305), pulses (RAM 305, RAM 243), cereal grain, straw and forage (RAM 305/03). The methods RAM 305, RAM 305/03 and RAM 243 were previously reported by the JMPR in 2008 and method POPIT MET.029 by JMPR in 2011. Method PLARA 082 v.07 is briefly described below and the recoveries are summarized in Table 1.

Method: PLARA 082 v.07
Reference: PLMV 027 039/2010
Commodity: Coffee bean
Analyte: Azoxystrobin, R230310
Determination: LC-MS/MS
LOQ: 0.01 mg/kg
Accuracy: The mean recovery in coffee was between 91–105 % at each fortification level.
Repeatability: The relative standard deviations (RSDs) of azoxystrobin recoveries at each fortification level and overall during method validation were all below 20 %.
Linearity: The linearity of detector response was confirmed by analysis of nine concentrations of standard solutions in the range 0.01 to 2.0 ng/mL of azoxystrobin with three injections for each concentration. Linearity of response was demonstrated with a correlation coefficient (R^2) of 0.9995.
Specificity: No interfering peaks were detected in control samples above the LOD.
Description: A sample of ground coffee beans (1 g) is extracted by shaking for 15 minutes with ethyl acetate (20 mL), ultrasonicing for 15 minutes and centrifuging. The extract is removed and the extraction repeated. The extracts from the two extractions are combined, an aliquot (3 mL) taken, evaporated to dryness and resuspended in 3 mL methanol/water (1:1 v/v) using vortex mixing. An aliquot (1 mL) of the resulting extract is taken, and mixed with 4 mL methanol/water (1:1 v/v) using a vortex mixer and then ultrasonicing for 15 minutes. This extract is analysed directly by LC-MS/MS with quantification by external standardisation.

Table 1 Recovery data for azoxystrobin in coffee (PLMV 027 039/2010)

Commodity	Fortification level (mg/kg)	Recovery (%)	No. of analyses (n)	Mean recovery (%)	RSD (%)	Range (%)
Coffee bean	0.01	96, 91, 95, 96, 98, 99	6	96	3	91–99
	0.1	105, 95, 92, 97,	7	97	5	91–105

Commodity	Fortification level (mg/kg)	Recovery (%)	No. of analyses (n)	Mean recovery (%)	RSD (%)	Range (%)
		94, 91, 101				
	Overall		13	96	4	91–105

USE PATTERN

The information available to the 2013 JMPR on registered uses of azoxystrobin is summarized in Table 2. Copies of labels including an English translation if appropriate were made available to the Meeting.

Table 2 Registered uses of azoxystrobin

Crop	Country	Form	Application		Spray			PHI, days	Remarks
			Method	Rate, kg ai/ha	Volume, L/ha	No	Interval, days		
Barley	USA	SE	Foliar spray	0.072–0.15		1	–		Early season ^a
Barley	USA	SE	Foliar spray	0.11–0.15		1	14		Main season ^a PHI 7 days minimum for forage/hay
Barley (foot rot/eyespot)	USA	SE	Foliar spray	0.15		1	14		PHI 7 days minimum for forage/hay
Coffee	Brazil	SC	Foliar spray ^b	0.10	400	3	60	30	
Coffee	Brazil	SC	Foliar spray ^b	0.15	400	2	90	30	
Coffee	Colombia	SC	Foliar spray	0.15	280–420	3	45	15	
Field bean	France	SC	Foliar spray	0.20	100–300	1–2		42	
Field bean	Germany	SC	Foliar spray	0.25	200–400	1–2	14–28	35	Appl. from BBCH ^c 13
Field pea, chickpeas	France	SC	Foliar spray	0.2–0.25	100–300	2	14	35	
Field pea	Germany	SC	Foliar spray	0.25	200–400	1–2	14–28	35	Appl. at BBCH 51–75
Lentil	France	SC	Foliar spray	0.2–0.25	100–300	2	14	28	
Lupin	France	SC	Foliar spray	0.20	100–300	1–2		42	
Lupin	Germany	SC	Foliar spray	0.25	200–400	1–2	14–28	35	Appl. from BBCH 13
Oats	USA	SE	Foliar spray	0.15		1	–		Early season ^a
Oats	USA	SE	Foliar spray	0.11–0.15		1	14	7	Main season ^a PHI 7 days minimum for forage/hay
Oats (foot rot/eyespot)	USA	SE	Foliar spray	0.15		1	14	7	PHI 7 days minimum for forage/hay
Potato	USA	SC	Post-harvest spray	0.49 g/100 kg tubers		1	–		

Crop	Country	Form	Application		Spray			PHI, days	Remarks
			Method	Rate, kg ai/ha	Volume, L/ha	No	Interval, days		
Sorghum	USA	SE	Foliar spray	0.11–0.28		2		14	Part of integrated diseases management

^a A single early season application followed by a single application at 50% to full flag leaf emergence.

^b Use of an adjuvant at 0.5% of the spray application volume is recommended.

^c BBCH scale (<http://www.pub.jki.bund.de>)

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised field trials for azoxystrobin uses that produced residues on the following commodities:

Commodity	Group	Table No
Beans, dry	VD Pulses	3
Peas, dry	VD Pulses	4
Potato	VR Root and tuber vegetables	5
Barley	GC Cereal grains	6
Oat	GC Cereal grains	7
Sorghum	GC Cereal grains	8
Coffee beans	SB Seed for beverages and sweets	9
Bean fodder	AL Legume animal feed	10
Pea fodder (dry)	AL Legume animal feed	11
Pea vines (green)	AL Legume animal feed	12
Barley straw	AF Straw, fodder and forage of cereals	13
Barley hay	AF Straw, fodder and forage of cereals	14
Oat straw	AF Straw, fodder and forage of cereals	15
Oat hay	AF Straw, fodder and forage of cereals	16
Oat forage (green)	AF Straw, fodder and forage of cereals	17
Sorghum stover	AF Straw, fodder and forage of cereals	18
Sorghum forage (green)	AF Straw, fodder and forage of cereals	19

Conditions of the supervised residue trials were generally well reported in detailed field reports. If two field samples were taken or results of two replicate plots were submitted, the mean value was calculated. From two trials carried out side-by-side the higher residues were chosen and not the average.

Laboratory reports included method validation with procedural recoveries from spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analysis or duration of residue sample storage were also provided. Residue data are recorded unadjusted for recovery. When residues were not quantifiable they are shown in the tables as below the LOQ (e.g. < 0.01 mg/kg). When residues were not detectable, they are shown as n/d.

Residues and application rates have generally been rounded to two significant figures. Residue values from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels. Those results included in the evaluation are underlined.

*Pulses**Beans, dry*

Eleven independent supervised trials were conducted on dry beans in the UK, Italy and France in 1998–2005. Azoxystrobin was applied twice as an SC formulation containing 250 g ai/L at a rate of 0.20–0.25 kg ai/ha with a spray interval of 14 days. Applications were made between BBCH growth stages 61 and 87. Samples of dry bean seed were collected at normal commercial harvest at PHIs of 14–36 days. The analytical methods used were RAM 305/01, RAM 305/02 and RAM 305/03 with a validated limit of quantification of 0.01 mg/kg. Detailed trial summaries are presented in Table 3.

Table 3 Azoxystrobin residues in beans, dry

Country, year, location (variety)	Application			PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage (BBCH)				
UK, 2005, Horsten, Nottinghamshire (Clipper)	0.2 0.2	2	61 79	30	Bean (dried)	<u>< 0.01</u>	05-0415, AF/8541/SY/1 Syngenta File No. SAN619/8116
UK, 2005, Draycott, Nottinghamshire (Quattro)	0.21 0.21	2	61 79	30 36	Bean (dried)	< 0.01 <u>< 0.01</u>	05-0415, AF/8541/SY/2 Syngenta File No. SAN619/8116
France North, 2005 Boce, Pays de la Loire (Castel)	0.13 0.2	2	62 87	26	Bean (dried)	<u>< 0.01</u>	05-0415, AF/8541/SY/4 Syngenta File No. SAN619/8116
Italy, 1998 Nogara (VR), Veneto (Etna, Borlotto)	0.25 0.25	2	61 75	73 (34) ^a	Dried seeds	< 0.01	RJ2845B, IT20-99-P301 Syngenta File No. ICI5504/0394
Italy, 1998 Moncestino (AL), Piemonte (Etna, Borlotto)	0.25 0.25	2	Beginning of flowering 79	30	Dried seeds	<u>< 0.01</u>	RJ2845B, IT20-99-P302 Syngenta File No. ICI5504/0394
Italy, 1999 Moncestino (AL), Piemonte (Etna)	0.25 0.25	2	55 65	28	Dried seeds	<u>< 0.01</u>	RJ2969B, IT30-99-P350 Syngenta File No. ICI5504/0408
Italy, 1999 Sant 'Antonio (RA), Emilia Romagna (Kirena)	0.25 0.25	2	79 79	14	Dried seeds	0.04	RJ2969B, IT20-99-P351 Syngenta File No. ICI5504/0408
France, 2005 Monteux, Provence-Alpes-Cote-d'Azur (Big Borloto)	0.21 0.2	2	69–71 75–77	30	Seed	<u>< 0.01</u>	05-0607, FR-FR-05-0482 Syngenta File No. SAN619/8117
France, 2005 Grisolles, Midi-Pyrenees (Linex)	0.2 0.2	2	62 76	31	Seed	<u>< 0.01</u>	05-0607, FR-FR-05-0483 Syngenta File No. SAN619/8117
France, 2005 Estillac, Aquitaine (Linex)	0.22 0.21	2	64 73–75	29	Seed	<u>< 0.01</u>	05-0607, FR-FR-05-0484 Syngenta File No. SAN619/8117
France, 2005 Marsillargues, Languedoc-Roussillon (Linex)	0.21 0.21	2	61 67	28	Seed	<u>< 0.01</u>	05-0607, FR-FR-05-0485 Syngenta File No. SAN619/8117

^a Sample harvested partially dried from the field, drying was completed indoors for a further 39 days.

Peas, dry

Twenty independent supervised trials were conducted on dry peas in the UK and France in 1996–2004. In each trial, azoxystrobin was applied twice as an SC formulation containing 250 g ai/L at a rate of 0.20–0.25 kg ai/ha with a spray interval of 14 days. Applications were made between BBCH growth stages 61 and 77. Samples of dry pea seed were collected at normal commercial harvest at PHIs of 30–45 days. Several trials were conducted as decline trials. In these trials, peas are separated from the pods by hand, except where noted in the table. The analytical methods used were RAM 305/02, RAM 243/04 and RAM 243/05 with a validated limit of quantification of 0.01 mg/kg. Detailed trial summaries are presented in Table 4.

Table 4 Azoxystrobin residues in peas, dry

Country, year, location (variety)	Application			PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
France North, 1996 Grivesnes, Picardie Vining pea (Bonette)	0.25	2	63–65 69–71	14	Seed	0.02	RJ2286B, S101.96 Syngenta File No. ICI5504/1111
	0.25			14	Seed	0.02	
				14	Seed (mech. thresh)	0.1	
				14	Seed (mech. thresh)	0.09	
				38	Seed (mech. thresh)	0.06	
				38	Seed (mech. thresh)	0.07	
						mean 0.065	
France North, 1996 Grivesnes, Picardie Vining pea (Bonette)	0.2	2	63–65 69–71	14	Seed	0.01	RJ2286B, S101.96 Syngenta File No. ICI5504/1111
	0.2			14	Seed	< 0.01	
				14	Seed (mech. thresh)	0.07	
				14	Seed (mech. thresh)	0.06	
				38	Seed (mech. thresh)	0.01	
				38	Seed (mech. thresh)	0.04	
France North, 1996 Bayonvillers, Picardie Vining pea (Lynx)	0.25	2	63 69–71	14	Seed	0.08	RJ2286B, S102.96 Syngenta File No. ICI5504/1111
	0.25			14	Seed	0.05	
				14	Seed (mech. thresh)	0.16	
				14	Seed (mech. thresh)	0.12	
				42	Seed (mech. thresh)	0.02	
				42	Seed (mech. thresh)	0.01	
						mean 0.015	
France North, 1996 Bayonvillers, Picardie Vining pea (Lynx)	0.2	2	63 69–71	14	Seed	0.03	RJ2286B, S102.96 Syngenta File No. ICI5504/1111
	0.2			14	Seed	0.04	
				14	Seed (mech. thresh)	0.07	
				14	Seed (mech. thresh)	0.09	
				42	Seed (mech. thresh)	< 0.01	
				42	Seed (mech. thresh)	< 0.01	
France North, 1996, Tourny, Haute-Normandie Vining pea (Mini)	0.25	2	65 69–71	15	Seed	0.02	RJ2286B, S208.96 Plot: 2 Syngenta File No. ICI5504/1111
	0.25			15	Seed	0.02	
				15	Seed (mech. thresh)	0.06	
				15	Seed (mech. thresh)	0.06	
				30	Seed (mech. thresh)	0.03	
				30	Seed (mech. thresh)	0.02	
						mean 0.025	
France North, 1996, Tourny, Haute-Normandie Vining	0.2	2	65 69–71	15	Seed	< 0.01	RJ2286B S208.96 Plot: 2
	0.2			15	Seed	< 0.01	
				15	Seed (mech. thresh)	0.03	

Azoxystrobin

Country, year, location (variety) pea (Mini)	Application		BBCH	PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No					Syngenta File No.
				15	Seed (mech. thresh)	0.04	ICI5504/1111
				30	Seed (mech. thresh)	0.01	
				30	Seed (mech. thresh)	0.01	
France North, 1997 Chaulnes, Picardie Vining pea (Novaroy)	0.25	2	62	14	Seed	0.01	RJ2548B, S101.97 Syngenta File No. ICI5504/1115
	0.25		71	14	Seed (mech. thresh)	0.06	
				40	Seed (mech. thresh)	0.01	
	0.2	2	62	14	Seed	0.01	
	0.2		71	14	Seed (mech. thresh)	0.06	
				40	Seed (mech. thresh)	< 0.01	
France North, 1997 Hennezis, Haute Normandie Vining pea (Camaro)	0.25	2	65	15	Seed	0.01	RJ2548B, S205.97 Syngenta File No. ICI5504/1115
	0.25		75	15	Seed (mech. thresh)	0.04	
				41	Seed	< 0.01	
	0.2	2	65	15	Seed	0.01	
	0.2		75	15	Seed (mech. thresh)	0.03	
				41	Seed	< 0.01	
UK, 1996, Asselby, East Yorkshire Field pea (Solara)	0.25	2	62	15	Seed (mech. thresh)	0.05	RJ2390B, with Addendum 1 AP/3248/ZE/1 Syngenta File No. ICI5504/1109
	0.25		64–72	15	Seed (mech. thresh)	0.06	
				42	Seed (mech. thresh)	< 0.01	
				42	Seed (mech. thresh)	< 0.01	
						mean < 0.01	
	0.2	2	62	15	Seed	< 0.01	
	0.2		64–72	15	Seed	< 0.01	
				15	Seed (mech. thresh)	0.04	
				15	Seed (mech. thresh)	0.05	
				42	Seed (mech. thresh)	< 0.01	
				42	Seed (mech. thresh)	< 0.01	
UK, 1997 Melbourne, Derbyshire Field pea (Alfetta)	0.25	2	62	14	Seed	< 0.01	RJ2521B AP/3783/ZE/1 Syngenta File No. ICI5504/1113
	0.25		67–72	14	Seed	< 0.01	
				14	Seed (mech. thresh)	0.03	
				14	Seed (mech. thresh)	0.03	
				45	Seed (mech. thresh)	< 0.01	
				45	Seed (mech. thresh)	< 0.01	
						mean < 0.01	
	0.2	2	62	14	Seed	< 0.01	
	0.2		67–72	14	Seed	< 0.01	
				14	Seed (mech. thresh)	0.03	
				14	Seed (mech. thresh)	0.02	
				45	Seed (mech. thresh)	< 0.01	
				45	Seed (mech. thresh)	< 0.01	
UK, 1997 Middleton on the Wolds, Yorkshire Field pea (Grafilla)	0.25	2	62	14	Seed	0.01	RJ2521B, AP/3783/ZE/2 Plot: 2 Syngenta File No. ICI5504/1113
	0.25		67–75	14	Seed	< 0.01	
				14	Seed (mech. thresh)	0.02	
				14	Seed (mech. thresh)	0.02	
				44	Seed (mech. thresh)	< 0.01	
				44	Seed (mech. thresh)	< 0.01	
						mean < 0.01	
	0.2	2	62	14	Seed	0.01	

Country, year, location (variety)	Application			PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
	0.2		67–75	14	Seed	0.02	
				14	Seed (mech. thresh)	0.02	
				14	Seed (mech. thresh)	0.02	
				44	Seed (mech. thresh)	< 0.01	
				44	Seed (mech. thresh)	< 0.01	
UK, 2004 Birkin, Yorkshire Pea dry (Solara)	0.2	2	61–63 69–73	7	Seed	0.03	04-0422, AF/8166/SY/1 Syngenta File No. SAN619/7886
	0.21			14	Seed	0.02	
				21	Seed	< 0.01	
				30	Seed	< 0.01	
				43	Seed	0.01	
UK, 2004 Hunmanby, Yorkshire Pea dry (Samson)	0.19	2	61 67–71	14	Seed	0.02	04-0422, AF/8166/SY/2 Syngenta File No. SAN619/7886
	0.21			21	Seed	< 0.01	
				30	Seed	< 0.01	
				43	Seed	0.01	
France North, 2004 Rouvres St Jean, Centre Pea, dry (Canyon)	0.2	2	71 75	0-	Seed	< 0.01	04-0422, AF/8166/SY/3 Syngenta File No. SAN619/7886
	0.2			0+	Seed	0.02	
				7	Seed	< 0.01	
				14	Seed	0.01	
				21	Seed	< 0.01	
				30	Seed	0.01	
France North, 2004 Montbellet, Bourgogne Pea dry (Atos)	0.2	2	63 75	0-	Seed	< 0.01	04-0422, AF/8166/SY/4 Syngenta File No. SAN619/7886
	0.2			0+	Seed	0.09	
				7	Seed	0.02	
				14	Seed	< 0.01	
				21	Seed	0.07	
				30	Seed	0.02	
France South, 1996 Brie, Poitou- Charentes (Baccara)	0.25	2	65 69–71	13	Seed	0.01	RJ2286B, S663.96 Syngenta File No. ICI5504/1111
	0.25			13	Seed	0.02	
				36	Seed (mech. threshed)	0.01	
				36	Seed (mech. threshed)	0.02	
France South, 1996 Brie, Poitou- Charentes (Baccara)	0.2	2	65 69–71	13	Seed	< 0.01	
	0.2			13	Seed	< 0.01	
				36	Seed (mech. threshed)	< 0.01	
				36	Seed (mech. threshed)	< 0.01	
France South, 1996 Brie, Poitou- Charentes (Baccara)	0.25	2	65 69–71	13	Seed	0.01	RJ2286B, S669.96 Syngenta File No. ICI5504/1111
	0.25			13	Seed	0.01	
				35	Seed (mech. threshed)	0.01	
				35	Seed (mech. threshed)	< 0.01 mean 0.01	
France South, 1996 Brie, Poitou- Charentes (Baccara)	0.2	2	65 69–71	13	Seed	0.01	
	0.2			13	Seed	0.01	
				35	Seed (mech. threshed)	< 0.01	
				35	Seed (mech. threshed)	< 0.01	
France South, 1997 Chabournay, Poitou	0.25	2	63 65	14	Seed	0.01	RJ2548B, S662.97
	0.25			44	Seed (mech. thresh)	< 0.01	

Country, year, location (variety)	Application			PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
Pea (Solara)	0.2	2	63	14	Seed	0.04	Syngenta File No. ICI5504/1115
	0.2		65	44	Seed (mech. thresh)	< 0.01	
France South, 1997 Vendeuvre du Poitou, Poitou (Baccara)	0.25	2	61	14	Seed	< 0.01	RJ2548B, S663.97
	0.25		63	44	Seed (mech. thresh)	< 0.01	
				44	Seed (mech. thresh)	< 0.01	
France South, 2004 Epennes, Pitou- Charentes Pea dry (NC farm seed)	0.2	2	61	0-	Seed	< 0.01	04-0421, AF/8167/SY/1 Syngenta File No. SAN619/7887
	0.2		72	0+	Seed	0.07	
				7	Seed	0.03	
				14	Seed	< 0.01	
				21	Seed	< 0.01	
				29	Seed	0.03	
France South, 2004 Biziat, Rhone-Alpes Pea dry (Atos)	0.2	2	67	0-	Seed	< 0.01	04-0421, AF/8167/SY/2 Syngenta File No. SAN619/7887
	0.2		77	0+	Seed	0.05	
				7	Seed	0.01	
				14	Seed	0.04	
				21	Seed	0.01	
				30	Seed	< 0.01	
France South, 2004, Finham, Midi Pyrenees Pea, dry (Austin)	0.2	2	61	7	Seed	0.01	04-0421, AF/8167/SY/3 Syngenta File No. SAN619/7887
	0.2		69-71	14	Seed	< 0.01	
				21	Seed	< 0.01	
				30	Seed	< 0.01	
France South, 2004, Meauzac, Midi- Pyrenees Pea dry (Bacara)	0.2	2	61	7	Seed	0.02	04-0421, AF/8167/SY/4 Syngenta File No. SAN619/7887
	0.2		67-71	14	Seed	0.01	
				21	Seed	0.01	
				30	Seed	0.03	

Root and tuber vegetables

Potatoes

Trials have been conducted in the USA and Canada in 2009 to support the registered use pattern.

Five independent supervised trials were conducted. In each trial, azoxystrobin was applied once as an SC formulation containing 250 g ai/L at a rate of 0.44–0.50 g ai/100 kg tubers. In one trial, four different application methods were used, namely spray application to tubers falling from a conveyor belt, surface application, application inside a spray chamber and spray application on a brush table. All other trials used spray application to tubers falling from a conveyor belt or moving along a roller table. In one trial, a bulk sample was collected and processed to flakes, chips and wet peel. Potatoes from the residue trials were sampled after the test substance had dried (0 day). In three trials, additional treated samples were placed in typical potato storage conditions for up to 231 days to generate residue decline data. Samples were collected in duplicate.

Following collection, with the exception of the bulk sample for processing, the potato tubers were frozen and shipped to the laboratory for analysis. The bulk samples were stored at ambient temperature prior to shipment to the processing facility. Processed samples were frozen after collection. The analytical method used was RAM 305/03 with a validated limit of quantification of 0.01 mg/kg. The data are presented in Table 5.

Table 5 Azoxystrobin residues in potatoes after post-harvest treatment

Country, region, year (variety)	Application		PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	g ai/100 kg	Method				
USA, Idaho, 2009/2010 (Russet Burbank)	0.45	Conveyor belt	0	Tuber	4.2	TK0003297, 09-ID19, Syngenta File No. ICI5504_50552
			0	Tuber	3.4 mean <u>3.8</u>	
			30	Stored tuber	1.5	
			30	Stored tuber	1.5	
			231	Stored tuber	0.75	
			231	Stored tuber	0.44	
	0.45	Surface	0	Tuber	1.2	
			0	Tuber	1.1	
	0.44	Spray chamber	0	Tuber	3.6 3.5	
	0.45	Brush table	0	Tuber	2.3	
			0	Tuber	2.2 mean <u>2.3</u>	
USA, Main, 2009 (Frito Lay 1533)	0.50	Conveyor belt	0 0	Tuber Tuber	0.99 1.0 mean <u>1.0</u>	TK0003297, 09-ME04, Syngenta File No. ICI5504_50552
Canada, 2010 (Ac Chaleur)	0.45	Roller table	0	Tuber	3.5	TK0003297, 09-ON14, Syngenta File No. ICI5504_50552 Samples were cut in half in the field before sending to the lab
			0	Tuber	3.7	
			14	Stored tuber	4.8	
			14	Stored tuber	4.5	
			31	Stored tuber	4.2	
			31	Stored tuber	4.1	
			59	Stored tuber	4.3	
USA, Washington, 2009/2010 (Russet Burbank)	0.45	Conveyor belt	0	Tuber	2.3	TK0003297, 09-WA32, Syngenta File No. ICI5504_50552
			0	Tuber	2.2	
			13	Stored tuber	2.5	
			13	Stored tuber	1.6	
			32	Stored tuber	2.6	
			32	Stored tuber	1.6 mean <u>2.1</u>	
			61	Stored tuber	1.5	
			61	Stored tuber	1.4	
USA, Wisconsin, 2009 (Russet Burbank)	0.46	Conveyor belt	0 0	Tuber Tuber	1.5 1.4 mean <u>1.5</u>	TK0003297, 09-WI19, Syngenta File No. ICI5504_50552

*Cereal grains**Barley*

Trials have been conducted in the USA in 2009 and 2010 to support the registered use pattern. Seven independent supervised trials were conducted. In each trial, azoxystrobin was applied twice as an SC formulation containing 250 g ai/L at a rate of 0.15 kg ai/ha. Grain samples were harvested at 16–54 days after the final application. The analytical method RAM 305/03 was used. The residue data are summarized in Table 6.

Table 6 Azoxystrobin residues in barley

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
USA, 2009, Northwood, ND (Pinnacle)	0.15	2	BBCH 39	33	Grain	< 0.01	T004408-08, C13-9062
	0.15		BBCH 71	40	Grain	< 0.01	
				47	Grain	0.013	

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
				47	Grain	0.014 mean <u>0.014</u>	
				54	Grain	< 0.01	
USA, 2009, Carrington, ND (Pinnacle)	0.15	2	BBCH 37	48	Grain	0.033	T004408-08, C13-9065
	0.15		BBCH 69	48	Grain	0.04 mean <u>0.037</u>	
USA, 2009, Gann Valley, SD (Lacey)	0.15	2	BBCH 43–49	33	Grain	0.021	T004408-08, C16-9064
	0.15		BBCH 71–73	33	Grain	0.017 mean <u>0.019</u>	
USA, 2009, Ault, CO (Moravian 37)	0.15	2	Feekes 10.3	25	Grain	0.30	T004408-08, W12-9067
	0.15		Feekes 10.5	25	Grain	0.32 mean <u>0.31</u>	
USA, 2010, Suffolk, VA (Nomini)	0.15	2	BBCH 55	30	Grain	0.19	T004408-08, E07-9061
	0.15		BBCH 71	30	Grain	0.19 mean <u>0.19</u>	
USA, 2010, Rupert, ID (Ida-Gold II)	0.15	2	BBCH 55–59	16	Grain	0.058	T004408-08, W15-9070
	0.15		BBCH 85	16	Grain	0.043 mean <u>0.05</u>	
USA, 2010, Porterville, CA (UC937)	0.15	2	Feekes 10.5	49	Grain	1.1	T004408-08, W32-9068
	0.15		Post Feekes 10.5	49	Grain	0.88 mean <u>0.99</u>	

Oats

Twelve independent supervised trials have been conducted in the USA in 2009 and 2010. In each trial, azoxystrobin was applied twice as an SC formulation containing 250 g ai/L at a rate of 0.15 kg ai/ha. Grain samples were harvested at 11–48 days after the final application. The analytical method RAM 305/03 was used. The residue data are shown in Table 7.

Table 7 Azoxystrobin residues in oats

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
USA, 2009, Geneva, MN (Morton)	0.15	2	Feekes 9	48	Grain	0.026	T005494-08, C09-9084
	0.15		Feekes 10.5	48	Grain	0.03 mean <u>0.028</u>	
USA, 2009, Ayer, ND (Morton)	0.15	2	BBCH 52	44	Grain	0.058	T005494-08, C12-9086
	0.15		BBCH 70	44	Grain	0.058 mean <u>0.058</u>	
USA, 2009, Gardner, ND (Morton)	0.15	2	BBCH 52 BBCH 70	11	Immature grain	0.25	T005494-08, C12-9087
				18	Immature grain	0.34	
				25	Grain	0.26	
				25	Grain	0.34 mean <u>0.28</u>	
				32	Grain	0.23	
USA, 2009, Northwood, ND (Jerry)	0.15	2	BBCH 39	33	Grain	0.024	T005494-08, C13-9083
	0.15		BBCH 71	33	Grain	0.031 mean <u>0.028</u>	
USA, 2009, Northwood, ND (Jerry)	0.15	2	BBCH 43	28	Grain	0.043	T005494-08, C13-9088
	0.15		BBCH 75	28	Grain	0.054 mean <u>0.049</u>	
USA, 2009, Carrington, ND (Jerry)	0.15	2	BBCH 37	39	Grain	0.057	T005494-08, C13-9091
	0.15		BBCH 69	39	Grain	0.048 mean <u>0.053</u>	
USA, 2009, White Lake, SD (Stallion)	0.15	2	BBCH 43	36	Grain	0.014	T005494-08, C16-9090
	0.15		BBCH 71	36	Grain	0.012 mean <u>0.013</u>	
USA, 2009, Bagley,	0.15	2	14 days prior to	32	Grain	0.047	T005494-08,

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
IA (Reeves)	0.15		Feekes 10.5 Feekes 10.5	32	Grain	0.048 mean <u>0.048</u>	C30-9085
USA, 2009, Germansville, PA (Armor)	0.15	2	Feekes 10.5 Feekes 10.5–11.1	28	Grain	0.62	T005494-08, E04-9081
	0.15			28	Grain	0.64 mean <u>0.63</u>	
USA, 2009, Ault, CO (Jerry)	0.15	2	Feekes 10.2 Feekes 10.5	28	Grain	0.12	T005494-08, W12-9092
	0.15			28	Grain	0.11 mean <u>0.12</u>	
USA, 2010, Elko, SC (Horizon 270)	0.15	2	Feekes 10 Feekes 10.3	44	Grain	0.06	T005494-08, E11-9082
	0.15			44	Grain	0.055 mean <u>0.06</u>	
USA, 2010, Uvalde, TX (BOB)	0.15	2	BBCH 60 BBCH 71	35	Grain	0.12	T005494-08, W07-9089
	0.15			35	Grain	0.11 mean <u>0.12</u>	

Sorghum

Twelve independent supervised trials were conducted in the US in 2004 to support the registered use pattern in the US. In each trial, azoxystrobin was applied three times as an SC formulation containing 250 g ai/L at a rate of 0.28 kg ai/ha with a 7 day application interval. Grain samples were harvested at 14 and 21 days after the last application. The analytical method RAM 305/03 was used. The results are summarized in Table 8.

Table 8 Azoxystrobin residues in sorghum

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
USA, 2004, York, NE (NC+ 6B50)	0.28	3	BBCH 87 BBCH 93 BBCH 93	0	Grain	2.1	T002036-03, NB-FR-04-5028
	0.28			0	Grain	1.9	
	0.28			3	Grain	2.5	
				3	Grain	2.3	
				7	Grain	1.6	
				7	Grain	1.3	
				14	Grain	1.7	
				14	Grain	1.6 mean <u>1.7</u>	
				21	Grain	1.3	
				21	Grain	1.2	
USA, 2004, Grand Island, NE (NC+ 6B50)	0.28	3	BBCH 87 BBCH 87 BBCH 89	14	Grain	0.33	T002036-03, NB-FR-04-5033
	0.28			14	Grain	0.63	
	0.28					mean <u>0.48</u>	
USA, 2004, Highland, KS (Asgrow 571)	0.29	3	Stage 7 Stage 7–8 Stage 8	14	Grain	1.7, 2.9	T002036-03, ND-FR-04-5027
	0.28			14	Grain	1.4, 1.5	
	0.27					mean <u>1.9</u>	
USA, 2004, La Plata, MO (Pioneer 8500)	0.28	3	BBCH 79 BBCH 85 BBCH 89	17	Grain	1.1	T002036-03, ND-FR-04-5029
	0.28			17	Grain	1.4	
	0.28					mean <u>1.3</u>	
USA, 2004, Wagner, SD (DeKalbDK28E)	0.28	3	BBCH 85–89 BBCH 86–89 BBCH 88–89	17	Grain	1.5	T002036-03, NF-FR-04-5030
	0.28			17	Grain	1.3	
	0.28					mean <u>1.4</u>	
USA, 2004, Keensburg, CO (NC+ 4R48)	0.28	3	Soft dough Hard dough Hard dough	14	Grain	7.9	T002036-03, NM-FR-04-5035
	0.28			14	Grain	8.1	
	0.29					mean <u>8.0</u>	
USA, 2004, St. Paul, TX (GA 697)	0.28	3	81 89 89	0	Grain	7.4	T002036-03, SA-FR-04-5031
	0.28			0	Grain	8.3	
	0.28			3	Grain	3.7	
				3	Grain	3.0	
				7	Grain	2.0	
				7	Grain	1.6	
				14	Grain	1.6	

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
				14	Grain	2.0 mean <u>1.8</u>	
				21	Grain	1.3	
				21	Grain	1.3	
USA, 2004, Comanche, OK (Garst 5515)	0.28	3	89	14	Grain	4.6	T002036-03, SC-FR-04-5032
	0.29		89	14	Grain	4.3	
	0.29		93			mean <u>4.5</u>	
USA, 2004, Olton, TX (Cropland 414)	0.27	3	BBCH 89	13	Grain	2.3	T002036-03, SC-FR-04-5034
	0.28		BBCH 89	13	Grain	2.3	
	0.28		BBCH 89			mean <u>2.3</u>	
USA, 2004, Pleasant Hill, NM (Pioneer 8505)	0.28	3	milk stage	14	Grain	2.2	T002036-03, SC-FR-04-5036
	0.29		BBCH 89	14	Grain	2.1	
	0.27		dough stage			mean <u>2.2</u>	
USA, 2004, Cheneyville, LA (Golden Acres 444E)	0.29	3	dough stage	14	Grain	3.0	T002036-03, SD-FR-04-5026
	0.29		dough stage	14	Grain	2.5	
	0.29		dough stage			mean <u>2.8</u>	
USA, 2004, Elko, SC (K73-J6)	0.28	3	BBCH 85	14	Grain	1.3	T002036-03, SJ-FR-04-5025
	0.28		BBCH 85	14	Grain	1.4	
	0.28		BBCH 85			mean <u>1.4</u>	

Seed for beverages and sweets

Coffee beans

Azoxystrobin residues in coffee were evaluated by the 2011 JMPR. Nineteen trials were conducted in Brazil. In four trials (2006/2007) azoxystrobin was applied three times at a rate of 0.15 kg ai/ha with a 60 days application interval. Beans were harvested at PHIs of 14, 21 and 30 days. In three trials (2002/2003) azoxystrobin was applied three times to parallel plots, to one plot at a rate of 0.1 kg ai/ha and to the second plot at a rate of 0.2 kg ai/ha, both with an application interval of 60 days. In six trials (WG formulation, 2010/2011) azoxystrobin was applied two times pre-flowering at the rate 0.05 kg ai/ha with 30 days interval and three times at the rate 0.12 kg ai/ha with a 60 day application interval. Beans were harvested at PHIs 21, 28 and 35 days. Adjuvant was added to all applications. In six trials (EC formulation, 2010/2011) azoxystrobin was applied two times pre-flowering at the rate 0.05 kg ai/ha with 30 days interval and three times at the rate 0.1 kg ai/ha with a 60 day application interval. Beans were harvested at PHIs 21, 28 and 35 days. The residue data were reported by the 2011 JMPR and were not repeated in this document.

New trials on coffee Arabica have been conducted in Colombia in 2010/2011 and in Guatemala and Brazil in 2011 to support the registered use pattern in Colombia. Seven independent supervised trials were conducted in which azoxystrobin was applied three times as an SC formulation containing 200 g ai/L at a rate of 0.15 kg ai/ha. In two trials, a 30 day interval between applications was used, and samples of beans collected at PHIs of 0, 14, 28 and 42 days. In five trials, an application interval of 41–48 days was used, and beans were harvested at a PHI of 14–15 days, or at intervals of 5, 10, 15, 20 and 25 days from the decline trial.

Following harvest, the coffee cherries were processed according to normal local practices to give dry bean samples which were shipped to the laboratory for analysis. The analytical methods used were PLARA 082 v.07 and RAM 305/3, both with validated limits of quantification of 0.01 mg/kg. The residues are summarized in Table 9.

Table 9 Azoxystrobin residues in coffee beans

Country, year, location (variety)	Application			PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
Colombia, 2010 Pereira, Risaralda (Caturra)	0.15	3	77	0	Bean	< 0.01	RF 027 039 10B Trial: 1 Syngenta File No.
	0.15			14	Bean	n/d	
	0.15			28	Bean	n/d	

Country, year, location (variety)	Application			PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
				42	Bean	<u>≤ 0.01</u>	CGA322704_10025
				56	Bean	n/d	
				70	Bean	< 0.01	
				84	Bean	< 0.01	
				98	Bean	n/d	
				112	Bean	n/d	
				126	Bean	n/d	
				140	Bean	n/d	
				154	Bean	n/d	
				168	Bean	n/d	
				182	Bean	n/d	
				196	Bean	n/d	
Colombia, 2010 Chinchina, Caldas (Caturra)	0.15	3	77	0	Bean	0.01	RF 027 039 10B Trial: 2 Syngenta File No. CGA322704_10025
	0.15			14	Bean	n/d	
	0.15			28	Bean	n/d	
				42	Bean	<u>≤ 0.01</u>	
				56	Bean	n/d	
				70	Bean	n/d	
				84	Bean	n/d	
				98	Bean	n/d	
				112	Bean	n/d	
				126	Bean	n/d	
				140	Bean	n/d	
				154	Bean	n/d	
Colombia, 2011 Santa Marta, Magdalena (Castillo)	0.15	3	75	15	Green bean	< 0.01	TK0046957 Trial: 1 Syngenta File No. A12910C_50004
	0.15		77	15	Green bean	<u>≤ 0.01</u>	
Colombia, 2011 Santa Marta, Magdalena (Castillo)	0.15	3	75	5	Green bean	0.018	TK0046957 Trial: 2 Syngenta File No. A12910C_50004
	0.15		77	5	Green bean	0.019	
	0.15		81	10	Green bean	< 0.01	
				10	Green bean	< 0.01	
				15	Green bean	<u>≤ 0.01</u>	
				15	Green bean	< 0.01	
				20	Green bean	< 0.01	
				20	Green bean	< 0.01	
				25	Green bean	< 0.01	
				25	Green bean	< 0.01	
Guatemala, 2011 Santa Rosa (Bourbon)	0.15	3	75	14	Green bean	< 0.01	TK0046957 Trial: 3 Syngenta File No. A12910C_50004
	0.15		81	14	Green bean	0.02	
	0.15		85			mean <u>0.015</u>	
Brazil, 2012 Santo Antonio Do Jardim (Obatã)	0.15	3	77	14	Green bean	< 0.01	TK0046957 Trial: 4 Syngenta File No. A12910C_50004
	0.15		80	14	Green bean	0.01	
	0.15		85			mean <u>0.01</u>	
Brazil, 2012 Dois Corregos Coffee, Arabica (Tupi)	0.15	3	77	14	Green bean	< 0.01	TK0046957 Trial: 5 Syngenta File No. A12910C_50004
	0.15		80	14	Green bean	0.01	
	0.15		85			mean <u>0.01</u>	

n/d: not detected

*Legume animal feeds**Bean fodder*

Seven independent supervised trials were conducted on dry beans in the UK and France in 2005. Azoxystrobin was applied twice as an SC formulation containing 250 g ai/L at a rate of about 0.20 kg ai/ha with a spray interval of 14 days. Applications were made between BBCH growth stages 61 and 87. The analytical methods used were RAM 305/01, RAM 305/02 and RAM 305/03 with an LOQ of 0.01 mg/kg. Residue data are presented in Table 10.

Table 10 Azoxystrobin residues in bean fodder

Country, year, location (variety)	Application			PHI, Days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
UK, 2005 Horsten, Nottinghamshire (Clipper)	0.20 0.20	2	61 79	30	Remaining plant	< 0.01	05-0415, AF/8541/SY/1 Syngenta File No. SAN619/8116
UK, 2005 Draycott, Nottinghamshire (Quattro)	0.21 0.21	2	61 79	30 36	Remaining plant	0.07 0.10	05-0415, AF/8541/SY/2 Syngenta File No. SAN619/8116
France North, 2005 Boce, Pays de la Loire (Castel)	0.13 0.20	2	62 87	26	Remaining plant	0.55	05-0415, AF/8541/SY/4 Syngenta File No. SAN619/8116
France, 2005 Monteux, Provence- Alpes-Cote-d'Azur (Big Borloto)	0.21 0.20	2	69–71 75–77	30	Remaining plant	0.08	05-0607, FR-FR-05-0482 Syngenta File No. SAN619/8117
France, 2005 Marsillargues, Languedoc-Roussillon (Linex)	0.20 0.20	2	62 76	31	Remaining plant	0.03	05-0607, FR-FR-05-0483 Syngenta File No. SAN619/8117
France, 2005 Estillac, Aquitaine (Linex)	0.22 0.21	2	64 73–75	29	Remaining plant	0.25	05-0607, FR-FR-05-0484 Syngenta File No. SAN619/8117
France, 2005 Marsillargues, Languedoc-Roussillon (Linex)	0.21 0.21	2	61 67	28	Remaining plant	0.06	05-0607, FR-FR-05-0485 Syngenta File No. SAN619/8117

Pea fodder (dry)

Twenty independent supervised trials were conducted in the UK and France in 1996–2004 on peas. In each trial, azoxystrobin was applied twice as an SC formulation containing 250 g ai/L at a rate of 0.20–0.25 kg ai/ha with a spray interval of 14 days. Applications were made between BBCH growth stages 61 and 77. Samples of dry pea seed were collected at normal commercial harvest at PHIs of 30–45 days. The remaining plant can be used as fodder (dry). The results are shown in Table 11. The analytical methods used were RAM 305/02, RAM 243/04 and RAM 243/05 with a validated limit of quantification of 0.01 mg/kg.

Table 11 Azoxystrobin residues in pea fodder (dry)

Country, year, location (variety)	Application			PHI, Days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
France North, 1996, Grivesnes, Picardie, Vining pea (Bonette)	0.25 0.25	2	63–65 69–71	38	Plant	<u>3.7</u>	RJ2286B, S101.96 Syngenta File No. ICI5504/1111
France North, 1996, Grivesnes, Picardie,	0.20 0.20	2	63–65 69–71	38	Plant	2.2	RJ2286B, S101.96

Country, year, location (variety)	Application			PHI, Days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
Vining pea (Bonette)							Syngenta File No. ICI5504/1111
France North, 1996, Bayonvillers, Picardie, Vining pea (Lynx)	0.25 0.25	2	63 69–71	42	Plant	<u>7.2</u>	RJ2286B, S102.96 Syngenta File No. ICI5504/1111
France North, 1996 Bayonvillers, Picardie, Vining pea (Lynx)	0.20 0.20	2	63 69–71	42	Plant	4.9	RJ2286B, S102.96 Syngenta File No. ICI5504/1111
France North, 1996, Tourny, Haute- Normandie, Vining pea (Mini)	0.25 0.25	2	65 69–71	30	Plant	<u>3.9</u>	RJ2286B, S208.96 Plot: 2 Syngenta File No. ICI5504/1111
France North, 1996, Tourny, Haute- Normandie, Vining pea (Mini)	0.20 0.20	2	65 69–71	30	Plant	2.5	RJ2286B, S208.96 Plot: 2 Syngenta File No. ICI5504/1111
France North, 1997, Chaulnes, Picardie, Vining pea (Novaroy)	0.25 0.25	2	62 71	40	Plant	<u>2.0</u>	RJ2548B, S101.97 Syngenta File No. ICI5504/1115
	0.20 0.20	2	62 71	40	Plant	1.4	
France North, 1997, Hennezis, Haute Normandie, Vining pea (Camaro)	0.25 0.25	2	65 75	41	Plant	<u>1.4</u>	RJ2548B, S205.97 Syngenta File No. ICI5504/1115
	0.20 0.20	2	65 75	41	Plant	1.4	
UK, 1996, Asselby, East Yorkshire, Field pea (Solara)	0.25 0.25	2	62 64–72	42	Plant	<u>2.3</u>	RJ2390B, with Addendum 1, AP/3248/ZE/1 Syngenta File No. ICI5504/1109
UK, 1996, Asselby, East Yorkshire, Field pea (Solara)	0.20 0.20	2	62 64–72	42	Whole plant	1.3	RJ2390B, with Addendum 1, AP/3248/ZE/1 Syngenta File No. ICI5504/1109
UK, 1997, Melbourne, Derbyshire, Field pea (Alfetta)	0.25 0.25	2	62 67–72	45	Plant	0.52	RJ2521B, AP/3783/ZE/1 Syngenta File No. ICI5504/1113
UK, 1997, Melbourne, Derbyshire, Field pea (Alfetta)	0.20 0.20	2	62 67–72	45	Whole plant	<u>0.62</u>	RJ2521B, AP/3783/ZE/1 Syngenta File No. ICI5504/1113
UK, 1997, Middleton on the Wolds, Yorkshire, Field pea (Grafilla)	0.25 0.25	2	62 67–75	44	Plant	0.56	RJ2521B, AP/3783/ZE/2 Plot: 2 Syngenta File No. ICI5504/1113
UK, 1997, Middleton on the Wolds, Yorkshire, Field pea (Grafilla)	0.20 0.20	2	62 67–75	44	Whole plant	<u>0.63</u>	RJ2521B, AP/3783/ZE/2 Plot: 2 Syngenta File No. ICI5504/1113
UK, 2004, Birkin, Yorkshire Pea dry (Solara)	0.20 0.21	2	61–63 69–73	43	Remaining Plant	<u>1.0</u>	04-0422, AF/8166/SY/1 Syngenta File No. SAN619/7886
UK, 2004, Hunmanby, Yorkshire, Pea dry	0.19 0.21	2	61 67–71	43	Remaining Plant	<u>0.34</u>	04-0422, AF/8166/SY/2

Country, year, location (variety)	Application			PHI, Days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
(Samson)							Syngenta File No. SAN619/7886
UK, 2004, Rouvres St Jean, Centre, Pea dry (Canyon)	0.20 0.20	2	71 75	30	Remaining Plant	<u>4.8</u>	04-0422, AF/8166/SY/3 Syngenta File No. SAN619/7886
France North, 2004, Montbellet, Bourgogne, Pea dry (Atos)	0.20 0.20	2	63 75	30	Remaining Plant	<u>1.8</u>	04-0422, AF/8166/SY/4 Syngenta File No. SAN619/7886
France South, 1996, Brie, Poitou- Charentes, Pea (Baccara)	0.25 0.25	2	65 69–71	36	Plant	<u>3.6</u>	RJ2286B S663.96 Syngenta File No. ICI5504/1111
France South, 1996, Brie, Poitou- Charentes, Pea (Baccara)	0.20 0.20	2	65 69–71	36	Plant	1.8	RJ2286B, S663.96 Syngenta File No. ICI5504/1111
France South, 1996, Brie, Poitou- Charentes, Pea (Baccara)	0.25 0.25	2	65 69–71	35	Plant	<u>3.8</u>	RJ2286B, S669.96 Syngenta File No. ICI5504/1111
France South, 1996, Brie, Poitou- Charentes, Pea (Baccara)	0.20 0.20	2	65 69–71	35	Plant	1.8	RJ2286B, S669.96 Syngenta File No. ICI5504/1111
France South, 1997, Chabournay, Poitou, Pea (Solara)	0.25 0.25	2	63 65	44	Plant	<u>2.1</u>	RJ2548B, S662.97 Syngenta File No. ICI5504/1115
France South, 1997, Chabournay, Poitou, Pea (Solara)	0.20 0.20	2	63 65	44	Plant	1.3	RJ2548B, S662.97 Syngenta File No. ICI5504/1115
France South, 1997, Venduvre du Poitou, Poitou, Pea (Baccara)	0.25 0.25	2	61 63	44	Plant	<u>0.61</u>	RJ2548B, S663.97 Syngenta File No. ICI5504/1115
France South, 1997, Venduvre du Poitou, Poitou, Pea (Baccara)	0.20 0.20	2	61 63	44	Plant	0.20	RJ2548B, S663.97 Syngenta File No. ICI5504/1115
France South, 2004, Epennes, Pitou- Charentes, Pea dry (NC farm seed)	0.20 0.20	2	61 72	29	Remaining Plant	<u>1.8</u>	04-0421, AF/8167/SY/1 Syngenta File No. SAN619/7887
France South, 2004, Biziat, Rhone- Alpes, Pea dry (Atos)	0.20 0.20	2	67 77	30	Remaining Plant	<u>4.0</u>	04-0421, AF/8167/SY/2 Syngenta File No. SAN619/7887
France South, 2004, Finham, Midi- Pyrenees, Pea dry (Austin)	0.20 0.20	2	61 69–71	30	Remaining Plant	<u>1.6</u>	04-0421, AF/8167/SY/3 Syngenta File No. SAN619/7887
France South, 2004, Meauzac, Midi- Pyrenees, Pea dry (Baccara)	0.20 0.20	2	61 67–71	30	Remaining Plant	<u>18</u>	04-0421, AF/8167/SY/4 Syngenta File No. SAN619/7887

Pea vines (green)

Twenty independent supervised trials were conducted in the UK and France in 1996–2004 on peas. In each trial, azoxystrobin was applied twice as an SC formulation containing 250 g ai/L at a rate of 0.20–0.25 kg ai/ha with a spray interval of 14 days. Applications were made between BBCH growth stages 61 and 77. Several trials were conducted as decline trials. The green plant (pea vines) can be used as animal feed. The analytical methods used were RAM 305/02, RAM 243/04 and RAM 243/05 with a validated limit of quantification of 0.01 mg/kg. The results are shown in Table 12.

Table 12 Azoxystrobin residues in pea vines (green)

Country, year, location (variety)	Application			PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
France North, 1996, Grivesnes, Picardie Vining pea (Bonette)	0.25	2	63–65 69–71	0+	Plant	5.9	RJ2286B, S101.96, Syngenta File ICI5504/1111
	0.25			3	Plant	<u>5.6</u>	
				7	Plant	3.7	
				14	Plant	3.5	
France North, 1996, Grivesnes, Picardie Vining pea (Bonette)	0.20	2	63–65 69–71	0+	Plant	3.6	RJ2286B, S101.96, Syngenta File ICI5504/1111
	0.20			3	Plant	3.6	
				7	Plant	3.2	
				14	Plant	1.9	
France, North, 1996, Bayonvillers, Picardie Vining pea (Lynx)	0.25	2	63 69–71	0+	Plant	6.9	RJ2286B, S102.96, Syngenta File ICI5504/1111
	0.25			3	Plant	<u>4.5</u>	
				7	Plant	4.3	
				14	Plant	3.6	
France, North, 1996, Bayonvillers, Picardie Vining pea (Lynx)	0.20	2	63 69–71	0+	Plant	3.9	RJ2286B, S102.96, Syngenta File ICI5504/1111
	0.20			3	Plant	3.1	
				7	Plant	2.9	
				14	Plant	2.4	
France North, 1996, Tourny, Haute-Normandie Vining pea (Mini)	0.25	2	65 69–71	0+	Plant	8.9	RJ2286B, S208.96, Plot 2, Syngenta File ICI5504/1111
	0.25			2	Plant	<u>3.3</u>	
				7	Plant	1.2	
				15	Plant	2.1	
France North, 1996, Tourny, Haute-Normandie Vining pea (Mini)	0.20	2	65 69–71	0+	Plant	6.8	RJ2286B, S208.96, Plot 2, Syngenta File ICI5504/1111
	0.20			2	Plant	2.4	
				7	Plant	1.0	
				15	Plant	0.76	
France North, 1997, Chaulnes, Picardie Vining pea (Novaroy)	0.25	2	62	14	Plant	<u>1.8</u>	RJ2548B, S101.97, Syngenta File ICI5504/1115
	0.25		71				
	0.20	2	62	14	Plant	1.2	
France North, 1997, Hennezeis, Haute Normandie Vining pea (Camaro)	0.25	2	65	15	Plant	<u>1.3</u>	RJ2548B, S205.97, Syngenta File ICI5504/1115
	0.25		75				
	0.20	2	65	15	Plant	1.1	
UK, 1996, Asselby, East Yorkshire Field pea (Solara)	0.25	2	62 64–72	0+	Plant	4.4	RJ2390B with Addendum 1, AP/3248/ZE/1, Syngenta File ICI5504/1109
	0.25			3	Plant	<u>3.1</u>	
				7	Plant	2.3	
				15	Plant	0.89	
UK, 1996, Asselby, East Yorkshire Field pea (Solara)	0.20	2	62 64–72	0+	Whole plant	3.3	RJ2390B with Addendum 1, AP/3248/ZE/1, Syngenta File ICI5504/1109
	0.20			3	Whole plant	2.4	
				7	Whole plant	1.6	
				15	Whole plant	0.70	
UK, 1997, Melbourne, Derbyshire Field pea (Alfetta)	0.25	2	62 67–72	0+	Plant	4.3	RJ2521B, AP/3783/ZE/1, Syngenta File ICI5504/1113
	0.25			3	Plant	<u>0.89</u>	
				7	Plant	0.70	
				14	Plant	0.83	
UK, 1997, Melbourne, Derbyshire Field pea (Alfetta)	0.20	2	62 67–72	0+	Whole plant	3.7	RJ2521B, AP/3783/ZE/1, Syngenta File ICI5504/1113
	0.20			3	Whole plant	0.54	
				7	Whole plant	0.45	
				14	Whole plant	0.73	

Country, year, location (variety)	Application			PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
UK, 1997, Middleton on the Wolds, Yorkshire Field pea (Grafilla)	0.25	2	62 67–75	0+	Plant	3.6	RJ2521B, AP/3783/ZE/2, Plot 2, Syngenta File ICI5504/1113
	0.25			3	Plant	<u>1.5</u>	
				7	Plant	0.95	
				14	Plant	0.74	
UK, 1997, Middleton on the Wolds, Yorkshire Field pea (Grafilla)	0.20	2	62 67–75	0+	Whole plant	3.4	RJ2521B, AP/3783/ZE/2, Plot 2, Syngenta File ICI5504/1113
	0.20			3	Whole plant	1.2	
				7	Whole plant	0.79	
				14	Whole plant	0.75	
UK, 2004, Birkin, Yorkshire Pea dry (Solara)	0.20	2	61–63 69–73	0–	Whole plant	0.22	04-0422, AF/8166/SY/1, Syngenta File SAN619/7886
	0.21			0+	Whole plant	3.4	
				7	Remaining Plant	2.0	
				14	Remaining plant	<u>3.1</u>	
				21	Remaining plant	0.50	
UK, 2004, Hunmanby, Yorkshire Pea dry (Samson)	0.19	2	61 67–71	0–	Whole plant	0.12	04-0422, AF/8166/SY/2, Syngenta File SAN619/7886
	0.21			0+	Whole plant	4.1	
				7	Whole plant	<u>1.4</u>	
				14	Remaining plant	0.54	
				21	Remaining plant	0.16	
UK, 2004, Rouvres St Jean, Centre Pea dry (Canyon)	0.20	2	71 75	0–	Remaining plant	1.10	04-0422, AF/8166/SY/3, Syngenta File SAN619/7886
	0.20			0+	Remaining plant	2.8	
				7	Remaining plant	3.3	
				14	Remaining plant	3.6	
				21	Remaining plant	4.1	
				30	Remaining plant	<u>4.8</u>	
France North, 2004, Montbellet, Bourgogne Pea dry (Atos)	0.20	2	63 75	0–	Remaining plant	0.49	04-0422, AF/8166/SY/4, Syngenta File SAN619/7886
	0.20			0+	Remaining plant	4.1	
				7	Remaining plant	<u>3.4</u>	
				14	Remaining plant	1.8	
				21	Remaining plant	2.3	
France South, 1996, Brie, Poitou-Charentes Pea (Baccara)	0.25	2	65 69–71	0+	Plant	6.9	RJ2286B, S663.96, Syngenta File ICI5504/1111
	0.25			2	Plant	6.9	
				6	Plant	3.3	
				13	Plant	<u>4.1</u>	
				36	Plant	3.6	
France South, 1996, Brie, Poitou-Charentes Pea (Baccara)	0.20	2	65 69–71	0+	Plant	6.0	RJ2286B, S663.96, Syngenta File ICI5504/1111
	0.20			2	Plant	4.2	
				6	Plant	1.9	
				13	Plant	2.4	
France South, 1996, Brie, Poitou-Charentes Pea (Baccara)	0.25	2	65 69–71	0+	Plant	5.1	RJ2286B, S669.96, Syngenta File ICI5504/1111
	0.25			2	Plant	<u>4.8</u>	
				6	Plant	3.3	
				13	Plant	4.4	
France South, 1996, Brie, Poitou-Charentes Pea (Baccara)	0.20	2	65 69–71	0+	Plant	4.6	RJ2286B, S669.96, Syngenta File ICI5504/1111
	0.20			2	Plant	3.6	
				6	Plant	2.1	
				13	Plant	2.5	
France South, 2004, Epennes, Pitou- Charentes, Pea dry (NC farm seed)	0.20	2	61 72	0–	Remaining plant	0.32	04-0421, AF/8167/SY/1, Syngenta File SAN619/7887
	0.20			0+	Remaining plant	3.5	
				7	Remaining plant	<u>4.9</u>	
				14	Remaining plant	2.7	
				21	Remaining plant	3.6	
France South, 2004, Biziat, Rhone-Alpes Pea dry (Atos)	0.20	2	67 77	0–	Remaining plant	1.4	04-0421, AF/8167/SY/2, Syngenta File SAN619/7887
	0.20			0+	Remaining plant	4.1	
				7	Remaining plant	4.3	
				14	Remaining plant	<u>5.8</u>	
				21	Remaining plant	3.0	
France South, 2004,	0.20	2	61 69–71	0–	Whole plant	0.11	04-0421, AF/8167/SY/3,
	0.20			0+	Whole plant	2.1	

Country, year, location (variety)	Application			PHI, days	Commodity	Residue, mg/kg	Report, trial, remarks
	kg ai/ha	No	BBCH				
Finham, Midi-Pyrenees Pea dry (Austin)				7	Remaining plant	1.6	Syngenta File SAN619/7887
				14	Remaining plant	2.2	
				21	Remaining plant	2.6	
France South, 2004, Meauzac, Midi-Pyrenees Pea dry (Baccara)	0.20	2	61	0–	Whole plant	0.38	04-0421, AF/8167/SY/4, Syngenta File SAN619/7887
	0.20		67–71	0+	Whole plant	3.2	
				7	Remaining plant	2.9	
				14	Remaining plant	2.4	
				21	Remaining plant	6.4	

Straw, fodder (dry) and forage of cereal grains

Barley straw and fodder, dry

Trials have been conducted on barley in the USA in 2009 and 2010 to support the registered use pattern. Seven independent supervised trials were conducted. In each trial, azoxystrobin was applied twice as an SC formulation containing 250 g ai/L at a rate of 0.15 kg ai/ha. Straw samples were harvested at 16–54 days after the final application. Hay samples were harvested from separate plots at 0–21 days after the final application. The analytical method RAM 305/03 was used. The residue data are shown in Tables 13 (straw) and 14 (hay).

Table 13 Azoxystrobin residues in barley straw

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
USA, 2009, Northwood, ND (Pinnacle)	0.15	2	BBCH 39	33	Straw	0.18	T004408-08, C13-9062
	0.15		BBCH 71	40	Straw	0.15	
				47	Straw	0.15	
				47	Straw	0.13	
				54	Straw	0.15	
USA, 2009, Carrington, ND (Pinnacle)	0.15	2	BBCH 37	48	Straw	0.63	T004408-08, C13-9065
	0.15		BBCH 69	48	Straw	0.76 mean 0.70	
USA, 2009, Gann Valley, SD (Lacey)	0.15	2	BBCH 43–49	33	Straw	0.29	T004408-08, C16-9064
	0.15		BBCH 71–73	33	Straw	0.26 mean 0.28	
USA, 2009, Ault, CO (Moravian 37)	0.15	2	Feekes 10.3	25	Straw	3.8	T004408-08, W12-9067
	0.15		Feekes 10.5	25	Straw	3.2 mean 3.5	
USA, 2010, Suffolk, VA (Nomini)	0.15	2	BBCH 55	30	Straw	3.3	T004408-08, E07-9061
	0.15		BBCH 71	30	Straw	3.3 mean 3.3	
USA, 2010, Rupert, ID (Ida-Gold II)	0.15	2	BBCH 55–59	16	Straw	0.36	T004408-08, W15-9070
	0.15		BBCH 85	16	Straw	0.35 mean 0.36	
USA, 2010, Porterville, CA (UC937)	0.15	2	Feekes 10.5	49	Straw	2.5	T004408-08, W32-9068
	0.15		Post Feekes 10.5	49	Straw	2.6 mean 2.6	

Table 14 Azoxystrobin residues in barley hay.

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
USA, 2009, Northwood, ND (Pinnacle)	0.15	2	BBCH 22	0	Hay	6.9	T004408-08, C13-9062
	0.15		BBCH 52	3	Hay	0.96	
				7	Hay	0.46	
				14	Hay	0.34	
				14	Hay	0.34	
				21	Hay	0.18	

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
USA, 2009, Carrington, ND (Pinnacle)	0.15	2	BBCH 16 BBCH 59	7	Hay	0.79	T004408-08, C13-9065
	0.15			7	Hay	0.69	
				14	Hay	0.74	
				14	Hay	0.83 mean <u>0.76</u>	
USA, 2009, Gann Valley, SD (Lacey)	0.15	2	BBCH 21–31 BBCH 43–49	7	Hay	0.91	T004408-08, C16-9064
	0.15			7	Hay	0.76	
				15	Hay	0.29	
				15	Hay	0.30	
USA, 2009, Ault, CO (Moravian 37)	0.15	2	Feekes 5 Feekes 10	7	Hay	3.8	T004408-08, W12-9067
	0.15			7	Hay	3.5	
				14	Hay	mean <u>3.7</u> 2.5	
				14	Hay	2.9	
USA, 2010, Suffolk, VA (Nomini)	0.15	2	Feekes 5 Feekes 5.2	7	Hay	3.7	T004408-08, E07-9061
	0.15			7	Hay	2.7	
				14	Hay	mean <u>3.2</u> 1.6	
				14	Hay	1.6	
USA, 2010, Rupert, ID (Ida-Gold II)	0.15	2	BBCH 30 BBCH 55	7	Hay	0.69	T004408-08, W15-9070
	0.15			7	Hay	0.69	
				14	Hay	mean <u>0.69</u> 0.27	
				14	Hay	0.31	
USA, 2010, Porterville, CA (UC937)	0.15	2	Feekes 5 Feekes 7	7	Hay	1.6	T004408-08, W32-9068
	0.15			7	Hay	2.6	
				14	Hay	mean <u>2.1</u> 1.1	
				14	Hay	1.6	

Oats straw and fodder, dry

Twelve independent supervised trials have been conducted in the USA in 2009 and 2010. In each trial, azoxystrobin was applied twice as an SC formulation containing 250 g ai/L at a rate of 0.15 kg ai/ha. Straw samples were harvested at 11–48 days after the final application. Hay samples were harvested from separate plots at 0–21 days after the final application. The analytical method RAM 305/03 was used. The results are summarized in Tables 15 (straw) and 16 (hay).

Table 15 Azoxystrobin residues in oats straw.

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
USA, 2009, Geneva, MN (Morton)	0.15	2	Feekes 9 Feekes 10.5	48	Straw	0.066	T005494-08, C09-9084
	0.15			48	Straw	0.11 mean <u>0.088</u>	
USA, 2009, Ayr, ND (Morton)	0.15	2	BBCH 52 BBCH 70	44	Straw	0.40	T005494-08, C12-9086
	0.15			44	Straw	0.21 mean <u>0.31</u>	
USA, 2009, Gardner, ND (Morton)	0.15	2	BBCH 52 BBCH 70	11	Straw	0.96	T005494-08, C12-9087
	0.15			18	Straw	0.87	
				25	Straw	1.3	
				25	Straw	1.2 mean <u>1.3</u>	
USA, 2009, Northwood, ND (Jerry)	0.15	2	BBCH 39 BBCH 71	33	Straw	0.84	T005494-08, C13-9083
	0.15			33	Straw	0.12 0.18 mean <u>0.15</u>	
USA, 2009,	0.15	2	BBCH 43	28	Straw	0.31	T005494-08,

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
Northwood, ND (Jerry)	0.15		BBCH 75	28	Straw	0.38 mean <u>0.35</u>	C13-9088
USA, 2009, Carrington, ND (Jerry)	0.15	2	BBCH 37	39	Straw	0.68	T005494-08, C13-9091
	0.15		BBCH 69	39	Straw	0.55 mean <u>0.62</u>	
USA, 2009, White Lake, SD (Stallion)	0.15	2	BBCH 43	36	Straw	0.08	T005494-08, C16-9090
	0.15		BBCH 71	36	Straw	0.069 mean <u>0.075</u>	
USA, 2009, Bagley, IA (Reeves)	0.15	2	14 days prior to Feekes 10.5	32	Straw	0.053	T005494-08, C30-9085
	0.15			32	Straw	0.094 mean <u>0.074</u>	
USA, 2009, Germansville, PA (Armor)	0.15	2	Feekes 10.5	29	Straw	0.78	T005494-08, E04-9081
	0.15		Feekes 10.5–11.1	29	Straw	0.61 mean <u>0.70</u>	
USA, 2009, Ault, CO (Jerry)	0.15	2	Feekes 10.2	28	Straw	0.83	T005494-08, W12-9092
	0.15		Feekes 10.5	28	Straw	0.93 mean <u>0.88</u>	
USA, 2010, Elko, SC (Horizon 270)	0.15	2	Feekes 10	44	Straw	0.60	T005494-08, E11-9082
	0.15		Feekes 10.3	44	Straw	0.85 mean <u>0.73</u>	
USA, 2010, Uvalde, TX (BOB)	0.15	2	BBCH 60	35	Straw	0.21	T005494-08, W07-9089
	0.15		BBCH 71	35	Straw	0.19 mean <u>0.20</u>	

Table 16 Azoxystrobin residues in oats hay

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
USA, 2009, Geneva, MN (Morton)	0.15	2	Feekes 5 Feekes 7	7	Hay	0.37	T005494-08, C09-9084
	0.15			7	Hay	0.17 mean <u>0.27</u>	
				14	Hay	0.15	
				14	Hay	0.13	
USA, 2009, Ayr, ND (Morton)	0.15	2	BBCH 31 BBCH 49	7	Hay	3.0	T005494-08, C12-9086
	0.15			7	Hay	3.0 mean <u>3.0</u>	
				14	Hay	1.8	
				14	Hay	1.4	
USA, 2009, Gardner, ND (Morton)	0.15	2	BBCH 31 BBCH 49	5	Hay	5.7	T005494-08, C12-9087
	0.15			7	Hay	<u>3.4</u>	
				14	Hay	1.5	
				14	Hay	2.3	
USA, 2009, Northwood, ND (Jerry)	0.15	2	BBCH 22 BBCH 55	21	Hay	1.9	T005494-08, C13-9083
	0.15			7	Hay	0.47	
				7	Hay	0.38	
				14	Hay	0.48	
USA, 2009, Northwood, ND (Jerry)	0.15	2	BBCH 30 BBCH 71	14	Hay	0.58 mean <u>0.53</u>	T005494-08, C13-9088
	0.15			7	Hay	2.6	
				7	Hay	1.7 mean <u>2.2</u>	
				14	Hay	1.4	
USA, 2009, Carrington, ND (Jerry)	0.15	2	BBCH 16 BBCH 55	14	Hay	0.76	T005494-08, C13-9091
	0.15			7	Hay	0.62	
				7	Hay	0.70 mean <u>0.66</u>	
				14	Hay	0.55	
USA, 2009, White	0.15	2	BBCH 23	14	Hay	0.64	T005494-08,

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
Lake, SD (Stallion)	0.15		BBCH 43	6	Hay	3.1 mean <u>3.1</u>	C16-9090
				16	Hay	0.45	
				16	Hay	0.42	
USA, 2009, Bagley, IA (Reeves)	0.15	2	Feekes 5 14 days after Feekes 5	7	Hay	0.25	T005494-08, C30-9085
	0.15			7	Hay	0.15 mean <u>0.20</u>	
				14	Hay	0.18	
				14	Hay	0.14	
USA, 2009, Germansville, PA (Armor)	0.15	2	Feekes 5 Feekes 7	7	Hay	0.91	T005494-08, E04-9081
	0.15			7	Hay	0.86 mean <u>0.89</u>	
				14	Hay	0.56	
				14	Hay	0.59	
USA, 2009, Ault, CO (Jerry)	0.15	2	Feekes 5 Feekes 10	7	Hay	1.4	T005494-08, W12-9092
	0.15			7	Hay	0.77 mean <u>1.1</u>	
				14	Hay	0.63	
				14	Hay	0.79	
USA, 2010, Elko, SC (Horizon 270)	0.15	2	Feekes 5 BBCH 32	7	Hay	3.2	T005494-08, E11-9082
	0.15			7	Hay	3.1 mean <u>3.2</u>	
				14	Hay	1.5	
				14	Hay	1.2	
USA, 2010, Uvalde, TX (BOB)	0.15	2	BBCH 30 BBCH 33	7	Hay	0.93	T005494-08, W07-9089
	0.15			7	Hay	1.6 mean <u>1.3</u>	
				14	Hay	0.50	
				14	Hay	0.60	

Oats forage (green)

Twelve independent supervised trials have been conducted in the USA in 2009 and 2010. In each trial, azoxystrobin was applied twice as an SC formulation containing 250 g ai/L at a rate of 0.15 kg ai/ha. Forage samples were harvested at 0–21 days after the final application. The analytical method RAM 305/03 was used. The residue data are summarized in Table 17.

Table 17 Azoxystrobin residues in oats forage

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
USA, 2009, Geneva, MN (Morton)	0.15	2	Feekes 5 Feekes 7	7	Forage	0.20	T005494-08, C09-9084
	0.15			7	Forage	0.20 mean <u>0.20</u>	
				14	Forage	0.042	
				14	Forage	0.062	
				14	Forage	0.062	
USA, 2009, Ayr, ND (Morton)	0.15	2	BBCH 31 BBCH 49	7	Forage	0.92	T005494-08, C12-9086
	0.15			7	Forage	1.1 mean <u>1.0</u>	
				14	Forage	0.70	
				14	Forage	0.80	
USA, 2009, Gardner, ND (Morton)	0.15	2	BBCH 31 BBCH 49	0	Forage	3.5	T005494-08, C12-9087
	0.15			3	Forage	2.8	
				7	Forage	<u>1.6</u>	
				14	Forage	0.66	
				14	Forage	0.68	
				21	Forage	1.1	
USA, 2009, Northwood, ND (Jerry)	0.15	2	BBCH 22 BBCH 55	7	Forage	0.23	T005494-08, C13-9083
	0.15			7	Forage	0.28 mean <u>0.26</u>	

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
				14	Forage	0.21	
				14	Forage	0.20	
USA, 2009, Northwood, ND (Jerry)	0.15	2	BBCH 30 BBCH 71	7	Forage	1.4	T005494-08, C13-9088
	0.15			7	Forage	1.3 mean <u>1.4</u>	
				14	Forage	1.0	
				14	Forage	0.92	
USA, 2009, Carrington, ND (Jerry)	0.15	2	BBCH 16 BBCH 55	7	Forage	0.42	T005494-08, C13-9091
	0.15			7	Forage	0.46 mean <u>0.44</u>	
				14	Forage	0.34	
				14	Forage	0.28	
USA, 2009, White Lake, SD (Stallion)	0.15	2	BBCH 23 BBCH 43	6	Forage	0.70	T005494-08, C16-9090
	0.15			6	Forage	0.86 mean <u>0.78</u>	
				16	Forage	0.16	
				16	Forage	0.20	
USA, 2009, Bagley, IA (Reeves)	0.15	2	Feekes 5 14 days after Feekes 5	7	Forage	0.11	T005494-08, C30-9085
	0.15			7	Forage	0.11 mean <u>0.11</u>	
				14	Forage	0.067	
				14	Forage	0.064	
USA (1), 2009 (Armor)	0.15	2	Feekes 5 Feekes 7	7	Forage	0.53	T005494-08, E04-9081
	0.15			7	Forage	0.50 mean <u>0.52</u>	
				14	Forage	0.21	
				14	Forage	0.18	
USA, 2009, Germansville, PA (Jerry)	0.15	2	Feekes 5 Feekes 10	7	Forage	1.1	T005494-08, W12-9092
	0.15			7	Forage	0.79 mean <u>0.95</u>	
				14	Forage	0.58	
				14	Forage	0.57	
USA, 2010, Elko, SC (Horizon 270)	0.15	2	Feekes 5 BBCH 32	7	Forage	2.2	T005494-08, E11-9082
	0.15			7	Forage	1.8 mean <u>2.0</u>	
				14	Forage	0.80	
				14	Forage	0.75	
USA, 2010, Uvalde, TX (BOB)	0.15	2	BBCH 30 BBCH 33	7	Forage	0.72	T005494-08, W07-9089
	0.15			7	Forage	1.0 mean <u>0.86</u>	
				14	Forage	0.25	
				14	Forage	0.27	

Sorghum straw and fodder, dry

Twelve independent supervised trials were conducted in the US in 2004. In each trial, azoxystrobin was applied three times as an SC formulation containing 250 g ai/L) at a rate of 0.28 kg ai/ha with a 7 day application interval. Stover samples were harvested at 14 and 21 days after the last application. The analytical method RAM 305/03 was used. The results are summarized in Table 18.

Table 18 Azoxystrobin residues in sorghum stover

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
USA, 2004, York, NE (NC+ 6B50)	0.28	3	BBCH 87 BBCH 93 BBCH 93	0	Stover	6.4	T002036-03, NB-FR-04-5028
	0.28			0	Stover	7.2	
	0.28			3	Stover	5.9	
				3	Stover	4.7	
				7	Stover	4.5	

Country, year, location (variety)	Application			PHI, days	Commodity	Residues, mg/kg	Report, trial, remarks
	kg ai/ha	No	Growth stage				
				7	Stover	3.5	
				14	Stover	4.6	
				14	Stover	2.8	
				21	Stover	4.3	
				21	Stover	3.7 mean <u>4.0</u>	
USA, 2004, Grand Island, NE (NC+ 6B50)	0.28	3	BBCH 87	14	Stover	1.6	T002036-03, NB-FR-04-5033
	0.28		BBCH 87	14	Stover	3.1	
	0.28		BBCH 89			mean <u>2.4</u>	
USA, 2004, Highland, KS (Asgrow 571)	0.29	3	Stage 7	14	Stover	5.2, 8.7	T002036-03, ND-FR-04-5027
	0.28		Stage 7–8	14	Stover	1.9, 3.4	
	0.27		Stage 8			mean <u>4.8</u>	
USA, 2004, La Plata, MO (Pioneer 8500)	0.28	3	BBCH 79	17	Stover	0.57	T002036-03, ND-FR-04-5029
	0.28		BBCH 85	17	Stover	0.84	
	0.28		BBCH 89			mean <u>0.71</u>	
USA, 2004, Wagner, SD (DeKalb DK28E)	0.28	3	BBCH 85–89	17	Stover	6.3, 6.4	T002036-03, NF-FR-04-5030
	0.28		BBCH 86–89	17	Stover	5.0, 3.5	
	0.28		BBCH 88–89			mean <u>5.3</u>	
USA, 2004, Keensburg, CO (NC+ 4R48)	0.28	3	Soft dough	14	Stover	3.0	T002036-03, NM-FR-04-5035
	0.28		Hard dough	14	Stover	4.3	
	0.29		Hard dough			mean <u>3.7</u>	
USA, 2004, St. Paul, TX (GA 697)	0.28	3	81	0	Stover	21	T002036-03, SA-FR-04-5031
	0.28		89	0	Stover	17	
	0.28		89	3	Stover	1.0	
				3	Stover	2.5	
				7	Stover	0.22	
				7	Stover	0.41	
				14	Stover	0.33	
				14	Stover	0.45 mean <u>0.39</u>	
				21	Stover	0.19	
				21	Stover	0.21	
USA, 2004, Comanche, OK (Garst 5515)	0.28	3	89	14	Stover	15	T002036-03, SC-FR-04-5032
	0.29		89	14	Stover	14	
	0.29		93			mean <u>14.5</u>	
USA, 2004, Olton, TX (Cropland 414)	0.27	3	BBCH 89	13	Stover	5.7	T002036-03, SC-FR-04-5034
	0.28		BBCH 89	13	Stover	3.2	
	0.28		BBCH 89			mean <u>4.5</u>	
USA, 2004, Pleasant Hill, NM (Pioneer 8505)	0.28	3	milk stage	14	Stover	7.0	T002036-03, SC-FR-04-5036
	0.29		BBCH 89	14	Stover	14	
	0.27		dough stage			mean <u>10.5</u>	
USA, 2004, Cheneyville, LA (Golden Acres 444E)	0.29	3	dough stage	14	Stover	2.1, 2.0	T002036-03, SD-FR-04-5026
	0.29		dough stage	14	Stover	2.6, 3.5	
	0.29		dough stage			mean <u>2.6</u>	
USA, 2004, Elko, SC (K73-J6)	0.28	3	BBCH 85	14	Stover	0.43	T002036-03, SJ-FR-04-5025
	0.28		BBCH 85	14	Stover	0.63	
	0.28		BBCH 85			mean <u>0.53</u>	

Sorghum forage (green)

Twelve independent supervised trials were conducted in the US in 2004. In each trial, azoxystrobin was applied three times as an SC formulation containing 250 g ai/L at a rate of 0.28 kg ai/ha with a 7 days application interval. Forage samples were taken at 0, 3, 7, 14 or 21 days after the final application. The analytical method RAM 305/03 was used. The results are summarized in Table 19.

Table 19 Azoxystrobin residues in sorghum forage.

Country, year,	Application	PHI,	Commodity	Residues,	Report, trial,

location (variety)	kg ai/ha	No	Growth stage	days		mg/kg	remarks
USA, 2004, York, NE (NC+ 6B50)	0.28	2	BBCH 51 BBCH 67	0	Forage	11	T002036-03, NB-FR-04-5028
	0.28			0	Forage	12	
				7	Forage	1.5	
				7	Forage	1.4	
						mean <u>1.5</u>	
				14	Forage	0.32	
				14	Forage	0.48	
				21	Forage	0.45, 0.44	
USA, 2004, York, NE (NC+ 6B50)	0.28	3	BBCH 87 BBCH 93 BBCH 93	21	Forage	0.79, 0.81	T002036-03, NB-FR-04-5028
	0.28			3	Forage	1.8	
	0.28			3	Forage	1.4	
USA, 2004, Grand Island, NE (NC+ 6B50)	0.28	2	BBCH 55 BBCH 71	14	Forage	0.14	T002036-03, NB-FR-04-5033
	0.28			14	Forage	0.35	
USA, 2004, Highland, KS (Asgrow 571)	0.27	2	BBCH 65 BBCH 65-85			mean <u>0.25</u>	T002036-03, ND-FR-04-5027
	0.28			14	Forage	0.19, 0.17	
				14	Forage	0.40, 0.50	
USA, 2004, La Plata, MO (Pioneer 8500)	0.27	2	BBCH 73 BBCH 77			mean <u>0.32</u>	T002036-03, ND-FR-04-5029
	0.29			15	Forage	0.26	
				15	Forage	0.28	
USA, 2004, Wagner, SD (DeKalb DK28E)	0.28	2	BBCH 45 BBCH 55-65			mean <u>0.27</u>	T002036-03, NF-FR-04-5030
	0.27			13	Forage	4.0, 4.0	
USA, 2004, Keensburg, CO (NC+ 4R48)	0.28	2	flowering milk stage	13	Forage	5.8, 8.5	T002036-03, NM-FR-04-5035
	0.28			13	Forage	mean <u>5.6</u>	
USA, 2004, St. Paul, TX (GA 697)	0.28	2	65 75	14	Forage	2.9	T002036-03, SA-FR-04-5031
	0.28			14	Forage	0.94	
USA, 2004, St. Paul, TX (GA 697)	0.28	3	81 89 89			mean <u>1.9</u>	T002036-03, SA-FR-04-5031
	0.28			0	Forage	9.0	
	0.28			0	Forage	12	
				3	Forage	<u>12</u>	
				3	Forage	<u>11</u>	
				7	Forage	4.5	
				7	Forage	11	
				14	Forage	5.1	
USA, 2004, Comanche, OK (Garst 5515)	0.28	2	69 85	14	Forage	3.8	T002036-03, SC-FR-04-5032
	0.29			14	Forage	1.2	
						1.7	
						mean <u>1.5</u>	
				14	Forage	1.9	
				14	Forage	1.4	
USA, 2004, Olton, TX (Cropland 414)	0.29	2	51 30 % bloom			mean <u>1.7</u>	T002036-03, SC-FR-04-5034
	0.27						
USA, 2004, Pleasant Hill, NM (Pioneer 8505)	0.27	2	Early bloom 67	14	Forage	9.0	T002036-03, SC-FR-04-5036
	0.29			14	Forage	5.4	
USA, 2004, Cheneyville, LA (Golden Acres 444E)	0.27	2	End of heading dough stage			mean <u>7.2</u>	T002036-03, SD-FR-04-5026
	0.28			14	Forage	1.8	
				14	Forage	1.4	
USA, 2004, Elko, SC (K73-J6)	0.29	2	BBCH 41 BBCH 61			mean <u>1.6</u>	T002036-03, SJ-FR-04-5025
	0.28			14	Forage	0.30, 0.41	
				14	Forage	0.26, 0.17	
						mean <u>0.29</u>	

FATES OF RESIDUES IN STORAGE AND PROCESSING

In processing-effect on the residue level

The Meeting received information on the fate of azoxystrobin residues during the processing of potatoes to flakes, chips and wet peel, sorghum to aspirated grain fractions and of green coffee to roasted and instant coffee. The information submitted on processing procedures is summarized below.

Potato

A processing study was carried out during 2009 on potatoes obtained from a trial conducted in Idaho, USA (Report No. TK0003297). One post-harvest application of azoxystrobin formulated as a 250 g ai/L SC was made to potato tubers at the rate of 0.45 g ai/100 kg. Potato tubers were sampled on day 0 after the applied spray had dried.

Potatoes were processed to flakes and wet peel as follows:

- Potatoes were washed and their specific gravity was determined. The potatoes were batch steam peeled, and then batch scrubbed. The potato peel was collected from the peeling and scrubbing process. The peeled potatoes were hand trimmed to remove additional peel, rot, green or damaged potatoes.
- The collected peel was hydraulically pressed, blended with the cut trim waste and a representative sample collected and frozen as the 'wet peel' sample.
- The peeled potatoes were cut into slabs and washed in cold tap water to remove free starch. The potato slabs were precooked at 70–77 °C for approximately 20 minutes, and then cooled to less than 32 °C for 20 minutes. The cooked potato slabs were steam-cooked at 94–100 °C for 40–42 minutes, mashed and then mixed with an emulsion of pre-weighed food additives. The cooked mash was fed into a drum dryer to dry the cooked mash into a thin sheet, and then broken into large flakes by hand. The flakes were uniformly milled into potato flakes in a hammer mill. The milled potato flakes were dried on a fluidized bed dryer before samples of 'potato flakes' were collected and frozen.

Potatoes were processed to chips (crisps) as follows:

- Washed potatoes were batch peeled and hand trimmed if necessary. The peeled potatoes were cut into thin slices (approximately 1.6 mm thick) and washed with hot water to remove free starch.
- The slices were drained and fried at approximately 163–191 °C in frying oil for approximately 120 seconds. The fried potato chips were drained and salted and samples of 'chips' then collected and frozen.

Samples of pre-processing potato tubers, wet peel, potato flakes and chips were analysed using method RAM 305/03. Samples were stored frozen for a maximum period of 7.3 months from sampling to analysis and residues in the processed products are deemed to be stable over the storage period. The results are summarized in Table 20.

Sorghum

A processing study was carried out in Texas, USA in 2004 (Report T002036-03, field test no SC-FR-04-534). Three applications with 0.27–0.28 kg ai/ha were made. Grain samples were taken 13 days after the last treatment. Samples were analysed by method RAM 305/3 (LOQ 0.01 mg/kg).

The aspirated grain fraction was generated as follows:

- After drying, the sample was placed in a dust generation room containing a holding bin, drag conveyors, and a bucket conveyor.
- As the sample was moved in the system, aspiration was used to remove light impurities (grain dust). The sample was moved for 120 minutes.

- The light impurities were classified by sieving. After classification of each sample, all material through the 2360 micron sieve was recombined to produce one aspirated grain fraction.

Coffee

A processing study was carried out during 2011 on coffee beans (Coffee Arabica, variety Bourbon) obtained from a trial conducted in Guatemala (Report TK0046957). Three applications of azoxystrobin formulated as a 200 g ai/L SC were applied to coffee plants at the rate of 750 g ai/ha (5 × rate). Applications were made at intervals of 42–44 days, and coffee cherries were harvested 14 days after the final application. Coffee cherries were pre-processed according to normal local practices to dry green beans (the raw agricultural commodity), and these were then processed to roasted coffee beans and instant coffee.

The coffee cherries were pre-processed to dry green coffee beans (RAC) as follows:

- The skin and some of the pulp of the coffee berry was removed by mechanically pressing the fruit through a screen in water batch, the remaining pulp was removed via a fermentation and washing process, and the bean then dried and the thin parchment layer remaining removed by hand.
- The process for producing dry green beans took 6–14 days.

Green coffee beans were processed to roasted and instant coffee as follows:

- Whole green coffee beans were aspirated to remove light impurities. The beans were roasted to a 'mild roast' using a modified table top roaster at a temperature of 199–216 °C for 10–30 minutes. Samples of dry roasted coffee beans were collected after cooling.
- Roasted coffee beans were ground using a disc mill and sifted using a sifter equipped with 18 and 36 mesh sieves. Material below the 18 mesh sieve but above the 36 mesh sieve was used for extraction. The ground coffee beans were extracted with water and steam in a pressurised extraction vessel. The exit temperature of the liquid extract was 129–163 °C. The extract was cooled to 13–24 °C in a heat exchanger. The extract was filtered through a 100 mesh screen, centrifuged and screened again using a 120 mesh screen. The resulting coffee extract was concentrated in a vacuum evaporator until the solids content was 15–30%, and then filtered through a 125 mesh screen. The resulting liquor extract was frozen dried and reduced to granules to form frozen dried (instant) coffee. Samples of instant coffee were collected for analysis.
- On completion of processing, samples of roasted coffee beans and instant coffee were frozen immediately and stored frozen before being shipped still frozen to the analytical laboratory.

Samples of dry green coffee beans, roasted coffee beans and instant coffee were analysed using method RAM 305/3. The validated limit of quantification was 0.01 mg/kg. Samples were stored frozen for a maximum period of 1.9 months from sampling to analysis and residues in the processed products are deemed to be stable over the storage period. The results are shown in Table 20. The processing factors are summarized in Table 21.

Table 20 Azoxystrobin residues in processed commodities of sorghum, potatoes and coffee

RAC, country, year	Application			PHI, Days	Commodity	Residues mg/kg	Report, Syngenta File
	Form	kg ai/ha	No				
Sorghum, USA, 2004, Olton, TX	SC	0.27 0.28 0.28	3	13	Grain Aspirated grain fraction	2.1 106	T002036-03, SC-FR-04-5034
Coffee, Guatemala, 2011	SC	0.75	3	14	Green beans (RAC) ^a Green beans (RAC) ^b Roasted beans Instant coffee	< 0.01, 0.016 < 0.01 0.01 0.017	TK0046957, A12910C_50004
Potatoes, USA, Idaho, 2009	SC	0.45 g ai/100 kg	1	0	Tuber (RAC) Flakes	0.94 < 0.01	TK0003297, ICI5504_50552

RAC, country, year	Application			PHI, Days	Commodity	Residues mg/kg	Report, Syngenta File
	Form	kg ai/ha	No				
					Chips Wet peel	0.011 0.85	

^a Dry green coffee bean sample collected from the field.

^b Dry green coffee bean sample collected from the bulk sample prior to processing.

Table 21 Summary of processing factors for azoxystrobin residues

RAC	Processed commodity	Calculated processing factors	Best estimate
Sorghum	Aspirated grain fraction	50	50
Potatoes	Flakes	< 0.011	< 0.011
	Chips	0.012	0.012
	Wet peel	0.904	0.904
Coffee	Roasted coffee beans	<1, (0.625) ^a	0.625
	Instant coffee	1.7, (1.06) ^a	1.06

^a Calculation based on RAC with residues of 0.016 mg/kg

APPRAISAL

Azoxystrobin was first evaluated for toxicology and residues by the JMPR in 2008. The Meeting derived an ADI of 0–0.2 mg/kg bw per day, decided that an ARfD was unnecessary and concluded that the residue definition for plant and animal commodities for compliance with MRL values and for consumer risk assessment was parent azoxystrobin. The compound was re-evaluated for residues by the JMPR in 2011 and 2012.

Azoxystrobin was listed by the Forty-fourth Session of the CCPR for the review of additional MRLs by the JMPR in 2013. The Meeting received information on GAP and residue supervised trials data on pulses, potatoes, coffee beans, barley, oats and sorghum.

Methods of residue analysis

The Meeting received recovery data on analytical methods for coffee beans. After extraction with ethyl acetate, the residues were determined by LC-MS/MS with an LOQ of 0.01 mg/kg.

Results of supervised residue trials on crops

Most trial designs used replicate plots. If two field samples were taken or results of two replicate plots were submitted, the mean value was calculated. From two trials carried out side-by-side the higher residues was chosen.

Pulses

The 2008 JMPR estimated a maximum residue level for azoxystrobin in soya beans, dry of 0.5 mg/kg and an STMR of 0.06 mg/kg. The 2008 assessment based on the US GAP for soya beans at 6 × 0.28 kg ai/ha and a PHI of 14 days.

The use pattern in Germany for field peas, field beans and lupins is one to two applications at 0.25 kg ai/ha, with a spray interval of 14–28 days and a PHI of 35 days. The GAP in France is two foliar applications applied at 0.2–0.25 kg ai/ha with a spray interval of 14 days and a PHI of 35 days for dry peas (including chickpeas), 42 days for dry beans and lupins and 28 days for lentils.

Eight European trials (2 × UK, 4 × France, 2 × Italy) on dry beans were treated twice with 0.2–0.25 kg ai/ha. One additional French trial was treated with 0.13 + 0.2 kg ai/ha. The residues were in dry beans at PHIs of 26–36 days < 0.01 mg/kg (9).

Twenty trials were conducted on dry peas in the UK and in France matching the French and German GAPs. Azoxystrobin was applied twice at a rate of 0.2–0.25 kg ai/ha with a spray interval of 14 days. Samples of dry pea seed were collected at normal commercial harvest at PHIs of 30–45 days. If results of two replicate plots were submitted, the mean value was calculated. From two trials carried out side-by-side the higher residues were chosen for evaluation. The residues (n=20) were < 0.01 (8), 0.01 (5), 0.015, 0.015, 0.02, 0.025, 0.03, 0.03 and 0.065 mg/kg.

The Meeting estimated a maximum residue level of 0.07 mg/kg and an STMR 0.01 mg/kg for azoxystrobin residues in pulses, dry except soya beans.

Potato

The 2008 JMPR estimated a maximum residue level for azoxystrobin in root and tuber vegetables of 1 mg/kg, an STMR of 0.23 mg/kg and a highest residue of 0.45 mg/kg. The 2008 assessment based on the US GAP for root vegetables at 6×0.37 kg ai/ha.

Azoxystrobin is registered in the USA for one post-harvest application at 0.49 g ai/100 kg tubers. Six trials were submitted with one application of 0.44–0.50 g ai/100 kg tubers. Samples were taken directly after treatment. In three trials, stored tubers were analysed also (0–59; 0–61 and 0–231 days after treatment). The maximum residues from samples taken after treatment and after storage were 1.0, 1.5, 2.3, 2.3 and 3.8 mg/kg.

The current Meeting estimated for azoxystrobin residues in potato a maximum residue level of 7 mg/kg Po and an STMR of 2.3 mg/kg. The previous recommendation of 1 mg/kg azoxystrobin for root and tuber vegetables was withdrawn. For root and tuber vegetables, except potatoes, the Meeting confirmed the previous recommendation.

Barley and oats

The 2008 JMPR estimated a maximum residue level for azoxystrobin in barley and oats of 0.5 mg/kg and an STMR of 0.08 mg/kg based on the European GAP and residue data.

Azoxystrobin is registered in the USA in barley and oats as foliar spray with 2×0.15 kg ai/ha, a PHI in days for grain was not specified. The recommended use pattern is for a single early season application followed by a single application at 50% to full flag leaf emergence. New residue data were received for barley and oats.

On barley, seven independent supervised trials were conducted. In each trial, azoxystrobin was applied twice at a rate of 0.15 kg ai/ha. The residues in grains were 0.014, 0.019, 0.037, 0.05, 0.19, 0.31 and 0.99 mg/kg.

On oats, twelve supervised trials were submitted treated at a rate of 0.15 kg ai/ha. The residues in grains were 0.013, 0.028, 0.028, 0.028, 0.048, 0.049, 0.053, 0.058, 0.06, 0.12, 0.12 and 0.63 mg/kg.

The Meeting noted that the populations of azoxystrobin residues in grains of barley and oats have similar distributions and can be combined (n=19): 0.013, 0.014, 0.019, 0.028, 0.028, 0.028, 0.037, 0.048, 0.049, 0.05, 0.053, 0.058, 0.06, 0.12, 0.12, 0.19, 0.31, 0.63 and 0.99 mg/kg.

The current Meeting estimated a maximum residue level of 1.5 mg/kg for azoxystrobin residues in barley and oats to replace the previous recommendation (0.5 mg/kg). An STMR value of 0.05 mg/kg for was estimated.

Sorghum

The US GAP for sorghum is 2×0.28 kg ai/ha with a PHI of 14 days. Twelve independent supervised trials were conducted. In each trial, azoxystrobin was applied three times at a rate of 0.28 kg ai/ha with a 7-day application interval. The residues in grains were 0.48, 1.3, 1.4, 1.4, 1.7, 1.8, 1.9, 2.2, 2.3, 2.8, 4.5 and 8.0 mg/kg.

The Meeting estimated a maximum residue level of 10 mg/kg and an STMR of 1.85 mg/kg for azoxystrobin residues in sorghum grain.

Coffee beans

The 2011 JMPR estimated for azoxystrobin residues in coffee beans a maximum residue level of 0.02 mg/kg and an STMR of 0.01 mg/kg based on the Brazilian residue data and Brazilian GAP of 2×0.15 kg ai/ha (interval 90 days) or 3×0.1 kg ai/ha (interval 60 days) and a PHI of 30 days.

The GAP in Columbia is registered as 3×0.15 kg ai/ha (interval 45 days) and a PHI of 15 days. Seven new trials have been conducted in Brazil, Colombia and Guatemala in 2010/2011 to support the registered use pattern in Colombia. Azoxystrobin was applied three times at a rate of 0.15 kg ai/ha. The residues in green coffee beans were < 0.01 (4), 0.01, 0.01 and 0.015 mg/kg at a PHI of 14–15 days.

Four further Brazilian trials conducted in 2006/2007 and matching the Colombian GAP were reported by the 2011 JMPR (trials M06024, Roncato, 2008). After application of 3×0.15 kg ai/ha and a 14 day PHI, the azoxystrobin residues were < 0.01 mg/kg (4).

In total, the residues of azoxystrobin in green coffee beans matching Colombian GAP were, in rank order (n=11): < 0.01 (8), 0.01, 0.01 and 0.015 mg/kg.

Based on residues data matching Colombian GAP, 0.02 mg/kg were calculated as maximum residue level using the OECD MRL calculator. The Meeting noted that the calculated value is very close to the highest level of 0.015 mg/kg (mean of < 0.01 and 0.02 mg/kg from 2 replicated plots) and proposed rounding up to 0.03 mg/kg.

The current Meeting estimated a maximum residue level of 0.03 mg/kg and an STMR of 0.01 mg/kg for azoxystrobin residues in coffee beans to replace the previous recommendation.

Legume animal feeds

The use pattern in Germany for field peas, field beans and lupins is one to two applications at 0.25 kg ai/ha with a spray interval of 14–28 days. The GAP in France is for dry peas (including chickpeas), dry beans, lentils and lupins two foliar applications at 0.2–0.25 kg ai/ha with an interval of 14 days.

Pea hay or pea fodder (dry)

Twenty trials were conducted on dry peas in the UK and France matching the GAP of France and Germany. Azoxystrobin was applied twice at a rate of 0.2–0.25 kg ai/ha with a spray interval of 14 days. Samples of pea fodder were collected at normal commercial harvest, PHIs of 30–45 days.

Residues found, on fresh weight basis, were (n=20): 0.34, 0.61, 0.62, 0.63, 1.0, 1.4, 1.6, 1.8, 1.8, 2.0, 2.1, 2.3, 3.6, 3.7, 3.8, 3.9, 4.0, 4.8, 7.2 and 18 mg/kg.

The residue values, on dry weight basis, were (88% dry matter): 0.39, 0.69, 0.70, 0.72, 1.1, 1.6, 1.8, 2.0, 2.0, 2.3, 2.4, 2.6, 4.1, 4.2, 4.3, 4.4, 4.5, 5.5, 8.2 and 20 mg/kg.

The Meeting estimated a maximum residue level of 20 mg/kg for azoxystrobin residues in pea hay or fodder (dry) on dry weight basis. The estimated median and highest residue values were 1.9 mg/kg and 18 mg/kg on fresh weight basis or 2.35 mg/kg and 20 mg/kg, respectively on dry weight basis.

Pea vines (green)

Pea vines (green) aren't in international trade and an MRL is not necessary. Nevertheless, the commodity is used as animal feed and the estimation of an STMR and a highest residue values is requested.

In 18 trials conducted on peas in the UK and France matching the GAP of France and Germany for peas (dry), pea vines were sampled. Azoxystrobin was applied twice at a rate of 0.2–0.25 kg ai/ha with a spray interval of 14 days. The highest residue values of pea vines samples

collected at PHIs of 2 to 30 days after treatment were selected for the evaluation. The residues were on fresh weight basis (n=18): 0.89, 1.3, 1.4, 1.5, 1.8, 2.6, 3.1, 3.1, 3.3, 3.4, 4.1, 4.5, 4.8, 4.8, 4.9, 5.6, 5.8 and 9.4 mg/kg.

The Meeting estimated a median and a highest residue of 3.35 and 9.4 mg/kg (fresh weight) equivalent to 13.4 and 37.6 mg/kg (25% dry weight basis) for azoxystrobin residues in pea vines.

Straw and fodder (dry) of cereal grains

Based on GAP and residue data for barley, oats, rice, rye, triticale and wheat straw, the 2008 JMPR estimated a maximum residue level for straw and fodder of cereal grains, except maize of 15 mg/kg, an STMR of 1.7 mg/kg and a highest residue value of 11 mg/kg on dry weight basis.

Azoxystrobin is registered in the USA in barley and oats as foliar spray with 2×0.15 kg ai/ha and a 7-days PHI for forage and hay. New trials are available for barley straw, oats straw, barley hay and oats hay matching the US GAP. The straw samples were taken at grain harvest 16 – 49 days after treatment. Samples of hay were taken 6 - 7 days after treatment.

The residues in barley straw on fresh weight basis (n=7) were 0.18, 0.28, 0.36, 0.70, 2.6, 3.3 and 3.5 mg/kg; this is equivalent to 0.20, 0.31, 0.40, 0.79, 2.9, 3.7 and 3.9 mg/kg (dry weight, based on 89% dry matter).

The residues in oats straw on fresh weight basis (n=12) were: 0.074, 0.075, 0.088, 0.15, 0.30, 0.31, 0.35, 0.62, 0.70, 0.73, 0.88 and 1.3 mg/kg; this is equivalent to 0.082, 0.083, 0.098, 0.17, 0.33, 0.34, 0.39, 0.69, 0.78, 0.81, 0.98 and 1.4 mg/kg (dry weight, based on 90% dry matter).

The residues in barley hay on fresh weight basis (n=7) were: 0.46, 0.69, 0.76, 0.84, 2.1, 3.2 and 3.7 mg/kg; this is equivalent to 0.52, 0.78, 0.86, 0.95, 2.4, 3.6 and 4.2 mg/kg (dry weight, based on 88% dry matter).

The residues in oats hay on fresh weight basis (n=12) were: 0.20, 0.27, 0.53, 0.66, 0.89, 1.1, 1.3, 2.2, 3.0, 3.1, 3.2 and 3.4 mg/kg; this is equivalent to 0.22, 0.30, 0.59, 0.73, 0.99, 1.2, 1.4, 2.4, 3.3, 3.4, 3.6 and 3.8 mg/kg (dry weight, based on 90% dry matter).

The Meeting noted that the residues in straw and fodder of barley and oats resulting of azoxystrobin treatment according to US GAP were covered by the MRL recommendation of the 2008 JMPR for straw and fodder of cereal grains, except maize of 15 mg/kg (90% dry matter). The estimated median residue value was 1.5 mg/kg (fresh weight) equiv. to 1.7 mg/kg (dry weight) and the highest value 9.9 mg/kg (fresh weight) equiv. to 11 mg/kg (dry weight). A new estimation of a maximum residue level, a median and a highest residue was not necessary. Because residue data on sorghum show higher residues, the commodity “straw and fodder of cereal grains, except maize” should be revised to “Straw and fodder (dry) of cereal grains, except maize and sorghum”. The previous recommendation for “Straw and fodder of cereal grains, except maize” should be withdrawn.

The US GAP for sorghum is 2×0.28 kg ai/ha with a PHI of 14 days. Twelve trials on sorghum stover, dry, matching the US GAP were submitted. The residues on fresh weight basis (n=12) were: 0.39, 0.53, 0.71, 2.4, 2.6, 3.7, 4.0, 4.5, 4.8, 5.3, 10.5 and 14.5 mg/kg; this is equivalent to 0.44, 0.60, 0.81, 2.7, 2.95, 4.2, 4.5, 5.1, 5.5, 6.0, 12 and 16 mg/kg (dry weight, based on 88% dry matter).

The Meeting estimated maximum residue level of 30 mg/kg for azoxystrobin residues in sorghum straw and fodder, dry on dry weight basis. The estimated median residue value was 3.85 mg/kg (fresh weight) equiv. to 4.35 mg/kg (dry weight) and the highest residue 14.5 mg/kg (fresh weight) equiv. to 16 mg/kg (dry weight).

Cereal forage (green)

Residue data were received for oat and sorghum forage (green). Because these aren't commodities in international trade, MRLs are not necessary. Nevertheless, the commodities are used as animal feed and the estimation of STMRs and highest residue values is requested.

Oats forage (green)

Azoxystrobin is registered in the USA in oats as foliar spray with 2×0.15 kg ai/ha and a 7-days PHI for forage and hay. Twelve trials are available for oats forage matching the US GAP. The residues on fresh weight basis (n=12) were: 0.11, 0.20, 0.26, 0.44, 0.52, 0.78, 0.86, 0.95, 1.0, 1.4, 1.6 and 2.0 mg/kg.

The 2008 JMPR estimated a median residue value of 1.7 mg/kg and a highest value of 4.0 mg/kg for oats forage (fresh weight). The current Meeting noted that the residues in oats forage resulting of azoxystrobin treatment according to US GAP are covered by the estimation of the 2008 JMPR.

Sorghum forage (green)

The US GAP for sorghum is 2×0.28 kg ai/ha with a PHI of 14 days for grain. Supervised residue trials conducted included residue data for forage from 3 to 21 days after treatment. The residues on fresh weight basis (n=14) were: 0.25, 0.27, 0.29, 0.32, 1.5, 1.5, 1.6, 1.6, 1.7, 1.9, 5.6, 7.2, 11 and 12 mg/kg.

The Meeting estimated a median and a highest residue value of 1.6 and 12 mg/kg (fresh weight) equivalent to 4.6 and 34 mg/kg (35% dry weight basis) for azoxystrobin residues in sorghum forage (green).

Fate of residues during processing

The Meeting received information on the fate of azoxystrobin residues during the processing of potatoes to flakes, chips and wet peel, sorghum to aspirated grain fractions and green coffee to roasted and instant coffee.

The processing factors obtained in the processing studies and estimated STMR-P values are summarized below.

Raw agricultural commodity (RAC)		Processed commodity		
Name	STMR, mg/kg	Name	Processing factor	STMR-P, mg/kg
Potato	2.3	Flakes	< 0.011	0.0253
		Chips	0.012	0.0276
		Wet peel	0.904	2.08
Barley	0.05	Barley malt	0.10 ^a	0.005
		Barley spent grain	0.15 ^a	0.0075
		Beer	0.03 ^a	0.0015
Sorghum	1.85	Aspirated grain fractions	50	92.5
Coffee beans, green	0.01	Roasted coffee beans	0.625	0.006
		Instant coffee	1.06	0.0106

^a Estimated by JMPR in 2008

Farm animal dietary burden

The 2013 JMPR evaluated residues of azoxystrobin in the following animal feed items: pulses, potato, cereal grains (barley, oats, sorghum), legume animal feeds as well as straw, fodder and forage of cereal grains which are listed in the OECD feeding table.

Estimated maximum and mean dietary burdens of farm animals

Dietary burden calculations based on the feed items evaluated by the JMPR in 2008 and 2013 for beef cattle, dairy cattle, broilers and laying poultry as presented in Annex 6. The calculations were made according to the livestock diets, in the OECD table, from Australia, the EU, Japan and US-Canada. The following table below shows the values calculated by the 2008 JMPR and by the current Meeting.

	Livestock dietary burden, azoxystrobin, ppm of dry matter diet (calculation 2008/2013)							
	Japan		US-Canada		EU		Australia	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	-/0.96	-/0.96	34/17	15/12	55/61	19/25	58/72	32/51 ^c
Dairy cattle	-/16.3	-/2.97	33/30	16/12	72 ^a /74	27 ^b /29	39/45.5	20/20
Poultry – broiler	-/1.4	-/1.4	0.44/1.7	0.44/1.7	0.62/2.2	0.40/1.9	0.59/1.7	0.59/1.7
Poultry – layer	-/1.4	-/1.4	0.44/1.7	0.44/1.7	23 ^d /21	9.1 ^e /9.5	0.59/1.7	0.59/1.7

^a Highest maximum beef or dairy cattle burden suitable for MRL estimates for mammalian meat, edible offal and milk

^b Highest mean dairy cattle burden suitable for STMR estimates for milk

^c Highest mean beef or dairy cattle burden suitable for STMR estimates for mammalian meat and edible offal

^d Highest maximum poultry broiler or layer burden suitable for MRL estimates for poultry meat and eggs

^e Highest mean poultry broiler or layer burden suitable for STMR estimates for poultry meat and eggs

Animal commodity residue levels

The Meeting noted that the new estimation did not result in a significant change of the dietary burdens of farm animals, except the mean burden for beef cattle what increased from 32 ppm in 2008 to 51 ppm in 2013 (factor 1.59).

The 2008 JMPR calculated for a dietary burden of 32 ppm mean residues of 0.013 mg/kg in liver, < 0.01 mg/kg in kidney and 0.01 mg/kg in fat. The estimated STMR values were 0.01 mg/kg for meat (fat) and edible offal from mammals other than marine mammals.

The table below shows the recalculation of the STMR values for meat (fat) and edible offal for mammals, other than marine mammals based on the results of the cattle feeding studies evaluated by the 2008 JMPR and the new dietary burden calculation.

	Mean estimated azoxystrobin concentrations (STMR, mg/kg)			
Beef cattle	Muscle	Liver	Kidney	Fat
Dietary burden (51 ppm)	< 0.01	0.02	< 0.01	0.015
Feeding level [25 ppm]	< 0.01	< 0.01	< 0.01	< 0.01
Feeding level [75 ppm]	< 0.01	0.03	0.01	0.02

The current Meeting calculated mean residues of 0.02 mg/kg in liver and < 0.01 mg/kg in kidney, < 0.01 mg/kg in muscle and 0.015 mg/kg in fat. The estimated STMR values were 0.02 mg/kg for edible offal (mammalian), 0.01 mg/kg for muscle and 0.015 mg/kg for fat.

The previous MRL recommendations for animal commodities and the STMRs for whole milk, milk fat, poultry meat (fat), poultry edible offal and eggs were maintained.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

*Definition of the residue (for compliance with the MRL and for estimation of dietary intake)
for plant and animal commodities: azoxystrobin.*

The residue is fat-soluble.

CCN	Commodity name	MRL, mg/kg		STMR or STMR-P mg/kg
		Proposed	Previous	
GC 0640	Barley	1.5	0.5	0.05
SB 0716	Coffee beans	0.03	0.02	0.01
GC 0647	Oats	1.5	0.5	0.05
AL 0072	Pea hay or fodder (dry) ^a	20 ^a		1.9 ^b
VR 0589	Potato	7 Po		2.3 Po
VD 0070	Pulses, dry, except soya beans	0.07		0.01
VR 0075	Root and tuber vegetables	W	1	0.23
VR 0075	Root and tuber vegetables, except potato	1		0.23
GC 0651	Sorghum	10		1.85
AS 0651	Sorghum straw and fodder, dry	30 ^a		3.85 ^b
AS 0081	Straw and fodder of cereal grains, except maize and sorghum	15 ^a		1.5 ^b
AS 0081	Straw and fodder of cereal grains, except maize	W		

^a Dry matter basis

^b Fresh weight basis

Dietary intake only

CCN	Commodity name	Median/STMR or STMR-P, mg/kg	Highest residue, mg/kg
	Barley malt	0.005	
	Barley spent grain	0.0075	
	Beer	0.0015	
	Coffee beans, roasted	0.006	
	Instant coffee	0.0106	
MO 0105	Edible offal (Mammalian)	0.02	
MF 0100	Mammalian fats (except milk fats)	0.015	
MM 0095	Meat (from mammals other than marine mammals)	0.01 (muscle) 0.015 (fat)	
AL 0072	Pea hay or fodder (dry) ^a	1.9 ^b	18 ^b
AL 0528	Pea vines (green)	3.35 ^b	9.4 ^b
	Potato flakes	0.0253	
	Potato chips	0.0276	

CCN	Commodity name	Median/STMR or STMR-P, mg/kg	Highest residue, mg/kg
	Potato wet peel	2.08	
	Sorghum, aspirated grain fractions	92.5	
AF 0651	Sorghum forage (green)	1.6 ^b	12 ^b
AS 0651	Sorghum straw and fodder, dry	3.85 ^b	14.5 ^b

^b Fresh weight basis

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDIs) of azoxystrobin were calculated for the 13 GEMS/Food cluster diets using STMRs and STMR-Ps estimated by the JMPR in 2008, 2011, 2012 and 2013. The results are shown in Annex 3 of the 2013 JMPR Report.

The ADI is 0–0.2 mg/kg bw and the calculated IEDIs were 2–10% of the maximum ADI. The Meeting concluded that the long-term intake of residues of azoxystrobin resulting from the uses considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The 2008 Meeting decided that an ARfD for azoxystrobin is unnecessary and concluded that the short-term intake of residues resulting from the use of azoxystrobin is unlikely to present a public health concern.

REFERENCES

Code	Author	Year	Title, Institute, Report reference
04-0421	Benazeraf, L	2005	Azoxystrobin (ICI5504) and Cyproconazole (SAN619): Residue Study in or on Pulses (Peas) in France (South). Unpublished.
04-0422	Benazeraf, L	2005	Azoxystrobin (ICI5504) and Cyproconazole (SAN619): Residue Study in or on Pulses (Peas) in France (North) and in United Kingdom). Unpublished.
05-0415	Bour, D	2006	Azoxystrobin (ICI5504) and cyproconazole (SAN619): Residue study on dried beans in the United Kingdom and France (North). Unpublished.
05-0607	Bour, D	2006	Azoxystrobin (ICI5504) and cyproconazole (SAN619): Residue study on dried beans in Southern France. Unpublished.
M02037	Boscolo, P, Francisco, E & Nascimento, F	2003	Priori Xtra—Residues of Azoxystrobin, R230310 and Cyproconazole in coffee—Brazil 2002–03. Unpublished.
M06024	Roncato, C, Imamura, P & Silva, M	2008	Priori Xtra—Residues of Azoxystrobin, R230310 and Cyproconazole in coffee—Brazil, 2006-07. Unpublished.
PLMV 027 039/2010	Ono, T	2011	Analytical method and validation: Magnitude of residues of thiamethoxam, CGA 322704, cyproconazole, azoxystrobin, R230310 and chlorantraniliprole in coffee—Colombia 2010. Unpublished.
RF 027 039 10B	Ono, T	2011	Verdadero 600 WG, Amistar Ztra and Voliam Flexi—Magnitude of residues of thiamethoxam + CGA322704, cyproconazole, azoxystrobin + R230310 and chlorantraniliprole in coffee—Colombia 2010. Unpublished.
RJ2286B	Sapiets, A, Picard, JM & Farrelly, E	1998	Azoxystrobin and Flutriafof: Residue Levels in Peas from Trials Conducted in France During 1996. Unpublished.
RJ2390B	Sapiets, A	1997	Azoxystrobin and Flutriafof: Residue Levels in Field Peas from a Trial Conducted in the United Kingdom During 1996. Unpublished.
RJ2521B	Sapiets, A	1998	Azoxystrobin and Flutriafof: Residue Levels in Peas from Trials Conducted in the United Kingdom during 1997. Unpublished.
RJ2548B	Sapiets, A, Lister, N &	1998	Azoxystrobin/Flutriafof: Residue levels in Peas from Trials Conducted

	Picard, JM		in France during 1997. Unpublished.
RJ2845B	Lister, N & Bonfanti, F	1999	Azoxystrobin: Residue Levels in Beans from Trials Carried out in Italy during 1998. Unpublished.
RJ2969B	Gill, JP & Volpi, E	2000	Azoxystrobin: Residue Levels in Dried Beans from Trials Carried out in Italy During 1999. Unpublished.
TK0003297	Hampton, M	2011	Azoxystrobin + Fludioxonil + Difenoconazole—Magnitude of the Residue on Potato Following Post-Harvest Treatment. Unpublished.
TK0046957	Mickelson, K	2012	Azoxystrobin and Cyproconazole (A12910C)—Magnitude of the Residues in or on Coffee. Unpublished.

BENTAZONE (172)*First draft prepared by Dr Yibing He,**Department of Science and Education, Ministry of Agriculture, China***EXPLANATION**

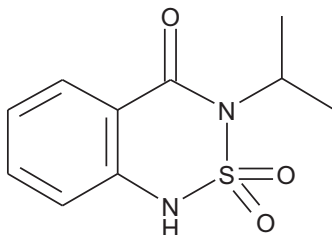
Bentazone, a post-emergence herbicide, was originally evaluated by the JMPR in 1991 and re-evaluated for residues and toxicity several times up to 2004. It was reviewed as part of the periodic re-evaluation programme of CCPR on toxicity by the 2012 JMPR. Bentazone is a selective herbicide which is used at post emergence applications to control dicotyledonous weeds in agriculture, horticulture, ornamentals and amenity grasslands. The mode of action is based primarily on an irreversible blockage of the photosynthetic electron transport and in further consequence the inhibition of photosynthesis at photo system II. As a result of this reaction, CO₂ assimilation is suppressed and after a short period of growth stagnation, the plant dies.

At the 43rd Session of the CCPR (REP 12/PR, Appendix VIII), bentazone was scheduled for periodic residue review by the 2013 JMPR. The Meeting received information on physical and chemical properties, metabolism, environmental fate, analytical methods and freezer storage stability, national registered use patterns, as well as supervised trials, processing studies and livestock feeding studies.

IDENTITY

ISO Common name	bentazone
Chemical name	
IUPAC name	3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide
CAS name	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide
CAS Registry Number	25057-89-0
CIPAC Number	366
Synonyms and trade names	
Manufacturer's codes	51929

Structural formula



Molecular formula	C ₁₀ H ₁₂ N ₂ O ₃ S
Molecular weight	240.3 g/mol
Minimum content of ai	

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient		Ref
Appearance (purity 99.9%)	Solid, white crystals	Tuerk, W, 1994, 1994/ 11115
Odour	odourless	Tuerk, W, 1994, 1994/11193

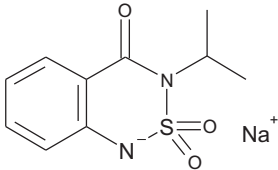
Pure active ingredient		Ref
Vapour pressure (purity 99.6%):	4.9×10^{-4} Pa at 20 °C	Kaestel, R, 1999, 1999/11055
Henry's law constant	2.108×10^{-9} kPa.m ³ . mol ⁻¹ at 20 °C	Brem, G, 2000, 2000/1023935
Boiling point (purity 99.8%)	157 °C (onset temperature)	Kroehl, T, 2011, 2011/1074521
Melting point (purity 99.8%)	139 °C (onset temperature)	Kroehl, T, 2011/2011/1074521
Octanol-water partition coefficient at 20 °C: (purity 99.6%)	log P _{ow} = 1.49 in deionized water log P _{ow} = 1.55 at pH 4 log P _{ow} = -0.94 at pH7 log P _{ow} = -1.32 at pH9	Daum, A, 2000, 2000/1018475
Solubility in water at 20 °C (purity 99.8%):	pH 7: 0.57 g/L demineralized pH 4: 3.0 g/L buffered pH 7: 7.7 g/L buffered pH 9: 17 g/L buffered	Class, T, 2011, 2011/1074524
Relative density (purity 99.8%)	1.405 g/cm ³ 20 °C	Kroehl, T, 1994, 1994/10783
Dissociation constant in water (purity 99.6%)	pK _a = 3.51 at 20 °C	Daum, A, 2000, 2000/1013485
	The partition coefficient of the non-ionized form of bentazone was calculated from the pKa for the pH range from pH 1–6. The calculations show, that bentazone is completely non-ionized at pH values below 1.2 and completely ionized at pH values above 5.8.	Daum, A, 2002, 2002/1007049
Hydrolysis rate at pH 4, 7 and 9 under sterile and dark conditions	At 25 °C bentazone is hydrolytically stable at pH 5, 7 and 9.	Panek, E, 1986, 1986/5018
Direct phototransformation in sterile water using artificial light	DT ₅₀ parent < 5.5 d (tested at pH 5, 7, and 9) metabolites = Peak B 27%, 18%, 9% at pH 5, 7, 9 respectively Peak C 20%, 25%, 23% at pH 5, 7, 9 respectively all others ≤ 6%	Singh, M, 2011, 2011/7002318
Surface tension, 20 °C (99.8%)	Surface tension, concentration (w/w) in pure water: 0.5%: 69.2 mN/m 2.0%: 70.0 mN/m	Kroehl, T, 1994, 1994/10783
Quantum yield efficiency (purity 97.3%)	Quantum Yield = 7.7×10^{-3} mol/Einstein in aqueous photolysis at pH 5	Singh, M, 2011, 2011/7002318

Technical material (purity 96.9%)

Melting point

Solubility in organic solvents at 20 °C:	Acetone	> 300 g/L	Class, T, 2011, 2011/1074525
	Dichloromethane	≥ 250 g/L	
	Ethyl acetate	> 300 g/L	
	n-Hexane	0.11 g/L	
	Methanol	> 300 g/L	
	Toluene	24.5 g/L	

IDENTITY (Bentazone sodium)

ISO Common name	Bentazone sodium
Chemical name	
	IUPAC name sodium 3-isopropyl-3 <i>H</i> -2,1,3-benzothiadiazin-4-olate 2,2-dioxide
	CAS name 3-(1-methylethyl)-1 <i>H</i> -2,1,3-benzothiadiazin-4(3 <i>H</i>)-one 2,2-dioxide sodium salt
CAS Registry Number	50723-80-3
CIPAC Number	
Structural formula	
Molecular formula	C ₁₀ H ₁₁ N ₂ NaO ₃ S
Molecular weight	262.3 g/mol

Formulations

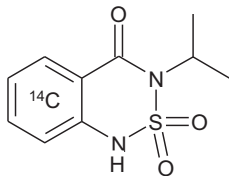
Bentazone is available in various formulations such as the following formulations:

Formulation	Products
Soluble concentrate	480 g/L SL, 600 g/L SL
Suspension concentrate	150 g/L SC, 200 g/L SC, 480 g/L SC
Water soluble granules	870 g/kg SG

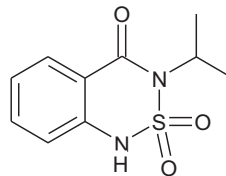
METABOLISM AND ENVIRONMENTAL FATE

The Meeting received information on animal metabolism, plant metabolism and environmental fate studies using [¹⁴C] bentazone (Phenyl Label) and unlabelled bentazone.

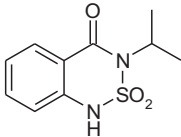
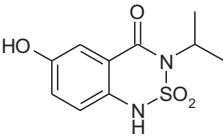
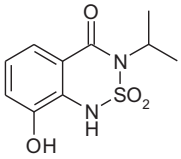
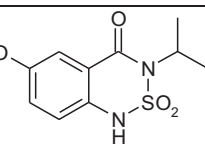
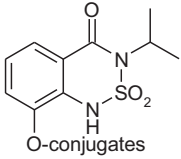
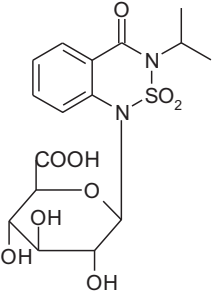
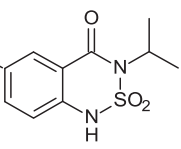
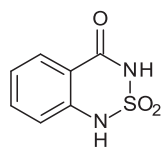
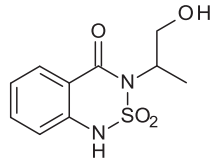
¹⁴C-labelled bentazone

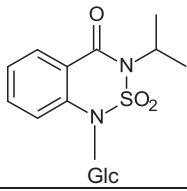
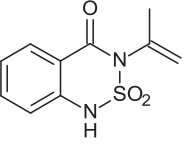
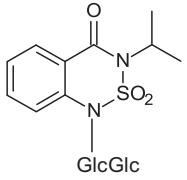
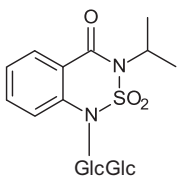


Unlabelled bentazone



Structures, names and codes for bentazone and its metabolites in metabolism and environmental fate studies, and MCPB in a plant metabolism study are summarized below.

Code Name	Chemical Name	Metabolite Identity	Matrix where found
Bentazone Parent	3-Isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide		Potato, Rice, Maize Soya bean, Wheat, Hen, Goat, Rat
6-OH-bentazone (M351H001)	3-Isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one-6-hydroxy-2,2-dioxide		Hen ^a Goat ^b Rat
8-OH-bentazone (M351H002)	3-Isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one-8-hydroxy-2,2-dioxide		Soya bean Goat ^b Rat
Bentazone-6-O-glucoside (M351H013)	–	conjugates- 	Potato, Maize, Rice Soya bean, Wheat
Bentazone-8-O-glucoside (M351H017)	–	 O-conjugates	Soya bean, Wheat
Bentazone-N-glucuronide (Metabolite A, M351H004)	3-isopropyl-1-methyl-2,2-dioxo-2,1,3-benzothiadiazin-4-one		Hen, Goat Rat (urine)
M351H003	3-isopropyl-6-methoxy-2,2-dioxo-1H-2,1,3-benzothiadiazin-4-one	GlcA— 	Rat (urine)
M351H005	2,2-dioxo-1H-2,1,3-benzothiadiazin-4-one		Rat (urine)
M351H006	3-(2-hydroxy-1-methyl-ethyl)-2,2-dioxo-1H-2,1,3-benzothiadiazin-4-one		Rat (faeces)

Code Name	Chemical Name	Metabolite Identity	Matrix where found
M351H007	3-isopropyl-1-methyl-2,2-dioxo-2,1,3-benzothiadiazin-4-one		Rat (urine)
M351H008	3-isopropenyl-2,2-dioxo-1H-2,1,3-benzothiadiazin-4-one		Rat (urine)
M351H014 and isomers: M351H015-016, -018-019, -022	—		Wheat
M351H020 and M351H021	—		Wheat

^a Excreta, after 6-OH bentazone dosing

^b Urine, after 6-OH bentazone or 8-OH-bentazone dosing

Animal metabolism

The Meeting received animal metabolism studies with bentazone in lactating goats and laying hens.

Lactating goats

[¹⁴C] Bentazone

Three lactating goats were dosed orally with [¹⁴C] bentazone once daily for 5 or 8 consecutive days at the nominal equivalent rate of 3 (goat A) or 50 (goat B1 and B2) mg ai/kg bw, corresponding to residue levels in feed of 123 (goat A), 1420 (goat B1) and 1580 (goat B2) mg ai/kg animal feed respectively (Giese, U, 1990, 1992/10161; Großhans, F, 1991, 1991/11137). During the administration period blood, milk, urine and faeces were collected. 24 hours after the last administration the goat was sacrificed and liver, kidney, muscle, fat, bile and GIT were obtained. Two further goats were dosed for 8 days with 3 mCi per day corresponding to about 1.7 g of the test substance (nominally 50 mg/kg; 1.42–1.58 g bentazone/kg feed). The animals were sacrificed 4 hours after the last administration and liver, kidney, muscle, fat, bile and GIT of one goat were obtained for determination of radioactivity. Goat B2 was regarded as a reserve animal intended to be used for method development and adaptation work, but it was not included in this study. Samples were stored at -18 °C or below until analysis. Residues were analysed for radioactivity by LSC or combustion/LSC. The amount of the excreta, milk, and edible tissues, and after extraction and liquid-liquid partition they were analysed by TLC and PLC. Metabolites were identified by MS. The results are summarized in Table 1 and Table 2.

Table 1 Total radioactive residues in milk and tissues from lactating goats following administration of [^{14}C] bentazone for 5 or 8 days (Giese, U, 1990, 1992/10161)

Matrix	Goat (3 mg/kg bw)		Goat (50 mg/kg bw)	
	mg eq/kg	% Dose	mg eq/kg	% Dose
Edible tissues and milk				
Milk ^a	0.017	0.005	0.257	0.005
Fat	0.912	0.03	2.960	< 0.005
Muscle	0.017	< 0.005	1.206	0.01
Kidney	0.566	0.01	54.35	0.04
Liver	0.044	0.01	3.790	0.02
Non-edible tissues/samples				
Faeces	1.064	0.62	95.40	5.63
Urine	84.98	91.41	542.3	80.59
Others	4.638	5.035	306.862	12.805
Total		97.3		99.1

^a Elimination in totalTable 2 Characterization and identification of radioactive residues in extras, milk and tissues from lactating goats dosed with [^{14}C] bentazone (Großhans, F, 1991, 1991/11137)

Animals	Goat (3 mg/kg bw)				Goat (50 mg/kg bw)			
	bentazone		metabolite		bentazone		metabolite	
Fraction	mg/kg	TRR%	mg/kg	TRR%	mg/kg	TRR%	mg/kg	TRR%
Urine	162.656	100	–	–	614.237	96.8	–	–
Faeces	1.268	70.7	–	–	43.179	70.5	–	–
Milk am ^a	0.034	70.8	0.002 ^c	4.2	0.155	85.7	–	–
			0.002 ^d	4.2				
Milk pm ^b	0.048	82.7	–	–	0.387	96.1	–	–
Muscle	0.010	71.4	–	–	1.244	97.0	–	–
Fat	1.579	93.7	–	–	2.792	97.9	–	–
Kidney	0.553	90.9	–	–	48.901	97.6	–	–
Liver	0.033	82.6	–	–	3.058	84.4	0.401 ^e	11.1

^a in pooled morning milk.^b in pooled afternoon milk.^c and ^d Minor unknown metabolites.^e Bentazone-N-glucuronide.

– = Not detected.

[^{14}C]-6-hydroxy-bentazone

Two lactating goats were orally dosed daily for 5 or 6 consecutive days with [^{14}C]-6-hydroxy-bentazone, which was uniformly labelled in the ring (specific activity, 1.439 mBq/mg; radiochemical purity, 97.2%) (Giese, U, 1991, 1991/10702; Hafemann, C, 1995, 1995/10011). A goat was administered orally about 1.5 mCi [^{14}C]-6-hydroxy-bentazone per day corresponding to about 84 mg 6-hydroxy-bentazone (nominally 2 mg/kg, 40.5 mg 6-hydroxy-bentazone/kg feed) for 5 consecutive days. During the administration period blood, milk, urine and faeces were collected. 24 hours after the last administration the goat was sacrificed and liver, kidney, muscle, fat, bile and GIT were obtained. Another goat was dosed for 6 days with 3 mCi per day corresponding to about 1.7 g of the test substance (nominally 40 mg/kg; 970 mg 6-hydroxy-bentazone/kg feed). The animal was sacrificed 4 hours after the last administration and liver, kidney, muscle, fat, bile and GIT were obtained for determination of radioactivity. The faeces, urine and milk samples were stored at -18 °C. Residues were analysed for radioactivity by LSC or combustion/LSC. The concentrations of 6-hydroxy-bentazone were too low in goat A to obtain significant radioactivity peaks by chromatography of the extracts. The isolated metabolites in goat B were chromatographically characterized. The results are summarized in Table 3 and Table 4.

Table 3 Total radioactive residues in milk and tissues from lactating goats following administration of [^{14}C]-6-OH-bentazone for 5 or 8 days (Giese, U, 1991, 1991/10702)

Matrix	Goat (2 mg/kg bw)		Goat (40 mg/kg bw)	
	mg eq/kg	% Dose	mg eq/kg	% Dose
Edible tissues and milk				
Milk ^a	0.020	0.030	0.517	0.051
Fat	0.019	0.001	0.623	0.002
Muscle	0.021	0.006	0.343	0.005
Kidney	0.136	0.005	20.72	0.028
Liver	0.017	0.003	0.831	0.009
Non-edible tissues/samples				
Faeces	11.04	15.670	175.52	14.961
Urine	16.13	70.397	198.11	54.913
Others	6.537	8.598	435.165	45.861
Total		94.71		97.79

^a Elimination in totalTable 4 Characterization and identification of radioactive residues in milk, tissues, urine and faeces from lactating goat B (40 mg/kg bw) dosed with [^{14}C]-6-OH-bentazone (Hafemann, C, 1995, 1995/10011)

Fraction	6-OH-Bentazone	Metabolites in different matrices			mg/kg n. i.	(TRR %)	
		Sulphate conj.	Conj.	n. i.		n. i.	n. i.
Urine	246.35(88.8)	19.42 (7.0)	–	1.665 (0.6)	6.658 (2.4)	–	–
Faeces	68.95 (64.7)	–	–	–	–	–	–
Bile	–	–	4.486 (74.4)	1.14 (18.9)	–	–	–
Milk	–	0.225 (42.5)	–	0.026 (4.9)	0.033 (6.2)	0.029 (5.5)	–
Muscle	0.105 (43.69)	0.016 (6.87)	–	0.013 (5.41)	0.022 (9.33)	0.017 (7.01)	–
Fat	0.888 (93.7)	–	–	–	–	–	–
Liver (methanol extract)	0.390 (42.7)	0.304 (33.2)	–	–	–	–	–
Kidney	16.346 (72.8)	1.080 (4.8)	0.493 (2.2)	1.661 (7.4)	1.415 (6.3)	0.779 (3.5)	0.542 (2.4)

n. i. = Not identified.

– = Not detected.

[^{14}C]-8-hydroxy-bentazone

Two lactating goats were orally dosed daily for 5 or 6 consecutive days with [^{14}C]-8-hydroxy-bentazone, which was uniformly labelled in the ring (specific activity, 1.390 mBq/mg; radiochemical purity, 95.4%) (Giese, U, 1991, 1991/10703; Kohl, W, 1995, 1995/10062). A goat was administered orally about 1.5 mCi [^{14}C]-8-hydroxy-bentazone per day corresponding to about 69 mg 8-hydroxy-bentazone (nominally 2 mg/kg, 41.7 mg 8-hydroxy-bentazone/kg feed) for 5 consecutive days. During the administration period blood, milk, urine and faeces were collected. 24 hours after the last administration the goat was sacrificed and liver, kidney, muscle, fat, bile and GIT were obtained. Another goat was dosed for 6 days with 3 mCi per day corresponding to about 1.8 g of the test substance (nominally 40 mg/kg; 731.6 mg 8-hydroxy-bentazone/kg feed). The animal was sacrificed 4 hours after the last administration and liver, kidney, muscle, fat, bile and GIT were obtained for determination of radioactivity. The faeces, urine and milk samples were stored at $-18\text{ }^{\circ}\text{C}$ or below. Residues were analysed for radioactivity by LSC or combustion/LSC. The isolated metabolites in goat B were chromatographically characterized. The results are summarized in Table 5 and Table 6.

Table 5 Total radioactive residues in milk and tissues from lactating goats following administration of [^{14}C]-8-OH-bentazone for 5 or 8 days (Giese, U, 1991, 1991/10703)

Matrix	Goat (2 mg/kg bw)		Goat (40 mg/kg bw)	
	mg eq/kg	% Dose	mg eq/kg	% Dose
Edible tissues and milk				
Milk ^a	0.028	0.069	0.599	0.046
Fat	0.003	0.000	0.303	0.005
Muscle	0.005	0.001	0.523	0.010
Kidney	0.100	0.004	20.392	0.026
Liver	0.005	0.020	2.106	0.018
Non-edible tissues/samples				
Faeces	7.774	13.785	435.76	18.284
Urine	20.98	77.527	415.84	65.041
Others	14.918	7.900	549.025	20.540
Total		99.3		103.97

^a Elimination in total

Table 6 Characterization and identification of radioactive residues in milk, tissues, urine and faeces from lactating goats dosed with [^{14}C]-8-OH-bentazone (Kohl, W, 1995, 1995/10062)

Fraction	8-OH-Bentazone	Metabolites in different matrices			mg/kg n. i.	(TRR %) n. i.	n. i.
		Conjugate	Conjugate	Conjugate			
Goat (2 mg/kg bw)							
Urine day 2	20.905 (100)	–	–	–	–	–	–
day 4	34.015 (100)	–	–	–	–	–	–
Faeces	2.909 (67.2)	–	–	–	–	–	–
Goat (40 mg/kg bw)							
Urine day 2	512.301 (100)	–	–	–	–	–	–
day 4	591.074 (100)	–	–	–	–	–	–
Faeces	96.185 (70.1)	–	–	–	–	–	–
Bile	2.106 (20.6)	6.299 (61.6)	–	–	1.820 (17.8)	–	–
Milk	0.182 (29.2)	0.148 (23.8)	0.060 (9.6)	0.044 (7.1)	–	–	–
Muscle	0.345 (60.5)	0.015 (2.5) ^a	0.014 (2.4) ^a	0.024 (4.3) ^a	0.038 (6.7)	0.006 (1.1)	0.022 (3.9)
Fat	0.270 (82.2)	0.006 (1.9) ^a	0.004 (1.2) ^a	0.006 (1.8) ^a	0.002 (0.5)	0.003 (0.8)	–
Liver	1.742 (69.6)	–	–	–	0.047 (1.9)	0.112 (4.5)	0.025 (1.0)
pronase	0.146 (5.8)	–	–	–	0.087 (3.5)	0.058 (2.3)	–
Kidney	16.851 (95.1)	–	–	–	0.117 (0.7)	0.430 (2.4)	–

^a unknown metabolites.

n. i. = Not identified.

– = Not detected.

Laying hens

[^{14}C]-Bentazone, 6-OH-[^{14}C]-bentazone and 8-OH-[^{14}C]-bentazone were each administered orally by gelatine capsule to separate groups of 10 laying hens (*Gallus gallus domesticus*) once daily for 5 consecutive days at the nominal rate of 10 mg/bird/day (Hawkins, DR, 1988, 1988/0432). The test substance was uniformly labelled in the ring (bentazone: specific activity, 43.68 mCi/mg, radiochemical purity, 99%; 6-OH-bentazone: specific activity, 42.98 mCi/mg, radiochemical purity, 99%; 8-OH-bentazone: specific activity, 40.91 mCi/mg, radiochemical purity, > 99%). The treated hens were separated into six cages of five hens each. Four hens were used as a control group. All birds were sacrificed 6 hours after the final dose. All samples were stored at -15 °C or below until taken for analysis. Radioactivity was measured by liquid scintillation counting (LSC) and the nature of

radioactivity in excreta, eggs and tissues was investigated further. The levels of radioactivity in the tissues and eggs of hens from 6-OH-bentazone and 8-OH-bentazone groups were generally too low for analysis. The results are summarized in Table 7 and Table 8.

Table 7 Total radioactive residues in tissues and excreta from laying hens following administration of [^{14}C]-bentazone and its hydroxylated metabolites for 5 consecutive days at 10 mg/day/bird.

Matrix	[^{14}C]-bentazone		[^{14}C]-6-OH-bentazone		[^{14}C]-8-OH-bentazone	
	mg/kg	% Dose	mg/kg	% Dose	mg/kg	% Dose
Excreta	n.r.	93.6	n.r.	90.2	n.r.	93.1
Egg day 5	0.15	n.r.	0.023	n.r.	0.029	n.r.
Subcutaneous fat	0.11	n.r.	0.008	n.r.	0.028	n.r.
Peritoneal fat	0.064	n.r.	0.002	n.r.	0.004	n.r.
Leg muscle	0.42	n.r.	0.027	n.r.	0.025	n.r.
Breast muscle	0.35	n.r.	0.037	n.r.	0.021	n.r.
Kidneys	3.9	n.r.	0.66	n.r.	1.6	n.r.
Liver	1.1	n.r.	0.13	n.r.	0.23	n.r.
Plasma	4.5	n.r.	0.052	n.r.	0.13	n.r.
Whole-blood	1.4	n.r.	0.040	n.r.	0.11	n.r.

n.r. = Not reported

Table 8 Characterization and identification of radioactive residues in eggs and tissues from hens orally dosed with [^{14}C]-bentazone and its hydroxylated metabolites for 5 consecutive days at 10 mg/day/bird.

Fraction ^b	Excreta		Liver		Breast muscle		Fat		Liver	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
Bentazone										
bentazone	64 (0–24h)	na	84	0.91	100	0.29	100	0.056	100	0.13
	57.5(24–48h)	n.r.								
8-OH-bentazone	– (0–24h)	–	– ^a	–	–	–	–	–	–	–
	– (24–48h)	–	–							
Metabolite A	14.5 (0–24h)	na	16	0.17	–	–	–	–	–	–
	17.5 (24–48h)	na								

^a A minor component corresponding to 8-OH-bentazone was initially detected in these extracts but was not detected after repeat analysis.

^b No detailed information available on 6-OH-bentazone and 8-OH-bentazone administration.

– = Not detected

na = Not available

n.r. = Not reported

Plant metabolism

The Meeting received plant metabolism studies with bentazone on soya beans, rice, maize, green beans, potatoes and wheat.

Soya bean

The metabolism of [^{14}C]-bentazone (uniformly labelled with ^{14}C in the phenyl ring, specific activity, 42.4 $\mu\text{Ci}/\text{mg}$; chemical and radiochemical purity > 99%) was studied in soya bean (variety: Centenial) after single and double applications at 2.24 and 1.68 (1.12) kg/ha (Brown, M, *et al.*, 1987/5079). Forage (foliage) at early and late pre-harvest intervals (PHI), hay and seed samples were collected for metabolism investigations. Radioactivity was measured by liquid scintillation counting (LSC) and the nature of radioactivity in interim and harvest samples was investigated further with TLC and GLC. The results are summarized in Table 9 to Table 12.

Table 9 Soya bean raw agricultural commodities; total radioactive residues after single and double applications of [^{14}C] bentazone

Sample	Application frequency	DAT ^d (second treatment)	TRR ^a mg/kg	ERR ^b mg/kg	%TRR	RRR ^c mg/kg	%TRR
Foliage	1	9	18.5	9.4	51	7.0	38
Foliage	1	36	7.0	3.4	49	3.7	53
Hay	1	93	21.2	0.8	4	20.4	96
Seed	1	93	0.4	0.016	4	0.4	96
Foliage	2	9	17.4	10.8	62	6.3	36
Foliage	2	56 (11)	24.0	14.4	60	12.7	53
Hay	2	93 (48)	79.5	7.2	9	62.6	78.7
Seed	2	93 (48)	1.1	0.06	6	1.0	95

^a Total radioactive residues^b Extractable radioactive residues (here extractant: methanol)^c Residual radioactive residues (non-extracted residues)^d Days after treatment (= PHI pre-harvest interval)

Table 10 Comparison of residues of bentazone and its hydroxy metabolites in soya bean forage quantified by GLC and radio-TLC

	Bentazone residues mg/kg and (% TRR)			
	1 application		2 application	
	2.24 kg ai/ha	ai/ha	1.68 +	1.12 kg ai/ha
Fraction harvested sample	9 days after treatment	36 days after treatment	9 days after 1. treatment	11 (45) days after 2. treatment
GLC analysis				
Bentazone	0.7	—	0.7	5.0
6-OH-bentazone	2.5	0.9	1	1.8
8-OH-bentazone	2.5	2	1.8	2.3
GLC analysis (bentazone + OH-metabolites)	5.7	2.9	3.5	9.1
(% TRR)	(31)	(41)	(20)	(38)
Radio-TLC analysis				
TLC analysis (bentazone + OH-metabolites)	8.3	2.2	8	8.6
(% TRR)	(45)	(31)	(46)	(36)

Table 11 Bentazone residues in soya bean hay by GLC and ^{14}C -equivalents (mg/kg)

	1 application	2 application
	2.24 kg ai/ha	1.68 + 1.12 kg ai/ha
	93 DAT	93 (48) DAT
	GLC analysis	
Bentazone	0.18	3.57
6-OH-bentazone	0.11	0.95
8-OH-bentazone	0.11	0.54
Total GLC	0.4	5.06
Total ^{14}C -equivalents	0.33	4.9

Table 12 Results for the fractionation of non-extracted radioactive residues in soya bean forage and hay

		% total	radioactive	Residues	(TRR)
		2.24 kg ai/ha		1.68 + 1.12 kg	ai/ha
	forage	forage	forage	forage	hay
Fraction	9 day	36 day	9 day	45 day	82 day
Methanol-	38.0	53.0	36.0	53.0	78.7

		% total	radioactive	Residues	(TRR)
		2.24 kg ai/ha		1.68 + 1.12 kg	ai/ha
	forage	forage	forage	forage	hay
Fraction	9 day	36 day	9 day	45 day	82 day
insoluble residues					
Polysaccharide	15.9	21.9	14.5	17.3	34.2
Pectin	0.3	0.4	0.4	0.3	2.0
Hemicellulose I	7.3	10.4	8.9	10.5	17.2
Lignin	1.8	3.1	2.2	2.0	0.6
Solid residues	1.1	2.4	3.2	1.5	3.1
Total extracted	26.9	38.5	29.2	31.6	61.2
Overall loss	11.1	14.5	6.8	21.4	17.5
Average overall loss			14.3		

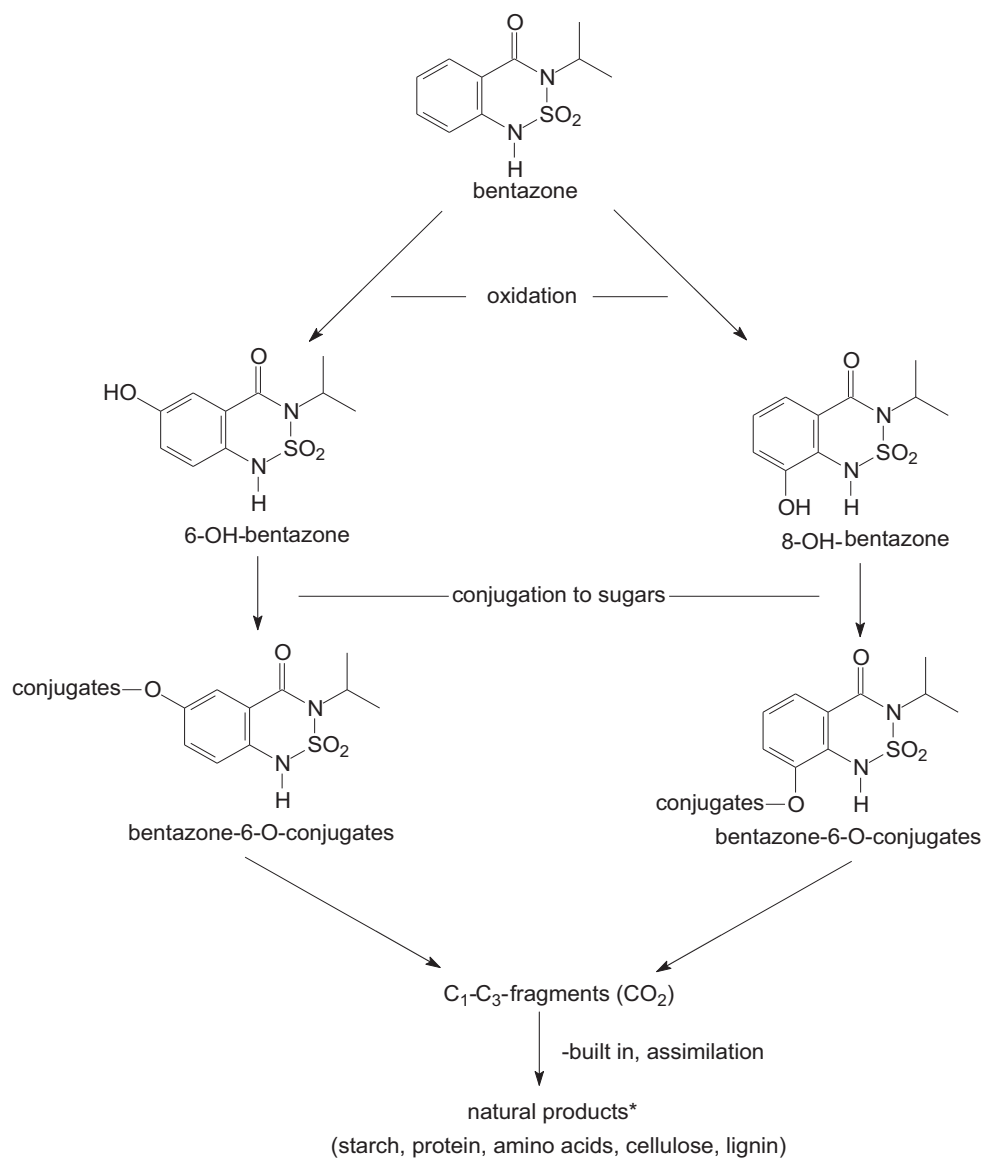


Figure 1 Metabolic pathway of bentazone in soya beans

Rice

A metabolism study in rice (variety: *Nihonbare*) was conducted with [^{14}C] bentazone (uniformly labelled with ^{14}C in the phenyl ring, specific activity, 43.68 $\mu\text{Ci/mg}$; radiochemical purity > 99%) at a rate of 1 kg ai/ha in a single treatment after development of the first rice shoots (Huber, R and Schepers, U, 1987, 1987/0420). Plant parts of the rice were sampled at 0 and 26 days after application of bentazone. In the final harvest samples, the grains, glumes, awns, straw and roots were divided for analysis. Radioactivity was measured by liquid scintillation counting (LSC) and the nature of radioactivity in interim and harvest samples was investigated further with radio-TLC, radio-HPLC and GC-MS. The results are summarized in Table 13 and Table 14.

Table 13 Characterization and distribution of radioactive residues in rice grain

Extract fraction (designation code)	mg/kg	% TRR
Methanolic extract (F3) ^a	0.03	6.6
Minor fractions (F5, F6, F8, F9, F11)	0.02	5.3
Purified fraction (F10)	0.003	0.7
Methanol-extracted residue (F2)	0.43	93.4
Dilute NaOH-protein extract (F16)	0.12	25.4
Protein filtrate (F17)	0.06	12.5
Hydrolysed aqueous phase (F21)	0.05	10.7
Hydrolysed EtOAc phase (F22)	0.01	3.1
Bentazone	0.01	1.5
Protein precipitate (F18)	0.04	9.0
Hydrolysed aqueous phase (F24)	0.03	5.9
Hydrolysed EtOAc phase (F23)	0.01	1.8
Solid residue (F15)	0.32	70.4
Starch II fraction (F27)	0.32	69.7
Total	0.44	97.21

^a F = Fraction

Table 14 Characterization and distribution of radioactive residues in dry rice straw

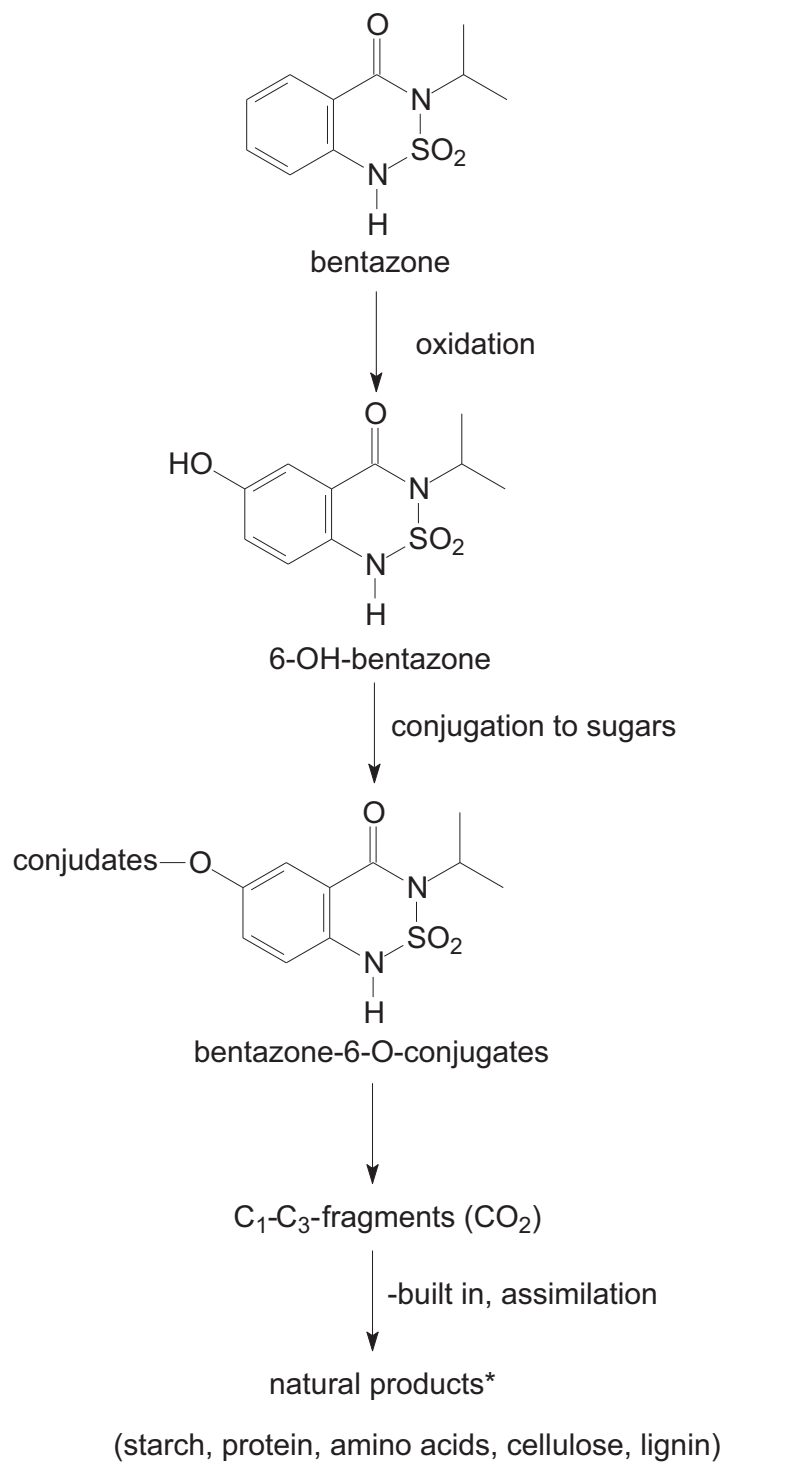
Extract fraction (designation code)	mg/kg	% TRR
Methanolic extract (F3) ^a	18.25	35.6
Methyl-bentazone (F12)	6.85 ^b	13.3
6-Methoxy-methyl-bentazone (F12)	2.16	4.2
Secondary fractions (F5, F6, F8, F9, F11)	8.58	16.7 ^c
Methanol-extracted residue (F2)	33.07	64.4
Boiling water extraction (F45)	18.31	35.7
Methyl-bentazone (F56)	0.50 ^b	1.0
6-Methoxy-methyl-bentazone (F56)	1.98 ^b	3.9
Polysaccharide	14.34 ^c	27.9
Lignin extraction ^d		
Lignin fraction	12.32	24.0
Cellulose fraction	0.42	0.8
Total of characterized residue	47.15	91.8

^a F = Fraction

^b Residue values were determined by HPLC analysis

^c None of these fractions accounted for > 6% of the TRR

^d Radioactive residues in the lignin pool were determined using three different lignin extraction procedures. Values for lignin and cellulose fractions are taken from the Honeycutt/Alder lignin extraction procedure.



*do not represent "bound residues", as by IUPAC-definition

Figure 2 Flow diagram of the metabolism of bentazone in rice

Maize

The metabolism of an aqueous solution of the sodium salt of [^{14}C] bentazone (uniformly labelled with ^{14}C in the phenyl ring, specific activity, 189.35 $\mu\text{Ci}/\text{mg}$; radiochemical purity > 98%) equivalent to 1.68 kg/ha of bentazone was investigated in maize (variety: *Michigan 407-2x*) (Clark, JR, Hoehne, C and Huber, R, 1976, 1976/5060). Whole plant samples (without roots) were removed from the plots at 0, 7, 14, 21, 42, 63 and 126 days (final harvest) after the application of bentazone. All plant samples were frozen soon after collection and shipped with dry ice to the metabolism laboratory for analysis. In the final harvest samples, the grain, cobs, husks and stover were separated before analysis. Radioactivity was measured by liquid scintillation counting (LSC) and the nature of radioactivity in interim and harvest samples was investigated further with GLC. The results were summarized in Table 15.

Table 15 Characterization and identification of radioactive residues in maize interim and harvest samples after treatment of [^{14}C] bentazone at 6-leaves stage

Weeks after application ^a	Total	radioactive	Residues ^b	GC	identified	Residues ^c
	Original sample	Methanol extractable	Methanol insoluble	bentazone	6-OH-bentazone	8-OH-bentazone
0	196.15	—	—	—	—	—
1	9.53	3.28	6.25	0.12	1.16	< 0.05
2	6.42	—	—	0.06	0.62	< 0.05
3	1.57	0.76	0.81	0.08	0.16	< 0.05
6	0.27	0.12	0.15	< 0.05	0.09	< 0.05
9	0.21	0.14	0.07	< 0.05	0.09	< 0.05
Final harvest grain	0.04	0.01	0.03	< 0.05	< 0.05	< 0.05
Final harvest cobs	0.11	0.06	0.05	< 0.05	< 0.05	< 0.05
Final harvest husks	0.13	0.06	0.05	< 0.05	< 0.05	< 0.05
Final harvest stover	0.24	0.17	0.07	< 0.05	< 0.05	< 0.05
Final harvest stover protein			0.02			
Final harvest stover polysaccharide			0.00 (1)			
Final harvest stover lignin			0.02			
Final harvest stover cellulose			0.01			
Final harvest grain protein			0.01			
Final harvest grain starch			0.02			
Final harvest grain lipid			0.00(04)			

^a Weeks after the application of 1.68 kg/ha of [^{14}C] bentazone

^b These values are mg/kg bentazone equivalents based on fresh plant weight

^c These numbers are mg/kg values based on the fresh plant weight

Green beans

The metabolism of [^{14}C]-bentazone (uniformly labelled with ^{14}C in the phenyl ring, specific activity, 9.885 mCi/mMole or 91.4 dpm/mg; radiochemical purity 99.7%, chemical purity 99.6%) was studied in green beans (variety: *Bluelake*) after single and double applications at 2.24 and 1.68 kg ai/ha (Clark, J, and Winkler, V, 1988, 1988/5543). Foliage, succulent beans, hay and seeds was collected or harvested at various PHIs. The samples were immediately placed in a cooler containing dry ice. After transport to the laboratory the samples were immediately put into -20 °C freezers. Radioactivity was measured by liquid scintillation counting (LSC). The results are summarized in Table 16.

Table 16 Percent of applied [^{14}C] bentazone remaining in plant parts after single and double applications

		Single	treatment		Double	treatments
Matrices	PHI	mg eq/kg	% dose	PHI ^a	mg eq/kg	% dose
Forage	9	17.3	9.5	—	—	—
Forage	36	5.0	4.1	36 (8)	44.5	21.9
Succulent bean	36	0.13	0.1	36 (8)	1.9	0.6
Seed	79	0.61	0.02	79 (51)	1.3	0.04

		Single	treatment		Double	treatments
Matrices	PHI	mg eq/kg	% dose	PHI ^a	mg eq/kg	% dose
Hull	79	1.4	0.03	79 (51)	9.9	0.15
Hay	79	20.4	4.6	79 (51)	115	17.4

^a The number in the parentheses represents days after the second treatment.

Potatoes

The metabolism of [¹⁴C]-bentazone (uniformly labelled with ¹⁴C in the phenyl ring, specific activity, 96967 dpm/μg; radiochemical purity 98.73%) was investigated in potatoes (variety: *Grata*) in 1989 (Hofmann, M, 1989, 1989/10248). Ten potato plants were each treated twice at 1.12 kg ai/ha. Samples of leaves were taken 4 hours after the first application as well as shortly before and 4 hours after the second application. The potatoes were harvested 41 days after the last application. All samples were stored in a freezer at -20 °C. Radioactivity was measured by liquid scintillation counting (LSC). At harvest time the total radioactive residues (TRR) of potatoes and potato tops were 0.156 mg eq/kg and 29.4 mg eq/kg, respectively.

The further metabolism study on potatoes (variety: *Grata*) was conducted with [14C] bentazone (uniformly labelled with ¹⁴C in the phenyl ring, specific activity, 96967 dpm/μg; both chemical and radiochemical purity > 99%) in 1994 (Ellenson, JL, 1994, 1994/5106). Foliar spray application of the parent compound was made at pre-harvest intervals of 62 and 41 days using two equal 1.12 kg ai/ha treatments. The samples were collected and stored in a freezer at -20 °C. Fractionation and residue analyses were carried out separately on peels and pulp. Separate peel and pulp freeze-dried samples were first extracted with methanol and then DCM. The residual slurries were partially hydrolysed with 3 N HCl and basified with NaOH. The slurries were partitioned with DCM, re-acidified with HCl and partitioned with ethyl acetate. The final slurry was neutralized, centrifuged, and separated into insoluble material, aqueous fraction, and ethyl acetate fraction which was combined with the previous ethyl acetate fraction. The aqueous fraction was further concentrated by evaporation and filtered, resulting in a final aqueous fraction and a filter residue which was combined with the marc fraction. Radioactivity was measured by liquid scintillation counting (LSC) and the nature of radioactivity in samples was investigated further with HPLC. The results were summarized in Table 17 and Table 18.

Table 17 Distribution of radioactive residues resulting from extraction and partitioning of tissues of potatoes after double treatments with [¹⁴C] bentazone (Ellenson, JL, 1994, 1994/5106)

	Peel (0.037	mg eq/kg)	Pulp(0.100	eq mg/kg)	Whole tuber	(0.137 mg eq/kg)
Fraction	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Methanol	0.010	7.1	0.051	37.2	0.061	44.2
DCM I	< 0.001	0.1	< 0.001	< 0.1	< 0.001	< 0.1
DCM II	< 0.001	0.2	< 0.001	0.3	< 0.001	0.5
EtOAc	0.001	0.6	0.001	0.8	0.002	1.4
Aqueous remainder	0.004	3.3	0.030	22.4	0.034	25.7
Residual (Marc)	0.017	12.7	0.025	18.0	0.042	30.7
Sum	0.032	24.0	0.108	78.6	0.140	102.6
Mass balance %		89		108		103

Table 18 Summary of results of radio-HPLC analysis of methanolic extracts of potato tubers after double treatments with [¹⁴C]-bentazone (Ellenson, JL, 1994, 1994/5106)

Retention time	%TRR	m/kg	Identity
0–3.7	0.3	< 0.001	–
3.7–6.0	5.7	0.008	Polar unknown region I
6.0–8.0	1.4	0.002	Polar unknown region II
8.0–10.3	25.0	0.034	6-OH-Bentazone conjugate
10.3–11.7	5.8	0.008	Polar unknown region III

Retention time	%TRR	m/kg	Identity
11.7–12.7	1.4	0.002	Polar unknown region IV
12.7–14.7	3.7	0.005	Bentazone
14.7–16.3	0.9	0.001	Polar unknown region V

Wheat

The metabolism of [^{14}C] bentazone (uniformly labelled with ^{14}C in the phenyl ring, specific activity, 18.1 317400 dpm/ug; radiochemical purity 97.3%, chemical purity 95.2%) was investigated in wheat (Rabe, U, Kloeppner, U, 2011, BASF DocID 2010/1062115).

Wheat (variety: *Thassos*) was grown in plastic containers located in a phytotron and treated with one foliar application of [^{14}C] bentazone at BBCH growth stage 31–32. The active substance was applied once at an application rate of 1 kg ai/ha, representing the critical GAP. Samples of wheat forage and hay were collected at BBCH 39 (20 days after application) and samples of grain, chaff and straw were sampled at BBCH 89 (83 days after application). All samples were stored in a freezer at, or below, $-18\text{ }^{\circ}\text{C}$ immediately after they were collected until analysis.

Prior to extraction and determination of the total radioactive residues (TRR), subsamples of wheat chaff and grain were homogenised. Frozen subsamples of all other matrices were mixed with dry ice and homogenised. The homogenised material was transferred into polycarbon boxes and stored at $-18\text{ }^{\circ}\text{C}$ or below. In order to determine the TRR values by combustion analysis, small aliquots of the homogenised subsamples were combusted to $^{14}\text{CO}_2$. Subsamples of homogenised plant material were extracted three times with a sufficient volume of methanol. After each extraction step, the liquid phase was separated from the solid, and the remaining plant material was subjected to the next extraction step. The methanol extracts of the three steps were combined, adjusted to a defined volume and measured by liquid scintillation counting (LSC). The residue was extracted two additional times in the same way with appropriate volumes of water. The aqueous extracts were also combined, adjusted to a defined volume with water, and aliquots of the combined aqueous extract were radio-assayed by LSC. Results of methanol and water extractions are referred to as extractable radioactive residues (ERR). The residue after solvent extraction (methanol and water) of each sample was deep frozen and freeze dried, and the weight of the remaining sample was determined. The samples were homogenised prior to combustion analysis of aliquots for the determination of the residual radioactive residues (RRR). The total radioactive residues (TRR) were the result of the combustion of aliquots or the sum of ERR and RRR values. Samples of forage, straw and grain were homogenized in liquid nitrogen, combusted and radio-assayed by liquid scintillation counting (LSC). The LOQ was 0.001 mg/kg, 0.002 mg/kg and 0.0003 mg/kg in wheat forage, straw and grain, respectively. The TRR in samples are summarized in Table 19. Identification and quantification of extractable residues in wheat matrices are summarized in Table 20. Characterisation of the residual radioactive residues after solvent extraction in wheat matrices are summarized in Table 21.

Table 19 Total radioactive residues in wheat matrices following a single application at 1.0 kg ai/ha of [^{14}C] bentazone

Matrix	DAT ^a	TRR Calculated ^b	TRR Combusted	Combined Methanol Extract		Combined Aqueous Extract		ERR ^c		RRR ^d	
		[mg/kg]	[mg/kg]	[mg/kg]	[$\%$ TRR]	[mg/kg]	[$\%$ TRR]	[mg/kg]	[$\%$ TRR]	[mg/kg]	[$\%$ TRR]
Forage	20	4.461	4.579	3.803	85.2	0.151	3.4	3.954	88.6	0.508	11.4
Hay	20	30.913	31.697	22.695	73.4	2.840	9.2	25.535	82.6	5.378	17.4
Straw	83	17.315	18.009	8.932	51.6	3.451	19.9	12.383	71.5	4.931	28.5
Chaff	83	1.555	1.669	0.219	14.1	0.100	6.4	0.319	20.5	1.236	79.5
Grain	83	1.112	1.144	0.058	5.3	0.047	4.2	0.105	9.5	1.007	90.5

^a DAT = days after last treatment

^b TRR was calculated as the sum of ERR + RRR

^c ERR = extractable radioactive residue

^d RRR = residual radioactive residue (after solvent extraction)

Table 20 Identification and quantification of extractable residues in wheat matrices following a single application at 1.0 kg ai/ha of [¹⁴C] bentazone

Metabolite Code	Forage (20 DAT) ^a [mg/kg] [%TRR]	Hay (20 DAT) [mg/kg] [%TRR]	Straw (83 DAT) [mg/kg] [%TRR]	Chaff (83 DAT) [mg/kg] [%TRR]	Grain (83 DAT) [mg/kg] [%TRR]
Bentazone (M351H000)	2.517 (56.4)	12.068 (39.0)	8.896 (51.4)	0.065 (4.2)	nd
M351H013	1.250 (28.0)	12.689 (41.1)	1.217 (7.0)	0.031 (2.1)	nd
M351H017 M351H018 M351H019 M351H020M351H021	0.075 (1.7)	0.928 (3.0)	0.494 (2.9)	0.040 (2.6)	nd
M351H007 M351H014 M351H015 M351H016 M351H022	0.136 (3.0)	1.184 (3.8)	0.817 (4.7)	0.016 (1.0)	nd
Carbohydrates (glucose)	nd	nd	nd	nd	0.647 (58.2)

DAT = days after treatment

nd = not detected

Metabolites M351H017, M351H018, M351H019, M351H020, M351H021 and M351H007, M351H014, M351H015, M351H016, M351H022 are co-eluting and were identified after several HPLC clean-up steps from a sample of hay.

Therefore, the composition of these components could be different in the other matrices and the radioactivity might be represented by only one or all of these metabolites.

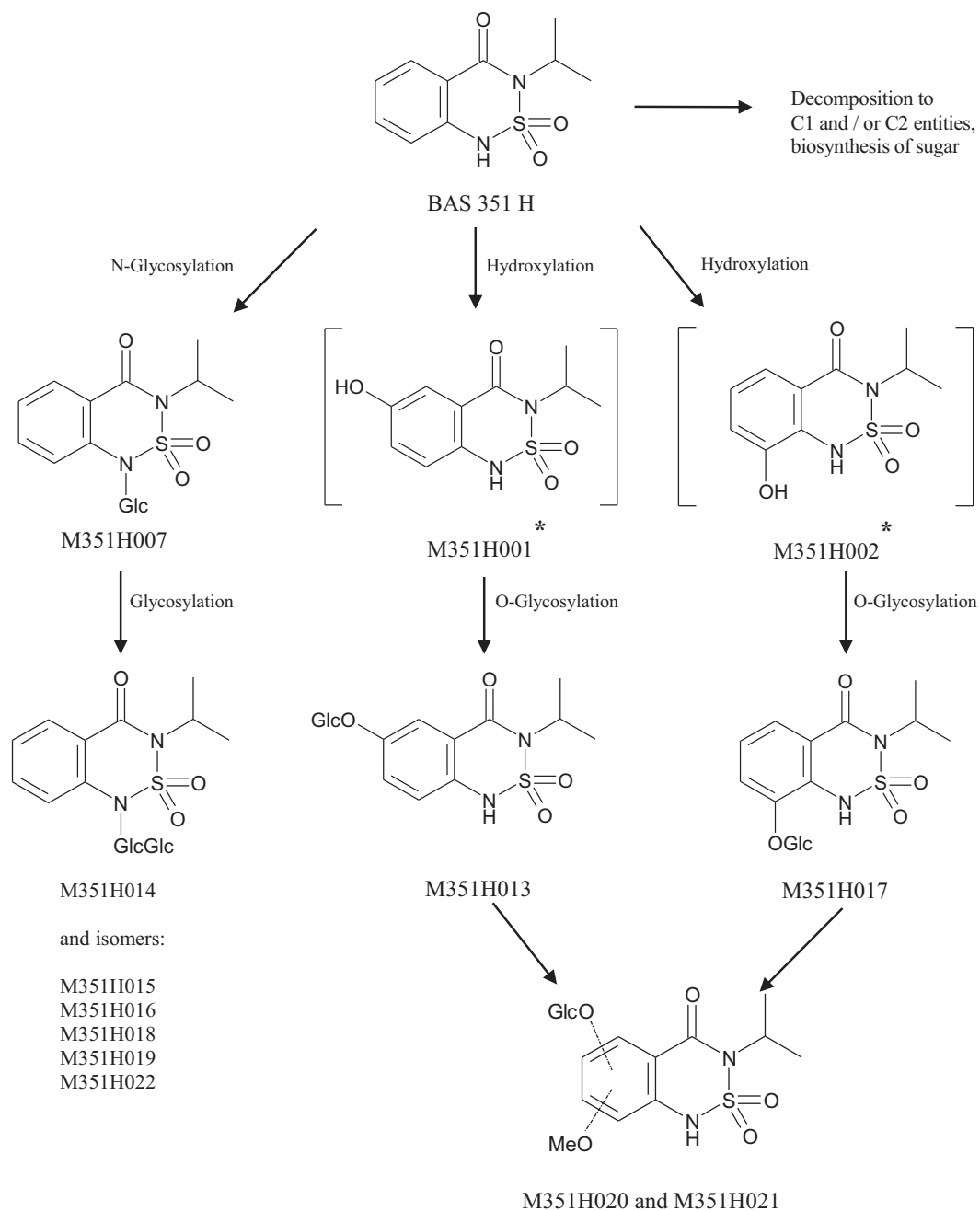
Table 21 Characterisation of the residual radioactive residues in wheat matrices following a single application at 1.0 kg ai/ha of [¹⁴C] bentazone

Fraction / Solubilisate	Crop Matrix									
	Wheat Forage		Wheat Hay		Wheat Straw		Wheat Chaff		Wheat Grain	
	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
RRR	0.508	11.4	5.378	17.4	4.931	28.5	1.236	79.5	1.007	90.5
NH ₄ OH solubilisate	0.100	2.2	1.623	5.2	1.450	8.4	0.045	2.9	0.097	8.7
NH ₄ OH residue	0.402	9.0	4.045	13.1	3.516	20.3	1.232	79.2	0.906	81.4
Glucosidase / Hesperidinase supernatant	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	0.104	9.4
Glucosidase / Hesperidinase residue	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	0.763	68.6
Macerozyme supernatant	0.140	3.1	1.131	3.7	1.113	6.4	0.136	8.7	0.495	44.5
Macerozyme residue	0.243	5.4	2.806	9.1	2.184	12.6	1.041	66.9	0.257	23.1
Tyrosinase / Laccase supernatant	0.049	1.1	0.752	2.4	0.245	1.4	0.020	1.3	n. a.	n. a.
Tyrosinase / Laccase residue	0.174	3.9	1.981	6.4	1.909	11.0	1.012	65.0	n. a.	n. a.
Amylase / Amyloglucosidase supernatant	0.017	0.4	0.218	0.7	0.078	0.5	0.018	1.2	0.143	12.8
Amylase / Amyloglucosidase residue	0.152	3.4	1.644	5.3	1.886	10.9	0.997	64.1	0.100	9.0
Sum of solubilised radioactive residues	0.306	6.9	3.725	12.0	2.887	16.7	0.218	14.0	0.838	75.4
Final residue ^a	0.152	3.4	1.644	5.3	1.886	10.9	0.997	64.1	0.100	9.0
Procedural recovery [%]	90.3		99.8		96.8		98.3		93.2	
6 M HCl solubilisate	n. a.	n. a.	n. a.	n. a.	0.510	2.9	0.447	28.7	0.041	3.7

Fraction / Solubilisate	Crop Matrix									
	Wheat Forage		Wheat Hay		Wheat Straw		Wheat Chaff		Wheat Grain	
	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
6 M HCl residue	n. a.	n. a.	n. a.	n. a.	1.304	7.5	0.482	31.0	0.051	4.6
1 M NaOH solubilisate	n. a.	n. a.	n. a.	n. a.	1.790	10.3	0.494	31.8	0.081	7.2
1 M NaOH residue	n. a.	n. a.	n. a.	n. a.	0.521	3.0	0.482	31.0	0.028	2.5
Microwave Extraction solubilisate	n. a.	n. a.	n. a.	n. a.	0.743	4.3	0.311	20.0	0.051	4.6
Microwave Extraction residue	n. a.	n. a.	n. a.	n. a.	1.283	7.4	0.675	43.4	0.052	4.7

^a For wheat straw, chaff and grain additional solubilisation steps were performed. In all cases sodium hydroxide solution released the highest amount of radioactivity from the respective residual material. Therefore the radioactive residues after sodium hydroxide solubilisation are cited as the final residue for these matrices.

Based on the identified metabolites the proposed metabolic pathway of bentazone in wheat involves the hydroxylation of the benzothiadiazine ring. The hydroxyl groups were subsequently glycosylated generating the metabolites M351H013 and M351H017. In addition, the benzothiadiazine ring was conjugated with monosaccharide/disaccharide at the nitrogen atom at position one. Further metabolism lead to the degradation of the carbon skeleton of bentazone and re-assimilation into natural compounds like carbohydrates. The proposed metabolic pathway for bentazone in wheat is shown in Figure 3.



* Not detected as free metabolites in wheat matrices

Figure 3 Proposed metabolic pathway of bentazone in wheat

Environmental fate in soil

The Meeting received information on the environmental fate of bentazone in soil, including studies on soil metabolism, and crop rotational studies.

Soil metabolism (aerobic degradation)

The aerobic soil metabolism of bentazone was investigated in a sandy loam (pH 7.3, 1.23% OC) freshly collected from the field and passed through a 2 mm sieve before use (Staudenmaier, H and

Kuhnke, G, 2010, 2010/1057318). The soil was treated with [^{14}C -phenyl]-bentazone (5.15 MBq/mg, radiochemical purity 96.5%) at a nominal rate of 2.7 mg per kg dry soil which corresponds to a field application rate of 1000 g bentazone per hectare, calculated on the basis of an equal distribution in the top 2.5 cm soil layer and a soil density of 1.5 g/cm³.

Soil aliquots of 100 g (dry weight basis) were weighed into test vessels and incubated in the dark under aerobic conditions at soil moisture of 40% of the maximum water holding capacity and a temperature of 20 °C. A closed incubation system with continuous aeration (moistened air) was used with an attached trapping system for the collection of volatile compounds. At two time points during incubation (57 and 126 DAT), the microbial biomass was determined by the substrate induced respiration method, verifying that the soil was viable throughout the incubation period. Samples were taken at 0, 1, 3, 7, 14, 30, 64, 91, 120 and 150 days after treatment. At sampling times 0, 30, 120 and 150 DAT, soil samples were worked up in duplicate.

The soil samples were extracted twice with methanol and twice with water/methanol (v:v, 1:1). The amount of radioactivity in the individual extracts was determined by liquid scintillation counting. The methanol and water/methanol extracts per soil sample were combined, respectively, and analysed by means of HPLC. The remaining soil was homogenized and combusted after extraction to determine the amount of non-extractable residues (NER) in soil. The NER were further characterized by NaOH extraction and subsequent fractionation into fulvic acids, humic acids and humins. The fulvic acid fraction was furthermore partitioned with ethyl acetate. A full material balance was provided for each sampling interval. The results showed that the amount of extractable radioactivity in soil continuously decreased from 102.2% of the total applied radioactivity (TAR) at 0 DAT to 6.9% TAR after 150 days of incubation. The amount of the test item bentazone decreased from 101.0% TAR at 0 DAT to 2.3% TAR at 150 DAT. Metabolites were formed only in minor amounts of which the most prominent metabolite (max. 2.8% TAR) was identified as N-methyl-bentazone (M351H009). All other metabolites were formed in even lower amounts and their sum in the total extracts never exceeded 2.2% TAR at any sampling time. Mineralization to ^{14}C -CO₂ reached a total of 9.0% TAR after 150 days of incubation. No other volatile compounds were detected.

Non-extractable radioactive residues were formed in considerable amounts during incubation. They increased from 3.3% TAR on day 0 to a maximum of 68.8% TAR after 150 days. After extraction with NaOH, still about half of the radioactivity (2.3–34.8% TAR) remained tightly bound to the soil matrix (humines). The NaOH extractable radioactivity was distributed between the humic acid (1.0–11.9% TAR) and the fulvic acid fraction (2.7–21.0% TAR) in a ratio of about 1:2. The fulvic acid fraction was further characterized by partitioning with ethyl acetate. Amounts of 1.6 to 7.3% TAR of the fulvic acid fraction were soluble in ethyl acetate, whereas 0.9 to 13.1% TAR remained in the water phase. The ethyl acetate soluble fractions from samples of 30 DAT to 120 DAT were investigated by HPLC. Parent compound was found to be the most prominent peak, accounting for 3.0 to 3.7% TAR. The material balance throughout the incubation period ranged from 92.6 to 105.5% TAR except for the 150 DAT sampling, for which a material balance of only 84.7% TAR was achieved. The average material balance for all soil samples was 98.0% TAR. Results are presented in Table 22 to Table 25.

Table 22 Distribution of radioactivity and material balance after application of [^{14}C] bentazone

DAT	extractable			NER	CO ₂	Other volatiles	Material balance
	CH ₃ OH	H ₂ O/CH ₃ OH	total				
0	87.2 (2.339)	15.0 (0.403)	102.2 (2.742)	3.3 (0.090)	nd	nd	105.5 (2.832)
1	84.8 (2.277)	13.4 (0.359)	98.2 (2.635)	5.8 (0.155)	0.1 (0.002)	0.0 (0.000)	104.1 (2.793)
3	85.9 (2.304)	11.0 (0.295)	96.9 (2.600)	8.8 (0.237)	0.3 (0.009)	0.0 (0.000)	106.0 (2.846)
7	81.2 (2.179)	10.6 (0.285)	91.8 (2.464)	11.4 (0.306)	0.7 (0.018)	0.0 (0.000)	103.9 (2.789)
14	73.6 (1.976)	10.1 (0.272)	83.8 (2.248)	15.3 (0.411)	1.2 (0.033)	0.0 (0.000)	100.3 (2.692)
30	61.1 (1.639)	10.8 (0.291)	71.9 (1.930)	24.9 (0.667)	2.3 (0.062)	0.0 (0.000)	99.1 (2.659)

DAT	extractable			NER	CO ₂	Other volatiles	Material balance
	CH ₃ OH	H ₂ O/CH ₃ OH	total				
64	37.6 (1.008)	8.6 (0.230)	46.1 (1.238)	49.0 (1.314)	4.4 (0.118)	0.0 (0.000)	99.5 (2.670)
91	24.4 (0.655)	6.1 (0.164)	30.5 (0.819)	56.9 (1.527)	6.5 (0.176)	0.0 (0.000)	93.9 (2.521)
120	15.3 (0.412)	4.7 (0.126)	20.1 (0.538)	64.3 (1.726)	8.2 (0.220)	0.0 (0.000)	92.6 (2.484)
150	4.6 (0.123)	2.3 (0.061)	6.9 (0.184)	68.8 (1.847)	9.0 (0.241)	0.0 (0.000)	84.7 (2.272)

Table 23 Distribution of radioactivity and material balance after application of [¹⁴C] bentazone

DAT		N-methyl-		
	bentazone	bentazone	Sum others	total
0	101.0 (2.710)	nd	1.2 (0.032)	102.2 (2.742)
1	97.2 (2.610)	nd	1.0 (0.026)	98.2 (2.635)
3	95.8 (2.571)	nd	1.1 (0.029)	96.9 (2.600)
7	91.0 (2.442)	nd	0.8 (0.022)	91.8 (2.464)
14	83.0 (2.227)	nd	0.8 (0.021)	83.8 (2.248)
30	70.4 (1.889)	0.6 (0.017)	0.9 (0.025)	71.9 (1.930)
64	43.2 (1.159)	1.7 (0.045)	1.3 (0.034)	46.1 (1.238)
91	26.6 (0.714)	2.2 (0.060)	1.7 (0.045)	30.5 (0.819)
120	15.2 (0.408)	2.8 (0.075)	2.0 (0.055)	20.1 (0.538)
150	2.3 (0.061)	2.4 (0.064)	2.2 (0.059)	6.9 (0.184)

nd = Not determined.

Table 24 Fractionation of non-extractable residues from soil treated with [¹⁴C] bentazone

DAT	NER	NaOH		Fulvic acids	Acidic	Humic	humins
		extract	total	Ethylacetate soluble	water soluble	acids	
1	5.8 (0.155)	3.6 (0.096)	2.7 (0.071)	1.6 (0.043)	0.9 (0.024)	1.0 (0.026)	2.3 (0.062)
3	8.8 (0.237)	5.0 (0.134)	3.4 (0.091)	1.9 (0.051)	1.4 (0.038)	1.5 (0.039)	3.8 (0.101)
7	11.4 (0.306)	6.4 (0.173)	4.3 (0.115)	2.3 (0.061)	1.8 (0.049)	1.9 (0.051)	5.1 (0.136)
14	15.3 (0.411)	8.3 (0.223)	5.7 (0.153)	3.0 (0.082)	2.5 (0.066)	2.5 (0.066)	7.1 (0.191)
30*	24.6 (0.661)	12.9 (0.346)	8.5 (0.229)	4.2 (0.112)	4.1 (0.111)	4.0 (0.107)	12.7 (0.341)
64	49.0 (1.314)	26.0 (0.699)	16.6 (0.444)	6.8 (0.183)	9.1 (0.245)	8.8 (0.237)	23.6 (0.634)
91	56.9 (1.527)	31.2 (0.837)	19.3 (0.517)	6.6 (0.178)	12.1 (0.325)	10.8 (0.289)	30.4 (0.815)
120 a	64.7 (1.736)	34.1 (0.915)	21.0 (0.564)	7.3 (0.195)	13.1 (0.353)	11.9 (0.320)	34.8 (0.935)

^a One sample was analysedTable 25 Radio HPLC analysis of ethyl acetate extracts of fulvic acids from soil treated with [¹⁴C] bentazone

DAT	Total extractable	bentazone	Sum others
30	4.2 (0.112)	3.1 (0.083)	1.1 (0.029)
64	6.8 (0.183)	3.5 (0.094)	3.3 (0.089)
91	6.6 (0.178)	3.7 (0.099)	2.9 (0.079)
120	7.3 (0.195)	3.0 (0.081)	4.3 (0.114)

The degradation rate of bentazone under aerobic conditions was investigated in four different soils (Bruch West: 1.37% OC, pH 7.8; Li 10: 0.97% OC, pH 6.8; LUFA 2.2: 0.15% OC, pH 6.2; LUFA 2.3: 0.98% OC, pH 7.4) at a temperature of 20 °C (Tornisielo, A, Sacchi, RR, 2011, 2011/1000621). The soils were typical agricultural soils from Germany, freshly collected from the field and passed through a 2 mm sieve before use. The soils were treated with a nominal rate of 2.0 mg ¹⁴C-labelled bentazone (5.29 MBq/mg, radiochemical purity: 97.3%) per kg dry soil which corresponds to a field application rate of 750 g bentazone/ha, assuming equal distribution in the upper 2.5 cm soil layer and a soil density of 1.5 g/cm³.

The incubations were carried out under dark conditions at soil moisture of 40% of the maximum water holding capacity. A closed incubation system with continuous aeration (moistened air) was used with an attached trapping system for the determination of volatile compounds. Samples were taken at 0, 3, 7, 14, 29, 62, 90, and 120 days after treatment. The soil samples were extracted twice with methanol and four times with methanol/water (1:1) and the extracts analysed by means of LSC and HPLC. The amount of non-extractable residues was determined by combustion and subsequent LSC measurements.

The mass balance throughout the study ranged from 91.8 to 113.2% TAR with average values of 98.3 to 100.3% TAR for each soil. The extractable radioactivity decreased from 93.8–100.9% TAR (total applied radioactivity) at day 0 to 6.9–19.4% after 120 days. The majority of radioactivity in the extracts was always unchanged test item. At the end of incubation, bentazone was detected in amounts of 4.8–18.8% TAR. Three metabolites appeared in the chromatograms. By comparison of retention times with the reference substance, one metabolite could be assigned to the known soil metabolite N-methyl-bentazone. It reached maximum amounts of about 5% TAR in soil LUFA 2.2. In all other soils, it never exceeded 2.3% TAR. The other two unknown compounds never exceeded 2.2% TAR at any sampling time. Formation of CO₂ was observed in all four soils reaching in total 9.1 to 21.2% TAR after 120 days. No other volatile compounds were detected. Non-extractable residues were formed in high amounts with a maximum of 63.8 to 92.5% TAR at the end of the study. The distribution of radioactive residues in the different soils treated with ¹⁴C-labelled bentazone at various time intervals from 0 DAT to 120 DAT is shown in Table 26 to Table 29.

Table 26 Distribution of radioactivity in soils after treatment with [¹⁴C] bentazone and incubation under aerobic conditions [% TAR]-Bruch West (20 °C)

Days after treatment	Extractable				NER	Volatiles ^a			Material balance
	Methanol	Methanol + water	Acetone	Total		CO ₂	Other volatiles	Total	
0	87.5	9.6	0.1	97.2	2.9	nd	nd	nd	100.1
0	87.5	9.5	0.0	97.0	2.9	nd	nd	nd	99.9
0 mean	87.5	9.6	0.1	97.1	2.9	nd	nd	nd	100.0
3	81.2	9.2	0.2	90.6	9.8	0.0	0.0	0.0	100.4
7	72.3	8.6	0.4	81.2	17.7	0.0	0.0	0.0	98.9
14	62.4	7.9	0.1	70.5	27.5	1.4	0.0	1.4	99.4
29	44.8	7.6	0.1	52.5	41.3	5.7	0.0	5.7	99.5
62	21.1	6.5	0.3	27.8	58.2	13.0	0.0	13.0	98.9
62	21.0	6.4	0.3	27.6	58.2	13.9	0.0	13.9	99.8
62 mean	21.0	6.4	0.3	27.7	58.2	13.5	0.0	13.5	99.3
90	8.6	4.3	0.1	13.1	62.8	17.9	0.0	17.9	93.8
120	3.0	3.8	0.1	6.9	69.2	21.2	0.0	21.2	97.4
120	3.1	4.1	0.1	7.3	67.8	21.2	0.0	21.2	96.3
120 mean	3.1	4.0	0.1	7.1	68.5	21.2	0.0	21.2	96.8

nd = Not determined

NER = Non-extractable residues

TAR = Total applied radioactivity (100% = 1.949 mg/kg dry weight)

^a Cumulated values

Table 27 Distribution of radioactivity in soils after treatment with [¹⁴C] bentazone and incubation under aerobic conditions [% TAR]—Li10 (20 °C)

Days after treatment	Extractable				NER	Volatiles ^a			Material balance
	Methanol	Methanol + water	Acetone	Total		CO ₂	Other volatiles	Total	
0	90.8	7.6	0.0	98.5	2.0	nd	nd	nd	100.4
0	90.1	6.9	0.1	97.0	2.5	nd	nd	nd	99.6
0 mean	90.4	7.3	0.1	97.8	2.2	nd	nd	nd	100.0
3	88.3	5.2	0.1	93.6	6.4	0.0	0.0	0.0	100.0

Days after treatment	Extractable				NER	Volatiles ^a			Material balance
	Methanol	Methanol + water	Acetone	Total		CO ₂	Other volatiles	Total	
7	79.9	5.8	0.3	86.0	11.5	0.0	0.0	0.0	97.5
14	69.4	6.5	0.1	76.0	22.8	0.6	0.0	0.6	99.4
29	53.2	7.1	0.1	60.4	29.2	2.5	0.0	2.5	92.1
62	28.0	6.1	0.2	34.2	63.0	6.5	0.0	6.5	103.7
62	30.1	6.5	0.2	36.8	58.0	6.8	0.0	6.8	101.5
62 mean	29.1	6.3	0.2	35.5	60.5	6.6	0.0	6.7	102.6
90	18.6	5.5	0.1	24.2	61.0	10.2	0.0	10.2	95.4
120	10.0	5.3	0.3	15.6	67.4	13.5	0.0	13.5	96.5
120	10.9	4.0	0.1	15.0	63.8	13.5	0.0	13.5	92.3
120 mean	10.4	4.6	0.2	15.3	65.6	13.5	0.0	13.5	94.4

nd = Not determined

NER = Non-extractable residues

TAR = Total applied radioactivity (100% = 1.958 mg/kg dry weight)

^a Cumulated values

Table 28 Distribution of radioactivity in soils after treatment with [¹⁴C] bentazone and incubation under aerobic conditions [% TAR]—LUFA 2.2 (20 °C)

Days after treatment	Extractable				NER	Volatiles ^a			Material balance
	Methanol	Methanol + water	Acetone	Total		CO ₂	Other volatiles	Total	
0	84.7	9.1	0.1	93.8	2.8	nd	nd	nd	96.6
0	91.3	9.6	0.1	100.9	2.4	nd	nd	nd	103.4
0 mean	88.0	9.4	0.1	97.4	2.6	nd	nd	nd	100.0
3	73.3	9.0	0.3	82.6	14.6	0.0	0.0	0.0	97.2
7	69.1	8.4	0.1	77.6	18.2	0.0	0.0	0.0	95.9
14	54.7	8.3	0.2	63.2	35.8	0.6	0.0	0.6	99.6
29	45.0	8.9	0.5	54.4	39.9	2.6	0.0	2.6	96.9
62	14.3	6.0	0.3	20.6	67.5	4.7	0.0	4.7	92.8
62	13.1	5.9	0.3	19.3	67.0	5.5	0.0	5.5	91.8
62 mean	13.7	5.9	0.3	19.9	67.2	5.1	0.0	5.1	92.3
90	8.3	4.8	0.2	13.4	81.8	7.4	0.0	7.4	102.6
120	6.5	4.9	0.3	11.7	92.5	9.1	0.0	9.1	113.2
120	6.3	4.6	0.3	11.3	90.0	9.1	0.0	9.1	110.4
120 mean	6.4	4.8	0.3	11.5	91.3	9.1	0.0	9.1	111.8

nd = Not determined

NER = Non-extractable residues

TAR = Total applied radioactivity (100% = 1.891 mg/kg dry weight)

^a Cumulated values

Table 29 Distribution of radioactivity in soils after treatment with [¹⁴C] bentazone and incubation under aerobic conditions [% TAR]—LUFA 2.3 (20 °C)

Days after treatment	Extractable				NER	Volatiles ^a			Material balance
	Methanol	Methanol + water	Acetone	Total		CO ₂	Other volatiles	Total	
0	86.9	9.3	0.2	96.4	2.5	nd	nd	nd	98.9
0	89.6	8.7	0.4	98.6	2.5	nd	nd	nd	101.1
0 mean	88.2	9.0	0.3	97.5	2.5	nd	nd	nd	100.0
3	81.9	7.8	0.3	90.0	8.1	0.0	0.0	0.0	98.1
7	76.5	8.1	0.2	84.8	12.5	0.0	0.0	0.0	97.3
14	65.8	8.2	0.2	74.1	21.2	0.7	0.0	0.7	96.0
29	51.9	9.5	0.8	62.2	31.2	3.2	0.0	3.2	96.6

Days after treatment	Extractable				NER	Volatiles ^a			Material balance
	Methanol	Methanol + water	Acetone	Total		CO ₂	Other volatiles	Total	
62	34.8	8.9	0.7	44.3	49.6	8.9	0.0	8.9	102.9
62	29.8	7.5	0.3	37.5	51.0	7.8	0.0	7.8	96.2
62 mean	32.3	8.2	0.5	40.9	50.3	8.3	0.0	8.4	99.5
90	19.1	6.4	0.2	25.8	58.0	12.6	0.0	12.6	96.3
120	13.1	6.1	0.2	19.4	62.8	16.0	0.0	16.0	98.2
120	11.7	5.1	0.1	16.9	67.7	16.0	0.0	16.0	100.6
120 mean	12.4	5.6	0.2	18.1	65.2	16.0	0.0	16.0	99.4

nd = Not determined

NER = Non-extractable residues

TAR = Total applied radioactivity (100% = 1.954 mg/kg dry weight)

^a Cumulated values

All combined methanol and methanol / water extracts were analysed by radio-HPLC. The results are summarized in Table 30 to Table 33.

Table 30 Radio-HPLC analysis of soil extracts after treatment of soil Bruch West with [¹⁴C] bentazone and incubation under aerobic conditions at 20 °C [%TAR]

Days after treatment	Total	UK1	Bentazone (BAS 351 H)	N-methyl-bentazone (M351H009)	UK2
		t _R 30.9	t _R 37.9	t _R 47.6	t _R 51.6
0	97.2	0.7	96.5	—	—
0	97.0	1.0	96.1	—	—
0 mean	97.1	0.8	96.3	—	—
3	90.6	0.4	90.2	—	—
7	81.2	0.7	80.5	—	—
14	70.5	1.2	69.2	—	—
29	52.5	0.9	51.6	—	—
62	27.8	—	25.9	—	1.9
62	27.6	—	27.6	—	—
62 mean	27.7	—	26.8	—	0.9
90	13.1	—	13.1	—	—
120	6.9	—	6.9	—	—
120	7.3	—	7.3	—	—
120 mean	7.1	—	7.1	—	—

t_R = Retention time [min]

— not detected

TAR = Total applied radioactivity (100% = 1.949 mg/kg dry weight)

Table 31 Radio-HPLC analysis of soil extracts after treatment of soil Li 10 with [¹⁴C] bentazone and incubation under aerobic conditions at 20 °C [%TAR] (Tornisiello, A and Sacchi, RR, 2011, 2011/1000621)

Days after treatment	Total	UK1	Bentazone (BAS 351 H)	N-methyl-bentazone (M351H009)	UK2
		t _R 30.9	t _R 37.9	t _R 9.5	t _R 51.6
0	98.5	0.5	98.0	—	—
0	97.0	—	96.8	—	0.2
0 mean	97.8	0.2	97.4	—	0.1
3	93.6	1.0	92.6	—	—
7	86.0	—	85.8	—	0.2
14	76.0	1.5	74.5	—	—
29	60.4	1.4	59.1	—	—
62	34.2	—	34.2	—	—
62	36.8	—	36.0	0.8	—

Days after treatment	Total	UK1	Bentazone (BAS 351 H)	N-methyl-bentazone (M351H009)	UK2
		t _R 30.9	t _R 37.9	t _R 9.5	t _R 51.6
62 mean	35.5	–	35.1	0.4	–
90	24.2	–	21.4	2.3	0.5
120	15.6	–	13.4	2.2	–
120	15.0	–	13.3	1.7	–
120 mean	15.3	–	13.3	2.0	–

t_R = Retention time [min]

– = Not detected

TAR = Total applied radioactivity (100% = 1.958 mg/kg dry weight)

Table 32 Radio-HPLC analysis of soil extracts after treatment of soil LUFA 2.2 with [¹⁴C] bentazone and incubation under aerobic conditions at 20 °C [%TAR] (Tornisielo, A and Sacchi, RR, 2011, 2011/1000621)

Days after treatment	Total	UK1	Bentazone (BAS 351 H)	N-methyl-bentazone (M351H009)	UK2
		t _R 30.9	t _R 37.9	t _R 9.5	t _R 51.6
0	93.8	1.2	92.6	–	–
0	100.9	1.0	100.0	–	–
0 mean	97.4	1.1	96.3	–	–
3	82.6	0.6	81.9	–	–
7	77.6	0.4	77.0	–	0.3
14	63.2	0.5	62.7	–	–
29	54.4	–	50.5	1.8	2.2
62	20.6	–	17.1	3.5	–
62	19.3	–	16.1	3.2	–
62 mean	19.9	–	16.6	3.3	–
90	13.4	–	8.7	4.7	–
120	11.7	–	6.7	4.1	0.8
120	11.3	–	4.8	5.4	1.0
120 mean	11.5	–	5.8	4.8	0.9

t_R = Retention time [min]

– = Not detected

TAR = Total applied radioactivity (100% = 1.891 mg/kg dry weight)

Table 33 Radio-HPLC analysis of soil extracts after treatment of soil LUFA 2.3 with [¹⁴C] bentazone and incubation under aerobic conditions at 20 °C [%TAR]

Days after treatment	Total	UK1	Bentazone (BAS 351 H)	N-methyl-bentazone (M351H009)	UK2
		t _R 30.9	t _R 37.9	t _R 9.5	t _R 51.6
0	96.4	–	95.0	–	1.4
0	98.6	–	96.6	–	2.0
0 mean	97.5	–	95.8	–	1.7
3	90.0	0.7	89.3	–	–
7	84.8	1.0	83.8	–	–
14	74.1	0.5	73.6	–	–
29	62.2	1.3	59.7	–	1.3
62	44.3	–	44.3	–	–
62	37.5	–	37.0	0.3	0.2
62 mean	40.9	–	40.6	0.2	0.1
90	25.8	0.3	25.2	0.2	–
120	19.4	–	18.8	0.5	–
120	16.9	–	16.6	0.3	–
120 mean	18.1	–	17.7	0.4	–

t_R = retention time [min]

– = Not detected

TAR = Total applied radioactivity (100% = 1.954 mg/kg dry weight)

Aerobic degradation of relevant metabolites in soils

The aerobic soil degradation of N-methyl-bentazone was investigated in a loamy sand (LUFA Speyer 2.2: 2.29% OC, pH 5.7), a loam (LUFA Speyer 3A: 2.2% OC, pH 7.1) and a clay loam (PTRL soil: 1.31% OC, pH 6.8) (Class, T, 2005, 2005/1026922). The soils were all freshly collected from the field, and sieved through a 2 mm screen. Before treatment, the soil moisture was adjusted to 40–50% of the maximum water holding capacity. The microbial biomass was determined (Anderson & Domsch) after acclimatization, during and at the end of the incubation.

Individual soil samples consisted of 50 g soil (dry weight equivalents) and placed in open incubation flasks covered only partially to allow air exchange, but to prevent excessive loss of soil humidity. The incubations were kept in the dark at 20 ± 2 °C. Non-labelled N-methyl-bentazone was dosed at 0.64 mg / kg or 32 µg per 50 g (dry-weight) soil incubation. This dose was calculated assuming a bentazone application rate of 1.5 kg/ha and a resulting metabolite formation of max. 0.32 kg/ha, corresponding to an initial concentration of 0.64 mg/kg dry soil.

Soil samples were taken and analysed for remaining N-methyl-bentazone after the following incubation periods: 0 (in duplicate), 1, 2, 3, 4, 6, 8, 15, 30, 37, 60 (duplicate), 90, 120 (duplicate), 150 (duplicate), and 181 (duplicate) days. All dosed and incubated soil specimens were extracted, cleaned-up using SPE and analysed right after the respective incubation period, using the ion trap LCQ LC/MS/MS. At the end of the 181-days incubation period, all stored raw soil extracts and the raw extracts obtained from the 21 concurrent recovery soil samples, were diluted 10-fold and analysed without any further SPE clean-up (thus eliminating any potential losses) using the more sensitive triple-quadrupole API 3000 LC/MS/MS instrument. The purpose of these re-analyses was to confirm the degradation data by eliminating day-to-day variations when using the LCQ instrument over the period of 6 months. The results of HPLC-MS analysis (API 3000 LC/MS/MS) are shown in Table 34.

Table 34 Degradation of N-methyl-bentazone in soil incubated under aerobic condition at 20 °C

Days after treatment	LUFA Speyer 2.2 (F221904)		LUFA Speyer 3A (F3A 1804)		PTRL soil	
	N-methyl-bentazone [mg/kg]	Recovery [%]	N-methyl-bentazone [mg/kg]	Recovery [%]	N-methyl-bentazone [mg/kg]	Recovery [%]
0 repl. 1	0.705 ^a	110%	0.690 ^a	108%	0.702 ^a	110%
0 repl. 2	0.727 ^a	114%	0.692 ^a	108%	0.719 ^a	112%
1	0.702	110%	0.675	106%	0.713	111%
2	0.693	108%	0.660	103%	n.p.	n.p.
3	0.656	102%	0.640	100%	0.693	108%
4	0.680	106%	0.636	99%	0.642	100%
6	0.702	110%	0.594	93%	0.658	103%
8	0.675	106%	0.570	89%	0.616	96%
15	0.638	100%	0.455	71%	0.563	88%
30	0.620	97%	0.444	69%	0.458	72%
37	0.572	89%	0.442	69%	0.433	68%
60	0.563	88%	0.389	61%	0.385	60%
60	0.576	90%	0.405	63%	0.367	57%
90	0.451	70%	0.068	11%	0.052	8%
120 repl. 1	0.451	70%	0.363	57%	0.172	27%
120 repl. 2	0.449	70%	0.345	54%	0.330	52%
150 repl. 1	0.323	51%	0.020	3.1%	0.008	1%
150 repl. 2	0.350	55%	0.018	2.8%	0.009	1%
181 repl. 1	0.275	43%	0.016	2.5%	0.010	2%
181 repl. 2	0.297	46%	0.017	2.6%	0.007	1%

n.p. = Not performed

R_{dosed} = 0.64 mg/kg

^a Mean of two values

Aerobic degradation in water/sediment

A degradation of [^{14}C] bentazone (43.7 $\mu\text{Ci/mg}$, radiochemical purity > 96%) was investigated in two different water/sediment system under aerobic conditions over a period of 100 days at 20 °C in the dark. Two sediments named “Krempe” (pH 6.9, 2.1% OC) and “Ohlau” (pH 6.4, 0.37% OC) were characterized as sandy and as sand. 0.34 mg test substance were applied per kg water, which is equivalent to an application rate of 1 kg ai/ha (Bieber, WD, 1994, 1994/11026).

Water and sediment samples were taken after the following incubation periods at 0, 0.25, 1, 2, 7, 14, 30, 60 and 100 days. Water samples were acidified and extracted with ethyl acetate. Wet sediment samples were extracted with methanol/water and methanol. The extracts were analysed with LSC, radio-TLC, radio- HPLC or GC-MS. The results are shown in Table 35 to Table 37.

Table 35 Radioactivity distribution, partitioning and balance during the degradation of bentazone in “Krempe” system

Test period	water		sediment		CO ₂	Total
(d)	extractable	retained	extractable	retained		recovered
0	92.4	1.2	0.5	0.2	nd	94.3
0.25	92.9	1.2	1.8	1.2	nd	97.1
1	86.3	1.1	3.5	2.4	nd	93.3
2	84.2	1.0	5.8	2.1	< 0.1	93.1
7	77.7	1.0	8.0	4.0	0.2	90.9
14	74.8	1.1	11.1	3.0	0.3	90.3
30	74.8	1.0	12.2	5.5	0.6	94.1
60	66.4	1.4	10.5	13.0	1.7	93.0
100	62.9	1.2	9.6	15.6	2.6	91.9
100 ^a	74.7	1.0	11.1	3.4	nd	90.2

^a The system was sterilized before application of bentazone

Table 36 Radioactivity distribution, partitioning and balance during the degradation of bentazone in “Ohlau” system

Test period	water		sediment		CO ₂	Total
(d)	extractable	retained	extractable	retained		recovered
0	90.1	1.2	2.3	0.7	nd	94.3
0.25	89.2	1.0	2.4	0.9	nd	93.6
1	83.2	0.9	6.3	2.7	nd	93.0
2	83.5	0.9	6.6	2.4	0.1	93.5
7	81.4	0.9	8.8	3.1	0.2	94.4
14	71.6	1.3	10.8	3.6	0.4	87.7
30	76.6	0.9	10.5	5.2	0.8	93.9
60	74.7	1.4	8.4	10.5	1.3	96.2
100	67.9	1.4	8.4	13.4	2.6	93.6
100 ^a	80.0	1.1	9.7	3.2	nd	94.0

^a The system was sterilized before application of bentazone

Table 37 bentazone and methylbentazone during the degradation of bentazone in “Krempe” and “Ohlau” systems

Test period	bentazone	Krempe	system	(% TAR)		Ohlau	system	(% TAR)
(d)	total	water	Methyl-	bentazone	bentazone	water	Methyl-	bentazone
0	85.9	85.5	total	water	total	total	total	water
0.25	88.5	86.7	2.7	2.7	85.4	83.1	2.3	2.2
1	83.8	80.5	2.9	2.9	83.9	78.2	2.0	1.9
2	86.1	80.8	1.6	1.6	86.7	80.9	0.9	0.5
7	80.4	72.8	2.0	2.0	87.7	79.3	< 0.1	< 0.1
14	79.2	68.5	3.3	3.3	74.1	63.9	4.3	4.3
30	75.4	63.7	7.2	7.2	67.8	57.8	12.5	12.5

Test		Krempe	system	(% TAR)		Ohlau	system	(% TAR)
period	bentazone		Methyl-	bentazone	bentazone		Methyl-	bentazone
(d)	total	water	total	water	total	water	total	water
60	74.0	63.9	1.0	1.0	79.2	71.1	1.3	1.3
100	61.9	53.1	4.2	4.0	68.5	60.9	2.0	2.0
100 ^a	82.7	72.3	< 0.1	< 0.1	86.1	77.1	< 0.1	< 0.1

^a The system was sterilized before application of bentazone

Soil photolysis

The photolytic degradation of [¹⁴C] bentazone (5.15 MBq/mg, radiochemical purity 96.5%) was studied on a sandy clay loam soil (1.85% OC, pH 7.8) (Hassink, J, 2012, 2011/1276919; Hassink, J, 2012, 2012/1023466). [¹⁴C] bentazone was homogeneously applied on the surfaces of soil in 1 cm deep stainless steel dishes at a concentration of 7.207 mg/kg dry soil (equivalent to an application rate of 1081 g ai/ha). The incubation conditions were irradiation from a Xenon lamp (about 3 mW/cm²) at 22 °C for 15 days. Duplicate samples were taken 0, 1, 3, 7, 10 and 15 days after treatment. Dark control samples were analysed at the same sampling days. Volatiles were trapped in appropriate trapping solutions.

Soil samples were extracted with methanol and methanol/water and the extracts analysed by LSC and HPLC. Bound residues were quantified by combustion and subsequent LSC measuring. The bound residues were further characterised by NaOH-extraction and distribution of radioactivity between fulvic acids, humic acids and humines. The overall results for the material balances in the photolysis and the dark control samples were in the range of 95.3–100.3% TAR. Carbon dioxide was the only volatile degradation product trapped with 8.1% TAR detected after 15 days in the photolysis test and 1.8% TAR in the dark control.

The sample extractability for the photolysis test differed from the dark control. At the end of the study about 32% TAR were not extractable from the illuminated soil samples. About 20% TAR were non-extractable at the end of the incubation of the dark control samples. The alkali-soluble radioactivity amounted to about 12–24% in the period of 3 to 15 days after treatment in the soil photolysis and was further fractionated to distinguish between acid-insoluble humic acids and acid-soluble fulvic acids. The major part of the radioactivity could be assigned to the fulvic acid fraction (max. 18.7% TAR at 7 DAT). In the dark control samples the amount of non-extractable residues was less than under light. It was confirmed that the alkali-soluble fraction (max. 12.2% TAR at 15 DAT) consisted of radioactive material mainly assigned to the fulvic acid fraction (max. 6.3% TAR at 15 DAT). HPLC analysis of the fulvic acid fractions showed that the radioactivity is divided between several unspecific polar peaks in negligible amounts. The concentration of bentazone decreased to 48.7% TAR in the course of the photolysis study and to 77.0% in the dark control samples. No degradation products was present in more or equal to 1% TAR, respectively. 4% TAR occurred in the photolysis samples or in the dark controls. The results are shown in Table 38 to Table 45.

Table 38 Distribution of radioactivity in soil Bruch West after treatment with [phenyl-U-¹⁴C]-bentazone and incubation under irradiated conditions [%TAR]

DAT	MeOH	MeOH/H ₂ O	ERR	NER	Volatiles ^a	Sum
0 DAT I	95.9	4.5	100.4	1.0	na	101.4
0 DAT II	93.6	4.4	98.0	0.6	na	98.6
0 DAT mean	94.7	4.4	99.2	0.8	na	100.0
1 DAT I	84.0	7.9	91.9	7.3	0.5	99.7
1 DAT II	86.7	7.3	94.0	7.8	0.5	102.3
1 DAT mean	85.3	7.6	92.9	7.5	0.5	101.0
3 DAT I	68.3	10.3	78.6	17.3	2.2	98.1
3 DAT II	66.9	11.8	78.7	17.7	2.2	98.6
3 DAT mean	67.6	11.0	78.7	17.5	2.2	98.4
7 DAT I	42.3	15.9	58.2	32.9	5.0	96.1
7 DAT II	39.4	16.2	55.7	33.9	5.0	94.6
7 DAT mean	40.9	16.1	56.9	33.4	5.0	95.4

DAT	MeOH	MeOH/H ₂ O	ERR	NER	Volatiles ^a	Sum
10 DAT I	45.8	17.9	63.6	28.8	6.5	98.9
10 DAT II	45.2	14.4	59.6	28.5	6.5	94.6
10 DAT mean	45.5	16.1	61.6	28.6	6.5	96.8
15 DAT I	47.2	13.9	61.1	28.7	8.1	97.9
15 DAT II	35.1	14.2	49.3	35.2	8.1	92.6
15 DAT mean	41.2	14.1	55.2	31.9	8.1	95.3

ERR = Extractable radioactive residues

NER = Non-extractable radioactive residues

^a Only CO₂ was found

Table 39 Distribution of radioactivity in soil Bruch West after treatment with [phenyl-U-¹⁴C]-bentazone and incubation under dark conditions [%TAR]

DAT	MeOH	MeOH/H ₂ O	ERR	NER	Volatiles ^a	Sum
0 DAT I	95.9	4.5	100.4	1.0	na	101.4
0 DAT II	93.6	4.4	98.0	0.6	na	98.6
0 DAT mean	94.7	4.4	99.2	0.8	na	100.0
1 DAT I	92.9	3.8	96.7	4.2	0.3	101.2
1 DAT II	91.4	3.7	95.1	4.0	0.3	99.3
1 DAT mean	92.2	3.8	95.9	4.1	0.3	100.3
3 DAT I	91.7	3.0	94.7	6.0	0.6	101.2
3 DAT II	89.9	2.7	92.6	5.7	0.6	99.0
3 DAT mean	90.8	2.8	93.7	5.8	0.6	100.1
7 DAT I	82.1	3.1	85.2	11.7	1.1	97.9
7 DAT II	84.2	3.2	87.4	10.3	1.1	98.8
7 DAT mean	83.2	3.2	86.3	11.0	1.1	98.3
10 DAT I	79.8	3.8	83.6	14.0	1.4	99.0
10 DAT II	81.5	4.1	85.7	13.7	1.4	100.7
10 DAT mean	80.7	4.0	84.7	13.9	1.4	99.9
15 DAT I	71.7	4.3	75.9	20.8	1.8	98.6
15 DAT II	73.0	5.0	78.0	18.4	1.8	98.3
15 DAT mean	72.3	4.6	77.0	19.6	1.8	98.4

ERR = Extractable radioactive residues

NER = Non-extractable radioactive residues

^a Only CO₂ was found

Table 40 Radio-HPLC-analysis of soil extracts after treatment of soil Bruch West with [phenyl-U-¹⁴C]-bentazone and incubation under irradiated conditions [%TAR]

days after treatment	Bentazone	others ^a	sum
0 DAT I	99.6	0.8	100.4
0 DAT II	96.8	1.2	98.0
0 DAT mean	98.2	1.0	99.2
1 DAT I	91.2	0.7	91.9
1 DAT II	92.6	1.4	94.0
1 DAT mean	91.9	1.0	92.9
3 DAT I	76.7	1.9	78.6
3 DAT II	76.9	1.8	78.7
3 DAT mean	76.8	1.8	78.7
7 DAT I	52.7	5.5	58.2
7 DAT II	51.9	3.8	55.7
7 DAT mean	52.3	4.6	56.9
10 DAT I	59.9	3.7	63.6
10 DAT II	59.6	0.0	59.6
10 DAT mean	59.7	1.9	61.6
15 DAT I	57.3	3.9	61.1
15 DAT II	40.2	9.1	49.3
15 DAT mean	48.7	6.5	55.2

^a Each single peak below 4% TAR

Table 41 Radio-HPLC-analysis of soil extracts after treatment of soil Bruch West with [phenyl-U-¹⁴C]-bentazone and incubated under dark conditions [%TAR]

days after treatment	Bentazone	others ^a	sum
0 DAT I	99.6	0.8	100.4
0 DAT II	96.8	1.2	98.0
0 DAT mean	98.2	1.0	99.2
1 DAT I	96.7	0.0	96.7
1 DAT II	95.1	0.0	95.1
1 DAT mean	95.9	0.0	95.9
3 DAT I	94.1	0.6	94.7
3 DAT II	92.2	0.4	92.6
3 DAT mean	93.2	0.5	93.7
7 DAT I	85.2	0.0	85.2
7 DAT II	87.4	0.0	87.4
7 DAT mean	86.3	0.0	86.3
10 DAT I	83.6	0.0	83.6
10 DAT II	85.7	0.0	85.7
10 DAT mean	84.7	0.0	84.7
15 DAT I	75.9	0.0	75.9
15 DAT II	78.0	0.0	78.0
15 DAT mean	77.0	0.0	77.0

^a Each single peak below 1% TAR

Table 42 Characterization of non-extractable residues in soil Bruch West after treatment with [¹⁴C] bentazone and incubation under irradiated conditions [%TAR]

DAT	% TAR					
	NER initial	NaOH extraction	Water extraction	Sum of NaOH and water extracts	Soil residues after extraction (humins)	Sum ^a
3 I	17.33	11.28	0.24	11.52	2.81	14.33
3 II	17.66	12.04	0.36	12.40	3.04	15.44
3 mean	17.50	11.66	0.31	11.96	2.92	14.88
7 I	32.94	21.92	0.54	22.46	5.67	28.13
7 II	33.88	22.88	0.74	23.63	5.04	28.67
7 mean	33.41	22.39	0.65	23.04	5.35	28.40
10 I	28.76	18.45	0.51	18.95	6.47	25.42
10 II	28.48	19.29	0.49	19.78	5.22	25.00
10 mean	28.62	18.87	0.50	19.37	5.84	25.21
15 I	28.69	21.79	1.27	23.07	5.54	28.61
15 II	35.21	23.66	1.35	25.01	7.80	32.80
15 mean	31.95	22.73	1.31	24.04	6.67	30.71

^a Deviations from initial NER values have to be attributed to differing LSC results

Table 43 Distribution of radioactivity between fulvic acids and humic acids in soil Bruch West after treatment with [¹⁴C] bentazone and incubation under irradiated conditions [%TAR]

DAT	% TAR			
	Sum of NaOH and water extracts	Fulvic acid	Humic acid	Sum ^a
3 I	11.52	8.52	3.17	11.69
3 II	12.40	9.20	3.37	12.57
3 mean	11.96	8.86	3.27	12.13
7 I	22.46	18.39	4.72	23.11
7 II	23.63	19.09	3.90	22.99
7 mean	23.04	18.74	4.31	23.05
10 I	18.95	15.48	3.20	18.68

DAT	% TAR			
	Sum of NaOH and water extracts	Fulvic acid	Humic acid	Sum ^a
10 II	19.78	16.64	2.97	19.61
10 mean	19.37	16.06	3.09	19.15
15 I	23.07	15.30	5.94	21.24
15 II	25.01	16.71	6.26	22.96
15 mean	24.04	16.01	6.10	22.10

^a Slight deviations from initial values have to be attributed to differing LSC results

Table 44 Characterization of non-extractable residues in soil Bruch West after treatment with [¹⁴C] bentazone and incubation under dark conditions [%TAR]

DAT	% TAR					
	NER initial	NaOH extraction	Water extraction	Sum of NaOH and water extracts	Soil residues after extraction (humin)	Sum ^a
7 I	11.67	5.39	0.20	5.60	2.99	8.59
7 II	10.29	5.10	0.19	5.29	3.28	8.57
7 mean	10.98	5.25	0.19	5.44	3.14	8.58
10 I	13.97	6.16	0.21	6.37	4.24	10.60
10 II	13.74	5.86	0.18	6.03	4.47	10.50
10 mean	13.86	6.01	0.20	6.20	4.35	10.55
15 I	20.79	11.47	1.00	12.48	6.62	19.09
15 II	18.45	10.98	1.01	11.98	6.18	18.16
15 mean	19.62	11.23	1.00	12.23	6.40	18.63

^a Deviations from initial NER values have to be attributed to differing LSC results

Table 45 Distribution of radioactivity between fulvic acids and humic acids in soil Bruch West after treatment with [¹⁴C] bentazone and incubation under dark conditions [%TAR]

DAT	% TAR			
	Sum of NaOH and water extracts	Fulvic acid	Humic acid	Sum ^a
7 I	5.60	4.24	1.41	5.65
7 II	5.29	4.00	1.45	5.45
7 mean	5.44	4.12	1.43	5.55
10 I	6.37	5.04	1.42	6.46
10 II	6.03	4.70	1.51	6.21
10 mean	6.20	4.87	1.46	6.33
15 I	12.48	6.45	4.07	10.52
15 II	11.98	6.14	4.47	10.61
15 mean	12.23	6.30	4.27	10.56

^a Slight deviations from initial values have to be attributed to differing LSC results

The results of the present study showed that sunlight may have an influence on the degradation rate of bentazone in soil. The incorporation into the humic substances was observed to be faster under irradiated than under dark conditions. However, no photo degradates were formed in significant amounts (all peaks < 4%).

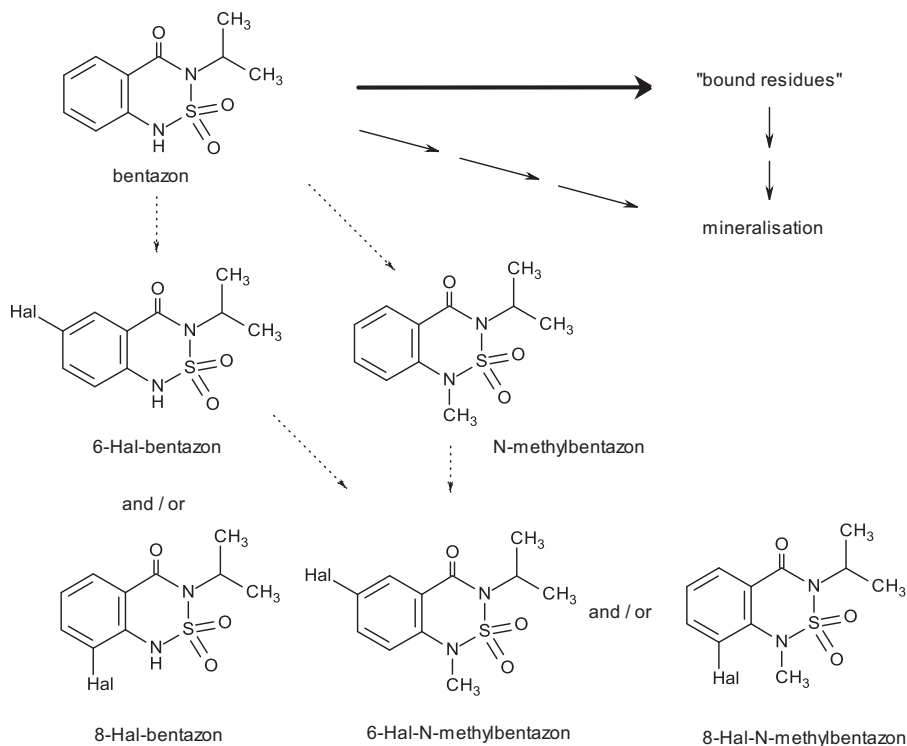


Figure 4 Proposed pathway for the degradation of bentazone in soil

Crop rotation studies

Information on the fate of bentazone in follow-on crop studies was made available to the Meeting.

A confined rotational crop study was conducted with U-¹⁴C-phenyl-labelled bentazone (5.29 MBq/mg, radiochemical purity 97.3%) (Radzom, M. *et al.*, 2011, 2010/1143715). The active substance was applied to bare silty loamy sand soil in plastic containers at an application rate of 1 × 1000 g ai/ha using an automatic spray track system. The nature and the level of radioactive residues were investigated in lettuce (immature and mature; Variety: *Matildas*, *Giesela*), white radish (top and root; Variety: *April Cross*) and spring wheat (forage, hay, straw and grain; Variety: *Thasos*) after plant back intervals of 30, 120 and 365 days. Plant samples were harvested at maturity, and additional immature lettuce samples as well as spring wheat forage samples (in part dried to hay) were taken 27 to 40 days and 56 to 74 days after planting or sowing, respectively. Soil (1.86% OC; pH 7.5) samples were taken after ploughing and after harvest of the mature crops for each plant back interval. The sampled material was stored in a freezer. All plant samples were homogenised and the radioactive residues in these samples and in the soil samples were determined by combustion analysis.

Significant translocation of radioactive residues from soil into the plants was observed for the plant back interval of 30 DAT which declined rapidly for longer aging periods of 120 and 365 days. The residue concentration in the top soil layer after aging and ploughing slightly decreased with increasing plant back intervals. The total radioactive residues (TRR) in lettuce (immature and mature samples) did not exceed 0.128 mg/kg for all plant back intervals. The TRR in white radish top was 0.168 mg/kg at a plant back interval of 30 DAT, decreasing to 0.019 mg/kg after 120 DAT and to 0.003 mg/kg (TRR combusted) after 365 DAT. The total radioactive residues in roots of mature crop decreased from 0.128 mg/kg (30 DAT), to 0.012 mg/kg (120 DAT) and finally to 0.001 mg/kg (365 DAT, TRR combusted). In spring wheat, the highest residue levels were measured in hay (ranging from 0.070 to 1.591 mg/kg, for 30 DAT and 365 DAT, respectively) and straw (0.049 to 1.107 mg/kg, for 30 DAT and 365 DAT, respectively). Total radioactive residues in grain accounted for 0.041 to 0.711 mg/kg.

The extractability of the radioactive residues with methanol and water ranged from 43.7% to 71.3% TRR for lettuce and white radish. For spring wheat matrices, the extractability was relatively low with 8.5% to 30.0%, indicating incorporation of radioactivity in plant constituents. The major portions of the radioactive residues were generally extracted with methanol, except for spring wheat grain where similar portions were extracted with methanol and water.

In all the crop matrices analysed, considerable amounts of the radioactive residues were not extractable with methanol and water. The residual radioactive residues after solvent extraction of all matrices of the plant back intervals 30 DAT and 120 DAT were further characterised using a sequential solubilisation procedure including solubilisation with aqueous ammonia, macerozyme/cellulase and glucosidase/hesperidinase. These incubations were, where applicable, followed by treatments with amylase/amyloglucosidase, tyrosinase/laccase, microwave incubation, and treatments with hydrochloric acid and sodium hydroxide. The solubilised residues had possibly been associated with or embedded / incorporated in insoluble plant material (e.g. proteins, cell wall polymers and starch). Analysis of the extracts and solubilisates after solvent extraction using the HPLC resulted for all crops, matrices and DAT intervals in an early eluting peak or peak group. This peak or peak group represented the main component in all matrices and for all aging intervals and was identified as polar fraction. The composition of the polar fraction was further investigated using an HPLC method suitable for saccharide analysis. The main portion of the residues corresponded to glucose, fructose and sucrose (> 50% ROI), showing composition of the polar fraction of carbohydrates.

Bentazone and/or its soil metabolites were taken up by and transformed in the rotational crops primarily into sugars (glucose, fructose and sucrose and further components of similar polarity) which were without exception the most abundant components in all matrices examined (methanol/water extracts and solubilisates after solvent extraction). The unchanged parent molecule was found as minor component in samples of immature (30 DAT) and mature lettuce (30 and 120 DAT) in concentrations of < 0.0013 mg/kg and 1.2% TRR only. Additional medium polar degradation products were detected at even lower concentrations.

Table 46 Total radioactive residues in crops after treatment with [^{14}C] bentazone

Crop Parts (Days After Sowing /Planting, DAP)	TRR Determined by Direct Combustion [mg/kg]	TRR Calculated ^a [mg/kg]
Plant back interval: 30 DAT		
Immature lettuce (40 DAP)	0.133	0.128
Mature lettuce (61 DAP)	0.079	0.076
White radish top (76 DAP)	0.169	0.168
White radish root (76 DAP)	0.138	0.128
Spring wheat forage (60 DAP)	0.279	0.270
Spring wheat hay (60 DAP)	1.712	1.591
Spring wheat straw (117 DAP)	1.337	1.107
Spring wheat grain (117 DAP)	0.732	0.711
Plant back interval: 120 DAT		
Immature lettuce (27 DAP)	0.013	0.011
Mature lettuce (41 DAP)	0.012	0.013
White radish top (77 DAP)	0.021	0.019
White radish root (77 DAP)	0.012	0.012
Spring wheat forage (56 DAP)	0.031	0.029
Spring wheat hay (56 DAP)	0.148	0.146
Spring wheat straw (103 DAP)	0.137	0.127
Spring wheat grain (103 DAP)	0.256	0.267
Plant back interval: 365 DAT		
Immature lettuce (34 DAP)	0.007	< 0.01
Mature lettuce (62 DAP)	0.002	< 0.01
White radish top (83 DAP)	0.003	< 0.01
White radish root (83 DAP)	0.001	< 0.01
Spring wheat forage (74 DAP)	0.007	< 0.01
Spring wheat hay (74 DAP)	0.053	0.070

Crop Parts (Days After Sowing/Planting, DAP)	TRR ^a	Methanol Extract		Water Extract		ERR ^b		RRR ^c	
	[mg/kg]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
Immature lettuce (27)	0.011	0.004	37.7	0.001	6.4	0.005	44.1	0.006	55.9
Mature lettuce (41)	0.013	0.007	50.8	0.001	6.8	0.008	57.6	0.006	42.4
White radish top (77)	0.019	0.005	28.4	0.003	15.3	0.008	43.7	0.010	56.3
White radish root (77)	0.012	0.008	67.8	0.000	3.5	0.009	71.3	0.003	28.7
Spring wheat forage (56)	0.029	0.007	23.8	0.001	3.7	0.008	27.5	0.021	72.5
Spring wheat hay (56)	0.146	0.022	15.0	0.011	7.7	0.033	22.7	0.113	77.3
Spring wheat straw (103)	0.127	0.020	15.6	0.009	6.8	0.028	22.4	0.099	77.6
Spring wheat grain (103)	0.267	0.011	4.3	0.011	4.2	0.023	8.5	0.244	91.5
Plant back interval: 365 DAT									
Spring wheat hay (74)	0.070	0.013	19.0	0.004	6.2	0.018	25.2	0.052	74.8
Spring wheat straw (133)	0.049	0.011	21.5	0.004	8.6	0.015	30.0	0.034	70.0
Spring wheat grain (133)	0.041	0.002	5.9	0.003	8.1	0.006	14.0	0.035	86.0

^a TRR = sum of ERR and RRR

^b ERR = extractable radioactive residue (methanol extract and water extract),

^c RRR = residual radioactive residue

^d Extraction 2; data for water extract 2, ERR and RRR are not shown because they are of no relevance

Table 49 Partition characteristics of radioactive residues extracted with methanol from rotational crop samples after [¹⁴C] bentazone treatment and plant back intervals of 30 days

Crop Parts	DA T ^a	Methanol Extract		Organosoluble				Organo-soluble Sum		Water Soluble		Recovery _b
				Dichloro-methane		Ethyl Acetate						
		[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[%]
Plant back interval: 30 DAT												
Immature lettuce	30	0.051	40.0	0.015	11.4	0.003	2.7	0.018	14.1	0.035	27.2	103.4
Mature lettuce		0.032	42.1	0.008	9.9	0.002	2.1	0.009	11.9	0.022	28.8	96.7
White radish top		0.057	34.2	0.011	6.7	0.004	2.1	0.015	8.8	0.044	26.3	102.8
White radish root		0.064	50.0	0.002	1.8	0.002	1.4	0.004	3.3	0.060	46.4	99.2
Spring wheat forage		0.065	24.3	0.020	7.4	0.005	1.8	0.025	9.3	0.038	13.9	95.4
Spring wheat hay		0.263	16.6	0.099	6.2	0.014	0.9	0.113	7.1	0.156	9.8	101.9
Spring wheat straw		0.172	15.5	0.063	5.7	0.021	1.9	0.084	7.6	0.083	7.5	97.2
Spring wheat grain		0.035	5.0	0.012	1.7	0.003	0.4	0.015	2.1	0.017	2.4	91.0

^a DAT = Days after treatment

^b Recovery calculated as (dichloromethane + ethyl acetate + water soluble) [mg/kg]

Table 50 Quantitative distribution of the non-released radioactivity in rotational crops after treatment with [¹⁴C] bentazone

Fraction / Supernatant	Crop Parts							
	Immature lettuce (40 DAP ^a)		Mature lettuce (61 DAP)		White radish Top (76 DAP)		White radish root (76 DAP)	
	[mg/kg]	[% TRR]	[mg/kg]	[% TRR]	[mg/kg]	[% TRR]	[mg/kg]	[% TRR]
Plant back interval: 30 DAT ^b								
RRR	0.070	54.6	0.040	52.7	0.087	51.6	0.059	45.8
NH ₄ OH Solubilisate	0.004	2.8	0.002	2.9	0.005	2.9	0.003	2.6
Macerozyme / Cellulase Solubilisate ^c	0.018	14.1	0.016	21.2	0.035	21.1	0.027	20.7
Glucosidase / Hesperidinase Solubilisate	0.0049	3.8	0.004	5.4	0.007	4.1	0.009	6.8
α -Amylase / β -Amylase / Amyloglucosidase Solubilisate	0.0043	3.3	0.001	1.4	0.004	2.1	0.003	2.2
Sum of Solubilised Radioactive Residues	0.031	24.0	0.024	30.9	0.051	30.1	0.041	32.3
Final Residue	0.023	17.6	0.018	23.4	0.028	16.8	0.016	12.5
Procedural Recovery [%] ^d	76.3		103.2		91.0		97.8	
Plant back interval: 120 DAT								
RRR	0.006	55.9	0.006	42.4	0.010	56.3	0.003	28.7
NH ₄ OH Solubilisate	0.001	5.0	0.000	3.7	0.001	4.2	0.000	1.4
Macerozyme Solubilisate	0.001	12.4	0.001	10.1	0.002	12.7	0.001	7.8
Glucosidase / Hesperidinase Solubilisate	na		na		0.001	2.8	0.000	1.8
Sum of Solubilised Radioactive Residues	0.002	17.4	0.002	13.8	0.004	19.6	0.001	10.9
Final Residue	0.004	38.4	0.003	23.6	0.005	26.1	0.002	14.3
Procedural Recovery [%]	99.8		88.2		81.3		88.0	

a DAP = Days after planting (or sowing, respectively)

b DAT = Days after treatment

c Cellulase was additionally applied in the case of mature lettuce, white radish top and root

d Recovery calculated as (sum of solubilised radioactive residues + final residue) [mg/kg] • 100 / RRR [mg/kg]

na = not applied

RRR residual radioactive residue

Table 51 Quantitative distribution of the non-released radioactivity in rotational crops after treatment with [¹⁴C] bentazone

Fraction / Supernatant	Crop Parts							
	Spring Wheat Forage (60 DAP ^a)		Spring Wheat Hay (60 DAP)		Spring Wheat Straw (117 DAP)		Spring Wheat Grain (117 DAP)	
	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
Plant back interval: 30 DAT ^b								
RRR	0.193	71.6	1.198	75.3	0.845	76.3	0.634	89.2
NH ₄ OH Solubilise	0.009	3.3	0.091	5.7	0.028	2.5	0.072	10.1
Macerozyme / Cellulase Solubilise ^{c, d}	0.056	20.6	0.134	8.4	0.085	7.7	0.201	28.2
Glucosidase / Hesperidinase Solubilise	0.013	5.0	0.039	2.5	0.033	3.0	0.061	8.6
α-Amylase / β -Amylase / Amyloglucosidase Solubilise	0.002	0.9	0.019	1.2	0.012	1.1	0.152	21.3
Tyrosinase / Laccase Solubilise	0.001	0.4	na		0.018	1.6	0.002	0.2
Microwave Incubation	0.008	2.8	0.049	3.1	0.155	14.0	0.025	3.5
6 N HCl	0.025	9.3	0.273	17.2	0.154	14.0	na	
2 N NaOH	0.020	7.4	0.180	11.3	0.159	14.4	na	
Sum of Solubilised	0.134	49.8	0.785	49.3	0.645	58.3	0.511	71.9

Fraction / Supernatant	Crop Parts							
	Spring Wheat Forage (60 DAP ^a)		Spring Wheat Hay (60 DAP)		Spring Wheat Straw (117 DAP)		Spring Wheat Grain (117 DAP)	
	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
Radioactive Residues								
Final Residue	0.011	4.2	0.068	4.3	0.035	3.1	0.041	5.7
Procedural Recovery [%] ^c	75.4		71.2		80.4		87.1	
Plant back interval: 120 DAT								
RRR	0.021	72.5	0.113	77.3	0.099	77.6	0.244	91.5
NH ₄ OH Solubilisate	0.001	3.5	0.008	5.3	0.005	3.7	0.019	7.3
Macerozyme / Cellulase Solubilisate ^c	0.005	18.1	0.016	11.0	0.006	4.8	0.114	42.9
Glucosidase / Hesperidinase Solubilisate	0.001	4.4	0.004	2.8	0.002	1.6	0.044	16.4
α -Amylase / β -Amylase / Amyloglucosidase Solubilisate	0.001	2.2	0.002	1.1	0.001	1.1	0.012	4.4
Microwave Incubation	0.001	2.2	0.005	3.6	0.005	3.9	na	
Sum of Solubilised Radioactive Residues	0.009	30.4	0.035	23.9	0.019	15.0	0.190	71.1
Final Residue	0.008	25.9	0.064	44.1	0.071	55.8	0.021	7.9
Procedural Recovery [%] ^c	77.7		87.9		91.2		86.3	

^a DAP = Days after planting (or sowing, respectively)

^b DAT = Days after treatment

^c Cellulase was additionally applied in the case of spring wheat forage, straw and grain

^d In the work-up of spring wheat grain (30 DAT) the enzymatic solubilisation procedures applying macerozyme / cellulase and glucosidase / hesperidinase were applied in a reversed order

^e Recovery calculated as (sum of solubilised radioactive residues + final residue) [mg/kg] • 100 / RRR [mg/kg]

na = not applied

RRR residual radioactive residue

Table 52 Total identified, characterised and final radioactive residues in lettuce after treatment with [¹⁴C] bentazone

Metabolite / Fraction	Immature Lettuce Leaves		Mature Lettuce Leaves	
	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
Plant back interval: 30 DAT				
Total radioactive residue (TRR)	0.128	100.0	0.076	100.0
Extractable radioactive residue (ERR)	0.058	45.4	0.036	47.3
Total identified from ERR	0.038	30.0	0.030	39.8
Total characterised from ERR	0.018	14.0	0.003	3.5
Total identified or characterised from ERR ^a	0.056	44.0	0.033	43.3
Residual radioactive residue (after solvent extraction, RRR)	0.070	54.6	0.040	52.7
Total Identified Radioactive Residues Solubilised from RRR	0.027	20.7	0.023	29.6
Total Characterised Radioactive Residues Solubilised from RRR	0.004	3.3	0.001	1.4
Total identified or characterised radioactive residues solubilised from RRR ^b	0.031	24.0	0.024	30.9
Total identified	0.065	50.7	0.053	69.4
Total characterised	0.022	17.4	0.004	4.9
Total identified or characterised	0.087	68.0	0.057	74.3
Final residue ^b	0.023	17.6	0.018	23.4
Grand Total	0.110	85.6	0.074	97.7
Plant back interval: 120 DAT				
Total radioactive residue (TRR)	0.011	100.0	0.013	100.0
Extractable radioactive residue (ERR)	0.005	44.1	0.008	57.6
Total identified from ERR	0.004	37.7	0.005	36.5
Total characterised from ERR	0.001	6.4	0.003	21.1
Total identified or characterised from ERR ^a	0.005	44.1	0.008	57.6
Residual radioactive residue (after solvent extraction, RRR)	0.006	55.9	0.006	42.4

Metabolite / Fraction	Immature Lettuce Leaves		Mature Lettuce Leaves	
	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
Total Characterised Radioactive Residues Solubilised from RRR	0.002	17.4	0.002	13.8
Total characterised radioactive residues solubilised from RRR ^b	0.002	17.4	0.002	13.8
Total identified	0.004	37.7	0.005	36.5
Total characterised	0.003	23.8	0.005	34.9
Total identified or characterised	0.007	61.5	0.010	71.4
Final residue	0.004	38.4	0.003	23.6
Grand Total	0.011	99.9	0.013	95.0

^a ERR = Extractable Radioactive Residue (methanol extract and water extract)

^b See Table 41

RRR residual radioactive residue

Table 53 Total identified, characterised and final radioactive residues in white radish after treatment with [¹⁴C] bentazone (Radzom, M *et al.*, 2011, 2010/1143715)

Metabolite / Fraction	White Radish Top		White Radish Root	
	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
Plant back interval: 30 DAT				
Total radioactive residue (TRR)	0.168	100.0	0.128	100.0
Extractable radioactive residue (ERR)	0.081	48.4	0.070	54.2
Total identified from ERR	0.071	42.4	0.066	51.7
Total characterised from ERR	0.006	3.9	0.000	0.0
Total identified or characterised from ERR ^a	0.078	46.3	0.066	51.7
Residual radioactive residue (after solvent extraction, RRR)	0.087	51.6	0.059	45.8
Total Identified Radioactive Residues Solubilised from RRR	0.051	30.1	0.038	29.7
Total Characterised Radioactive Residues Solubilised from RRR	0.000	0.0	0.003	2.6
Total identified or characterised radioactive residues solubilised from RRR ^b	0.051	30.1	0.041	32.3
Total identified	0.122	72.5	0.105	81.4
Total characterised	0.006	3.9	0.003	2.6
Total identified or characterised	0.128	76.4	0.108	84.0
Final residue ^b	0.028	16.8	0.016	12.5
Grand Total	0.157	93.2	0.124	96.5
Plant back interval: 120 DAT				
Total radioactive residue (TRR)	0.019	100.0	0.012	100.0
Extractable radioactive residue (ERR)	0.008	43.7	0.009	71.3
Total identified from ERR	0.005	28.4	0.008	67.8
Total characterised from ERR	0.003	15.3	0.000	3.5
Total identified or characterised from ERR ^a	0.008	43.7	0.009	71.3
Residual radioactive residue (after solvent extraction, RRR)	0.010	56.3	0.003	28.7
Total Characterised Radioactive Residues Solubilised from RRR	0.004	19.6	0.001	10.9
Total characterised radioactive residues solubilised from RRR ^b	0.004	19.6	0.001	10.9
Total identified	0.005	28.4	0.008	67.8
Total characterised	0.007	34.9	0.001	14.4
Total identified or characterised	0.012	63.3	0.010	82.2
Final residue	0.005	26.1	0.002	14.3
Grand Total	0.017	89.4	0.011	96.6

^a ERR = Extractable Radioactive Residue (methanol extract and water extract)

^b See Table 41

RRR residual radioactive residue

Table 54 Total identified, characterised and final radioactive residues in spring wheat after treatment with [¹⁴C] bentazone

Metabolite / Fraction	Spring Wheat Forage		Spring Wheat Hay	
	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
Plant back interval: 30 DAT				
Total radioactive residue (TRR)	0.270	100.0	1.591	100.0
Extractable radioactive residue (ERR)	0.077	28.4	0.393	24.7
Total identified from ERR	0.053	19.8	0.342	21.5
Total characterised from ERR	0.015	5.7	0.045	2.8
Total identified or characterised from ERR ^a	0.069	25.5	0.387	24.3
Residual radioactive residue (after solvent extraction, RRR)	0.193	71.6	1.198	75.3
Total Identified Radioactive Residues Solubilised from RRR	0.078	28.9	0.283	17.8
Total Characterised Radioactive Residues Solubilised from RRR	0.056	20.9	0.502	31.6
Total identified or characterised radioactive residues solubilised from RRR ^b	0.134	49.8	0.785	49.3
Total identified	0.131	48.7	0.625	39.3
Total characterised	0.072	26.6	0.547	34.4
Total identified or characterised	0.203	75.3	1.171	73.6
Final residue ^b	0.011	4.2	0.068	4.3
Grand Total	0.214	79.5	1.239	77.9
Plant back interval: 120 DAT				
Total radioactive residue (TRR)	0.029	100.0	0.146	100.0
Extractable radioactive residue (ERR)	0.008	27.5	0.033	22.7
Total identified from ERR	0.007	23.8	0.022	15.0
Total characterised from ERR	0.001	3.7	0.011	7.7
Total identified or characterised from ERR ^a	0.008	27.5	0.033	22.7
Residual radioactive residue (after solvent extraction, RRR)	0.021	72.5	0.113	77.3
Total Characterised Radioactive Residues Solubilised from RRR	0.009	30.4	0.035	23.9
Total characterised radioactive residues solubilised from RRR ^b	0.009	30.4	0.035	23.9
Total identified	0.007	23.8	0.022	15.0
Total characterised	0.010	34.1	0.046	31.6
Total identified or characterised	0.017	57.9	0.068	46.6
Final residue	0.008	25.9	0.064	44.1
Grand Total	0.025	83.8	0.133	90.7
Plant back interval: 365 DAT				
Total radioactive residue (TRR)	–	–	0.070	100.0
Total identified from ERR	–	–	0.013	19.0
Total characterised from ERR	–	–	0.004	6.2
Total identified or characterised from ERR ¹⁾	–	–	0.018	25.2
Residual radioactive residue (after solvent extraction, RRR)	–	–	0.052	74.8
Sum of RRR and Total identified or characterised from ERR	–	–	0.070	100.0

^a ERR = Extractable Radioactive Residue (methanol extract and water extract)^b See Table 42

RRR residual radioactive residue

Table 55 Total identified, characterised and final radioactive residues in spring wheat after treatment with [¹⁴C] bentazone

Metabolite / Fraction	Spring Wheat Straw		Spring Wheat Grain	
	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
Plant back interval: 30 DAT				
Total radioactive residue (TRR)	1.107	100.0	0.711	100.0
Extractable radioactive residue (ERR)	0.262	23.7	0.077	10.8
Total identified from ERR	0.185	16.8	0.052	7.4
Total characterised from ERR	0.066	5.9	0.003	0.4
Total identified or characterised from ERR ^a	0.251	22.7	0.055	7.8
Residual radioactive residue (after solvent extraction, RRR)	0.845	76.3	0.634	89.2
Total Identified Radioactive Residues Solubilised from RRR	0.147	13.2	0.485	68.2

Metabolite / Fraction	Spring Wheat Straw		Spring Wheat Grain	
	[mg/kg]	[%TRR]	[mg/kg]	[%TRR]
Total Characterised Radioactive Residues Solubilised from RRR	0.498	45.0	0.026	3.7
Total identified or characterised radioactive residues solubilised from RRR ^b	0.645	58.3	0.511	71.9
Total identified	0.332	30.0	0.537	75.6
Total characterised	0.564	51.0	0.029	4.1
Total identified or characterised	0.896	81.0	0.567	79.7
Final residue	0.035	3.1	0.041	5.7
Grand Total	0.931	84.1	0.608	85.5
Plant back interval: 120 DAT				
Total radioactive residue (TRR)	0.127	100.0	0.267	100.0
Extractable radioactive residue (ERR)	0.028	22.4	0.023	8.5
Total identified from ERR	0.020	15.6		
Total characterised from ERR	0.009	6.8	0.023	8.5
Total identified or characterised from ERR ^a	0.028	22.4		
Residual radioactive residue (after solvent extraction, RRR)	0.099	77.6	0.244	91.5
Total characterised radioactive residues solubilised from RRR	0.019	15.0		
Total characterised radioactive residues solubilised from RRR ^b	0.019	15.0	0.190	71.1
Total identified	0.020	15.6		
Total characterised	0.028	21.8	0.212	79.6
Total identified or characterised	0.047	37.4		
Final residue	0.071	55.8	0.021	7.9
Grand Total	0.118	93.1	0.233	87.5
Plant back interval: 365 DAT				
Total radioactive residue (TRR)	0.049	100.0	0.041	100.0
Total identified from ERR	0.011	21.5	-	-
Total characterised from ERR	0.004	8.6	0.006	14.0
Total identified or characterised from ERR ¹⁾	0.015	30.0	-	-
Residual radioactive residue (after solvent extraction, RRR)	0.034	70.0	-	-
Sum of RRR and Total identified or characterised from ERR	0.049	100.0	-	-

^a ERR = Extractable Radioactive Residue (methanol extract and water extract)

^b See Table 42.

RRR residual radioactive residue

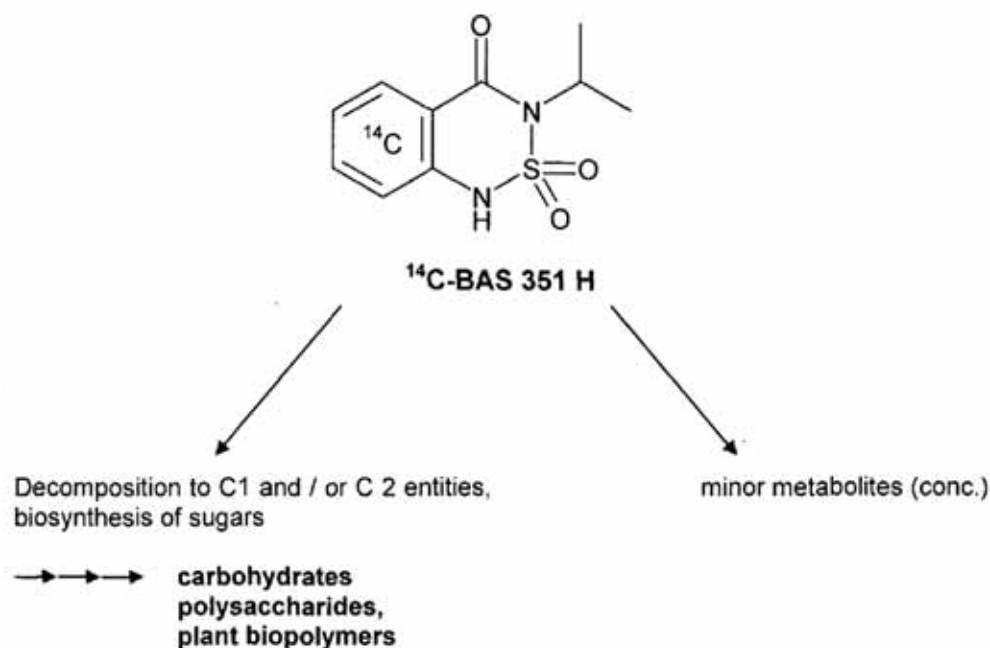


Figure 5 Metabolic pathway of [¹⁴C] bentazone in rotational crops

RESIDUE ANALYSIS

Analytical methods

The Meeting received descriptions and validation data for analytical methods for residues of bentazone and the conjugates of 6-OH- and 8-OH-bentazone in plant and animal matrices. Bentazone residues can be measured in most matrices to an LOQ of 0.01 to 0.05 mg/kg. The methods effectively measure 'total' bentazone.

Technical procedure-Method for the determination of Bentazon, 6-OH-Bentazon and 8-OH-Bentazon in plant matrices—Method 438/1. (Linder, G *et al.*, 2000, 2000/1000243)

Analyte:	bentazone, 6-OH-bentazone and 8-OH-bentazone	GC/MSD	Method No. 438/1
LOQ:	0.02 mg/kg		
Description	BASF Method No. 438/1 allows the determination of bentazone and all sugar conjugates which can be hydrolysed to 6-OH-bentazone and 8-OH-bentazone. It is a miniaturised version of the BASF Method No. 438/0 and was adapted to a number of additional crops. Bentazone and its metabolites are extracted from plant matrices with aqueous methanol. After purification of a 20% aliquot by an iso-octane liquid-liquid partition, the two relevant metabolites which are present as glucosides are hydrolysed using enzymatic cleavage to 6-OH-bentazone and 8-OH-bentazone. After a Ca(OH) ₂ -precipitation step to remove acidic plant constituents, a reversed phase C ₁₈ -column clean-up is performed. The analytes are then methylated with diazomethane and their derivatives are purified using a silica gel-column. The final determination of the residues of bentazone and its OH-metabolites is performed by GC-MS.		

Bentazone and its two OH-metabolites: Validation of residue method 438/2 for plant materials using LC/MS/MS. (Class T., 2007, 2007/1013924)

Analyte:	bentazone, 6-OH-bentazone and 8-OH-bentazone	LC-MS/MS	Method No. 438/2
LOQ:	0.01 mg/kg.		
Description	Extraction and enzymatic cleavage of residues of bentazone and its conjugated 6-OH- and 8-OH-metabolites from plant specimen was adopted from BASF Method No. 438/2 which uses GC-MS for the determination of the analytes in plant materials: bentazone and its hydroxy-metabolites present in plant as glucosides were extracted from plant material with aqueous methanol. After purification of an aliquot by liquid-liquid partition with iso-octane, glucosides were cleaved enzymatically to 6-OH-bentazone and 8-OH-bentazone. After $\text{Ca}(\text{OH})_2$ -precipitation of acidic plant constituents, a reversed phase C_{18} -SPE clean-up was performed. Final determination of bentazone and its OH-metabolites was performed by LC-MS/MS, monitoring two parent-daughter ion transitions for each compound.		

Determination of Bentazone, 6-OH-Bentazone and 8-OH-Bentazone in plant matrices—Independent laboratory validation of the analytical method No. 438/2. (Schulz, H., Meyer, M., 2007, 2007/1013926).

Analyte:	bentazone, 6-OH-bentazone and 8-OH-bentazone	LC-MS/MS	Method No. 438/2
LOQ:	0.01 mg/kg.		
Description	Bentazone and its metabolites are extracted from plant or animal matrices with aqueous methanol. After purification of an aliquot by an iso-octane liquid-liquid partition, the two relevant metabolites which are present as glucosides were hydrolysed using enzymatic cleavage to 6-OH-bentazone and 8-OH-bentazone. After a $\text{Ca}(\text{OH})_2$ -precipitation step to remove acidic matrix constituents, a reversed phase C_{18} -SPE clean-up is performed. The final determination of bentazone and its hydroxy-metabolites is performed by LC-MS/MS, monitoring two parent-daughter ion transitions for each compound.		

Method for determination of Bentazon and its metabolites residues in rice grain and bran, soya bean seed, hulls, forage and refined oil, corn grain, and dry peas. (Abdel-Baky, S, 1995, 1996/5278)

Analyte:	bentazone, 6-OH-bentazone and 8-OH-bentazone	GC-TSD GC-MSD	Method No. D9310
LOQ:	0.05 mg/kg.		
Description	Residues are extracted from all matrices with methanol. The extracts are concentrated and hydrolysed with MeOH/HCl to release the 6-OH-bentazon and 8-OH-bentazone metabolites. The samples are made basic with 50% KOH (pH 14) and extracted with dichloromethane (DCM) to remove neutral and basic matrix impurities. The sample solutions are acidified with concentrated HCl (pH < 1), and then extracted with ethyl acetate. The final extracts are evaporated and the residues are derivatised with diazomethane. The methylated products, N-methylbentazon (BH 351-NMB), 8-methoxy-N-methylbentazon (BH 351-8OMNM), and 6-methoxy-N-methylbentazon (BH 351-6OMNM), are purified on a mini-silica column (1 gram) by elution with DCM/hexane. Final quantitation has been done on two analytical instruments: a capillary gas chromatograph with a thermionic specific detector (GC-TSD) and a capillary gas chromatograph with a mass selective detector (GC-MSD).		

Method for peppermint and lemon balm: Analysis of residues after treatment with Basagran: Active ingredient: bentazone. (Class, T and Bacher, R, 1998, 1998/11399)

Analyte:	bentazone and 8-OH-bentazone	(GC-MS/MS).
LOQ:	0.05 mg/kg.	
Description	Residues are extracted from all matrices with methanol. The extracts were methylated with diazomethane and detected with gas chromatography with a mass selective detector (GC-	

MS/MS).

Bentazone and its two OH-metabolites: Validation of residue method 438/2 for animal materials using LC/MS-MS. (Bacher, R, 2007, 2007/1013925)

Analyte: bentazone, 6-OH-bentazone and 8-OH-bentazone LC-MS/MS Method 438/2

LOQ: 0.01 mg/kg.

Description Extraction and enzymatic cleavage of residues of bentazone and its conjugated 6-OH- and 8-OH-metabolites from plant specimen was adopted from BASF Method No. 438/2 which uses GC-MS for the determination of the analytes in plant materials: bentazone and its OH-metabolites present in animal matrices as glucuronides or sulphates were extracted with aqueous methanol. After purification of an aliquot by liquid-liquid partition with iso-octane, glucuronides and sulphates were cleaved enzymatically to 6-OH-bentazone and 8-OH-bentazone. After $\text{Ca}(\text{OH})_2$ -precipitation of acidic matrix constituents, a reversed phase C_{18} -SPE clean-up was performed. The final determination of bentazone and its hydroxy-metabolites was performed by LC-MS/MS, monitoring two parent-daughter ion transitions for each compound.

Determination of Bentazone, 6-OH-Bentazone and 8-OH-Bentazone in animal matrices—Independent laboratory validation of the analytical method. No. 438/2. (Schulz, H and Meyer, M, 2007, 2007/1013927)

Analyte: bentazone, 6-OH-bentazone and 8-OH-bentazone LC-MS/MS Method. No. 438/2

LOQ: 0.01 mg/kg.

Description Bentazone and its metabolites are extracted from animal matrices with aqueous methanol. After purification of an aliquot by an iso-octane liquid-liquid partition, the two relevant metabolites which are present as glucosides were hydrolysed using enzymatic cleavage to 6-OH-bentazone and 8-OH-bentazone. After a $\text{Ca}(\text{OH})_2$ -precipitation step to remove acidic matrix constituents, a reversed phase C_{18} -SPE clean-up is performed. The final determination of bentazone and its OH-metabolites is performed by LC-MS/MS, monitoring two parent-daughter ion transitions for each compound.

A summary of analytical method and procedural recoveries are presented in Table 56.

Table 56 Recoveries of bentazone, 6-OH-bentazone and 8-OH-bentazone in-plant matrices spiked with 0.02, 0.2 and 2.0 mg/kg (Linder, G *et al.*, 2000, 2000/1000243)

Crop	Matrix	Bentazone			6-OH-bentazone			8-OH-bentazone		
		0.02	0.2	2.0	0.02	0.2	2.0	0.02	0.2	2.0
		mg/kg			mg/kg			mg/kg		
wheat	shoots	114.9	—	82.4	81.3	—	59.7	92.1	—	59.9
	shoots	112.7	—	105.4	89.2	—	80.2	112.1	—	84.8
	ears	104.1	—	100.5	87.0	—	82.6	71.7	—	—
	straw	109.3	103.4	—	98.1	90.2	—	78.5	79.4	—
	grain	121.4	97.1	88.1	109.3	101.3	76.8	96.3	—	—
	roots	98.1	111.7	107.4	75.7	89.7	101.8	91.5	87.6	75.9
potato	shoots	—	—	—	81.1	—	—	82.2	—	—
	tuber	81.4	91.2	—	57.2	71.7	—	86.1	71.4	—
potato	tuber	75.6	76.2	—	90.0	74.7	—	88.4	69.0	—
	tuber	78.7	—	—	77.9	—	—	110.4	—	—
maize	shoots	—	94.9	—	—	64.8	—	—	55.4	—
	shoots	90.0	64.1	—	70.1	54.6	—	103.4	57.5	—
	roots	120.1	78.9	90.9	87.8	70.9	88.8	98.1	71.8	84.6
	roots	91.6	89.5	75.4	88.9	67.2	68.7	116.9	73.8	57.4
	roots	110.4	67.4	74.8	105.5	72.3	75.1	108.6	61.1	62.2
	ears ^a	70.0	72.2	—	76.4	63.4	—	107.3	64.3	—
	straw	76.8	82.3	—	100.7	86.3	—	81.5	69.8	—

Crop	Matrix	Bentazone			6-OH-bentazone			8-OH-bentazone		
		0.02	0.2	2.0	0.02	0.2	2.0	0.02	0.2	2.0
		mg/kg			mg/kg			mg/kg		
	grain	100.7	89.7	–	92.2	88.7	–	84.6	75.1	–
barley	shoots	90.7	–	103.5	67.0	–	102.5	69.5	–	77.8
	shoots	89.0	–	82.2	86.0	–	95.7	89.7	–	77.6
	ears	90.0	–	103.9	103.1	–	101.6	115.8	–	85.0
	straw	92.8	–	98.7	70.5	–	111.7	114.4	–	87.1
	grain	95.0	–	69.4	108.1	69.6	–	117.7	–	60.8
flax	shoots	97.3	65.5	81.0	–	58.0	74.5	113.1	–	60.2
	straw	94.4	103.7	–	81.6	88.6	–	82.1	78.5	–
	seed	116.7	100.1	–	103.8	86.5	–	98.2	84.5	–
bean	seed	81.1	96.0	–	86.5	89.5	–	108.1	73.8	–
	straw	77.1	88.1	–	95.6	92.0	–	68.1	69.8	–
	shoots	51.5	74.3	87.5	63.7	81.5	80.6	55.3	74.5	68.6
	siliques	–	80.4	–	94.6	–	–	–	71.9	–
soya	shoots	–	73.9	93.1	–	87.2	100.0	–	–	84.0
	seed	110.7	85.2	–	89.9	69.7	–	–	–	–
	straw	106.9	76.7	–	83.7	71.4	–	–	–	–
onion	shallot	75.8	99.0	–	79.6	83.1	–	70.4	70.7	–
	bulb	80.1	92.9	–	60.6	80.3	–	61.9	–	52.9
onion	shallot	103.4	105.6	–	66.4	75.5	–	70.4	–	–
	bulb	94.1	99.5	–	89.8	107.0	–	100.0	95.5	–
bean	shoots	98.2	–	90.7	98.2	–	90.9	121.3	–	78.1
	beans ^b	107.8	97.4	–	95.2	74.3	–	117.0	72.3	–
	dry bean	112.7	89.5	–	99.9	70.1	–	119.9	75.8	–
	straw ^b	116.6	90.7	–	124.3	80.8	–	123.9	79.7	–
pea	plant ^c	–	–	101.8	120.4	–	91.0	–	116.4	72.4
	fruit	114.5	115.4	–	83.7	107.6	–	94.5	117.9	–
max (%):		121.4	115.4	107.4	124.3	107.6	111.7	123.9	117.9	87.1
min (%):		51.5	64.1	69.4	57.2	54.6	59.7	55.3	55.4	52.9
mean (%):		96.1	88.8	90.9	88.0	79.6	87.2	95.2	76.7	72.3
SD (+/-):		16.2	13.4	11.7	15.3	13.1	14.0	18.8	14.9	11.4
RSD (+/-):		16.9	15.1	12.9	17.4	16.5	16.1	19.7	19.4	15.8

^a With husks^b With pods^c Without roots

Table 57 Recoveries of bentazone, 6-OH-bentazone and 8-OH-bentazone in plant matrices (Class, T, 2007, 2007/1013924)

Test Substance	Crop	Fortification Level (mg/kg)	No. of Tests	Average Recovery (%)		Relative Standard Deviation (%)	
Transition				239 m/z > 132 m/z	239 m/z > 175 m/z	239 m/z > 132 m/z	239 m/z > 175 m/z
bentazone	maize	0.01	5	100	99	2	1
	silage	0.1	5	96	95	5	6
	maize	0.01	5	92	96	5	5
	grain	0.1	5	89	88	2	3
	whole	0.01	5	99	101	2	3
	orange	0.1	5	107	106	9	10
	soya	0.01	5	89	88	3	3
	bean	0.1	5	90	90	4	5
	onion	0.01	5	89	89	7	6
	onion	0.1	5	94	94	4	5
Transition				255 m/z > 213 m/z	255 m/z > 148 m/z	255 m/z > 213 m/z	255 m/z > 148 m/z
6-OH-bentazone	maize	0.01	5	88	90	4	2
	silage	0.1	5	86	85	4	3

Test Substance	Crop	Fortification Level (mg/kg)	No. of Tests	Average Recovery (%)		Relative Standard Deviation (%)	
	maize	0.01	5	83	87	5	3
	grain	0.1	5	92	91	4	2
	whole	0.01	5	98	98	2	1
	orange	0.1	5	94	96	6	6
	soya	0.01	5	82	100	11	6
	bean	0.1	5	98	99	3	3
	onion	0.01	5	85	87	9	8
		0.1	5	94	92	7	8
Transition				255 m/z > 148 m/z	255 m/z > 191 m/z	255 m/z > 148 m/z	255 m/z > 191 m/z
8-OH-bentazone	maize	0.01	5	80	79	1	2
	silage	0.1	5	75	76	5	5
	maize	0.01	5	76	73	6	6
	grain	0.1	5	82	81	6	6
	whole	0.01	5	100	102	3	1
	orange	0.1	5	84	83	4	4
	soya	0.01	5	72	73	6	6
	bean	0.1	5	88	87	3	2
	onion	0.01	5	74	73	5	6
		0.1	5	87	87	10	11

Table 58 Recoveries of bentazone, 6-OH-bentazone and 8-OH-bentazone in plant matrices (Schulz, H and Meyer, M, 2007, 2007/1013926)

Test Substance	Crop	Fortification Level (mg/kg)	No. of Tests	Average Recovery (%)		Relative Standard Deviation (%)	
Transition				239 m/z > 132 m/z	239 m/z > 175 m/z	239 m/z > 132 m/z	239 m/z > 175 m/z
bentazone	lemon	0.01	5	89.9	90.4	1.1	1.7
		0.1	5	79.4	79.0	3.3	3.8
	onion	0.01	5	98.4	98.8	0.6	0.9
		0.1	5	100.6	99.6	1.1	1.7
	soya bean	0.01	5	100.3	99.1	1.8	1.9
		0.1	5	101.4	101.0	1.3	1.6
	maize silage	0.01	5	102.5	102.2	3.1	2.2
		0.1	5	98.9	99.2	1.0	0.7
	maize grain	0.01	5	97.5	98.0	3.5	2.9
		0.1	5	97.9	98.5	2.1	1.6
Transition				255 m/z > 213 m/z	255 m/z > 148 m/z	255 m/z > 213 m/z	255 m/z > 148 m/z
6-OH-bentazone	lemon	0.01	5	90.1	90.9	2.9	2.5
		0.1	5	108.2	107.4	10.6	9.5
	onion	0.01	5	83.0	82.4	1.7	1.8
		0.1	5	71.6	77.6	3.9	4.0
	soya bean	0.01	5	102.0	90.6	2.9	1.6
		0.1	5	83.2	79.4	2.2	2.1
	maize silage	0.01	5	94.4	93.4	4.5	4.4
		0.1	5	76.6	77.9	1.9	2.2
	maize grain	0.01	5	87.4	89.0	4.4	6.1
		0.1	5	74.8	75.6	1.5	0.8
Transition				255 m/z > 148 m/z	255 m/z > 191 m/z	255 m/z > 148 m/z	255 m/z > 191 m/z
8-OH-bentazone	lemon	0.01	5	84.6	84.3	1.6	2.7
		0.1	5	95.9	95.7	5.1	5.4
	onion	0.01	5	100.6	101.2	1.6	1.3
		0.1	5	84.6	85.1	1.9	2.5
	soya bean	0.01	5	85.2	85.6	2.4	2.4

Test Substance	Crop	Fortification Level (mg/kg)	No. of Tests	Average Recovery (%)		Relative Standard Deviation (%)	
	maize silage	0.1	5	99.6	98.4	0.6	1.2
		0.01	5	97.2	96.6	12.4	12.6
		0.1	5	77.7	77.5	2.9	4.1
	maize grain	0.01	5	83.4	82.8	3.7	4.3
		0.1	5	88.7	88.5	1.9	1.2

Table 59 Recoveries of bentazone, 8-OH-bentazone and 6-OH-bentazone in plant matrices spiked with 0.05, 1.0 and 3.0 mg/kg using GC-TSD and GC-MSD (Abdel-Baky, S, 1995, 1996/5278)

Crop	Matrix	Bentazone	6-OH-bentazone	8-OH-bentazone
		0.05, 1.0	0.05, 1.0	0.05, 1.0
		mg/kg	mg/kg	mg/kg
GC-TSD [mean (%), $\pm$ S.D.]				
rice	bran	82 $\pm$ 15 (n = 8)	87 $\pm$ 10 (n = 8)	94 $\pm$ 11 (n = 8)
rice	grain	88 $\pm$ 13 (n = 12)	89 $\pm$ 11 (n = 12)	89 $\pm$ 8 (n = 12)
soya bean	refined oil	98 $\pm$ 3 (n = 8)	93 $\pm$ 11 (n = 8)	95 $\pm$ 9 (n = 8)
soya bean	Hulls	84 $\pm$ 14 (n = 16)	84 $\pm$ 11 (n = 16)	84 $\pm$ 8 (n = 16)
soya bean	forage ^a	87 $\pm$ 18 (n = 8)	81 $\pm$ 8 (n = 8)	92 $\pm$ 14 (n = 8)
soya bean	seeds	88 $\pm$ 14 (n = 8)	87 $\pm$ 14 (n = 8)	87 $\pm$ 15 (n = 8)
peas	dry	83 $\pm$ 7 (n = 12)	88 $\pm$ 21 (n = 12)	90 $\pm$ 16 (n = 12)
corn	grain	92 $\pm$ 15 (n = 8)	93 $\pm$ 14 (n = 8)	92 $\pm$ 9 (n = 8)
average (n = 80) $\pm$ S.D.		87 $\pm$ 13	87 $\pm$ 13	90 $\pm$ 11
overall average (n = 240) $\pm$ S.D.				88 $\pm$ 13
GC-MSD [mean (%), $\pm$ S.D.]				
rice	bran	100 $\pm$ 12 (n = 8)	100 $\pm$ 5 (n = 8)	116 $\pm$ 11 (n = 8)
rice	grain	98 $\pm$ 13 (n = 12)	109 $\pm$ 23 (n = 12)	103 $\pm$ 14 (n = 12)
soya bean	refined oil	98 $\pm$ 11 (n = 8)	90 $\pm$ 12 (n = 8)	91 $\pm$ 9 (n = 8)
soya bean	hulls	88 $\pm$ 9 (n = 16)	94 $\pm$ 12 (n = 16)	94 $\pm$ 14 (n = 16)
soya bean	forage ^a	87 $\pm$ 19 (n = 8)	91 $\pm$ 18 (n = 8)	88 $\pm$ 17 (n = 8)
soya bean	seeds	81 $\pm$ 14 (n = 8)	84 $\pm$ 8 (n = 8)	84 $\pm$ 7 (n = 8)
peas	dry	92 $\pm$ 15 (n = 12)	95 $\pm$ 17 (n = 12)	96 $\pm$ 11 (n = 12)
corn	grain	85 $\pm$ 10 (n = 8)	92 $\pm$ 11 (n = 8)	91 $\pm$ 9 (n = 8)
average (n = 80) $\pm$ S.D.		91 $\pm$ 14	95 $\pm$ 16	96 $\pm$ 15
overall average (n = 240) $\pm$ S.D.				94 $\pm$ 15

^a Fortification level 0.05, 3.0 mg/kg

Table 60 Recoveries of bentazone and 8-OH-bentazone in lemon balm and peppermint spiked with 0.05 and 0.25 mg/kg using GC-MS/MS (Class, T and Bacher, R, 1998, 1998/11399)

Matrix	Bentazone	8-OH-bentazone
	0.05	0.05
	mg/kg	mg/kg
lemon balm	109%	70%
peppermint ^a	90% (n=)	not analysed

^a Fortification level 0.25 mg/kg

Table 61 Recoveries of bentazone, 6-OH-bentazone and 8-OH-bentazone in animal matrices (Bacher, R, 2007, 2007/1013925)

Test Substance	Matrix	Fortification Level (mg/kg)	No. of Tests	Average Recovery (%)		Relative Standard Deviation (%)	
Transition				239 m/z > 132 m/z	239 m/z > 175 m/z	239 m/z > 132 m/z	239 m/z > 175 m/z
bentazone	milk	0.01	5	102	100	7	7
		0.1	5	97	97	3	4

Test Substance	Matrix	Fortification Level (mg/kg)	No. of Tests	Average Recovery (%)		Relative Standard Deviation (%)	
	egg	0.01	5	102	105	3	2
		0.1	5	96	93	2	4
	bovine meat	0.01	5	98	96	6	4
		0.1	5	98	95	5	6
	bovine liver	0.01	5	106	103	5	4
		0.1	5	104	103	7	6
Transition				255 m/z > 213 m/z	255 m/z > 148 m/z	255 m/z > 213 m/z	255 m/z > 148 m/z
6-OH-bentazone	milk	0.01	5	98	90	5	6
		0.1	5	89	88	12	11
	egg	0.01	5	84	83	7	4
		0.1	5	80	80	6	5
	bovine meat	0.01	5	81	77	6	3
		0.1	5	76	75	18	17
	bovine liver	0.01	5	102	103	8	11
		0.1	5	103	106	4	3
Transition				255 m/z > 148 m/z	255 m/z > 191 m/z	255 m/z > 148 m/z	255 m/z > 191 m/z
8-OH-bentazone	milk	0.01	5	78	80	4	4
		0.1	5	76	78	7	7
	egg	0.01	5	79	77	3	4
		0.1	5	75	73	7	7
	bovine meat	0.01	5	82	84	8	5
		0.1	5	78	79	16	14
	bovine liver	0.01	5	90	89	7	9
		0.1	5	91	92	7	11

Table 62 Recoveries of bentazone, 6-OH-bentazone and 8-OH-bentazone in animal matrices (Schulz, H and Meyer, M, 2007, 2007/1013927)

Test Substance	Matrix	Fortification Level (mg/kg)	No. of Tests	Average Recovery (%)		Relative Standard Deviation (%)	
Transition				239 m/z > 132 m/z	239 m/z > 175 m/z	239 m/z > 132 m/z	239 m/z > 175 m/z
bentazone	bovine meat	0.01	5	88.3	88.6	0.5	0.7
		0.1	5	93.1	93.0	0.6	1.6
	bovine liver	0.01	5	101.0	101.2	1.2	1.3
		0.1	5	97.7	98.6	1.2	1.8
	milk	0.01	5	101.4	101.1	4.2	4.1
		0.1	5	97.0	97.3	4.9	3.9
	egg	0.01	5	101.5	101.9	4.2	3.2
		0.1	5	103.7	103.4	1.9	1.7
Transition				255 m/z > 213 m/z	255 m/z > 148 m/z	255 m/z > 213 m/z	255 m/z > 148 m/z
6-OH-bentazone	bovine meat	0.01	5	75.5	75.9	1.7	1.6
		0.1	5	73.5	75.4	1.9	0.6
	bovine liver	0.01	5	87.8	86.2	5.0	4.3
		0.1	5	74.4	71.8	2.6	2.6
	milk	0.01	5	89.8 ^a	90.0 ^a	1.9	2.7 ^a
		0.1	5	85.3	85.7 ^a	6.8	5.6 ^a
	egg	0.01	5	88.2	87.2	7.4	7.7
		0.1	5	92.7	91.0	6.1	6.1
Transition				255 m/z > 148 m/z	255 m/z > 191 m/z	255 m/z > 148 m/z	255 m/z > 191 m/z
8-OH-bentazone	bovine meat	0.01	5	81.3	79.8	1.0	1.6
		0.1	5	81.1	80.5	1.7	0.8
	bovine liver	0.01	5	105.3	104.4	3.0	3.1
		0.1	5	89.8	88.9	1.4	2.4
	milk	0.01	5	88.6	87.3	18.0	18.3

Test Substance	Matrix	Fortification Level (mg/kg)	No. of Tests	Average Recovery (%)		Relative Standard Deviation (%)	
	egg	0.1	5	76.7	76.6	11.5	11.4
		0.01	5	91.4	91.9	4.1	4.7
		0.1	5	91.0	92.1	1.6*	2.6 ^a

^a Without outlier

Stability of residues in stored analytical samples

The Meeting received information on the stability of residues of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone residues in maize (green plant, grain and straw), pea (seed), flax (seed) and potato (tuber) over a period of two years. In addition to these individual studies, storage stability determinations, together with procedural recovery analyses, were also carried out concurrently with the field trials samples and are reported in the residue trials reports.

The deep frozen storage stability of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone, determined as glucoside derivatives, were investigated over a period of two years in different plant matrices such as maize (green plant, grain and straw), pea (seed), flax (seed) and potato (tuber) (Sasturain, J *et al.*, 2002, 2002/1008779). The glucoside derivatives of 6-OH-bentazone and 8-OH-bentazone were produced in wheat cell suspension cultures and rape cell suspension cultures, respectively. Untreated matrix samples were fortified with 0.5 mg/kg of the test substances and stored at -20 °C in the dark. The storage conditions correspond to the usual storage conditions for field samples. Samples were analysed after 0, 27, 97, 180, 355, 539 and 713 days.

Bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone are extracted from plant matrices with aqueous methanol. After purification of a 4% aliquot by an iso-octane liquid-liquid partition, the two relevant metabolites which are present as glucosides are hydrolysed using enzymatic cleavage to 6-OH-bentazone and 8-OH-bentazone. After a Ca(OH)₂-precipitation step to remove acidic plant constituents, a reversed phase C₁₈-column clean-up is performed. The analytes are then methylated with diazomethane and their derivatives are purified using a silica gel-column. The final determination of the residues of bentazone and its hydroxy metabolites is performed by GC-MS. The limit of quantitation (LOQ) of the method for bentazone, 6-OH-bentazone and 8-OH-bentazone is 0.02 mg/kg each.

Procedural recoveries for bentazone averaged at about 90% for maize plant, at 94% for grain, at 97% for straw, at 87% for potato tuber, at 98% for flax seed and at 88% for pea. The mean recoveries for 6-OH-bentazone were about 77% in maize plant, 81% in grain, 83% in straw, 76% in potato tuber, 79% in flax seed and 74% in pea. Recoveries for 8-OH-bentazone averaged at about 72% in maize plant, at 73% in grain, at 80% in straw, at 72% in potato tuber, at 76% in flax seed and at 75% in pea.

Recoveries in stored samples for bentazone showed stability (> 70%) for 713 and 722 days in maize plant, grain, straw, in flax seed and in pea. Only in potato the recovery dropped to 66% but this was correlating with a low procedural recovery. The recoveries in stored samples for 6-OH-bentazone and 8-OH-bentazone were well above 70% in maize plant, grain, straw, potato tuber, flax seed and in pea after 713–722 days of storage.

Table 63 Recoveries for bentazone, 6-OH-bentazone and 8-OH-bentazone in stored and freshly spiked plant matrix samples (Sasturain, J *et al.*, 2002, 2002/1008779)

Day	Maize, Green Plant		Maize, Grain		Maize, Straw		Potato, Tuber		Flax, Seed		Pea, Seed	
	A: in stored samples,% of nominal						B: procedural in freshly spiked sample					
	A	B	A	B	A	B	A	B	A	B	A	B
Bentazone												
0	100	107	110	91	122	115	93	93	106	93	89	89
27	— ^a	76	— ^a	109	95	83	88	84	87	80	81	73
97	84	84	98	92	98	95	93	81	95	105	82	88
180	85	84	93	91	116	92	92	91	99	96	103	91

Day	Maize, Green Plant		Maize, Grain		Maize, Straw		Potato, Tuber		Flax, Seed		Pea, Seed	
	A: in stored samples,% of nominal						B: procedural in freshly spiked sample					
	A	B	A	B	A	B	A	B	A	B	A	B
Bentazone												
355/356	86	89	91	83	105	90	84	82	97	99	97	89
538/539	101	105	110	99	127	105	78	98	104	96	116	86
547	—	—	—	—	—	—	—	—	132	124	103	98
713	96	86	109	97	111	102	60	79	105	89	95	90
722	—	—	—	—	—	—	66	87	—	—	101	92
6-OH-bentazone												
0	90	85	109	84	124	97	85	61	101	76	95	68
27	— ^a	82	— ^a	95	107	86	81	77	97	82	97	85
97	75	69	104	84	102	77	91	77	96	102	81	76
180	86	71	92	79	132	81	87	75	93	79	108	75
355/356	85	79	88	71	96	73	71	69	95	72	94	68
538/539	98	79	113	86	123	91	52	101	118	70	145	74
547	—	—	—	—	—	—	—	—	125	75	119	64
713	83	72	96	70	100	78	88	78	118	79	111	90
722	—	—	—	—	—	—	92	71	—	—	116	70
8-OH-bentazone												
0	86	74	88	62	42	93	46	45	79	64	91	54
27	— ^a	69	— ^a	75	84	70	71	70	73	69	86	59
97	79	60	97	80	76	65	97	62	90	83	79	67
180	85	68	82	72	56	77	68	70	75	72	114	77
355/356	39	73	66	69	53	78	40	67	56	72	94	76
538/539	97	79	121	72	72	83	56	113	99	76	160	82
547	—	—	—	—	—	—	—	—	130	91	123	94
713	116	79	120	84	81	92	95	73	126	80	114	88
722	—	—	—	—	—	—	113	79	—	—	129	81

^a Residues are outlier, results not used for calculation.

USE PATTERNS

Labels and English translations were available for all the uses. Bentazone is applied either as a solo product or in combinations with other active substances and controls broad leaf weeds and is used in many crops in pre-emergence and post emergence. A summary of the current approved label rates are provided in Table 64.

Table 64 Summary of registered uses of bentazone

Crop Code No.	Crop	Country	F/G/P ^a	Application			Application rate per treatment			PHI [days] min ^c
				Method	No. per crop and season min max	App'n interval [days]	kg as/hL ^b max	Water L/ha min max	kg ai/ha ^b min max	
0385	Onion	Netherlands	F	Spray	1	—	0.18–0.36	200–400	0.72	NA
0388	Shallots	Netherlands	F	Spray	1	—	0.18–0.360	200–400	0.72	NA
0388	Shallots	Netherlands	F	spraying	1	—	0.174–0.348	200–400	0.696	—
0424	Cucumber	Sweden	F	Overall spraying	1	—	0.25–0.334	300–400	1.0	42
0447	Corn including sweet corn	Canada	F	Foliar broadcast	—	—	0.27–1.08	100–400	1.08	—
0447	Corn including sweet corn	Canada	F	Foliar broadcast	1–2	7 days	0.21–0.84	100–400	0.84	—

Crop Code No.	Crop	Country	F/G/P _a	Application			Application rate per treatment			PHI [days] min ^c
				Method	No. per crop and season min max	App'n interval [days]	kg as/hL ^b max	Water L/ha min max	kg ai/ha ^b min max	
0447	Corn including sweet corn	Canada	F	Foliar broadcast	—	—	0.36–1.08	100–300	1.08	—
0447	Corn including sweet corn	Canada	F	Foliar broadcast	1–2	7 days	0.28–0.84	100–300	0.84	—
0447	Corn including sweet corn	Canada	F	Foliar broadcast	1–2	7 days	0.15–0.4	200–400	0.6–0.8	45- sweet corn 60- field corn
0447	Corn including sweet corn	Netherland	F	Spray	1	—	360–720	200–400	1.44	—
0447	Corn including sweet corn	Netherland	F	Spray	1	—	200–400	200–400	0.8	—
0447	Sweet corn	France	F	Overall spray	1	—	0.348–0.696	200–400	1.392	90
0447	Sweet corn	France	F	Overall spray	1	—	0.3–0.4	300–400	1.2	28
0447	Sweet corn	Netherland	F	spraying	1	—	0.36–0.72	200–400	1.44	F
0061	Beans, except broad bean and soya bean	France	F	Overall spray	1	—	0.305–0.609	200–400	1.218	42
0061	Beans, except broad bean and soya bean	Netherland	F	spraying	2	7	0.325–0.72	200–400	0.13–1.44	21
0061	Beans, except broad bean and soya bean	Netherland	F	spraying	2	7	0.36–0.72	200–400	1.44	21
0063	Peas	Canada	F	Foliar broadcast	—	—	0.21–1.08	100–400	0.84–1.08	—
0063	Peas	Canada	F	Foliar broadcast	—	—	0.27–1.08	100–300	1.08	—
0063	Peas	Canada	F	Foliar broadcast	1–2	7 days	0.280–0.84	100–300	0.840	—
0063	Peas	France	F	Overall spray	1	—	0.305–0.609	200–400	1.218	42
0063	Peas	France	F	spray	1	—	0.150–0.600	100–400	0.600	—
0063	Peas	France	F	Overall spray	1	—	0.305–0.609	200–400	1.218	42
0064	Peas, shelled	United Kingdom	—	spraying	—	—	0.288–0.36	200–250	0.720	F
0064	Peas, shelled	United Kingdom	—	spraying	1	—	0.32–1.44	100–450	1.440	F
0064	Peas, shelled	United Kingdom	—	spraying	One	—	0.319–1.436	100–450	1.436	F

Crop Code No.	Crop	Country	F/G/P ^a	Application			Application rate per treatment			PHI [days] min ^c
				Method	No. per crop and season min max	App'n interval [days]	kg as/hL ^b max	Water L/ha min max	kg ai/ha ^b min max	
0064	Peas, shelled	USA	F	Spray by ground or air	1–2	7	0.6–1.208	93–187	1.123	10
0522	Broad bean	France	F	spray	1	—	0.15–0.6	100–400	0.6	—
0526	Common bean	Germany	F	spray	2	8–14	0.24–0.48	200–400	0.96	F
0526	Common bean	France	F	spray	1	—	0.15–0.6	100–400	0.6	—
0526	Common bean	United Kingdom	—	spraying	One or Two as a split dose	7 days	0.319–1.436	100–450	1.436	F
0526	Common bean	United Kingdom	—	spraying	One or Two as a split dose	7 days	0.32–1.44	100–450	1.44	F
0541	Soya bean	USA	F	Spray by ground or air	1–2	7	0.6–1.208	93–187	1.123	30 (grazing of forage or hay)
0071	Beans (dry)	Germany	F	spray	2	8–14 days	0.24–0.48	200–400	0.96	35
0071	Beans (dry)	Poland	F	Spray	—	—	0.4–0.72	200–300	1.2–1.44	
0071	Beans (dry)	Poland	F	Spray	2	7–10	1) 0.2–0.3 2) 0.2–0.3	200–300	0.6	
0072	Pea	Canada	F	Foliar broadcast	—	—	0.21–1.08	100–400	0.84–1.08	—
0072	Pea	Canada	F	Foliar broadcast	—	—	0.27–1.08	100–300	1.08	—
0072	Pea	Canada	F	Foliar broadcast	1–2	7 days	0.28–0.84	100–300	0.840	—
0072	Pea	USA	F	Spray by ground or air	1–2	7	0.6–1.208	93–187	1.123	30
0541	Soya bean	France	F	Overall spray	1	—	0.348–0.696	200–400	1.392	90
0541	Soya bean	France	F	spray	1	—	0.15–0.6	100–400	0.6	—
0541	Soya bean	Germany	F	spray	1	—	0.24–0.48	200–400	0.96	(F)
0541	Soya bean	Italy	F	Normal volume spraying Broadcast	1	—	0.087–0.4785	200–600	0.522–0.957	60
0541	Soya bean	Italy	F	Normal volume spraying Broadcast	1	—	0.1595–0.7395	200–600	0.957–1.479	60
0541	Soya bean	Italy	F	Normal volume spraying Broadcast	1	—	0.088–0.48	200–600	0.528–0.96	60
0541	Soya bean	Spain	F	Spray	—	—	—	—	0.72–0.96	NA
0541	Soya bean	Spain	F	Spray	—	—	—	—	0.957–1.0005	NA

Crop Code No.	Crop	Country	F/G/P ^a	Application			Application rate per treatment			PHI [days] min ^c
				Method	No. per crop and season min max	App'n interval [days]	kg as/hL ^b max	Water L/ha min max	kg ai/ha ^b min max	
0541	Soya bean	USA	F	Spray by ground or air	1–2	7	0.6–1.208	93–187	1.123	30 (grazing of forage or hay)
0589	Potato	Ireland	—	spraying	One or Two as a split dose	7	0.32–1.44	100–450	1.44	F
0589	Potato	Netherland	F	Spray	1	—	0.24–0.48	200–400	0.96	—
0589	Potato	Netherland	F	spraying	1	—	0.24–0.48	200–400	0.96	—
0589	Potato	Netherland	F	spraying	2	7	0.36–0.72	200–400	1.44	—
0589	Potato	Spain	F	Spray	—	—	—	—	0.96	—
0589	Potato	Spain	F	Spray	—	—	—	—	0.957–1.0005	—
0589	Potato	Switzerland	F	Spraying	1	—	160–240	400–600	0.96	—
0589	Potato	Switzerland	F	Spraying	1	—	239.25–319	300–400	0.957	—
0589	Potato	United Kingdom	—	spraying	One or Two as a split dose	7	320–1440	100–450	1.44	F
0589	Potato	United Kingdom	—	spraying	One or Two as a split dose	7	319–1436	100–450	1.436	F
0080	Cereal grains	Finland	F	Overall spraying	1	—	—	300–400	1.218–1.48	—
0080	Cereal grains	Netherland	F	spraying	1	—	0.36–0.72	200–400	1.44	F
0640	Barley	Spain	F	Spray	—	—	—	—	0.96	NA
0640	Barley	Spain	F	Spray	—	—	—	—	0.957–1.0005	NA
0645	Maize	France	F	Overall spray	2	10	0.240–0.32 0.12–0.16	300–400	1 appl. 0.960 2nd appl. 0.480	28 (silage)
0645	Maize	France	F	Overall spray	1	—	0.3–0.4	300–400	1.2	28 (silage)
0645	Maize	France	F	Overall spray	1	—	0.348–0.696	200–400	1.392	90
0645	Maize	France	F	Overall spray	1	—	0.266–0.533	150–300	0.8	90*
0645	Maize	Germany	F	spray	1	—	0.1875–0.375	200–400	0.75	60
0645	Maize	Germany	F	spray	1	—	0.1875–0.375	150–400	0.75	60
0645	Maize	Germany	F	spray	1	—	0.1125–0.3	150–400	0.45	—
0645	Maize	Italy	F	Normal volume spraying Broadcast	1	—	0.16–0.72	200–600	0.96–1.44	—
0645	Maize	Italy	F	Normal volume spraying Broadcast	1	na	0.16–0.4	200–400	0.64–0.8	90

Crop Code No.	Crop	Country	F/G/P _a	Application			Application rate per treatment			PHI [days] min ^c
				Method	No. per crop and season min max	App'n interval [days]	kg as/hL ^b max	Water L/ha min max	kg ai/ha ^b min max	
0645	Maize	Italy	F	Normal volume spraying Broadcast	1	—	0.1595–0.7395	200–600	0.957–1.479	—
0645	Maize	Netherland	F	Spray	1	—	0.36–0.72	200–400	1.44	—
0645	Maize	Netherland	F	spraying	1	—	0.36–0.72	200–400	1.44	F
0645	Maize	Netherland	F	Spray	1	—	0.2–0.4	200–400	0.8	NA
0645	Maize	Spain	F	Spray	—	—	—	—	0.96	NA
0645	Maize	Spain	F	Spray	—	—	—	—	0.957–1.0005	NA
0645	Maize	USA	F	Spray by ground or air	1–2	7	0.6–1.208	93–187	1.123	12 (grazing of forage)
0647	Oat	Germany	F	spray	1	—	0.24975–0.4995	200–400	0.999	F
0649	Rice	Brazil	F	Weed Post-emergence	1–2	—	—	150–250 (terrestrial application) 40 (aerial application)	0.72–0.96	60
0649	Rice	Brazil	F	Weed Post-emergence	1–2	—	—	150–250 (terrestrial application) 40 (aerial application)	0.72–0.96	60
0649	Rice	China	F	Spray	1	—	0.16–0.72	200–600 L/ha	0.96–1.44	—
0649	Rice	China	F	Spray	1	—	—	—	0.96–1.2	—
0649	Rice	Japan	F	soil application after surface drainage or with shallow flooding	1	—	—	—	Transplanting: 3.3–4.4; Direct seeding 3.3	60
0649	Rice	Japan	F	soil application after surface drainage or with shallow flooding	1–2	—	0.2–0.4	700–1000	2.0–2.8	50
0649	Rice	Japan	F	soil application with shallow flooding	1	—	—	—	3.3	60
0649	Rice	Portugal	F	Spray	1	—	0.36–0.96	200–400	1.44–1.92	—
0651	Sorghum	France	F	Overall spray	1	—	0.3–0.4	300–400	1.2	90
0651	Sorghum	France	F	Overall spray	2	10	0.24–0.32 0.12–0.16	300–400	1 appl. 0.960 2nd appl. 0.480	90

Crop Code No.	Crop	Country	F/G/P _a	Application			Application rate per treatment			PHI [days] min ^c
				Method	No. per crop and season min max	App'n interval [days]	kg as/hL ^b max	Water L/ha min max	kg ai/ha ^b min max	
0651	Sorghum	France	F	Overall spray	1	—	0.348–0.696	200–400	0.35	90
0654	Wheat	Denmark	F	Overall spraying	1	—	0.24–0.41	150–250	0.609	70
0654	Wheat	Germany	F	spray	1	—	0.24975–0.4995	200–400	0.999	F
0654	Wheat	Italy	F	Normal volume spraying Broadcast	1	—	0.16–0.72	200–600	0.96–1.44	60
0654	Wheat	Italy	F	Normal volume spraying Broadcast	1	—	0.1595–0.7395	200–600	0.957–1.479	60
0654	Wheat	Italy	F	Normal volume spraying Broadcast	1	—	0.2465–0.7395	200–600	1.479	60
0654	Wheat	Netherland	F	Spray	1	—	0.36–0.72	200–400	1.44	—
0654	Wheat	Spain	F	Spray	—	—	—	—	0.96	—
0654	Wheat	Spain	F	Spray	—	—	—	—	0.957–1.0005	—
0654	Wheat	United Kingdom	—	spraying	1 per crop	—	0.289–0.590	220–450	1.3	F
0693	Linseed	Canada	F	Foliar broadcast	—	—	0.27–1.08	100–400	1.08	—
0693	Linseed	Canada	F	Foliar broadcast	1–2	7	0.21–0.84	100–400	0.84	—
0693	Linseed	Canada	F	Foliar broadcast	—	—	0.27–1.08	100–300	1.08	—
0693	Linseed	Canada	F	Foliar broadcast	1–2	7	0.28–0.84	100–300	0.84	—
0693	Linseed	France	F	Overall spray	1	—	0.305–0.609	200–400	1.218	70
0697	Peanut	Israel	F	spray	—	—	—	—	1.2–2.4	—
0697	Peanut	USA	F	Spray by ground or air	1–2	7	0.6–1.208	93–187	1.123	50 (grazing of forage or hay)
0092	Herbs	Germany	F	spray	1	—	0.24–0.48	200–400	0.96	F (St. John's wort: 42)
0092	Herbs	France	F	Overall spray	1	—	0.109–0.566	200–400	0.435–1.131	28
0738	Mint	Germany	F	spray	1–2	8–14	0.24–0.48	200–400	0.960	42
0157	Legume animal feeds	France	F	Overall spray	1	—	0.174–0.348	200–400	0.696	60
0157	Legume animal feeds	France	F	spray	1	—	0.15–0.6	100–400	0.6	—
0157	Legume animal feeds	Spain	F	Spray	—	—	—	—	0.72–0.96	—
0157	Legume animal feeds	Spain	F	Spray	—	—	—	—	0.957–1.0005	—

Crop Code No.	Crop	Country	F/G/P ^a	Application			Application rate per treatment			PHI [days] min ^c
				Method	No. per crop and season min max	App'n interval [days]	kg as/hL ^b max	Water L/ha min max	kg ai/ha ^b min max	
1023	Clover	USA	F	Spray by ground or air	1–2	5–14	0.6–1.208	93–187	1.123	36 (grazing of forage or hay)
0162	Hay or fodder (dry) of grasses	Denmark	F	Overall spraying	1	—	0.24–0.32	150–200	0.48	14 days
0162	Hay or fodder (dry) of grasses	Denmark	F	Overall spraying	1	—	0.348–0.58	150–250 L/ha	0.87	14
0162	Hay or fodder (dry) of grasses	Denmark	F	over plant spray	1	—	0.375–0.666	150–200	0.75–1.0	14 days (42 days for seed production)
0162	Hay or fodder (dry) of grasses	Netherland	F	Spray	1	—	0.36–0.72	200–400	1.44	7
0162	Hay or fodder (dry) of grasses	Netherland	F	Spray	2	7–10	0.18–0.36	200–400	0.72	7
0162	Hay or fodder (dry) of grasses	Netherland	F	spraying	1	—	0.174–0.72	200–400	0.696–1.44	—
0162	Hay or fodder (dry) of grasses	Netherland	F	spraying	2	7	0.36–0.72	200–400	1.44	—

^a F = outdoor or field use, G = glasshouse, P = protected, I = indoor application

^b Information given on active substance refers to Bentazone only

^c PHI = pre-harvest interval, F = Determined by latest time of application

a.s. or as = active substance

na = not applicable

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised field trials for bentazone uses on the following crops.

Crop Group	Commodity	Country	Table No.
Bulb vegetables	Bulb onion	Brazil, France, Germany, Greece, Italy, Netherlands, Spain	Table 65
	Green onion	Germany, Greece, Netherlands, Spain	Table 66
Fruiting vegetables	Cucumber	Canada	Table 67
Fruiting vegetables, other than Cucurbits	Sweet corn	Canada, France	Table 68
Legume vegetables	Green peas	France, UK, USA	Table 69
	Green beans	France, Germany, Italy, Netherlands, Spain, UK	Table 70

Crop Group	Commodity	Country	Table No.
Pulses	Beans, (dry)	France, Germany, Spain, UK	Table 71
	Peas (dry)	Canada, USA	Table 72
	Soya bean (dry)	France, Germany, Greece, Italy, Spain, USA	Table 73
Root and tuber vegetable	Potato	Brazil, Canada, France, Germany, Greece, Italy, Netherlands, Spain, Sweden, Switzerland, UK	Table 74
	Sugar beet	USA	Table 75
Cereals	Barley	Canada, Italy, Spain	Table 76
	Oats	Germany	Table 77
	Maize	France, Germany, Italy, Netherlands, Spain, UK, USA	Table 78
	Rice	Brazil, China, France, Japan, Portugal	Table 79
	Sorghum	France	Table 80
	Wheat	Denmark, France, Germany, Italy, Netherlands, Spain	Table 81
Oilseeds	Linseed	Canada, France, USA	Table 82
	Peanut	USA	Table 83
Herbs	Herbs	France, Germany	Table 84
Legume animal feed	Alfalfa	France, Italy, Spain, Sweden, UK	Table 85
	Clover	USA	Table 86
	Green bean forage	France, Italy, Spain	Table 87
	Pea vines	USA	Table 88
	Bean fodder	France, Germany, Spain, UK	Table 89
	Pea hay	USA	Table 90
	Peanut hay	Israel, USA	Table 91
	Soya bean forage hay and fodder	France, Germany, Greece, Italy, Spain, USA	Table 92
Straw, fodder and forages of cereal grains and grasses	Barley straw	Italy, Spain	Table 93
	Oats straw	Germany	Table 94
	Maize forage and fodder	France, Germany, Italy, Netherlands, Spain, UK	Table 95
	Rice straw	China, Japan	Table 96
	Wheat straw	Germany, Italy, Spain	Table 97
	Grass	Denmark, Netherlands, USA	Table 98

In addition to the description and details of the field trials, each report includes a summary of the analytical method(s) used, together with the corresponding procedural recoveries, and in most cases, concurrent recoveries in stored frozen samples. In the field trials where multiple analyses are conducted on a single sample or where multiple samples were taken from a single plot, the average residue value is reported. Where results from separate plots with distinguishing characteristics, such

Results have not been corrected for concurrent method recoveries unless indicated. Residues and application rates have generally been rounded to 2 significant figures or, for residues near the LOQ, to 1 significant figure. The actual application rates were within $\pm 10\%$ of the nominal dosage rate. Residue values from the trials conducted according to the maximum GAP have been used for the estimation of maximum residue levels. Those results included in the tables are single underlined. If higher residue values were detected at longer PHI than specified in the cGAP, those values were used for the calculations.

For purposes of MRL estimation and risk assessment in this report, ND values in the reports were considered as < LOQ. For total bentazone, metabolites were calculated as parent equivalent; the conversion factor for both metabolites is 0.938; for calculation purposes, residues were treated as follows: 0.01 + 0.01 + 0.01 = 0.03; 0.01 + < 0.01 + < 0.01 = 0.03; < 0.01 + < 0.01 + < 0.01 = < 0.03; < 0.02 + < 0.02 + < 0.02 = < 0.06.

Onions

Table 65 Residues of bentazone in bulb onion after one application of bentazone in Southern Europe, Northern Europe

[illegible]

BULB ONIONS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water, L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
(Sturon)										
FR-84480	87% SG:	200	43	0	plant	4.3	0.02	0.06	4.38	
Bonnleux	1× 0.957			29	bulb	< 0.01	< 0.01	< 0.01	< 0.03	
Vaucluse, France										
2009										
(Glacier)										
ES-11140 Conil	87% SG:	200	43	0	plant	9.0	0.03	0.04	9.07	
Cadiz, Spain	1× 0.957			30	bulb	< 0.01	< 0.01	< 0.01	< 0.03	
2009										
(Valenciana Tardia)										
IT-48010	87% SG:	200	43-45	0	Plant	4.2	0.05	0.02	4.27	
Cotignola	1× 0.957			30	bulb	< 0.01	< 0.01	< 0.01	< 0.03	
Ravenna, Italy				40	bulb	< 0.01	< 0.01	< 0.01	< 0.03	
2009										
(Density)										
GR-57500	87% SG:	200	41	0	Plant	7.4	0.04	0.04	7.48	
Epanomi	1× 0.957			30	bulb	< 0.01	< 0.01	< 0.01	< 0.03	
Thessaloniki, Greece				44	bulb	< 0.01	< 0.01	< 0.01	< 0.03	
2009										
(Banko 936)										
FR-26740	87% SG:	200	43	0	Plant	3.8	0.02	0.03	3.85	
Marsanne	1× 0.957			29	bulb	< 0.01	< 0.01	< 0.01	< 0.03	
Vaucluse, France										
2009										
(Doree de Parme)										
Northern Europe										
NL-3897 LP	480 g/L SL	303	13	30	Plant	< 0.02	< 0.02	< 0.02	< 0.06	Blaschke, UG
Zeewolde	1.567			48	Plant	< 0.02	< 0.02	< 0.02	< 0.06	2001
The Netherlands				100	onion	< 0.02	< 0.02	< 0.02	< 0.06	2001/1000927
1999										
(Renate)										
F-41350	480 g/L SL	303	13	28	Plant	< 0.02	< 0.02	< 0.02	< 0.06	
Les Tabardieres	1.557			56	Plant	< 0.02	< 0.02	< 0.02	< 0.06	
France				99	onion	< 0.02	< 0.02	< 0.02	< 0.06	
1999										
(Spirit)										
16818 Wustrau	480 g/L SL	297	13	39	Plant	< 0.02	< 0.02	< 0.02	< 0.06	Erdmann, HP
Brandenburg	1.533			46	Plant	< 0.02	< 0.02	< 0.02	< 0.06	et al., 2000

BULB ONIONS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water, L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Germany				96	onion	< 0.02	< 0.02	< 0.02	< 0.06	2000/1018486
1999										
(Stuttgarter Riesen)										
19089 Crivitz	480 g/L SL	311	13	34	Plant	< 0.02	< 0.02	< 0.02	< 0.06	
Mecklenburg- Vorpommern	1.610			42	Plant	< 0.02	< 0.02	< 0.02	< 0.06	
Germany				85	onion	< 0.02	< 0.02	< 0.02	< 0.06	
1999										
(Zittauer Gelbe)										
South America										
Piedade	480 g/L SL	400	41	48	bulb	0.03	< 0.02	< 0.02	0.07	Anonymous,
Sp. Brazil	1× 1.44									1986
1985										1985/10335
(Baia Periforme)										
Empasc-	480 g/L SL	400	41	49	bulb	0.05	< 0.02	< 0.02	0.09	Anonymous,
Ituporanga	1× 1.44									1986
Sante Catarina										1985/10337
Brazil										
1985										
(Norte 14)										

^a At application^b Without roots^c Bulb = bulb onion*Spring onion*

A total of four trials in green onions were conducted in Europe during the 2010 growing season (Schroth, E and Martin, T, 2010, 2010/1164274). Results of the trials in green onions are summarized in Table 66, with residues matching the GAP underlined.

Table 66 Residues of bentazone in green onion after one application of bentazone in Southern Europe, Northern Europe

Green Onions country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water, L/ha	Crop Growth Stage ^a (BBCH)	DALA	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
North Europe										
DE-47574	87% SG	200	13	0	Plant	2.9	0.02	0.02	2.94	Schroth, E,
Goch- Nierswalde	1× 0.7221			23	Plant	0.04	< 0.01	< 0.01	0.06	Martin, T, 2010
Kleve, Germany										2010/1164274
2009										
(PAL)										
NL-6595 Ottersum	87% SG	200	13	0	Plant	3.0	0.01	0.01	3.02	
Gennep,	1× 0.7221			24	Plant	< 0.01	< 0.01	< 0.01	< 0.03	

Green Onions country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water, L/ha	Crop Growth Stage ^a (BBCH)	DALA	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
The Netherlands										
2009										
(PAL)										
South Europe										
ES-41710 Utrera	87% SG	200	43	0	Plant	6.2	0.02	0.03	6.25	
Sevilla, Spain	1× 0.957			30	Plant	< 0.01	< 0.01	< 0.01	< 0.03	
2009										
(Elody)										
GR-57007	87% SG	200	45	0	Plant	11	0.05	0.09	11.13	
Chalkidona	1× 0.957			30	Plant	< 0.01	< 0.01	< 0.01	< 0.03	
Thessaloniki,										
Greece										
2009										
(Degrano)										

^a At application^b Plants without roots*Fruiting vegetables, Cucurbits**Cucumbers*

Four trials in cucumbers were conducted in representative growing areas of Canada in 1976 to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC). (Anonymous, 1977, 1976/10556; Anonymous, 1977, 1976/10557; Anonymous, 1977, 1976/10558; Anonymous, 1977, 1976/10559). Results of the trials in green onions are summarized in Table 67, with residues matching the GAP underlined.

Table 67 Residues in cucumber after one application of bentazone in Canada

CUCUMBER country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water, L/ha	Crop Growth Stage ^a (BBCH)	DALA	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Block	n.r.	n.r.	11–13	41	cucumber	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
56-Hes-Simcoe	1× 1.0									1977
Canada										1976/10556
1976										
(Heinz 3534)										
Block	n.r.	n.r.	11–13	41	cucumber	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
56-Hes-Simcoe	1× 1.0									1977
Canada										1976/10557
1976										
(Heinz 3534)										
Block	n.r.	n.r.	11–13	41	cucumber	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
56-Hes-Simcoe	1× 1.0									1977
Canada										1976/10558
1976										
(Heinz 3534)										
Block	n.r.	n.r.	11–13	41	cucumber	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous

CUCUMBER country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water, L/ha	Crop Growth Stage ^a (BBCH)	DALA	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
56-Hes-Simcoe	1× 1.0									1977
Canada										1976/10559
1976										
(Heinz 3534)										

^a At application

n.r. = Not reported

Fruiting vegetables, other than Cucurbits

Sweet corn

A total of four field trials were conducted in representative sweet corn growing areas in Canada and France in 1977 and 2007 (Anonymous, 1977, 1977/10274; Anonymous, 1977, 1977/10275; Oxspring, S, 2008, 2008/1049973; Oxspring, S, 2008, 2008/1055036), to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC). The results are shown in Table 68.

Table 68 Residues in sweet corn on cob and maize cobs without husks after one application of bentazone in Canada and Europe

SWEET CORN country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- benta- zone	Total bentazone	
Dalmore, Victoria Canada	n.r. 1× 0.96	n.r.	Vegetative 18 cm	83	Sweet corn	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous 1977
1977										1977/10274
(n.r.)										
Dalmore, Victoria Canada	n.r. 1× 1.92	n.r.	Vegetative 18 cm	83	Sweet corn	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous 1977
1977										1977/10275
(n.r.)										
45530 Sury aux Bois, France, 2007	480 g/L, SC 1× 1.2	200	53–55	0	plant	7.75	2.20	0.53	10.31	Oxspring, S, 2008 2008/1049973
(Challenger)				21	cobs w/o husk	< 0.01	< 0.01	< 0.01	< 0.03	Oxspring, S, 2008 2008/1055036
				21	rest of plant	< 0.01	0.33	0.01	0.33	
				28	cobs w/o husk	< 0.01	< 0.01	< 0.01	< 0.03	
				28	rest of plant	0.01	0.56	0.03	0.57	
				35	cobs w/o husk	< 0.01	< 0.01	< 0.01	< 0.03	
				35	rest of plant	< 0.01	0.49	0.02	0.49	
				42	kernels w. cobs	< 0.01	< 0.01	< 0.01	< 0.03	

SWEET CORN country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- benta- zone	Total bentazone	
				42	rest of plant	< 0.01	0.35	0.02	0.36	
82100 Cordes Tolosannes	480 g/L, SC	200	73	0	plant	3.51	1.86	0.19	5.43	
France, 2007 (GH 5704)	1× 1.2			22	cobs w/o husk	< 0.01	0.02	< 0.01	0.04	
				22	rest of plant	0.10	0.54	0.02	0.63	
				29	cobs w/o husk	< 0.01	0.04	< 0.01	0.06	
				29	rest of plant	0.09	0.53	< 0.01	0.60	
Maize during cob	w/o	husk								
Bamague	480 g/L SL	200	55	0	plant	5.58	2.03	0.29	7.90	Klaas, P,
47120 Duras	1× 1.2			28	cobs w/o husks	< 0.01	0.02	< 0.01	0.04	Ziske, J, 2009 2009/1024805
France, 2008 (Mitic)										
“Finca Valsequillo”	480 g/L SL	200	55	0	plant	0.03	0.025	< 0.01	0.065	
Carretera vieja Antequera	1× 1.200			28	cobs w/o husks	< 0.01	0.08	< 0.01	0.10	
Campillos										
Spain, 2008 (Tardio 130)										
Civray 49490 Melgne le	480 g/L SL	200	55	0	plant	17.68	4.71	1.08	23.47	
Vicomte, France 2008 (Aspeed)	1× 1.2			27	cobs w/o husks	< 0.01	< 0.01	< 0.01	< 0.03	
Mittelweg 16 49685 Hoheging	480 g/L SL	200	55	0	plant	12.56	5.79	0.95	19.30	
Germany, 2008 (Delitop)	1× 1.2			19	cobs w/o husks	< 0.01	< 0.01	< 0.01	< 0.03	
				28	cobs w/o husks	< 0.01	< 0.01	< 0.01	< 0.03	
Az. Ag. Francesso Busato, Minerbio	480 g/L SC	200	55	0	plant	3.80	3.34	0.17	7.09	Oxspring, S, 2008,
40061 Bologna Italy, 2007	1× 1.2			28	cobs w/o husk	< 0.01	< 0.01	< 0.01	< 0.03	2008/1049973 Oxspring, S,
(Eleonora)										2008
C/Calvo Sotelo No.14	480 g/L	200	55	0	plant	4.26	2.58	0.28	6.94	2008/1055036
Calatorao 50280 Zaragoza	SC			28	cobs w/o husk	< 0.01	0.03	< 0.01	0.05	

SWEET CORN country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- benta- zone	Total bentazone	
Spain, 2007 (P 33N44)				35	cobs w/o husk	< 0.01	0.01	< 0.01	0.03	
				42	cobs w/o husk	< 0.01	< 0.01	< 0.01	< 0.03	
Avda. Zaragoza 29 Utebo. Poligono:1.	480 g/L SC	200	55	0	plant	5.37	4.74	0.32	10.12	
50180 Zaragoza Spain, 2007 (DKC 5784)				28	cobs w/o husk	< 0.01	< 0.01	< 0.01	< 0.03	
				35	cobs w/o husk	< 0.01	< 0.01	< 0.01	< 0.03	
				42	cobs w/o husk	< 0.01	< 0.01	< 0.01	< 0.03	
6 rue de Paris 45300 Semaïses	480 g/L SC	200	55	0	plant	6.15	0.59	0.02	6.72	
France, 2007 (Anjou 285)	1× 1.2			24	cobs w/o husk	< 0.01	0.02	< 0.01	0.04	
				28	cobs w/o husk	< 0.01	0.01	< 0.01	0.03	
				48	cobs w/o husk	< 0.01	0.01	< 0.01	0.03	
Ash Farm, Ingeiby Derbyshire, UK	480 g/L SC	200	55–59	0	plant	11.95	0.99	0.86	13.69	
2007 (Toccate & Sapphire)	1× 1.2			28	cobs w/o husk	< 0.01	0.08	< 0.01	0.10	
				36	cobs w/o husk	< 0.01	0.08	< 0.01	0.10	
				55	cobs w/o husk	< 0.01	0.08	< 0.01	0.10	
Manor Farm, Isley Walton, Derbyshire, UK 2007 (Salgado)	480 g/L SC	200	55–61	0	plant	9.80	0.39	0.56	10.70	
	1× 1.2			29	cobs w/o husk	< 0.01	0.19	< 0.01	0.20	
				44	cobs w/o husk	< 0.01	0.09	< 0.01	0.10	
				61	cobs w/o husk	< 0.01	0.07	< 0.01	0.09	
Zandsteeg 18 6595 MS Ottersum	200 g/L SC	300	14	0	plant ⁵	128	6	0.32	133.9	Reichert, N
Limburg The Netherlands 2005 (Ohio)	1x0.800			103	cobs with husks	< 0.02	< 0.02	< 0.02	< 0.06	2006, 2005/1034455

SWEET CORN country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- benta- zone	Total bentazone	
Asperberg 12				0	plant	78	1.3	0.3	79.5	Reichert, N,
47574 Goch- Pfalzdorf				117	cobs with husks	< 0.02	< 0.02	< 0.02	< 0.06	2006, 2006/1024264
Nordrhein- Westfalen										
Germany, 2005 (HSMR 20)										
F-62 116	480g/L	262	15	0	plant	166.3	3.53	0.419	170.0	Schulz, H,
Alblainzevelle France, 1999	SL			115	cobs with husks	< 0.02	< 0.02	< 0.02	< 0.06	2001, 2001/1000919
(Chantal)	1x1.607									
F-08 190, Aire France, 1999	480g/L SL	246	15-16	0 76	plant cobs with husks	99.94 < 0.02	1.25 < 0.02	0.13 < 0.02	101.23 < 0.06	
	1x1.511									

^a At application^b Plants without roots

n.r. = Not reported

*Legume vegetables**Green peas*

A total of 14 field trials were conducted on fresh peas in United Kingdom and the USA to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC) in 1993, 1994 and 2007 (Oxspring, S, 2008, 2008/1049972; Versoi, PL, *et al.*, 1995, 1995/5159; Oxspring, S, 2008, 2008/1049972). The results are shown in Table 69.

Table 69 Residues of bentazone in green peas after one application of bentazone

GREEN PEAS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Mautby	87% SC	200	51–59	0	Plant ^b	4.85	0.16	< 0.01	5.01	Oxspring, S,
Great Yarmouth	1× 0.957			28	seed ^c	< 0.01	< 0.01	< 0.01	< 0.03	2008,
NR29 3JB, UK				28	seed ^d	< 0.01	< 0.01	< 0.01	< 0.03	2008/1049972
2007				28	wh. pod ^d	< 0.01	0.02	< 0.01	0.04	
(Swallow)										
North Newbald	87% SC	200	55–65	0	Plant ^b	4.28	1.96	0.13	6.24	
Yorkshire YO 43	1× 0.957			28	seed ^c	< 0.01	< 0.01	< 0.01	< 0.03	
4 th , UK				28	seed ^d	< 0.01	< 0.01	< 0.01	< 0.03	
2007				28	wh. pod ^d	< 0.01	0.03	< 0.01	0.05	

GREEN PEAS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
(Waverx)										
Porterville, CA	42.2% SL	186	65–67	10	Pods ^c	0.74	1.95	< 0.05	2.74	Versoi, PL,
USA	2× 1.25	188								et al., 1995,
1993										1995/5159
(Wando)										
Madera, CA	42.2% SL	189	65–67	10	Pods	0.46	1.14	0.07	1.68	
USA	2× 1.25	189								
1993										
(Progress No. 9)										
Seaford	42.2% SL	245	65–67	10	Pods	< 0.05	0.67	< 0.05	0.77	
Delaware, USA	2× 1.25	178								
1993										
(Early Freezer 680)										
Buhl, Idaho	42.2% SL	190	65–67	10	Pods	< 0.05	0.23	< 0.05	0.33	
USA	2× 1.25	188								
1993	42.2% SL	191		10	Pods	< 0.05	0.73	< 0.05	0.83	
(FL24)	2× 1.25	192								
	with									
	adjuvant									
Redwood County	42.2% SL	185	65–71	10	Pods ^d	0.06	0.86	< 0.05	0.97	
Minnesota	2× 1.25	187								
USA										
1994										
(5063)										
Redwood County	42.2% SL	192	65–71	10	Pods ^d	0.05	1.01	< 0.05	1.11	
Minnesota	2× 1.25	188								
USA, 1994										
(7071)										
Delavan, WI	42.2% SL	195	65–67	10	Pods	< 0.05	0.44	< 0.05	0.54	
USA	2× 1.25	181								
1993										
(9888F)										
Verona, WI	42.2% SL	234	62–67	10	Pods	< 0.05	0.82	< 0.05	0.92	
USA	2× 1.25	173								
1993										
(77 EP)										
Corvallis, Oregon	42.2% SL	189	65–67	10	Pods	< 0.05	0.68	< 0.05	0.78	
USA	2× 1.25	184								
1993		190		10	Pods	< 0.05	0.77	< 0.05	0.87	

GREEN PEAS	Form. Appli.		Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
country, year (variety)	Rate (kg ai/ha)	Water L/ha			Matrix	bentazone	6-OH-bentazone	8-OH-bentazone	Total bentazone	
(Grant)		187								
Ephrata, WA	42.2% SL	184	71–77	10	Pods	< 0.05	0.81	< 0.05	0.91	
USA	2× 1.25	185								
1993		192		10	Pods	< 0.05	0.98	< 0.05	1.08	
(Perfection)		192								

^a At application^b Without roots or pods^c Mechanically harvested^d Manually harvested

Green beans

A total of 16 trials in green beans were conducted in different representative growing areas in Northern and Southern Europe in 2008 and 2009 to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone. (Schulz, H, 2009, 2009/1024806; Schroth, E, Martin, T, 2010, 2009/1123296). The results are shown in Table 70.

Table 70 Residues of bentazone in green beans after one application of bentazone in Southern and Northern Europe

GREEN BEANS	Form. Appli.		Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
country, year (variety)	Rate (kg ai/ha)	Water L/ha			Matrix ^b	bentazone	6-OH-bentazone	8-OH-bentazone	Total bentazone	
Southern Europe										
33220 St Avit	87% SG	200	55	0	plant	48.20	0.44	0.16	48.80	Schulz, H
St Nazaire	1× 0.957			27	Pods ^c	< 0.01	0.08	0.02	0.11	2009,
France				36	Pods ^c	< 0.01	0.05	0.02	0.08	2009/1024806
2008				36	Pods ^d	< 0.01	0.08	0.02	0.11	
(Flagoly)				36	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				41	Pods ^d	< 0.01	0.10	0.03	0.14	
				41	seed	< 0.01	< 0.01	< 0.01	< 0.03	
Bamague	87% SG	200	55	0	plant	46.80	0.48	0.23	47.50	
47120 Duras	1× 0.957			27	Pods ^c	< 0.01	0.04	0.01	0.06	
France				35	Pods ^c	< 0.01	0.03	0.01	0.05	
2008				35	Pods ^d	< 0.01	0.03	0.01	0.05	
(Flagoly)				35	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				40	Pods ^d	< 0.01	0.01	< 0.01	0.03	
				40	seed	< 0.01	< 0.01	< 0.01	< 0.03	
Toore del Mar	87% SG	200	55	0	plant	26.00	13.30	3.23	42.52	
Malaga	1× 0.957			28	Pods ^c	< 0.01	< 0.01	< 0.01	< 0.03	
Spain				35	Pods ^c	< 0.01	< 0.01	< 0.01	< 0.03	
2008				35	Pods ^d	< 0.01	< 0.01	< 0.01	< 0.03	
(De Oro)				35	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				42	Pods ^d	< 0.01	< 0.01	< 0.01	< 0.03	
				42	seed	< 0.01	< 0.01	< 0.01	< 0.03	
Toore del Mar	87% SG	200	55	0	plant	36.00	9.86	1.38	47.24	
Malaga	1× 0.957			28	Pods ^c	< 0.01	< 0.01	< 0.01	< 0.03	

GREEN BEANS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Spain				35	Pods ^c	< 0.01	< 0.01	< 0.01	< 0.03	
2008				35	Pods ^d	< 0.01	< 0.01	< 0.01	< 0.03	
(De Oro)				35	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				42	Pods ^d	< 0.01	< 0.01	< 0.01	< 0.03	
				42	seed	< 0.01	< 0.01	< 0.01	< 0.03	
FR-31220	87% SG	200	55	0	plant	92.13	0.65	0.63	93.34	Schroth, E
Palaminy	1 × 1.20			28	Pods ^c	< 0.01	0.18	0.03	0.21	Martin, T
Haute-Garonne				28	Pods ^d	< 0.01	0.20	0.06	0.25	2010,
France				28	seed	< 0.01	< 0.01	< 0.01	< 0.03	2009/1123296
2009				35	Pods ^c	< 0.01	0.07	0.03	0.10	
(Linex)				35	Pods ^d	< 0.01	0.21	0.06	0.26	
				35	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				42	Pods ^d	< 0.01	0.31	0.10	0.40	
				42	seed	< 0.01	< 0.01	< 0.01	< 0.03	
IT-48010	87% SG	200	55	0	plant	105.25	0.95	0.30	106.42	
Barbiano di	1 × 1.20			28	Pods ^c	< 0.01	0.04	0.01	0.06	
Cotignola				28	Pods ^d	< 0.01	0.06	0.02	0.09	
Ravenna, Italy				28	seed	< 0.01	< 0.01	< 0.01	< 0.03	
2009				35	Pods ^c	< 0.01	0.05	0.02	0.08	
(Flavert)				35	Pods ^d	< 0.01	0.09	0.03	0.12	
				35	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				42	Pods ^d	< 0.01	0.30	0.07	0.36	
				42	seed	< 0.01	< 0.01	< 0.01	< 0.03	
ES-41710	87% SG	200	55	0	plant	131.89	0.81	0.38	133.01	
Utrera										
Sevilla, Spain	1 × 1.20			36	Pods ^c	< 0.01	< 0.01	< 0.01	< 0.03	
(2009)				42	Pods ^d	< 0.01	< 0.01	< 0.01	< 0.03	
(Tremaya)				42	seed	< 0.01	< 0.01	< 0.01	< 0.03	
GR-57550	87% SG	200	55	0	plant	100.55	0.45	0.33	101.28	
Epanomi	1 × 1.20			29	Pods ^c	< 0.01	0.02	< 0.01	0.04	
Thessaloniki				29	Pods ^d	< 0.01	0.03	0.01	0.05	
Greece				29	seed	< 0.01	0.02	< 0.01	0.04	
2009				35	Pods ^c	< 0.01	0.01	< 0.01	0.03	
(Etna)				35	Pods ^d	< 0.01	0.03	0.01	0.05	
				35	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				42	Pods ^d	< 0.01	0.04	0.02	0.07	
				42	seed	0.02	< 0.01	< 0.01	0.04	
E-11140 Conil	87% SG	200	55	0	plant	77.50	0.86	0.36	78.65	
Cadiz, Spain	1 × 1.20			28	Pods ^c	< 0.01	0.01	< 0.01	0.03	
2009				28	Pods ^d	< 0.01	0.03	0.01	0.05	
(Tremaya)				28	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				35	Pods ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				35	Pods ^d	< 0.01	0.01	< 0.01	0.03	
				35	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				42	Pods ^d	< 0.01	0.01	< 0.01	0.03	
				42	seed	< 0.01	< 0.01	< 0.01	< 0.03	
Northern Europe										
Green Lane Farm	87% SG	200	55	0	plant	51.60	2.68	0.53	54.81	Schulz, H
Nafferton	1 × 0.957			27	Pods ^c	< 0.01	0.05	0.01	0.07	2009,
Driffeld				35	Pods ^c	< 0.01	0.04	0.01	0.06	2009/1024806
East Yorkshire				35	Pods ^d	< 0.01	0.01	0.01	0.03	
YO25 4LF, UK				35	seed	< 0.01	< 0.01	< 0.01	< 0.03	
2008				41	Pods ^d	< 0.01	< 0.01	< 0.01	< 0.03	
(Flamenco)				41	seed	< 0.01	< 0.01	< 0.01	< 0.03	

GREEN BEANS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Green Lane Farm	87% SG	200	55	0	plant	83.00	2.57	0.45	86.02	
Nafferton	1× 0.957			27	Pods ^c	< 0.01	0.07	0.01	0.09	
Drifffield				35	Pods ^c	< 0.01	0.04	0.02	0.07	
East Yorkshire				35	Pods ^d	< 0.01	0.04	0.02	0.07	
YO25 4LF, UK				35	seed	< 0.01	< 0.01	< 0.01	< 0.03	
2008				41	Pods ^d	< 0.01	0.04	0.01	0.06	
(Flavert)				41	seed	< 0.01	< 0.01	< 0.01	< 0.03	
La Bonde	87% SG	200	55	0	plant	56.60	0.37	0.20	57.17	
49650 Allonnes	1× 0.957			27	Pods ^c	< 0.01	0.02	0.01	0.04	
France				35	Pods ^c	< 0.01	0.03	0.01	0.05	
2008				35	Pods ^d	< 0.01	0.07	0.03	0.11	
(Flavert)				35	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				42	Pods ^d	< 0.01	0.09	0.04	0.14	
				42	seed	< 0.01	< 0.01	< 0.01	< 0.03	
Ferme Bonneil	87% SG	200	55	0	plant	53.60	1.17	0.45	55.22	
80400 Esmery	1× 0.957			29	Pods ^c	< 0.01	0.01	< 0.01	0.03	
Hllon, France				35	Pods ^c	< 0.01	0.01	< 0.01	0.03	
2008				42	Pods ^c	< 0.01	0.01	< 0.01	0.03	
(Valence)										
DE-47589 Uedem	87% SG	200	55	0	plant	67.89	0.48	0.40	68.72	Schroth, E
Kleve, Germany	1× 1.20			29	Pods ^c	0.02	0.02	< 0.01	0.05	Martin, T,
2009				36	Pods ^c	< 0.01	0.04	< 0.01	0.06	2010,
(Kansas)				36	Pods ^d	< 0.01	0.03	0.01	0.05	2009/1123296
				36	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				43	Pods ^d	< 0.01	0.04	0.01	0.06	
				43	seed	< 0.01	< 0.01	< 0.01	< 0.03	
DE-47533	87% SG	200	55	0	plant	71.64	0.61	0.68	72.86	
Kleve-Kellen	1× 1.20			29	Pods ^c	< 0.01	< 0.01	< 0.01	< 0.03	
Kleve, Germany				35	Pods ^c	< 0.01	0.02	< 0.01	0.04	
2009				35	Pods ^d	< 0.01	0.03	0.01	0.05	
(Nassau)				35	seed	< 0.01	0.01	< 0.01	0.03	
				43	Pods ^d	< 0.01	0.04	0.02	0.07	
				43	seed	< 0.01	< 0.01	< 0.01	< 0.03	
NL-5853	87% SG	200	55	0	plant	37.57	0.35	0.27	38.15	
Siebgewald	1× 1.20			28	Pods ^c	< 0.01	0.07	< 0.01	0.09	
Bergen				28	Pods ^d	< 0.01	0.07	0.02	0.09	
Netherlands				28	seed	< 0.01	< 0.01	< 0.01	< 0.03	
2009				34	Pods ^c	< 0.01	0.09	0.01	0.10	
(Artemis)				34	Pods ^d	< 0.01	0.09	0.03	0.12	
				34	seed	< 0.01	< 0.01	< 0.01	< 0.03	
				41	Pods ^d	< 0.01	0.05	0.02	0.08	
				41	seed	< 0.01	< 0.01	< 0.01	< 0.03	

^a At application^b Plant parts were taken without roots^c With seeds^d Without seeds

*Pulses**Beans, dry*

A total of 19 field trials in dry beans were conducted in representative growing areas in Southern Europe and Northern Europe and USA to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone (Stroemel, C *et al.*, 2000, 2000/1014883; Blaschke, UG, 2001, 2001/1000926; Schulz, H, 2002, 2002/1006296; Oxspring, S, 2008, 2008/1049971; Schroth E, Martin, T, 2011, 2011/1059498). The results are shown in Table 71.

Table 71 Residues of bentazone in dry beans after one application in Southern Europe and Northern Europe

BEANS (dry) country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Southern Europe										
ES-41710 Utrera	87% SG	200	15	0	plant	45	0.65	0.62	46.27	Schroth, E
Sevilla, Spain	1× 1.20			204	rest pl.	< 0.01	< 0.01	< 0.01	< 0.03	Martin, T
2010				204	seed	< 0.01	< 0.01	< 0.01	< 0.03	2011,
(Luz de Otono)										2011/1059498
FR-32130	87% SG	200	14–15	0	plant	65	0.75	0.52	66.27	
Samatan	1× 1.20			122	rest pl.	< 0.01	< 0.01	< 0.01	< 0.03	
Gers, France				122	seed	< 0.01	< 0.01	< 0.01	< 0.03	
2010										
(Castel)										
13210 St Remy de Provance	48% SL 1× 1.669	326	12	21	plant	0.194	0.752	0.148	1.04	Schulz, H., 2002
Provence, France				48	pod ^c	< 0.02	< 0.02	< 0.02	< 0.06	
2000				48	rest plant	0.027	0.03	0.025	0.08	2002/1006296
(Coco Blanc Gautier)				67	beans ^d	< 0.02	< 0.02	< 0.02	< 0.06	
13210 St Remy de Provance	48% SL 1× 1.546	302	12-13	27	plant	0.141	1.705	0.362	2.08	
Provence, France				52	pod ^c	< 0.02	< 0.02	< 0.02	< 0.06	
2000				52	rest plant	< 0.02	< 0.02	0.041	0.08	
(Langue de feu)				69	beans ^d	0.021	< 0.02	0.023	0.06	
E-41710 Utrera	48% SL	310	12	18	plant	0.0474	0.417	0.13	0.56	
Sevilla, France	1×1.587			48	pod ^c	< 0.02	< 0.02	< 0.02	< 0.06	
2000				48	rest plant	< 0.02	0.031	< 0.02	0.07	
(B.B.L.)				88	beans ^d	< 0.02	< 0.02	< 0.02	< 0.06	
E-41710 Utrera	48% SL	302	12-13	18	plant ^s	0.09	1.033	0.202	1.24	
Sevilla, France	1× 1.587			48	pod ^c	< 0.02	< 0.02	< 0.02	< 0.06	
2000				48	rest plant	< 0.02	0.045	< 0.02	0.08	
(Garrafal Oro)				88	beans ^d	< 0.02	< 0.02	< 0.02	< 0.06	
F-84700	48% SL	300	12	17	shoots	0.021	1.01	0.092	1.05	Blaschke, U
Sorgues, France	1× 1.553			52	pod ^s	< 0.02	< 0.02	< 0.02	< 0.06	G 2001,
1999				66	seeds	< 0.02	< 0.02	< 0.02	< 0.06	2001/1000926
(Novirex)										
F-84700	48% SL	302	12	18	shoots	< 0.02	0.860	0.072	0.89	
Sorgues, France	1× 1.561			59	pod ^s	< 0.02	< 0.02	< 0.02	< 0.06	

BEANS (dry) country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
1999 (Hiltrud)				105	seeds	< 0.02	< 0.02	< 0.02	< 0.06	
E-41720, Los Palacios, Spain	48% SL 1× 1.521	294	12	24	shoots	< 0.02	0.044	0.037	0.10	
				77	Pods	< 0.02	< 0.02	< 0.02	< 0.06	
1999 (BBL-274)				107	seeds	< 0.02	< 0.02	< 0.02	< 0.06	
E-41720, Los Palacios, Spain	48% SL 1× 1.617	313	12–13	24	shoots	0.021	0.094	0.030	0.14	
				66	Pods	< 0.02	< 0.02	< 0.02	< 0.06	
1999 (Garrafal Oro)				85	seeds	< 0.02	< 0.02	< 0.02	< 0.06	
				85	Pods ^c	< 0.02	< 0.02	< 0.02	< 0.06	
La Peyruque	87% SC	200	76	0	plant	2.80	0.50	0.10	3.36	Oxspring, S
St-Martin- Lalande	1× 0.957			28	Pods ^c	0.02	1.20	0.40	1.53	2008,
11400, France				28	seed ^d	0.08	0.04	< 0.01	0.13	2008/1049971
2007 (Linex)				28	seed ^c	< 0.01	0.01	0.20	0.22	
11150 Villasavary	87% SC	200	76	0	plant	1.90	0.70	0.60	3.12	
France	1× 0.957			28	Pods ^c	0.01	1.20	0.30	1.42	
2007 (Linex)				28	seed ^d	0.05	0.03	< 0.01	0.09	
				28	seed ^c	< 0.01	0.03	< 0.01	0.05	
E-41500 Kattendijke, Spain	48% SL 1× 1.518	293	12	12	shoots	0.040	4.31	0.251	4.32	Blaschke, U
				48	Pods	< 0.02	< 0.02	< 0.02	< 0.06	G 2001,
1999 (Berna)				82	seeds	< 0.02	< 0.02	< 0.02	< 0.06	2001/1000926
F-02150, La Selve	48% SL	298	12	31	shoots	< 0.02	0.663	0.150	0.78	
France	1× 1.541			57	Pods	< 0.02	< 0.02	< 0.02	< 0.06	
1999 (Flagrano)				101	seeds	< 0.02	< 0.02	< 0.02	< 0.06	
F-37510 Berthenay, France	48% SL 1× 1.561	298	13	14	shoots	0.032	3.62	0.356	3.76	
				68	Pods	< 0.02	< 0.02	< 0.02	< 0.06	
1999 (Phenomene)				89	seeds	< 0.02	< 0.02	0.023	0.06	
				89	straw	< 0.02	0.042	< 0.02	0.08	
Norther Europe										
Brandenburg Germany	48% SL 1× 1.536	300	12	20	plant	0.026	0.804	0.168	0.94	Stroemel, C
				47	beans ^c	< 0.02	< 0.02	< 0.02	< 0.06	et al., 2000,
1999 (Berggold)				89	dry beans	< 0.02	< 0.02	< 0.02	< 0.06	2000/1014883
				89	straw ^c	< 0.02	0.046	< 0.02	0.08	
Mecklenburg/ Vorpommern	48% SL 1× 1.536	300	12	25	plant	< 0.02	0.941	0.212	1.10	
				51	beans ^c	< 0.02	< 0.02	< 0.02	< 0.06	
Germany				98	dry beans	< 0.02	< 0.02	< 0.02	< 0.06	
1999 (Goodtime)				98	straw ^c	0.078	0.045	0.022	0.14	
Friesland Farm	87% SC	200	76	0	plant	3.00	0.40	0.09	3.46	Oxspring, S
Rushby Lane	1× 0.957			28	Pods ^c	0.80	3.20	0.05	3.85	2008,
Sandiacre				28	seed ^d	0.04	0.30	< 0.01	0.33	2008/1049971

BEANS (dry)	Form.		Crop	DALT	Residues Found (mg/kg)					Reference
country, year (variety)	Appli. Rate (kg ai/ha)	Water L/ha	Growth Stage ^a (BBCH)		Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	Author, year Reference No.
Nottinghamshire				28	seed ^c	< 0.01	0.30	< 0.01	0.30	
UK, 2007, (Cinco)										
91690 Guillerval	87% SC	200	76	0	plant	2.40	0.40	0.30	3.06	
France	1× 0.957			28	Pods ^c	1.40	0.80	0.06	2.21	
2007				28	seed ^d	0.08	0.30	< 0.01	0.37	
(Melodie)				28	seed ^e	0.02	0.30	< 0.01	0.31	

^a At application^b Plant parts were taken without roots^c With seeds^d Dry seed without pods^e Manually harvested dry seed without pod*Peas (dry)*

A total of nine field trials in peas were conducted in representative growing areas in USA, Canada and France to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC) (Single, YH, 1989, 1989/5046; Anonymous, 1989, 1988/10957; Oxspring, S, 2008, 2008/1049972). The results are shown in Table 72.

Table 72 Residues of bentazone in dried peas after one application in USA, Canada and France

PEAS (dry)	Form.		Crop	DALT	Residues Found (mg/kg)					Reference
country, year (variety)	Appli. Rate (kg ai/ha)	water L/ha	Growth Stage ^a (BBCH)		Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	Author, year Reference No.
Colton, Whitman	42% SC	n.r.	May 10	40	dry peas	< 0.05	< 0.05	< 0.05	< 0.15	Single, YH
Washington	2× 1.125									1989
USA, 1986										1989/5046
(Columbia)										
Colton, Whitman	42% SC	n.r.	May 31	31	dry peas	< 0.05	< 0.05	< 0.05	< 0.15	
Washington	2× 1.125									
USA, 1986										
(Columbia)										
Colton, Whitman	42% SC	n.r.	May 31	31	dry peas	< 0.05	< 0.05	< 0.05	< 0.15	
Washington	2× 1.125									
USA, 1986										
(Columbia)										
Latah, Moscow	42% SC	n.r.	May 9	30	dry peas	< 0.05	0.18	< 0.05	0.27	
Idaho	2× 1.125									
USA, 1987										
(Columbia)										
Latah, Moscow	42% SC	n.r.	May 15	33	dry peas	< 0.05	0.06	< 0.05	0.15	

PEAS (dry)	Form. Appli. Rate (kg ai/ha)	water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
country, year (variety)					Matrix	bentazone	6-OH-bentazone	8-OH-bentazone	Total bentazone	
Idaho	2× 1.125									
USA, 1987										
(Columbia)										
Potlatch, Latah	42% SC	n.r.	May 16	34	dry peas	< 0.05	0.43	0.31	0.74	
Idaho	2× 1.125									
USA, 1987										
(Latah)										
Olds, Alberta	48%	100	18–24	111	peas	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous,
Canada, 1988	1× 1.08									1989
(Tipu)										1988/10957
82700 Fihan	87% SC	200	69–70	0	Plant ^b	25.11	0.92	0.32	26.27	Oxspring, S.,
France	1× 0.957			0	wh. pod	6.26	0.20	0.03	6.48	2008,
2007				28	pea seed ^c	0.11	0.31	< 0.01	0.41	2008/1049972
(Lucy)				28	seed ^d	0.20	0.32	< 0.01	0.51	
				28	wh. pod ^d	2.28	0.54	0.02	2.80	
Chem de Pelut	87% SC	200	69–73	0	Plant ^b	24.34	1.62	0.38	26.22	
82000 Montauban	1× 0.957			0	wh. pod	1.96	0.13	0.03	2.11	
France				28	pea seed ^c	0.04	0.34	< 0.01	0.37	
2007				28	seed ^d	0.01	0.14	< 0.01	0.15	
(Ideal)				28	wh. pod ^d	0.21	0.31	< 0.01	0.51	

^a At application^b Plant parts were taken without roots^c With seeds^d Dry seed without pods*Soya bean (dry)*

A total of 23 trials in soya beans were conducted in different representative growing areas in southern Europe and northern Europe and the USA to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC) in 2009 (Kreke, N, 2009, 2008/1034457; Kreke, N, 2010, 2010/1155811; Kreke, N, 2009, 2008/1034456; Kreke, N, 2010, 2010/1155810; Schroth, E, Martin, T, 2010, 2010/1164275; Kreke, N, 2008, 2007/1028359; Kreke, N, 2010, 2010/1155807; Kreke, N, 2008, 2007/1023134; Kreke, N, 2010, 2010/1155806; Stewart, J, 1992, 1992/5169; Single, YH, 1989, 1989/5045). The results are shown in Table 73.

Table 73 Residues of bentazone in soya bean after one application in Southern and Northern Europe and USA

[illegible]

SOYA BEAN country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Europe										
DE-47574 Goch-	87% SG	200	55	0	plant	25	0.33	0.52	25.80	Schroth, E
Nierswalde, Kleve	1× 0.957			30	Pods ^c	0.20	0.01	0.01	0.22	Martin, T
Germany				79	seeds	< 0.01	< 0.01	< 0.01	< 0.03	2010
2009										2010/1164275
(Merlin)										
Heuilley-sur-	48% SL	203	13	90	seeds	< 0.01	< 0.01	< 0.01	< 0.03	Kreke, N
Saone/Burgundy	1× 0.914									2009
France										2008/1034457
2008 (Essor)										Kreke, N
										2010
										2010/1155811
Heuilley-sur-	48% SL	205	13	90	seeds	< 0.01	< 0.01	< 0.01	< 0.03	Kreke, N
Saone/Burgundy	1× 0.924									2009
France										2008/1034456
2008 (Essor)										Kreke, N
										2010
										2010/1155810
USA										
Gladstone,	44.8% SC	189	13–89	55	seeds	< 0.05	< 0.05	< 0.05	< 0.15	Stewart, J
Henderson County	5× 2.24	188			hulls	< 0.05	< 0.05	< 0.05	< 0.15	1992
Illinois, USA		188			meal	0.055	0.080	0.072	0.20	1992/5169
1991		190			crude oil	0.072	< 0.05	0.059	0.17	
(Williams 82)		191			ref. oil ^d	< 0.05	< 0.05	< 0.05	< 0.15	
Danville, Des	44.8% SC	187	12–89	56	seeds	< 0.05	< 0.05	< 0.05	< 0.15	
Moines County	5× 2.24	188			hulls	< 0.05	< 0.05	< 0.05	< 0.15	
Iowa, USA		187			meal	< 0.05	0.059	0.066	0.17	
1991		188			crude oil	0.118	< 0.05	< 0.05	0.21	
(Pioneer 9341)		188			ref. oil ^d	< 0.05	< 0.05	< 0.05	< 0.15	
Tebbetts, Callaway	42% SC	n.r.	June 16	114	seed	< 0.05	< 0.05	< 0.05	< 0.15	Single, YH
MO, USA	2× 1.125		July 6							1989
1987										1989/5045
(Hill)										
Ashland, Boone	42% SC	n.r.	June 15	119	seed	< 0.05	< 0.05	< 0.05	< 0.15	
MO, USA	2× 1.125		July 6							
1987										
(Williams)										
Ashland, Boone	42% SC	n.r.	June 15	119	seed	< 0.05	< 0.05	< 0.05	< 0.15	
MO, USA	2× 1.125		July 6							
1987										
(Williams)										
Jackson, Madison	42% SC	n.r.	June 8	84	seed	< 0.05	< 0.05	< 0.05	< 0.15	
TN, USA	2×		July 24							

^a At application
^b Whole plant parts were taken without roots
^c Pod with seeds
^d See processing study

Potato

Table 74 Residues of bentazone in potatoes after one application in Southern Europe

[illegible]

POTATO country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
GR-58300	87% SG	200	13–17	0	plant	60	3.1	0.87	63.73	
Galatades, Pella	1× 0.957			56	tuber	0.02	< 0.01	< 0.01	0.04	
Greece, 2009 (Spunta)										
ES-11140 Conil	87% SG	200	15	0	plant	35	0.50	0.89	36.30	
Cadiz, Spain	1× 0.957			63	tubers	0.06	< 0.01	< 0.01	0.08	
2009, (Carlita)										
IT-44022 Volania	87% SG	200	9–15	0	plant	71	5.7	1.0	77.29	
Ferrara, Italy	1× 0.957			73	tubers	< 0.01	< 0.01	< 0.01	< 0.03	
2009 (Mona Lisa)										
FR-47180 Meilhan	87% SG	200	19	0	plant	81	0.68	1.2	82.77	
sur Garonne, Lot	1× 0.957			74	tubers	< 0.01	< 0.01	< 0.01	< 0.03	
et Gronne, France										
2009 (Carrera)										
GR-61300 Livadia	87% SG	200	15	0	plant	31	0.85	0.57	32.33	
Kilkis, Greece	1× 0.957			94	tubers	< 0.01	< 0.01	< 0.01	< 0.03	
2009 (Spunta)										
Northern Europe										
Dielsdorf	48% SL	n.r.	5–12 cm	140	potato	< 0.02	< 0.02	< 0.02	< 0.06	Bassler, R,
Switzerland	1× 0.96									1994,
1978 (n.r.)										1994/106 26
Dielsdorf	48% SL	n.r.	8–20 cm	140	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Switzerland	1× 0.96									
1978 (n.r.)										
Dielsdorf	48% SL	n.r.	5–15 cm	140	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Switzerland	1× 0.96									
1978 (n.r.)										
Limbutgerhof	48% SL	400	post- emerg.	68	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Germany	1× 0.96			75	potato	< 0.02	< 0.02	< 0.02	< 0.06	
1979 (n.r.)				89	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Bohl, Germany	48% SL	330	post- emerg.	58	potato	< 0.02	< 0.02	< 0.02	< 0.06	
1979 (n.r.)	1× 0.96			67	potato	< 0.02	< 0.02	< 0.02	< 0.06	
				81	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Aligse, Germany	48% SL	400	post- emerg.	42	potato	< 0.02	< 0.02	< 0.02	< 0.06	
1979 (n.r.)	1× 0.96			49	potato	< 0.02	< 0.02	< 0.02	< 0.06	
				63	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Holzen, Germany	48% SL	400	5 cm	89	potato	0.02	0.02	0.02	0.06	
1979 (n.r.)	1× 0.96			97	potato	0.02	0.02	0.02	0.06	
				111	potato	0.02	0.02	0.02	0.06	
Fjalkinge, Sweden	48% SL	600	5–10 cm	121	potato	< 0.02	< 0.02	< 0.02	< 0.06	

[illegible]

POTATO country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Buinerveen	48% SL	600	15– 18 cm	143	potato	< 0.02	< 0.02	< 0.02	< 0.06	
The Netherlands	1× 1.44									
1979 (n.r.)										
Mylnefield	48% SL	467	15 cm	117	potato	< 0.02	< 0.02	< 0.02	< 0.06	
UK, 1984 (n.r.)	1× 1.44									
Mylnefield	48% SL	467	15 cm	117	potato	< 0.02	< 0.02	< 0.02	< 0.06	
UK, 1984 (n.r.)	1× 1.44									
Lincoln, UK	48% SL	240	30 cm	84	potato	< 0.02	0.03	< 0.02	0.07	
1984 (n.r.)	1× 1.44									
Catteris, UK	48% SL	280	20 cm	146	potato	< 0.02	< 0.02	< 0.02	< 0.06	
1984 (n.r.)	1× 1.44									
Lincoln, UK	48% SL	240	25 cm	87	potato	< 0.02	< 0.02	< 0.02	< 0.06	
1984 (n.r.)	1× 1.44									
Cambridgeshir e	48% SL	280	20 cm	146	potato	< 0.02	< 0.02	< 0.02	< 0.06	
UK, 1984 (n.r.)	1× 1.44									
Frankenthal	48% SL	400	69–75	1	potato	0.03	0.04	< 0.02	0.09	
Germany, 1985	1× 1.44			7	potato	< 0.02	< 0.02	< 0.02	< 0.06	
(n.r.)				14	potato	< 0.02	0.06	< 0.02	0.10	
				21	potato	< 0.02	0.05	< 0.02	0.09	
				27	potato	< 0.02	0.10	< 0.02	0.14	
Frankenthal	48% SL	400	69–75	1	potato	0.08	0.03	< 0.02	0.09	
Germany, 1985	1× 1.44			7	potato	< 0.02	0.07	< 0.02	< 0.06	
(n.r.)				14	potato	< 0.02	0.07	< 0.02	0.10	
				21	potato	< 0.02	0.06	< 0.02	0.09	
				33	potato	< 0.02	0.04	< 0.02	0.14	
Meckenheim	48% SL	400	59–60	1	potato	0.06	0.07	< 0.02	0.09	
Germany, 1985	1× 1.44			8	potato	0.03	0.07	< 0.02	< 0.06	
(n.r.)				15	potato	< 0.02	< 0.02	< 0.02	0.10	
				22	potato	< 0.02	< 0.02	< 0.02	0.09	
				29	potato	< 0.02	< 0.02	< 0.02	0.14	
Altheim, Germany	48% SL	400	10 cm	78	potato	< 0.02	< 0.02	< 0.02	< 0.06	
1977 (n.r.)	1× 1.92			85	potato	< 0.02	< 0.02	< 0.02	< 0.06	
				99	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Iggelheim	48% SL	330	5–10 cm	35	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Germany, 1977	1× 1.92			41	potato	< 0.02	< 0.02	< 0.02	< 0.06	
(n.r.)				56	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Limburgerhof	48% SL	400	10 cm	35	potato	0.02	0.06	< 0.02	0.10	
Germany, 1977	1× 1.92			41	potato	< 0.02	0.06	< 0.02	0.10	
(n.r.)				55	potato	0.03	0.03	< 0.02	0.08	
Iggelheim	48% SL	330	15– 17 cm	38	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Germany, 1978	1× 1.92			45	potato	< 0.02	< 0.02	< 0.02	< 0.06	
(n.r.)				59	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Limburgerhof	48% SL	400	15– 17 cm	69	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Germany, 1978	1× 1.92			77	potato	< 0.02	< 0.02	< 0.02	< 0.06	
(n.r.)				91	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Holzen, Germany	48% SL	400	15– 17 cm	50	potato	< 0.02	< 0.02	< 0.02	< 0.06	
1978, (n.r.)	1× 1.92			57	potato	< 0.02	< 0.02	< 0.02	< 0.06	
				71	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Otternhagen	48% SL	400	15– 17 cm	29	potato	< 0.02	0.03	< 0.02	0.07	
Germany, 1978	1× 1.92			36	potato	< 0.02	0.03	< 0.02	0.07	

POTATO country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
(n.r.)				52	potato	< 0.02	0.03	< 0.02	0.07	
Bobenheim	48% SL	400	40	1	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Germany, 1986	1× 0.96			8	potato	< 0.02	0.03	< 0.02	0.07	
(n.r.)				14	potato	< 0.02	< 0.02	< 0.02	< 0.06	
				21	potato	< 0.02	< 0.02	< 0.02	< 0.06	
				28	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Bobenheim	48% SL	400	40	1	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Germany, 1986	1× 0.96			8	potato	< 0.02	0.04	< 0.02	0.08	
(n.r.)				14	potato	< 0.02	0.03	< 0.02	0.07	
				21	potato	< 0.02	0.03	< 0.02	0.07	
				28	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Bobenheim	48% SL	400	40	1	potato	0.02	< 0.02	< 0.02	< 0.06	
Germany, 1986	1× 0.96			8	potato	< 0.02	0.04	< 0.02	0.08	
(n.r.)				14	potato	< 0.02	0.04	< 0.02	0.08	
				21	potato	< 0.02	0.03	< 0.02	0.07	
				28	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Brazil and Canada										
Aliston, Canada	48% SL	300	30 cm	98	potato	< 0.02	< 0.02	< 0.02	< 0.06	
1979 (n.r.)	1× 1.20									
Viamao, Brazil	48% SL	320	15– 20 cm	46	potato	< 0.02	< 0.02	< 0.02	< 0.06	
1985 (n.r.)	1× 1.44									
Porto Alegre	48% SL	200	25 cm	50	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Brazil, 1985 (n.r.)	1× 1.44									
ao Jose d. Campo	48% SL	350	tuber form	51	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Brazil,	1× 1.44									
Ridgetown	48% SL	300	20– 30 cm	76	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Canada, 1977	1× 1.584									
(n.r.)										
Ridgetown	48% SL	300	20– 30 cm	76	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Canada, 1977	1× 1.584									
(n.r.)										
Ridgetown	48% SL	300	20– 30 cm	76	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Canada, 1977	1× 1.584									
(n.r.)										
Ridgetown	48% SL	300	20– 30 cm	76	potato	< 0.02	< 0.02	< 0.02	< 0.06	
Canada, 1977	1× 1.584									
(n.r.)										

^a At application^b Plant parts were taken without roots

Sugar beet

A field trial on sugar beet was performed in the United States in order to determine the magnitude of the residue of bentazone and its metabolites in sugar beet raw agricultural commodities (RACs) in 1973 (Cannizzaro, R, 1974, 1974/5055). The results are shown in Table 75.

Table 75 Residues of bentazone in sugar beet after treatment in USA during 1973

SUGAR BEET country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- benta- zone	Total bentazone	
Greenville,	480 g/L	262	173 DBH	173 ^b	tops	< 0.05	< 0.05	< 0.05	< 0.15	Cannizzar
Mississippi	SL			173 ^b	roots	< 0.05	< 0.05	< 0.05	< 0.15	o, R, 1974,
USA, 1973	1× 1.125			173 ^b	tops	< 0.05	< 0.05	< 0.05	< 0.15	1974/5055
(n.r.)				173 ^b	roots	< 0.05	< 0.05	< 0.05	< 0.15	

^a At application

^b Interval from planting: 81 days (soil treatment was done before planting)

*Cereals**Barley*

A total number of five field trials were conducted at different representative barley growing areas in Southern Europe (Spain and Italy) and Canada during 1977 and 1999 (Blaschke, UG, 2000, 2000/1018490; Anonymous, 1978, 1977/10291). The results are shown in Table 76.

Table 76 Residues of bentazone in barley after one application in Southern Europe

BARLEY country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- benta- zone	Total bentazone	
E-21880, Paterna	48% SL	300	33	0	shoots	40.49	2.86	0.252	43.41	Blaschke,
Spain, 1999	1× 1.554			20	ears	0.024	0.263	< 0.02	0.29	UG, 2000,
(Irene)				20	remaining shoots	0.05	4.91	0.026	4.68	2000/1018490
				58	grains	< 0.02	< 0.02	< 0.02	< 0.06	
				58	straw	0.039	0.633	< 0.02	0.65	
E-41270, Los	48% SL	299	35-37	0	shoots	28.75	3.34	0.217	32.09	
Palacios, Spain	1× 1.546			17	ears	0.035	0.461	0.029	0.49	
1999, (Apex)				17	remaining shoots	1.03	3.58	0.022	4.41	
				58	grains	< 0.02	< 0.02	< 0.02	< 0.06	
				58	straw	0.144	0.23	< 0.02	0.38	
I-20089, Rozzano	48% SL	300	37	0	shoots	18.13	0.714	0.188	18.98	
Italy, 1999	1× 1.553			26	ears	0.020	0.027	0.030	0.07	

BARLEY country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- benta- zone	Total bentazone	
(Gotic)				26	remaining shoots	< 0.02	0.697	< 0.02	0.69	
				65	grains	< 0.02	< 0.02	< 0.02	< 0.06	
				65	straw	0.058	0.091	< 0.02	0.16	
I-20090, Caleppio	48% SL		37–39	0	shoots	8.66	0.555	0.109	9.28	
di Settala, Italy	1× 1.55			20	ears	0.020	0.116	< 0.02	0.15	
1999, (Federal)				20	remaining shoots	< 0.02	1.40	0.020	1.35	
				65	grains	< 0.02	< 0.02	< 0.02	< 0.06	
				65	straw	0.042	0.046	< 0.02	0.10	
I-27028, San	48% SL		39	0	shoots	4.82	0.278	0.027	5.11	
Marino, Sicconario	1× 1.55			17	ears	0.029	0.192	< 0.02	0.23	
Italy, 1999 (Folgore)				17	remaining shoots	< 0.02	0.614	< 0.02	0.61	
				57	grains	< 0.02	< 0.02	< 0.02	< 0.06	
				57	straw	0.062	0.061	< 0.02	0.14	
Northern America										
Lacome, Alberta	48% n.r.	100	14–15	73	grain	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
Canada, 1977	1× 1.60									1978,
(Galt)										1977/10291

^a At application

Oats

One field trial was conducted at a representative oat growing area in Germany (Schlag-Limburgerhof) during 1974 (Anonymous, 1974, 1974/10290). The results are shown in Table 77.

Table 77 Residues of bentazone in oats after one application in Germany

OAT country, year (variety)	Form. Appli. Rate (kg ai/ha)	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
				Matrix	bentazone	6-OH- bentazone	8-OH- benta-zone	Total bentazone	
Schlag	n.r.	Feekes	0	grain	9.78	—	—	9.88	Anonymous
-Limburgerhof	1× 1.92	-Scale G/H	30	grain	< 0.05	—	—	< 0.15	1974,
Germany			41	grain	< 0.05	—	—	< 0.15	1974/10290
1974			104	grain	< 0.05	—	—	< 0.15	
(Flamingskrone)									

^a At application

n.r. = Not reported

Maize

Thirty field trials were conducted in representative maize growing areas in the Northern and Southern Europe and USA to determine the residue level of bentazone in or on raw agricultural commodities (RAC) during 2010 (Stewart, J, 1992, 1992/5168; Oxspring, S, 2011, 2011/1059496; Klaas, P, Ziske, J, 2009, 2009/1024805; Oxspring, S, 2008, 2008/1049973; Oxspring, S, 2008, 2008/1055036; Reichert, N, 2006, 2005/1034455; Reichert, N, 2006, 2006/1024264; Schulz, H, 2001, 2001/1000919; Blaschke, UG, 2000, 2000/1018489). The results are shown in Table 78.

Table 78 Residues of bentazone in maize after one application in Europe

MAIZE	Form. Appli. Rate (kg ai/ha)	water L/ha	Crop Growth Stage ^a (BBCH)	DALT ^a	Residues Found (mg/kg)					Reference Author, year Reference No.
country, year (variety)					Matrix ^b	bentazone	6-OH-bentazone	8-OH-bentazone	Total bentazone	
South Europe										
Bologna, Italy	48% SL	200	35	0	plant	31	0.45	0.82	32	Oxspring, S
2010 (KWS 6565)	1 × 0.96			69	Cobs ^c	< 0.01	< 0.01	< 0.01	< 0.03	2011
				60	cobs ^c	< 0.01	< 0.01	< 0.01	< 0.03	2011/1059496
				84	grain	< 0.01	< 0.01	< 0.01	< 0.03	
Castelsarrasin	48% SL	200	35	0	plant	6.2	6.0	0.20	12	
France, 2010	1 × 0.96			61	cobs ^c	< 0.01	< 0.01	< 0.01	< 0.03	
(Tyrex)				119	grain	< 0.01	< 0.01	< 0.01	< 0.03	
Albacete, Spain	48% SL	200	35	0	plant	12	0.8	0.42	14	
2010 (Mitic)	1 × 0.96			56	cobs ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				60	cobs ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				124	grain	< 0.01	< 0.01	< 0.01	< 0.03	
Bamague	480 g/L SL	200	55	0	plant	5.58	2.03	0.29	7.90	Klaas, P
47120 Duras	1 × 1.2			64	grain	< 0.01	< 0.01	< 0.01	< 0.03	Ziske, J 2009
France, 2008				76	grain	< 0.01	< 0.01	< 0.01	< 0.03	2009/1024805
(Mitic)										
“Finca	480 g/L SL	200	55	0	plant	0.03	0.025	< 0.01	0.065	
Valsequillo”	1 × 1.2			63	grain	< 0.01	< 0.01	< 0.01	< 0.03	
Carretera vieja										
Antequera										
Campillos										
Spain, 2008										
(Tardio 130)										
Az. Ag. Francesco	480 g/L SC	200	55	0	whole plant	3.80	3.34	0.17	7.09	Oxspring, S
Busato, Minerbio	1 × 1.2			43	grain	< 0.01	< 0.01	< 0.01	< 0.03	2008,
40061 Bologna				50	grain	< 0.01	< 0.01	< 0.01	< 0.03	2008/1049973
Italy, 2007				65	grain	< 0.01	< 0.01	< 0.01	< 0.03	Oxspring S
(Eleonora)										2008
C/Calvo Sotelo No.14	480 g/L	200	55	0	whole plant	4.26	2.58	0.28	6.94	2008/1055036
Calatorao	SC			86	grain	< 0.01	< 0.01	< 0.01	< 0.03	
50280 Zaragoza	1 × 1.2									
Spain, 2007										
(P 33N44)										
Avda. Zaragoza 29	480 g/L SC	200	55	0	whole plant	5.37	4.74	0.32	10.12	
Utebo. Poligono:1.	1 × 1.2			96	grain	< 0.01	< 0.01	< 0.01	< 0.03	

MAIZE country, year (variety)	Form. Appli. Rate (kg ai/ha)	water L/ha	Crop Growth Stage ^a (BBCH)	DALT ^a	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
50180 Zaragoza										
Spain, 2007 (DKC 5784)										
F-79 100	480 g/L	244	14–16	0	plant	155.6	6.14	0.378	161.71	Schulz, H
Tourtenay	SL			144	grain	< 0.02	< 0.02	< 0.02	< 0.06	2001,
France, 1999 (LG 2447)	1× 1.502									2001/1000919
F-33 210	480 g/L	250	15–16	0	plant	78.84	1.82	0.20	80.73	
Saint Loubert	SL			141	grain	< 0.02	< 0.02	< 0.02	< 0.06	
France, 1999 (DK 604)	1× 1.536									
6231										
E-41720	485 g/L	305	15	0	shoots	57.5	2.15	1.68	61.09	Blaschke, U
Los Palacios	SL			122	grain	< 0.02	< 0.02	< 0.02	< 0.06	G 2000,
Spain, 1998 (Dracuna)	1× 1.576									2000/1018489
E-41849	485 g/L	306	15	0	shoots	73.30	2.58	2.10	77.69	
Aznalcázar-1	SL			109	grain	< 0.02	< 0.02	< 0.02	< 0.06	
Spain, 1998 (Eleonara)	1× 1.585									
E-41849	485 g/L	305	15	0	shoots	57.82	1.88	1.60	61.08	
Aznalcázar-1	SL			109	grain	< 0.02	< 0.02	< 0.02	< 0.06	
Spain, 1998 (Juanita)	1× 1.578									
I-20090	485 g/L	303	13–15	0	shoots	72.85	3.44	0.602	76.64	
Caleppio di Settala	SL			100	grain	< 0.02	< 0.02	< 0.02	< 0.06	
Italy, 1998 (Costanza)	1× 1.566									
I-26049	485 g/L	301	13–15	0	shoots	103.09	1.92	2.08	106.84	
Stagno Lombado	SL			114	grain	< 0.02	< 0.02	< 0.02	< 0.06	
Italy, 1998 (Costanza)	1× 1.559									
I-13041	485 g/L	300	13–15	0	shoots	46.54	2.98	0.575	49.87	
Bianze	SL			127	grain	< 0.02	< 0.02	< 0.02	< 0.06	
Italy, 1998 (Alicia)	1× 1.552									
North Europe										
Brandenberg	48% SL	200	35	0	plant	12	8.9	0.11	21	Oxspring, S
Blumberg	1× 0.96			60	cobs ^c	< 0.01	< 0.01	< 0.01	< 0.03	2011
Germany, 2010 (Franz)				99	grain	< 0.01	< 0.01	< 0.01	< 0.03	2011/1059496
Ticknall	48% SL	200	35	0	plant	16	0.50	0.14	17	
Derbyshire, UK	1× 0.96			71	cobs ^c	< 0.01	< 0.01	< 0.01	< 0.03	
2010 (N K Cheer)				60	cobs ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				89	grain	< 0.01	< 0.01	< 0.01	< 0.03	
Elst	48% SL	200	35	0	plant	24	0.73	0.18	25	
The Netherlands	1× 0.96			60	cobs ^c	< 0.01	< 0.01	< 0.01	< 0.03	
2010 (Aabsint)				106	grain	< 0.01	< 0.01	< 0.01	< 0.03	
Civray	480 g/L SL	200	55	0	plant	17.68	4.71	1.08	23.47	Klaas, P

MAIZE country, year (variety)	Form. Appli. Rate (kg ai/ha)	water L/ha	Crop Growth Stage ^a (BBCH)	DALT ^a	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
49490 Melgnet	1 × 1.200			63	grain	< 0.01	< 0.01	< 0.01	< 0.03	Ziske, J 2009
Vicomte, France										2009/1024805
2008 (Aspeed)										
Mittelweg 16	480 g/L SL	200	55	0	plant	12.56	5.79	0.95	19.30	
49685 Hoheging	1 × 1.200			62	grain	< 0.01	< 0.01	< 0.01	< 0.03	
Germany, 2008 (Delitop)				105	grain	< 0.01	< 0.01	< 0.01	< 0.03	
6 rue de Paris	480 g/L	200	55	0	whole plant	6.15	0.59	0.02	6.72	Oxspring, S 2008,
45300 Semaïses	SC			69	grain	< 0.01	< 0.01	< 0.01	< 0.03	2008/1049973
France, 2007 (Anjou 285)	1 × 1.200									Oxspring S 2008
Ash Farm, Ingeiby	480 g/L	200	55–59	0	whole plant	11.95	0.99	0.86	13.69	2008/1055036
Derbyshire, UK 2007 (Toccate & Sapphire)	SC 1 × 1.200			81	grain	< 0.01	0.02	< 0.01	0.04	
Manor Farm, Isley Walton, Derbyshire, UK 2007 (Salgado)	480 g/L SC 1 × 1.200	200	55–61	0	whole plant	9.80	0.39	0.56	10.70	
Zandsteeg 18	200 g/L	300	14	0	plant	128	6	0.32	133.9	Reichert, N. 2006
6595 MS Ottersum Limburg	SC 1 × 0.800			s138	grains	< 0.02	< 0.02	< 0.02	< 0.06	2005/1034455
The Netherlands 2005 (Ohio)										Reichert, N 2006,
Asperberg 12				0	plant	78	1.3	0.3	79.5	2006/1024264
47574 Goch- Pfalzdorf Nordrhein- Westfalen Germany, 2005 (HSMR 20)				142	grains	< 0.02	< 0.02	< 0.02	< 0.06	
F-62 116	480 g/L	262	15	0	plant	166.3	3.53	0.419	170.0	Schulz, H
Alblainzevelle	SL			140	grain	< 0.02	< 0.02	< 0.02	< 0.06	2001,
France, 1999 (Chantal)	1 × 1.607									2001/1000919
F-08 190, Aire	480 g/L	246	15–16	0	plant	99.94	1.25	0.13	101.23	
France, 1999 (Anjou 258)	SL 1 × 1.511			107	grain	< 0.02	< 0.02	< 0.02	< 0.06	
America Des Moines,	44.8%	188	V–4	69	grain	< 0.05	0.054	< 0.05	0.154	Stewart, J

MAIZE country, year (variety)	Form. Appli. Rate (kg ai/ha)	water L/ha	Crop Growth Stage ^a (BBCH)	DALT ^a	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Iowa	SL									
USA, 1991	5× 2.24	187	V-6	–	grits	< 0.05	< 0.05	< 0.05	< 0.15	1992
(Querna 7670)		187	V-7	–	meal	< 0.05	< 0.05	< 0.05	< 0.15	1992/5168
		186	Brown silk	–	flour	< 0.05	< 0.05	< 0.05	< 0.15	
		188	Milk	–	starch	< 0.05	< 0.05	< 0.05	< 0.15	
				–	crude oil ^d	< 0.05	< 0.05	< 0.05	< 0.15	
				–	refined oil ^d	< 0.05	< 0.05	< 0.05	< 0.15	
				–	crude oil	< 0.05	< 0.05	< 0.05	< 0.15	
				–	refined oil	< 0.05	< 0.05	< 0.05	< 0.15	
Henderson	44.8% SL	189	V-4	70	grain	< 0.05	< 0.05	< 0.05	< 0.15	
Illinois, USA	5× 2.24	190	V-6	–	grits	< 0.05	< 0.05	< 0.05	< 0.15	
1991		189	V-7	–	meal	< 0.05	< 0.05	< 0.05	< 0.15	
(Querna 7310)		189	Brown silk	–	flour	< 0.05	< 0.05	< 0.05	< 0.15	
		190	Milk	–	starch	< 0.05	< 0.05	< 0.05	< 0.15	
				–	crude oil ^d	< 0.05	< 0.05	< 0.05	< 0.15	
				–	refined oil ^d	< 0.05	< 0.05	< 0.05	< 0.15	
				–	crude oil	< 0.05	< 0.05	< 0.05	< 0.15	

^a At application^b Plant parts were taken without roots^c Cob with husk^d See processing study

Rice

A total of 18 field trials was conducted in representative rice growing areas in Brazil, China, Southern Europe and Japan to determine the residue level of bentazone in or on raw agricultural commodities (RAC) in 1984/1985, 1986, 1987, 2007 (Anonymous, 1987, 1986/10395; Anonymous, 1987, 1986/10854; Anonymous, 1987, 1986/10855; Anonymous, 1987, 1986/10856; Anonymous, 1988, 1987/10354; Anonymous, 1988, 1987/10355; Anonymous, 1986, 1984/10213; Anonymous, 1986, 1984/10259; Tianxi L. *et al.*, 1986, 1986/10849; Tianxi L. *et al.*, 1986, 1986/10850; Odanaka, Y *et al.*, 2008, 2012/1272538;). The results are shown in Table 79.

Table 79 Residues of bentazone in rice after one to two application(s) in Brazil, China, Southern Europe and Japan

RICE country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
South Europe										
Mejanas	n.r.	n.r.	14–23	86	grain	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
France, 1986	1× 1.92									1987
(Smeraldo)										1986/10395
13-Mejanes	n.r.	n.r.	14–23	87	grain	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous

RICE country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
France, 1986	1× 1.04									1987
(Smeraldo)										1986/10854
13-Mas Thibert	n.r.	n.r.	14–21	92	grain	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
France, 1986	1× 1.04									1987
(Smeraldo)										1986/10855
13-Mejanes	n.r.	n.r.	14–21	87	grain	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
France, 1986	1× 1.04									1987
(Bonnet Bel)										1986/10856
Moinhola- Agua	n.r.	400	30–39	n.r.	grain	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
De Moura, Portugal, 1987	1× 1.20									1988
(Ribe)										1987/10354
Benavente- Ribatejo	n.r.	400	30–39	n.r.	grain	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
Potugal, 1987	1× 1.20									1988
(Ribe)										1987/10355
America and Asia										
Cachoeirinha RS., Brazil	n.r.	250	21–29	120	grain	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
1984/1985	1× 2.4									1986
(Irga 409)										1984/10213
Cachoeirinha RS., Brazil	n.r.	250	21–29	120	grain	< 0.02	< 0.02	< 0.02	< 0.06	Anonymous
1984/1985	1× 2.4									1986
(Irga 409)										1984/10259
Hangzhou	480g/L	n.r.	n.r.	40	grain	< 0.02	< 0.02	< 0.02	< 0.06	Tianxi, L <i>et al.</i> ,
China	Water			50	grain	< 0.02	< 0.02	< 0.02	< 0.06	1986,
1986	Solution			60	grain	< 0.02	< 0.02	< 0.02	< 0.06	1986/10849
(TP 22)	1× 2.16									
Hangzhou	480 g/L	n.r.	n.r.	40	grain	< 0.02	< 0.02	< 0.02	< 0.06	
China	Water			50	grain	< 0.02	< 0.02	< 0.02	< 0.06	
1986	Solution			60	grain	< 0.02	< 0.02	< 0.02	< 0.06	
(TP 22)	1× 1.44									
Hangzhou	480 g/L	n.r.	n.r.	50	grain	< 0.02	< 0.02	< 0.02	< 0.06	
China	Water			60	grain	< 0.02	< 0.02	< 0.02	< 0.06	
1986	Solution									
(TP 22)	1× 1.08									
Guiyang	480 g/L	n.r.	n.r.	40	grain	< 0.02	< 0.02	< 0.02	< 0.06	
China	Water			50	grain	< 0.02	< 0.02	< 0.02	< 0.06	
1986	Solution			60	grain	< 0.02	< 0.02	< 0.02	< 0.06	
(TP 22)	1× 2.16									
GuiYang	480 g/L	n.r.	n.r.	40	grain	< 0.02	< 0.02	< 0.02	< 0.06	
China	Water			50	grain	< 0.02	< 0.02	< 0.02	< 0.06	
1986	Solution			60	grain	< 0.02	< 0.02	< 0.02	< 0.06	
(TP 22)	1× 1.44									
Guiyang	480 g/L	n.r.	n.r.	50	grain	< 0.02	< 0.02	< 0.02	< 0.06	
China	Water			60	grain	< 0.02	< 0.02	< 0.02	< 0.06	
1986	Solution									
(TP 22)	1× 1.08									
Ushiku, Japan 2007	40% SL 2× 2.8	n.r.	n.r.	0	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	Odanaka, Y <i>et al.</i> , 2008
(Koshihikari)					brown	< 0.01	< 0.01	< 0.01	< 0.03	2012/1272538

RICE country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
					rice ^c					
					straw ^c	< 0.02	< 0.02	< 0.02	< 0.06	
				30	brown rice ^b	0.11	< 0.01	< 0.01	0.13	
					brown rice ^c	0.12	< 0.01	< 0.01	0.14	
				45	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				59	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
Ushiku, Japan	40% SL 2× 4.4	n.r.	n.r.	0	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
2007 (Koshihikari)					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				30	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				45	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				59	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
Ishikawa, Japan	40% SL	n.r.	n.r.	0	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
2007	2× 2.8				brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
(Koshihikari)										
				30	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				45	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				59	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
Ishikawa, Japan	40% SL	n.r.	n.r.	0	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
2007	2× 4.4				brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
(Koshihikari)										
				30	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				45	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	

RICE country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	
				59	brown rice ^b	< 0.01	< 0.01	< 0.01	< 0.03	
					brown rice ^c	< 0.01	< 0.01	< 0.01	< 0.03	

^a At application^b Analysed by the Institute of Environmental Toxicology^c Analysed by Nisso Chemical Analysis Service

n.r. = Not reported

Sorghum

A total of six field trials were conducted in representative sorghum growing areas in France (Southern Europe) to determine the residue level of bentazone in or on raw agricultural commodities (RAC) in 1992 in southern Europe (Anonymous, 1993, 1992/12125; Anonymous, 1993, 1992/12126; Anonymous, 1993, 1992/12127; Anonymous, 1993, 1992/12128; Anonymous, 1993, 1992/12129; Anonymous, 1993, 1992/12130). The results are shown in Table 80.

Table 80 Residues of bentazone in sorghum after one application in Southern Europe

SORGHUM country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Southern Europe										
34 Marsillargues	480 g/L	n.r.	15–16	112	grain	< 0.05	< 0.08	< 0.08	< 0.20	Anonymous
France, 1992	n.r.									1993,
(Argence)	1 × 1.2									1992/12130
31 Labarthe	480 g/L	n.r.	15–16	184	grain	< 0.05	< 0.08	< 0.08	< 0.20	Anonymous
s/Leze, France	n.r.									1993,
1992 (DK 18)	1 × 1.2									1992/12129
31 Labarthe	480 g/L	n.r.	15–16	131	grain	< 0.05	< 0.08	< 0.08	< 0.20	Anonymous
s/Leze, France	n.r.									1993,
1992 (DK 18)	1 × 1.2									1992/12128
47 Canderoue	480 g/L	n.r.	15–17	163	grain	< 0.05	< 0.08	< 0.08	< 0.20	Anonymous
France, 1992	n.r.									1993,
(Argence)	1 × 1.2									1992/12127
32 Auterive	480 g/L	n.r.	16–17	116	grain	< 0.05	< 0.08	< 0.08	< 0.20	Anonymous
France, 1992	n.r.									1993,
(DK 18)	1 × 1.2									1992/12126
32 Ligardes	480 g/L	n.r.	16	190	grain	< 0.05	< 0.08	< 0.08	< 0.20	Anonymous
France, 1992	n.r.									1993,
(Aralba)	1 × 1.2									1992/12125

^a At application

Wheat

A total number of 12 field trials were conducted at different representative wheat growing areas in Southern Europe (Spain and Italy) and Northern Europe during 1998 and 2010 (Blaschke, UG, 2000, 2000/1018487; Oxspring, S, 2011, 2011/1059497). The results are shown in Table 81.

Table 81 Residues of bentazone in wheat after one application in Southern Europe and Northern Europe

[illegible]

WHEAT country, year (variety)	Form. Appli. Rate ⁰ (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH-bentazone	8-OH-bentazone	Total bentazone	
(Tabasco)										
Sweepstone	480 g/L	200	32	0	whole plant	24	0.95	0.17	25	
Leicestershire, UK	SL			87	grain	< 0.01	< 0.01	< 0.01	< 0.03	
2010 (Oakley)	1 × 0.96									
Burweg	480 g/L	200	32	0	plant	26	1.9	0.27	28	
Niedersachsen	SL			91	grain	< 0.01	< 0.01	< 0.01	< 0.03	
Germany, 2010	1 × 0.96									
(Tobasco)										
Tarupvej	480 g/L	200	32	0	plant	27	0.64	0.11	28	
Middelfart	SL			90	grain	< 0.01	< 0.01	< 0.01	< 0.03	
Denmark, 2010	1 × 0.96									
(Frument)										
Audeville, Loiret	480 g/L	200	32	0	plant	31	0.49	0.12	32	
45300, France	SL			87	grain	< 0.01	< 0.01	< 0.01	< 0.03	
2010 (Suba)	1 × 0.96									

^a At application^b Plants without roots

Oilseeds

Linseed

A total number of 14 field trials were conducted at different representative linseed growing areas in Southern France, Canada and USA during 1983, 1988, 1989 and 1999 (Blaschke, UG, 2000, 2000/1018491; Anonymous, 1983, 1983/10238; Anonymous, 1983, 1983/10239; Anonymous, 1983, 1983/10574; Anonymous, 1989, 1988/10960; Anonymous, 1989, 1988/10961; Single, YH, 1992, 1992/5123; Versoi PL, Abdel-Baky S, 2000, 2000/5188;). The results are shown in Table 82.

Table 82 Residues of bentazone in linseed after one application in Southern France, Canada and USA

LINSEED country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH-bentazone	8-OH-bentazone	Total bentazone	
Southern Europe										
F-31540, St Julia	485 g/L	287	15	34	shoots	< 0.02	0.104	< 0.02	0.14	Blaschke,
France, 1999	SL			97	seeds	< 0.02	< 0.02	< 0.02	< 0.06	UG 2000,
(Mikael)	1 × 1.483			97	straw	< 0.02	0.258	< 0.02	0.28	2000/1018491
F-32320	485 g/L	295	14	28	shoots	< 0.02	0.179	< 0.02	0.21	
Peyrusse Grande	SL			103	seeds	< 0.02	< 0.02	< 0.02	< 0.06	
France, 1999	1 × 1.527			103	straw	< 0.02	0.119	< 0.02	0.15	
(Mikael)										
F-26400,	485 g/L	308	13	29	shoots	< 0.02	0.434	< 0.02	0.45	

[illegible]

LINSEED country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazo ne	6-OH- bentazone	8-OH- bentazone	Total bentazone	
										Baky,
1999 (Linola)	1 × 1.092									S 2000,
										2000/5188

^a At application^b Residues in control sample was above LOQ (0.05 mg/kg)

n.r. = Not reported

Peanuts

A total of 13 trials in peanuts were conducted in the USA to determine the residue level of bentazone in or on raw agricultural commodities (RAC) during 1973, 1974 and 1975 (Dye, DM, 1994, 1976/5087; Dye, DM, 1976, 1976/5086; Dye, DM, 1976, 1976/5085; Daniel, JW, 1974, 1975/5065; Anonymous, 1976, 1975/5063; Horton, WE, 1976, 1975/5060; Anonymous, 1976, 1975/5059; Tiller, H, Thompson, J, 1976, 1975/5057). The results are shown in Table 83.

Table 83 Residues of bentazone in peanuts after treatment in the USA

PEANUT country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazon e	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Mulberry, Texas	480 g/L	374	5–50 cm	58	Pods	< 0.05	< 0.05	< 0.05	< 0.15	Dye, DM
USA, 1973 (Starr)	SL 1 × 1.12		height	58	nuts	< 0.05	< 0.05	< 0.05	< 0.15	1994, 1976/5087
Mulberry, Texas	480 g/L	374	5–50 cm	58	Pods	< 0.05	< 0.05	< 0.05	< 0.15	
USA, 1973 (Starr)	SL 1 × 2.24		height	58	nuts	< 0.05	< 0.05	< 0.05	< 0.15	
Yoakum, Texas	480 g/L	187	n.r.	128	Pods	< 0.05	< 0.05	< 0.05	< 0.15	Dye, DM
USA, 1973 (Starr)	SL 1 × 1.68			128	nuts	< 0.05	< 0.05	< 0.05	< 0.15	1976, 1976/5086
Yoakum, Texas	480 g/L	187	n.r.	128	Pods	< 0.05	< 0.05	< 0.05	< 0.15	
USA, 1973 (Starr)	SL 1 × 3.36			128	nuts	< 0.05	< 0.05	< 0.05	< 0.15	
Lewiston, NC 1973 (NC-5)	480 g/L SL	170	n.r.	132	Pods nuts	< 0.05 < 0.05	< 0.05 < 0.05	< 0.05 < 0.05	< 0.15 < 0.15	Dye, DM 1976, 1976/5085
Lewiston, NC 1973 (NC-5)	480 g/L SL	170	n.r.	132	Pods nuts	< 0.05 < 0.05	< 0.05 < 0.05	< 0.05 < 0.05	< 0.15 < 0.15	
Pleasanton, Texas	480 g/L	281	10 cm	92	Pods	0.08	< 0.05	< 0.05	0.18	Daniel, JW
USA, 1974 (Florirunner)	SL 1 × 1.12		high	92	nuts	< 0.05	< 0.05	< 0.05	< 0.15	1974, 1975/5065
Pleasanton, Texas	480 g/L	281	10 cm	92	Pods	0.36	< 0.05	< 0.05	0.46	
USA, 1974 (Florirunner)	SL 1 × 2.24		high	92	nuts	< 0.05	< 0.05	< 0.05	< 0.15	
Clarita, Oklahoma	480 g/L	n.r.	n.r.	112	Pods	< 0.05	< 0.05	< 0.05	< 0.15	Anonymous
USA, 1973 (n.r.)	SL 1 × 1.12			112	nuts	< 0.05	< 0.05	< 0.05	< 0.15	1976, 1975/5063
Clarita, Oklahoma	480 g/L	n.r.	n.r.	112	Pods	< 0.05	< 0.05	< 0.05	< 0.15	

PEANUT country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazon e	6-OH- bentazone	8-OH- bentazone	Total bentazone	
USA, 1973 (n.r.)	SL 1× 2.24			112	nuts	< 0.05	< 0.05	< 0.05	< 0.15	
Yoakum, Texas	480 g/L	187	n.r.							Horton, W
USA, 1975 (Star)	SL 1× 0.84			19 59	Pods nuts	< 0.05 < 0.05	0.20 < 0.05	< 0.05 < 0.05	0.29 < 0.15	E 1976, 1975/5060
	2× 0.84			59	Pods w/o nuts	< 0.05	0.16	< 0.05	0.25	
				59	nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				59	Pods w/o nuts	< 0.05	0.16	< 0.05	0.25	
	1× 1.12			78	nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				78	Pods w/o nuts	< 0.05	< 0.05	< 0.05	< 0.15	
	1× 2.24			78	nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				78	Pods w/o nuts	< 0.05	0.18	< 0.05	0.27	
Bethel, North Carolina, USA	480 g/L SL	187	n.r.	136	nuts	< 0.05	< 0.05	< 0.05	< 0.15	Anonymous 1976,
1975	2× 0.84			136	Pods w nuts	< 0.05	< 0.05	0.05	0.15	1975/5059
	1× 1.12			136	nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				136	Pods w/o nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				136	Pods w nuts	< 0.05	0.05	< 0.05	0.15	
	1× 2.24			136	nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				136	Pods w/o nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				136	Pods w nuts	< 0.05	0.06	< 0.05	0.16	
Sumter South Carolina	480 g/L SL	n.r.	n.r.	94	nuts	< 0.05	< 0.05	< 0.05	< 0.15	Tiller, H
USA, 1975 (Florigiant)	2× 0.84			34	Pods w nuts	< 0.05	0.10	0.05	0.19	Thompson, J 1976,
	1× 1.12			115	nuts	< 0.05	< 0.05	< 0.05	< 0.15	1975/5057
				115	Pods w/o nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				55	Pods w nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				65	Pods w nuts	< 0.05	< 0.05	< 0.05	< 0.15	
	1× 2.24			115	nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				115	Pods w/o nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				55	Pods w nuts	< 0.05	< 0.05	< 0.05	< 0.15	
				65	Pods w nuts	< 0.05	< 0.05	< 0.05	< 0.15	

^a At application

Herbs

A total of eight field trials were conducted with peppermint, Melissa and thyme in Germany and France to determine the residue level of bentazone and its metabolites 6-OH- and 8-OH-bentazone in

or on raw agricultural commodities (RAC) during 1995/1996, 2005 and 2006 (Class, T, Bacher, R, 1998, 1998/11399; Malet, JC, Allard, L, 2007, 2007/1063041; Malet, JC, Allard, L., 2007, 2008/1065207). The results are shown in Table 84.

Table 84 Residues of bentazone in herbs after treatment in Germany and France

HERBS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DAL T ^a	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazon e	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Peppermint										
Germany	480 g/L	93–	V31–32	39	leaves	< 0.05	< 0.05	< 0.05	< 0.15	Class, T
1996 (?)	SL	187								Bacher, R
	1 × 0.96									1998,
Germany	480 g/L	93–	6 weeks	58	leaves	< 0.05	< 0.05	< 0.05	< 0.15	1998/11399
1995 (?)	SL	187	After							
	1 × 0.96		planting							
Germany	480 g/L	93–	10–19	35	leaves	< 0.05	< 0.05	< 0.05	< 0.15	
1996 (?)	SL	187								
	1 × 0.96									
Melissa										
Germany	480 g/L	93–	ES 26	82	leaves	< 0.05	< 0.05	< 0.05	< 0.15	
1996 (?)	SL	187								
	1 × 0.96									
thyme										
RE05074	870 g/L	514.3	72	28	whole	0.037	0.023	< 0.014	0.07	Malet, JC
Southern	SG				plant					Allard, L
Zone, 13540	1 × 1.056									2007,
Puyricard, France										
2005 (Population)										
RE05073	1 × 1.076	523.8	73	28	whole	< 0.02	< 0.014	< 0.014	< 0.05	2007/106304 1
Southern					plant					
Zone, 13530										
Trets, France										
2005 (Volt 2001 ameliore)										
RE06094, 84240	870 g/L	400	33	28	whole	n.r.	n.r.	n.r.	0.06	Malet, JC
La Tour d Aigues	SG				plant					Allard, L
Southern Zone										2007,
France, 2006										2008/106520 7
(Population)										
RE06093				28	whole	n.r.	n.r.	n.r.	0.09	
Southern					plant					
Zone, 13540										
Puyricard, France										
2006 Varico)										

^a At application

*Legume animal feeds**Alfalfa*

A total of 12 field trials of alfalfa were conducted in Northern and Southern Europe to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC) during 1977, 1980, 1988 and 2007 (Kreke, N, 2008, 2007/1028360; Kreke, N, 2010, 2010/1155809; Kreke, N, 2008, 2007/1023135; Kreke, N, 2008, 2008/1097982; Kreke, N, 2010, 2010/1155808; Bassler, R, 1994, 1994/10678). The results are shown in Table 85.

Table 85 Residues of bentazone in alfalfa forage and hay after treatment in Southern and Northern Europe

ALFALFA country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Southern Europe										
94017, Regalbuto	480 g/L	429	11–13	41	green	0.03	0.137	< 0.01	0.17	Kreke, N
Sicily, Italy	SL				matter					2008
2007 (Emilliana)	1× 0.643			41	hay	0.07	0.653	< 0.01	0.69	2007/1028360
25670 Termens	480 g/L	408	12–19	28	green	0.01	0.249	< 0.01	0.26	Kreke, N
Catalogna, Spain	SL				matter					2010
2007 (Brago)	1× 0.612			30	hay	0.08	0.680	< 0.01	0.72	2010/1155809
Regalbuto, Italy	480 g/L	429	11–13	41	green	0.03	0.169	< 0.01	0.20	Kreke, N
2007 (Emiliana)	SL				matter					2008
	1× 0.643			41	hay	0.12	0.502	< 0.01	0.60	2007/1023135
Termens, Spain	480 g/L	421	12–19	28	green	0.01	0.436	< 0.01	0.43	Kreke, N
2007 (Arago)	SL				matter					2008
	1× 0.631			30	hay	0.04	0.708	< 0.01	0.72	2008/1097982
										Kreke, N
										2010
										2010/1155808
Casteggio, Italy	480 g/L	400	1–3 leaves	0	alfalfa	14.10	0.67	< 0.02	14.75	Bassler, R
1988 (n.r.)	SL			15	alfalfa	1.23	1.10	0.11	2.36	1994
	1× 1.44			29	alfalfa	0.45	0.27	0.05	0.75	1994/10678
				44	alfalfa	0.28	0.19	0.05	0.51	
Northern Europe										
51110,	480 g/L	438	37	14	green	0.07	5.646	0.034	5.40	Kreke, N
Warmeriville	SL				matter					2008
Champagne	1× 0.657			23	hay	0.23	3.492	0.042	3.54	2007/1028360
Ardennes, France										Kreke, N
2007										2010
(Symphonie)										2010/1155809
Warmeriville	480 g/L	411	37	14	green	0.06	1.439	0.011	1.42	Kreke, N
France	SL				matter					2008

ALFALFA country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
2007	1× 0.616			23	hay	0.10	1.309	< 0.01	1.33	2007/1023135
(Symphonie)										Kreke, N
										2008
										2008/1097982
										Kreke, N
										2010
										2010/1155808
n.r., Sweden	480 g/L	n.r.	n.r.	26	alfalfa	0.24	0.51	< 0.02	0.74	Bassler, R
1977 (n.r.)	SL									1994
	1× 1.44			58	alfalfa	0.10	0.28	< 0.02	0.38	1994/10678
	2× 0.96			32	alfalfa	< 0.02	0.03	< 0.02	0.07	
Bradwell on sea,	480 g/L	n.r.	n.r.	40	alfalfa	< 0.02	0.71	< 0.02	0.70	
UK	SL									
1977 (n.r.)	1× 1.44			40	alfalfa	< 0.02	1.48	< 0.02	1.43	

^a At application

n.r. = Not reported

Clover

A total of two field trials were conducted in representative clover growing areas in USA (OR) to determine the residue level of bentazone in or on raw agricultural commodities (RAC) during 1992/1993 (Kunkel, DL, 1996, 1996/5000220). The results are shown in Table 86

Table 86 Residues of bentazone in clover forage and hay after treatment in the USA during 1992/1993

CLOVER country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DA LT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazon e	6-OH- bentazon e	8-OH- bentazone	Total bentazon e	
OR, USA	480 g/L	187	71–76 cm	36	forage	0.06	0.24	< 0.05	0.34	Kunkel, DL
1992/1993	EC			36	hay	0.07	0.46	0.05	0.55	1996,
(Common)	1× 1.225			145	seed	< 0.05	< 0.05	< 0.05	< 0.15	1996/5000220
				145	scr. s.	< 0.05	< 0.05	< 0.05	< 0.15	
	1× 2.25			36	forage	0.08	0.41	0.05	0.51	
				36	hay	0.05	1.01	0.05	1.04	
				145	seed	< 0.05	< 0.05	< 0.05	< 0.15	
				145	scr. s.	< 0.05	< 0.05	< 0.05	< 0.15	
	1× 1.225		30-46	36	forage	< 0.05	0.11	< 0.05	0.20	
				36	hay	< 0.05	0.78	< 0.05	0.83	
				145	seed	< 0.05	< 0.05	< 0.05	< 0.15	
				145	scr. s.	< 0.05	< 0.05	< 0.05	< 0.15	
	1× 2.25			36	forage	< 0.05	0.13	< 0.05	0.22	
				36	hay	< 0.05	0.87	0.06	0.92	
				145	seed	< 0.05	< 0.05	< 0.05	< 0.15	
				145	scr. s.	< 0.05	< 0.05	< 0.05	< 0.15	

^a At application

scr.s. = A screening

Green bean forage

A total of 16 trials in green beans were conducted in different representative growing areas in Northern and Southern Europe in 2008 and 2009 to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC) (Schulz, H 2009, 2009/1024806; Schroth, E, Martin, T, 2010, 2009/1123296). The results are shown in Table 87.

Table 87 Residues of bentazone in green beans forage after one application of bentazone in Southern and Northern Europe

[illegible]

GREEN BEANS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DA LT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazon e	6-OH- bentazon e	8-OH- bentazon e	Total bentazon e	
ES-41710 Utrera	87% SG	200	55	0	plant	131.89	0.81	0.38	133.01	
Sevilla, Spain	1× 1.20			28	rest pl.	0.06	1.21	0.14	1.34	
(2009)				36	rest pl.	0.01	0.38	0.06	0.42	
(Tremaya)				42	rest pl.	0.01	0.20	0.02	0.22	
GR-57550 Epanomi	87% SG	200	55	0	plant	100.55	0.45	0.33	101.28	
Thessaloniki	1× 1.20			29	rest pl.	0.01	2.21	0.12	2.21	
Greece				35	rest pl.	< 0.01	1.53	0.09	1.53	
2009				42	rest pl.	< 0.01	1.14	0.08	1.16	
(Etna)										
E-11140 Conil	87% SG	200	55	0	plant	77.50	0.86	0.36	78.65	
Cadiz, Spain	1× 1.20			28	rest pl.	0.04	4.74	0.38	4.86	
2009				35	rest pl.	0.02	3.45	0.46	3.69	
(Tremaya)				42	rest pl.	0.02	3.47	0.39	3.64	
Northern Europe										
Green Lane Farm	87% SG	200	55	0	plant	51.60	2.68	0.53	54.81	Schulz, H
Nafferton	1× 0.957			27	rest pl.	0.02	2.87	0.92	3.81	2009
Driffield				35	rest pl.	0.01	2.21	0.70	2.92	2009/102480 6
East Yorkshire				41	rest pl.	< 0.01	1.36	0.53	1.90	
YO25 4LF, UK										
2008										
(Flamenco)										
Green Lane Farm	87% SG	200	55	0	plant	83.00	2.57	0.45	86.02	
Nafferton	1× 0.957			27	rest pl.	0.02	5.48	1.69	7.18	
Driffield				35	rest pl.	0.01	4.00	1.13	5.14	
East Yorkshire				41	rest pl.	0.01	3.21	1.13	4.35	
YO25 4LF, UK										
2008										
(Flavert)										
La Bonde	87% SG	200	55	0	plant	56.60	0.37	0.20	57.17	
49650 Allonnes	1× 0.957			27	rest pl.	< 0.01	3.15	0.88	4.04	
France				35	rest pl.	< 0.01	4.75	1.14	5.90	
2008				42	rest pl.	< 0.01	2.96	0.91	3.87	
(Flavert)										
Ferme Bonneil	87% SG	200	55	0	plant ⁵	53.60	1.17	0.45	55.22	
80400 Esmerly	1× 0.957			29	rest pl.	< 0.01	2.53	0.80	3.34	
Hllon, France				35	rest pl.	< 0.01	2.19	0.64	2.84	
2008				42	rest pl.	< 0.01	1.99	0.62	2.62	
(Valence)										
DE-47589 Uedem	87% SG	200	55	0	plant	67.89	0.48	0.40	68.72	Schroth, E

^b Plant parts were taken without roots

A total of 10 field trials were conducted in representative fresh pea growing areas and the United Kingdom (fresh peas) and USA to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC) in 1993, 1994 and 2007 (Versoi, PL *et al.*, 1995, 1995/5159). The results of green pea vine are shown in Table 88.

[illegible]

GREEN PEAS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazo ne	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Buhl, Idaho	42.2% SL	190	65–67	10	vines ^c	0.22	3.23	< 0.05	3.50	
USA	2× 1.25	188								
1993	42.2% SL	191		10	vines	0.21	9.13	0.08	9.42	
(FL24)	2× 1.25	192								
	with									
	adjuvan t									
Redwood County	42.2% SL	185	65–71	10	vines ^c	1.05	3.23	0.05	4.33	
Minnesota	2× 1.25	187								
USA										
1994										
(5063)										
Redwood County	42.2% SL	192	65–71	10	vines ^c	0.31	3.44	0.06	3.81	
Minnesota	2× 1.25	188								
USA, 1994										
(7071)										
Delavan, WI	42.2% SL	195	65–67	10	vines	0.19	5.50	0.07	5.76	
USA	2× 1.25	181								
1993										
(9888F)										
Verona, WI	42.2% SL	234	62–67	10	vines	0.22	3.74	< 0.05	4.01	
USA	2× 1.25	173								
1993										
(77 EP)										
Corvallis, Oregon	42.2% SL	189	65–67	10	vines	0.05	5.96	< 0.05	6.06	
USA	2× 1.25	184								
1993		190		10	vines	0.11	10.94	0.10	11.2	
(Grant)		187								
Ephrata, WA	42.2% SL	184	71–77	10	vines	0.10	11.54	0.11	11.75	
USA	2× 1.25	185								
1993		192		10	vines	0.12	6.48	0.07	6.67	
(Perfection)		192								

^a At application^b Mechanically harvested^c Manually harvested

Bean fodder

A total of 19 field trials in broad beans were conducted in representative growing areas in Southern Europe and Northern Europe and USA to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC) (Stroemel, C *et al.*, 2000, 2000/1014883; Blaschke, UG, 2001, 2001/1000926; Schulz, H, 2002, 2002/1006296; Oxspring, S, 2008, 2008/1049971; Schroth E, Martin T, 2011, 2011/1059498). The results are shown in Table 89.

Table 89 Residues of bentazone in broad beans fodder after one application in southern Europe and northern Europe

DRIED BEANS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Southern Europe										
ES-41710 Utrera	87% SG	200	15	0	plant	45	0.65	0.62	46.27	Schroth, E
Sevilla, Spain	1 × 1.20			204	rest pl.	< 0.01	< 0.01	< 0.01	< 0.03	Martin, T
2010										2011
(Luz de Otono)										2011/1059498
FR-32130	87% SG	200	14–15	0	plant	65	0.75	0.52	66.27	
Samatan	1 × 1.20			122	rest pl.	< 0.01	< 0.01	< 0.01	< 0.03	
Gers, France										
2010										
(Castel)										
13210 St Remy de Provance	48% SL 1 × 1.669	326	12	21	plant	0.194	0.752	0.148	1.04	Schulz, H
				48	rest plant	0.027	0.03	0.025	0.08	2002
Provence, France										2002/1006296
2000										
(Coco Blanc Gautier)										
13210 St Remy de Provance	48% SL 1 × 1.546	302	12–13	27	plant	0.141	1.705	0.362	2.08	
				52	rest plant	< 0.02	< 0.02	0.041	0.08	
Provence, France										
2000										
(Langue de feu)										
E-41710 Utrera Sevilla, France	48% SL 1 × 1.587	310	12	18	plant	0.0474	0.417	0.13	0.56	
				48	rest plant	< 0.02	0.031	< 0.02	0.07	
2000										
(B.B.L.)										
E-41710 Utrera Sevilla, France	48% SL 1 × 1.587	302	12–13	18	plant	0.09	1.033	0.202	1.24	
				48	rest plant	< 0.02	0.045	< 0.02	0.08	
2000										
(Garrafal Oro)										
F-84700	48% SL	300	12	17	shoots	0.021	1.01	0.092	1.05	Blaschke, U
Sorgues, France	1 × 1.553			66	straw	< 0.02	< 0.02	< 0.02	< 0.06	G 2001,
1999										2001/1000926
(Novirex)										
F-84700	48% SL	302	12	18	shoots	< 0.02	0.860	0.072	0.89	
Sorgues, France	1 × 1.561			105	straw	< 0.02	0.046	< 0.02	0.08	
1999										
(Hiltrud)										
E-41720, Los Palacios, Spain	48% SL 1 × 1.521	294	12	24	shoots	< 0.02	0.044	0.037	0.10	
				107	straw	0.083	< 0.02	< 0.02	0.12	
1999										
(BBL-274)										
E-41720, Los Palacios, Spain	48% SL 1 × 1.617	313	12–13	24	shoots	0.021	0.094	0.030	0.14	
				85	Pods ^c	< 0.02	< 0.02	< 0.02	< 0.06	

DRIED BEANS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
1999										
(Garrafal Oro)										
La Peyruque	87% SC	200	76	0	plant	2.80	0.50	0.10	3.36	Oxspring, S
St-Martin- Lalande	1× 0.957									2008
11400, France										2008/1049971
2007										
(Linex)										
11150 Villasavary	87% SC	200	76	0	plant	1.90	0.70	0.60	3.12	
France	1× 0.957									
2007										
(Linex)										
E-41500	48% SL	293	12	12	shoots	0.040	4.31	0.251	4.32	Blaschke, U
Kattendijke, Spain	1× 1.518			82	straw	< 0.02	0.229	0.030	0.26	G 2001,
1999										2001/1000926
(Berna)										
F-02150, La Selve	48% SL	298	12	31	shoots	< 0.02	0.663	0.150	0.78	
France	1× 1.541			101	straw	< 0.02	0.036	< 0.02	0.07	
1999										
(Flagrano)										
F-37510	48% SL	298	13	14	shoots	0.032	3.62	0.356	3.76	
Berthenay, France	1× 1.561			89	straw	< 0.02	0.042	< 0.02	0.08	
1999										
(Phenomene)										
Norther Europe										
Brandenburg	48% SL	300	12	20	plant	0.026	0.804	0.168	0.94	Stroemel, C
Germany	1× 1.536			89	straw ^c	< 0.02	0.046	< 0.02	0.08	<i>et al.</i> , 2000,
1999										2000/1014883
(Berggold)										
Mecklenburg/ Vorpommern	48% SL	300	12	25	plant	< 0.02	0.941	0.212	1.10	
	1× 1.536			98	straw ^c	0.078	0.045	0.022	0.14	
Germany										
1999										
(Goodtime)										
Friesland Farm	87% SC	200	12-19	0	plant	3.00	0.40	0.09	3.46	Oxspring, S
Rushby Lane	1× 0.957									2008
Sandiacre										2008/1049971
Nottinghamshire										
UK, 2007, (Cinco)										
91690 Guillerval	87% SC	200	12-19	0	plant	2.40	0.40	0.30	3.06	
France	1× 0.957									
2007										
(Melodie)										

^a At application^b Plant parts were taken without roots^c With seeds

Pea hay

A total of six field trials in peas were conducted in representative growing areas in USA and Canada to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC) (Single, YH, 1989, 1989/5046; Anonymous, 1989, 1988/10957). The results are shown in Table 90.

Table 90 Residues of bentazone in dried pea hay after one application in USA and Canada

DRIED BEANS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	DALT	Residues Found (mg/kg)					
				Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Colton, Whitman	42% SC	n.r.	40	hay	< 0.05	0.05	< 0.05	0.15	Single, YH 1989, 1989/5046
Washington	2× 1.125								
USA, 1986									
(Columbia)									
Colton, Whitman	42% SC	n.r.	31	hay	0.66	4.66	0.08	5.11	
Washington	2× 1.125								
USA, 1986									
(Columbia)									
Colton, Whitman	42% SC	n.r.	31	hay	1.45	2.60	0.06	3.95	
Washington	2× 1.125								
USA, 1986									
(Columbia)									
Latah, Moscow	42% SC	n.r.	30	hay	0.31	1.01	< 0.05	1.30	
Idaho	2× 1.125								
USA, 1987									
(Columbia)									
Latah, Moscow	42% SC	n.r.	33	hay	0.48	0.78	< 0.05	1.26	
Idaho	2× 1.125								
USA, 1987									
(Columbia)									
Potlatch, Latah	42% SC	n.r.	34	hay	1.99	1.42	< 0.05	3.37	
Idaho	2× 1.125								
USA, 1987									
(Latah)									

Peanut forage and fodder

A total of 15 trials in peanuts were conducted in Israel and the USA to determine the residue level of bentazone in or on raw agricultural commodities (RAC) during 1973, 1974 and 1975 (Resnick, H, Adato, I, 1976, 1976/10602; Dye, DM, 1994, 1976/5087; Dye, DM, 1976, 1976/5086; Dye, DM, 1976, 1976/5085; Daniel, JW, 1974, 1975/5065; Anonymous, 1976, 1975/5063; Horton, WE, 1976, 1975/5060; Anonymous, 1976, 1975/5059; Tiller, H, Thompson, J, 1976, 1975/5057). The results are shown in Table 91.

Table 91 Residues of bentazone in peanut forage and fodder after treatment in Israel and USA

PEANUT country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Galil Yam	480 g/L	n.r.	n.r.	0	foliage	7.95	n.r.	n.r.		Resnick, H
Israel, 1974	n.r.			7	foliage	1.05	n.r.	n.r.		Adato, I

PEANUT country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
(n.r.)	3× 1.92			13	foliage	0.12	n.r.	n.r.		1976
				21	foliage	0.09	n.r.	n.r.		1976/10602
Galil Yam	480 g/L	n.r.	n.r.	0	foliage	9.0	n.r.	n.r.		
Israel, 1974	n.r.			7	foliage	0.76	n.r.	n.r.		
(n.r.)	3× 3.6			13	foliage	0.29	n.r.	n.r.		
				21	foliage	0.08	n.r.	n.r.		
Mulberry, Texas	480 g/L	374	5–50 cm	58	fodder	< 0.05	< 0.05	< 0.05	< 0.15	Dye, DM
USA, 1973	SL		height							1994,
(Starr)	1× 1.12									1976/5087
Mulberry, Texas	480 g/L	374	5–50 cm	58	fodder	< 0.05	< 0.05	< 0.05	< 0.15	
USA, 1973	SL		height							
(Starr)	1× 2.24									
Yoakum, Texas	480 g/L	187	n.r.	128	fodder	< 0.05	< 0.05	0.33	0.43	Dye, DM
USA, 1973	SL									1976,
(Starr)	1× 1.68									1976/5086
Yoakum, Texas	480 g/L	187	n.r.	128	fodder	< 0.05	0.78	0.06	0.84	
USA, 1973	SL									
(Starr)	1× 3.36									
Lewiston, NC	480 g/L	170	n.r.	93	fodder	< 0.05	< 0.05	< 0.05	< 0.15	Dye, DM
USA, 1973 (NC-5)	SL									1976
	1× 1.68									1976/5085
Lewiston, NC	480 g/L	170	n.r.	93	fodder	< 0.05	< 0.05	< 0.05	< 0.15	
USA, 1973 (NC-5)	SL									
	1× 3.36									
Pleasanton, Texas	480 g/L	281	10 cm	92	fodder	< 0.05	< 0.05	< 0.05	< 0.15	Daniel, JW
USA, 1974	SL		high							1974
(Florirunner)	1× 1.12									1975/5065
Pleasanton, Texas	480 g/L	281	10 cm	92	fodder	< 0.05	0.12	< 0.05	0.21	
USA, 1974	SL		high							
(Florirunner)	1× 2.24									
Clarita, Oklahoma	480 g/L	n.r.	n.r.	112	fodder	< 0.05	< 0.05	< 0.05	< 0.15	Anonymous
USA, 1973	SL									1976
(n.r.)	1× 1.12									1975/5063
Clarita, Oklahoma	480 g/L	n.r.	n.r.	112	fodder	< 0.05	< 0.05	< 0.05	< 0.15	
USA, 1973	SL									
(n.r.)	1× 2.24									
Yoakum, Texas	480 g/L	187	n.r.	0	forage	9.7	1.40	0.06	11.1	Horton, W
USA, 1975	SL									E 1976
(Star)	1× 0.84									1975/5060
	2× 0.84			19	forage	0.07	2.90	0.10	2.88	
				59	fodder	< 0.05	0.73	< 0.05	0.78	
	1× 1.12			0	forage	6.53	1.30	0.06	7.81	
				38	forage	< 0.05	2.21	0.07	2.19	
				78	fodder	< 0.05	0.36	< 0.05	0.44	

PEANUT country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
	1× 2.24			0	forage	13.7	2.36	0.06	16.0	
				38	forage	< 0.05	3.52	0.08	3.43	
				78	fodder	0.06	0.91	0.06	0.97	
Bethel, North Carolina, USA 1975	480 g/L SL	187	n.r.	0	forage	25.5	2.80	0.07	28.2	Anonymous, 1976
	1× 0.84									1975/5059
	2× 0.84			14	forage	16.0	1.85	0.12	17.8	
				28	forage	< 0.05	0.62	< 0.05	0.68	
				56	forage	< 0.05	< 0.05	< 0.05	< 0.15	
				136	fodder	< 0.05	< 0.05	< 0.05	< 0.15	
	1× 1.12			0	forage	23.0	0.46	0.12	23.5	
				28	forage	< 0.05	0.09	< 0.05	0.18	
				56	forage	< 0.05	< 0.05	0.05	0.15	
				136	fodder	< 0.05	< 0.05	< 0.05	< 0.15	
	1× 2.24			0	forage	41.0	1.3	n.r.	42.2	
				28	forage	< 0.05	0.17	< 0.05	0.26	
				56	forage	< 0.05	< 0.05	0.05	0.15	
				136	fodder	< 0.05	0.15	< 0.05	0.24	
Sumter South Carolina USA, 1975	480 g/L SL	n.r.	n.r.	0	forage	71.1	6.55	< 0.05	77.3	Tiller, H Thompson, J 1976
(Florigiant)	2× 0.84			34	forage	13.7	2.38	0.08	16.0	1975/5057
				94	fodder	< 0.05	0.31	< 0.05	0.39	
	1× 1.12			0	forage	63.4	6.89	0.19	70.0	
				55	forage	0.09	0.09	< 0.05	0.22	
				65	forage	< 0.05	0.11	< 0.05	0.20	
				115	fodder	< 0.05	0.06	< 0.05	0.16	
	1× 2.24			0	forage	101.2	9.80	0.19	110.6	
				55	forage	0.07	0.53	< 0.05	0.62	
				65	forage	< 0.05	0.19	< 0.05	0.28	

^a At application

n.r. = Not reported

Soya bean forage and fodder

A total of 14 trials in soya beans were conducted in Southern Europe and Northern Europe and USA to determine the residue level of bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone in or on raw agricultural commodities (RAC) in 2009 (Kreke, N, 2009, 2008/1034457; Kreke, N, 2010, 2010/1155811; Kreke, N, 2009, 2008/1034456; Kreke, N, 2010, 2010/1155810; Schroth, E, Martin, T, 2010, 2010/1164275; Kreke, N, 2008, 2007/1028359; Kreke, N, 2010, 2010/1155807; Kreke, N, 2008, 2007/1023134; Kreke, N, 2010, 2010/1155806; Stewart, J, 1992, 1992/5169; Single, YH, 1989, 1989/5045). The results are shown in Table 92.

Table 92 Residues of bentazone in soya bean forage, hay and fodder after one application in Southern and Northern Europe and the USA

SOYA BEAN country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Southern Europe										
GR-59032	87% SG	200	55	0	plant	54	1.7	1.4	56.90	Schroth, E
Platanos	1× 0.957			30	rest ^c	< 0.01	0.47	0.34	0.77	Martin, T
Imathia, Greece 2009				93	rest ^c	< 0.01	0.05	0.04	0.10	2010
(Nikko)										2010/1164275
IT-40018, Pietro	87% SG	200	55	0	plant	50	0.63	1.3	51.81	
In Casale	1× 0.957			29	rest ^c	0.01	2.0	1.4	3.20	
Bologna, Italy 2009				80	rest ^c	< 0.01	0.13	0.13	0.25	
(Blancas)										
ES-41710 Utrera	87% SG	200	55	0	plant	95	0.67	1.0	96.57	
Sevilla, Spain	1× 0.957			31	rest ^c	0.19	0.92	0.87	1.87	
2009				68	rest ^c	0.12	0.13	0.12	0.35	
(CV Condor)										
FR-32200, Saint	87% SG	200	55	0	plant	92	0.67	1.3	93.85	
Caprais, Gers	1× 0.957			30	rest ^c	0.03	1.8	1.5	3.13	
France 2009				77	rest ^c	0.02	0.46	0.39	0.82	
(Samera)										
Northern Europe										
DE-47574 Goch-	87% SG	200	55	0	plant	25	0.33	0.52	25.80	Schroth, E
Nierswalde, Kleve	1× 0.957			30	rest ^c	0.03	2.4	1.9	4.06	Martin, T
Germany 2009				79	rest ^c	0.01	0.19	0.17	0.35	2010
(Merlin)										2010/1164275
USA										
Gladstone, SC	44.8% SC	189	13–89	55	soapst. ^d	< 0.05	< 0.05	< 0.05	< 0.15	Stewart, J
Henderson County	5× 2.24	188								1992
Illinois, USA 1991		188								1992/5169
(Williams 82)		190								
		191								
Danville, Des	44.8% SC	187	12–89	56	soapst. ^d	< 0.05	< 0.05	< 0.05	< 0.15	
Moines County	5× 2.24	188								
Iowa, USA 1991		187								
(Pioneer 9341)		188								
Tebbetts, Callaway	42% SC	n.r.		24	forage	0.12	2.14	1.83	3.84	Single, YH

^a At application
^b Plant parts were taken without roots
^c Rest: plants without pods
^d See processing study

Barley

Table 93 Residues of bentazone in barley straw after one application in Southern Europe

[illegible]

BARLEY country, year (variety)	Form. Appli. Rate (kg ai/ha) ^b	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
	1.554									
(Irene)										2000/1018490
E-41270, Los Palacios, Spain	48% SL 1× 1.546	299	35–37	58	straw	0.14	0.23	< 0.02	0.38	
1999, (Apex)										
I-20089, Rozzano Italy, 1999	48% SL 1× 1.553	300	37	65	straw	0.06	0.091	< 0.02	0.16	
(Gotic)										
I-20090, Caleppio di Settala, Italy 1999, (Federal)	48% SL 1× 1.55		37–39	65	straw	0.04	0.046	< 0.02	0.10	
I-27028, San Marino, Sicconario Italy, 1999 (Folgore)	48% SL 1× 1.55		39	57	straw	0.06	0.061	< 0.02	0.14	

^a At application^b Actual application rates varied by 10% at most

Oats

One field trial was conducted at representative oat growing area in Germany (Schlag-Limburgerhof) during 1974 (Anonymous, 1974, 1974/10290). The results are shown in Table 94.

Table 94 Residues of bentazone in oat straw after one application in Germany (Anonymous, 1974, 1974/10290)

OAT country, year (variety)	Form. Appli. Rate (kg ai/ha)	water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- benta-zone	Total bentazone	
Schlag Limburgerhof	n.r. 1× 1.92	n.r.	Feekes Scale G/H	104	straw	< 0.05	–	–	< 0.15	Anonymous 1974,
Germany 1974 (Flamingskrone)										1974/10290

^a At application

Maize fodder

Twenty-eight field trials were conducted in representative maize growing areas in the Northern and Southern Europe and USA to determine the residue level of bentazone in or on raw agricultural commodities (RAC) during 2010 (Stewart, J, 1992, 1992/5168; Oxspring, S, 2011, 2011/1059496; Klaas, P, Ziske, J, 2009, 2009/1024805; Oxspring, S, 2008, 2008/1049973; Oxspring, S, 2008,

2008/1055036; Reichert, N, 2006, 2005/1034455; Reichert, N, 2006, 2006/1024264; Schulz, H, 2001, 2001/1000919). The results are shown in Table 95.

Table 95 Residues of bentazone in maize forage and fodder after one application in Europe

MAIZE country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT ^a	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Southern Europe										
Bologna, Italy	48% SL	200	35	0	plant	31	0.45	0.82	32	Oxspring, S
2010 (KWS 6565)	1× 0.96			34	plant	< 0.01	0.19	< 0.01	0.21	2011
				69	rest plant	< 0.01	0.05	< 0.01	0.07	2011/1059496
				60	rest plant	< 0.01	0.11	< 0.01	0.13	
				84	rest plant	< 0.01	< 0.01	< 0.01	< 0.03	
Castelsarrasin	48% SL	200	35	0	plant	6.2	6.0	0.20	12	
France, 2010	1× 0.96			27	plant	< 0.01	0.22	< 0.01	0.24	
(Tyrex)				61	rest plant	< 0.01	0.12	< 0.01	0.14	
				119	rest plant	< 0.01	< 0.01	< 0.01	< 0.03	
Albacete, Spain	48% SL	200	35	0	plant	12	0.8	0.42	14	
2010 (Mitic)	1× 0.96			14	plant	< 0.01	0.20	< 0.01	0.22	
				56	rest plant	< 0.01	0.15	< 0.01	0.17	
				60	rest plant	< 0.01	0.10	< 0.01	0.12	
				124	rest plant	< 0.01	< 0.01	< 0.01	< 0.03	
Bamague	480 g/L SL	200	55	0	plant	5.58	2.03	0.29	7.90	Klaas, P
47120 Duras	1× 1.200			28	rest w. husks	0.02	2.63	< 0.01	2.66	Ziske, J 2009
France, 2008				28	plant	< 0.01	1.78	< 0.01	1.80	2009/1024805
(Mitic)				64	rest plant	0.02	1.26	0.01	1.29	
				76	rest plant	0.04	1.03	< 0.01	1.08	
“Finca	480 g/L SL	200	55	0	plant	0.03	0.025	< 0.01	0.065	
Valsequillo”	1× 1.200			28	rest w. husks	0.01	2.36	< 0.01	2.38	
Carretera vieja				28	plant	< 0.01	0.665	< 0.01	0.69	
Antequera				63	rest plant	< 0.01	0.37	< 0.01	0.39	
Campillos										
Spain, 2008										
(Tardio 130)										
Az. Ag. FrancESCO	480 g/L	200	55	0	whole plant	3.80	3.34	0.17	7.09	Oxspring, S
Busato, Minerbio	SC			28	rest of plant ^c	0.02	0.30	0.03	0.33	2008
40061 Bologna	1× 1.200			43	rest of plant	0.01	0.50	0.03	0.51	2008/1049973
Italy, 2007				50	rest of plant	0.02	0.57	0.02	0.57	Oxspring S
(Eleonora)				65	rest of plant	0.05	0.13	< 0.01	0.18	2008
C/Calvo Sotelo No.14	480 g/L	200	55	0	whole plant	4.26	2.58	0.28	6.94	
Calatorao	SC			28	rest of plant ^c	0.33	0.38	0.02	0.71	
50280 Zaragoza				35	rest of plant ^c	0.29	1.32	0.04	1.56	
Spain, 2007				42	rest of plant ^c	0.13	0.58	0.02	0.69	
(P 33N44)				86	rest of	0.24	0.28	0.01	0.51	

MAIZE country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT ^a	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
					plant					
Avda. Zaragoza 29	480 g/L	200	55	0	whole plant	5.37	4.74	0.32	10.12	
Utebo. Poligono: 1.	SC			28	rest of plant ^c	0.09	0.28	0.02	0.37	
50180 Zaragoza				35	rest of plant ^c	0.06	0.96	0.08	1.04	
Spain, 2007				42	rest of plant ^c	0.02	0.24	0.01	0.26	
(DKC 5784)				96	rest of plant	0.01	0.44	< 0.01	0.43	
F-79 100	480 g/L	244	14–16	0	plant	155.6	6.14	0.378	161.71	Schulz, H
Tourtenay	SL			46	plant	0.833	< 0.02	0.022	0.87	2001
France, 1999	1× 1.502			111	rest of plant ^c	< 0.02	< 0.02	< 0.02	< 0.06	2001/1000919
(LG 2447)				144	straw	< 0.02	< 0.02	< 0.02	< 0.06	
F-33 210	480 g/L	250	15–16	0	plant	78.84	1.82	0.20	80.73	
Saint Loubert	SL			48	plant	0.371	< 0.02	0.022	0.41	
France, 1999	1× 1.536			108	rest of plant ^c	< 0.02	< 0.02	< 0.02	< 0.06	
(DK 604)				141	straw	< 0.02	< 0.02	< 0.02	< 0.06	
6231										
E-41720	485 g/L	305	15	0	shoots	57.5	2.15	1.68	61.09	Blaschke, U
Los Palacios	SL			0	roots	0.151	0.028	< 0.02	0.20	G 2000,
Spain, 1998	1× 1.576			44	shoots	0.105	< 0.02	< 0.02	0.14	2000/1018489
(Dracuna)				44	roots	< 0.02	0.078	< 0.02	0.11	
				81	ears ^d	< 0.02	< 0.02	< 0.02	< 0.06	
				81	shoots ^e	< 0.02	< 0.02	< 0.02	< 0.06	
				81	roots	< 0.02	0.099	< 0.02	0.13	
				122	straw	< 0.02	< 0.02	< 0.02	< 0.06	
				122	roots	< 0.02	0.084	< 0.02	0.12	
E-41849	485 g/L	306	15	0	shoots	73.30	2.58	2.10	77.69	
Aznalcázar-1	SL			0	roots	0.086	0.038	< 0.02	0.14	
Spain, 1998	1× 1.585			38	shoots	0.166	< 0.02	< 0.02	0.20	
(Eleonara)				38	roots	< 0.02	0.238	< 0.02	0.26	
				68	ears ^d	< 0.02	< 0.02	< 0.02	< 0.06	
				68	shoots ^e	< 0.02	< 0.02	< 0.02	< 0.06	
				68	roots	< 0.02	0.175	< 0.02	0.20	
				109	straw	0.14	0.038	0.056	0.23	
				109	roots	0.038	0.192	0.049	0.26	
E-41849	485 g/L	305	15	0	shoots	57.82	1.88	1.60	61.08	
Aznalcázar-1	SL			0	roots	0.683	0.028	0.021	0.73	
Spain, 1998	1× 1.578			38	shoots	0.411	0.051	0.038	0.49	
(Juanita)				38	roots	< 0.02	0.058	< 0.02	0.09	
				68	ears ^d	0.033	< 0.02	< 0.02	0.07	
				68	shoots ^e	< 0.02	0.034	< 0.02	0.07	
				68	roots	0.022	0.217	< 0.02	0.24	
				109	straw	0.13	0.034	0.058	0.22	
				109	roots	< 0.02	0.099	< 0.02	0.13	
I-20090	485 g/L	303	13–15	0	shoots	72.85	3.44	0.602	76.64	
Caleppio di Settala	SL			0	roots	0.363	0.162	< 0.02	0.53	

MAIZE country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT ^a	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Italy, 1998	1× 1.566			23	shoots	0.064	0.030	< 0.02	0.11	
(Costanza)				23	roots	< 0.02	0.061	< 0.02	0.10	
				84	ears ^d	< 0.02	< 0.02	< 0.02	< 0.06	
				84	shoots ^c	< 0.02	< 0.02	< 0.02	< 0.06	
				84	roots	0.020	0.074	< 0.02	0.11	
				100	straw	< 0.02	< 0.02	< 0.02	< 0.06	
				100	roots	0.020	0.043	< 0.02	0.08	
I-26049	485 g/L	301	13–15	0	shoots	103.09	1.92	2.08	106.84	
Stagno Lombado	SL			0	roots	1.14	0.164	0.036	1.33	
Italy, 1998	1× 1.559			36	shoots	0.105	0.183	< 0.02	0.30	
(Costanza)				36	roots	< 0.02	0.067	< 0.02	0.10	
				93	ears ^d	< 0.02	< 0.02	< 0.02	< 0.06	
				93	shoots ^c	< 0.02	< 0.02	< 0.02	< 0.06	
				93	roots	< 0.02	0.033	< 0.02	0.07	
				114	straw	< 0.02	< 0.02	< 0.02	< 0.06	
				114	roots	< 0.02	0.024	< 0.02	0.06	
I-13041	485 g/L	300	13–15	0	shoots	46.54	2.98	0.575	49.87	
Bianze	SL			0	roots	2.67	0.670	0.061	3.36	
Italy, 1998	1× 1.552			36	shoots	0.125	< 0.02	< 0.02	0.16	
(Alicia)				36	roots	< 0.02	0.031	< 0.02	0.07	
				97	ears ^d	< 0.02	< 0.02	< 0.02	< 0.06	
				97	shoots ^c	< 0.02	< 0.02	< 0.02	< 0.06	
				97	roots	< 0.02	< 0.02	< 0.02	< 0.06	
				127	straw	< 0.02	< 0.02	< 0.02	< 0.06	
				127	roots	0.020	< 0.02	< 0.02	0.06	
Northern Europe										
Brandenberg	48% SL	200	35	0	plant	12	8.9	0.11	21	Oxspring, S
Blumberg	1× 0.96			8	plant	0.03	3.3	0.04	3.3	2011
Germany, 2010				60	rest plant ^c	< 0.01	0.74	0.03	0.77	2011/1059496
(Franz)				99	rest plant ^c	< 0.01	0.10	< 0.01	0.12	
Ticknall	48% SL	200	35	0	plant	16	0.50	0.14	17	
Derbyshire, UK	1× 0.96			18	plant	0.02	1.6	0.01	1.6	
2010 (N K Cheer)				71	rest plant ^c	< 0.01	1.2	0.02	1.3	
				60	rest plant ^c	< 0.01	1.5	0.02	1.5	
				89	rest plant ^c	< 0.01	1.1	0.01	1.1	
Elst	48% SL	200	35	0	plant	24	0.73	0.18	25	
The Netherlands	1× 0.96			18	plant	< 0.01	1.5	0.02	1.5	
2010 (Aabsint)				60	rest plant ^c	< 0.01	0.72	0.01	0.74	
				106	rest plant ^c	< 0.01	0.39	< 0.01	0.41	
Civray	480 g/L SL	200	55	0	plant	17.68	4.71	1.08	23.47	Klaas, P
49490 Melgne le	1× 1.200			27	rest w. husks	< 0.01	1.00	< 0.01	1.02	Ziske, J 2009

MAIZE country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT ^a	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix ^b	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
F-62 116	480 g/L	262	15							Schulz, H
Alblainzevelle	SL			45	plant	0.133	0.027	< 0.02	0.18	2001
France, 1999	1× 1.607			115	rest of plant	< 0.02	< 0.02	< 0.02	< 0.06	2001/1000919
(Chantal)				140	straw	< 0.02	< 0.02	< 0.02	< 0.06	
F-08 190, Aire	480 g/L	246	15–16							
France, 1999	SL			30	plant	0.128	0.12	< 0.02	0.26	
(Anjou 258)	1× 1.511			76	rest of plant	< 0.02	< 0.02	< 0.02	< 0.06	
				107	straw	< 0.02	< 0.02	< 0.02	< 0.06	

^a At application^b Plant parts were taken without roots^c Plants without cobs*Rice straw and fodder, dry*

A total of 18 field trials was conducted in representative rice growing area in China and Japan to determine the residue level of bentazone in or on raw agricultural commodities (RAC) in 1986 and 2007 (Tianxi, L *et al.*, 1986, 1986/10849; Tianxi, L *et al.*, 1986, 1986/10850; Odanaka, Y *et al.*, 2008, 2012/1272538). The results are shown in Table 96.

Table 96 Residues of bentazone in rice straw after one to two application(s) in China and Japan^a

RICE country, year (variety)	Form. Appli. Rate (kg ai/ha)	DAL T	Residues Found (mg/kg)					Reference Author, year Reference No.
			Matrix	bentazone	6-OH- bentazone	8-OH- benta- zone	Total bentazone	
Hangzhou	480 g/L	40	straw	0.267	0.830	< 0.02	1.06	Tianxi, L <i>et al.</i> ,
China	Water	50	straw	< 0.02	< 0.02	< 0.02	< 0.06	1986
1986	Solution	60	straw	< 0.02	< 0.02	< 0.02	< 0.06	1986/10849
(TP 22)	1× 2.16							
Hangzhou	480 g/L	40	straw	< 0.02	0.429	< 0.02	0.44	
China	Water	50	straw	< 0.02	< 0.02	< 0.02	< 0.06	
1986	Solution	60	straw	< 0.02	< 0.02	< 0.02	< 0.06	
(TP 22)	1× 1.44							
Hangzhou	480 g/L	50	straw	< 0.02	< 0.02	< 0.02	< 0.06	
China	Water	60	straw	< 0.02	< 0.02	< 0.02	< 0.06	
1986	Solution							
(TP 22)	1× 1.08							
Guiyang	480 g/L	40	straw	0.269	0.943	< 0.02	1.17	
China	Water	50	straw	0.144	0.221	< 0.02	0.37	
1986	Solution	60	straw	< 0.02	< 0.02	< 0.02	< 0.06	
(TP 22)	1× 2.16							
GuiYang	480 g/L	40	straw	0.215	0.579	< 0.02	0.78	
China	Water	50	straw	0.125	0.360	< 0.02	0.48	
1986	Solution	60	straw	< 0.02	< 0.02	< 0.02	< 0.06	
(TP 22)	1× 1.44							
Guiyang	480 g/L	50	straw	< 0.02	< 0.02	< 0.02	< 0.06	
China	Water	60	straw	< 0.02	< 0.02	< 0.02	< 0.06	
1986	Solution							
(TP 22)	1× 1.08							
Ushiku, Japan	40% SL	0	straw ^b	< 0.02	< 0.02	< 0.02	< 0.06	Odanaka, Y
2007	2× 2.8		straw ^c	< 0.02	< 0.02	< 0.02	< 0.06	et al., 2008,
(Koshihikari)		30	straw ^b	0.23	< 0.02	< 0.02	0.27	
			straw ^c	0.29	< 0.02	< 0.02	0.33	

WHEAT country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
1998 (Centauro)	1× 1.560									
				71	straw	0.04	0.032	< 0.02	0.08	
Northern Europe										
Brandenburg	480 g/L	200	32	87	straw	< 0.01	0.04	< 0.01	0.06	Oxspring, S
16356 Blumburg	SL									2011,
Germany, 2010	1× 0.96									2011/105949 7
(Akteur)										
Melbourne	480 g/L	200	32	103	straw	< 0.01	< 0.01	< 0.01	< 0.03	
Derbyshire, UK	SL									
2010 (Robigus)	1× 0.96									
Leouvlie, Loiret	480 g/L	200	32	95	straw	< 0.01	0.01	< 0.01	0.03	
45480, France	SL									
2010 (Courtot)	1× 0.96									
Reethsestraat	480 g/L	200	32	91	straw	< 0.01	< 0.01	< 0.01	< 0.03	
6662 Elst	SL									
The Netherlands	1× 0.96									
2010 (Tabasco)										
Sweepstone	480 g/L	200	32	87	straw	< 0.01	< 0.01	< 0.01	< 0.03	
Leicestershire, UK	SL									
2010 (Oakley)	1× 0.96									
Burweg	480 g/L	200	32	91	straw	< 0.01	< 0.01	< 0.01	< 0.03	
Niedersachsen	SL									
Germany, 2010	1× 0.96									
(Tobasco)										
Tarupvej	480 g/L	200	32	90	straw	< 0.01	< 0.01	< 0.01	< 0.03	
Middelfart	SL									
Denmark, 2010	1× 0.96									
(Fruvent)										
Audeville, Loiret	480 g/L	200	32	87	straw	< 0.01	< 0.01	< 0.01	< 0.03	
45300, France	SL									
2010 (Suba)	1× 0.96									

^a At application*Grass*

A total of 25 field trials of grass were conducted in Europe to determine the residue level of bentazone in or on raw agricultural commodities (RAC) from 1979 to 1984 (Bassler, R, 1994, 1994/10678; Fuchs, A, 1985, 1984/10469; Fuchs, A, 1985, 1984/10468; Fuchs, A, 1985, 1984/10467; Fuchs, A, 1985, 1984/10466; Fuchs, A, 1985, 1984/10465; Fuchs, A, 1985, 1984/10464; Fuchs, A, 1985, 1984/10463; Anonymous, 1981, 1981/10438). The results are shown in Table 98.

Table 98 Residues of bentazone in grass after treatment in Europe from 1979 to 1984

GRASS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
Epe, The Netherlands	480 g/L SL	600	n.r.	7 13	grass	0.14 0.03	5.22 0.26	0.07 < 0.02	5.10 0.29	Bassler, R 1994
1979 (n.r.)	1× 1.44			20		< 0.02	0.03	< 0.02	0.07	1994/10678
				7	grass	1.04	5.70	0.06	6.42	
				13		0.02	0.20	< 0.02	0.23	

GRASS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
				20		< 0.02	0.07	< 0.02	0.11	
				7	grass	1.25	5.88	0.07	6.83	
				13		0.08	0.72	0.03	0.78	
				20		< 0.02	0.05	< 0.02	0.09	
				7	grass	0.27	7.32	0.10	7.23	
				13		0.14	1.51	0.04	1.59	
				20		< 0.02	0.25	< 0.02	0.27	
Herwynen, The Netherlands	480 g/L	600	n.r.	7	grass	0.40	4.15	0.04	4.33	
	SL			14		0.07	1.05	0.03	1.08	
1979 (n.r.)	1 × 1.44			21		< 0.02	0.31	0.04	0.35	
				7	grass	0.56	5.57	0.04	5.82	
				14		0.13	1.65	0.03	1.71	
				21		0.03	1.19	< 0.02	1.17	
				7	grass	0.16	2.15	0.03	2.20	
				14		0.06	1.20	0.03	1.23	
				21		0.03	0.70	0.02	0.71	
				7	grass	0.18	2.60	0.03	2.65	
				14		0.07	0.75	0.03	0.80	
				21		0.03	0.59	0.03	0.61	
Berkel- Engschot The Netherlands	480 g/L	600	n.r.	10	grass	0.36	0.83	< 0.02	1.16	
	SL			18		0.09	0.16	0.03	0.27	
1979 (n.r.)	1 × 1.44			24		0.09	0.17	0.05	0.30	
				10	grass	0.81	1.72	< 0.02	2.44	
				18		0.18	0.21	0.03	0.41	
				24		0.10	0.19	0.04	0.32	
				10	grass	0.92	1.60	< 0.02	2.44	
				18		0.12	0.18	0.04	0.33	
				24		0.11	0.22	0.04	0.35	
				10	grass	0.41	0.92	0.02	1.29	
				18		0.14	0.24	0.03	0.39	
				24		0.20	0.29	0.04	0.51	
Regstrup Denmark	480 g/L	400	n.r.	1	grass	24.73	3.97	0.12	28.6	
	SL			14		0.39	2.03	0.04	2.33	
1981 (n.r.)	1 × 1.44			22		0.37	1.24	0.03	1.56	
		300		15	grass	0.39	1.22	0.04	1.57	
				25	silage	0.08	0.08	0.03	0.18	
n.r., Germany 1984 (n.r.)	150 g/L	400	20–25 cm	0	grass	0.39	0.80	< 0.02	1.16	Fuchs, A
	SC			7	grass	0.52	2.06	0.03	2.48	1985
	1 × 0.9			14	grass	0.03	1.38	< 0.02	1.34	1984/10469
				21	grass	0.22	0.99	< 0.02	1.17	
				28	grass	0.19	0.76	< 0.02	0.92	
				28	hay	0.61	5.88	0.08	6.20	
n.r., Germany 1984 (n.r.)	150 g/L	400	10–15 cm	0	grass	39.22	0.37	0.06	39.62	Fuchs, A
	SC			7	grass	0.13	7.18	0.03	6.89	1985
	1 × 0.9			14	grass	0.50	2.70	0.04	3.07	1984/10468
				21	grass	0.20	1.39	0.04	1.54	
				28	grass	< 0.02	0.54	< 0.02	0.55	
				32	hay	0.03	1.50	< 0.02	1.46	
n.r., Germany 1984 (n.r.)	150 g/L	400	26–28	0	grass	51.22	0.47	0.02	51.68	Fuchs, A
	SC			7	grass	5.17	1.36	< 0.02	6.46	1985
	1 × 0.9			14	grass	0.19	0.46	< 0.02	0.64	1984/10467
				21	grass	0.17	0.24	< 0.02	0.41	
				28	grass	0.07	0.10	< 0.02	0.18	
				36	hay	0.07	< 0.02	< 0.02	0.11	
n.r., Germany	150 g/L	300	5 cm	0	grass	26.08	0.21	0.11	26.39	Fuchs, A

GRASS country, year (variety)	Form. Appli. Rate (kg ai/ha)	Water L/ha	Crop Growth Stage ^a (BBCH)	DALT	Residues Found (mg/kg)					Reference Author, year Reference No.
					Matrix	bentazone	6-OH- bentazone	8-OH- bentazone	Total bentazone	
1984 (n.r.)	SC		expansion	7	grass	0.47	1.15	0.05	1.60	1985
	1× 0.9			14	grass	0.23	0.92	0.04	1.13	1984/10466
				21	grass	0.04	0.88	0.05	0.91	
				28	grass	< 0.02	0.39	< 0.02	0.40	
				28	hay	0.39	4.81	0.10	5.00	
n.r., Germany	150 g/L	400	29–30	0	grass	38.40	0.70	< 0.02	39.08	Fuchs, A
1984 (n.r.)	SC			7	grass	1.92	1.71	< 0.02	3.54	1985,
	1× 0.9			14	grass	0.54	1.24	< 0.02	1.72	1984/10465
				21	grass	0.12	0.40	< 0.02	0.51	
				28	grass	0.02	0.12	< 0.02	0.15	
				28	hay	0.08	0.09	< 0.02	0.18	
n.r., Germany	150 g/L	400	20 cm	0	grass	2.78	0.08	0.03	2.88	Fuchs, A
1984 (n.r.)	SC		plant	7	grass	2.67	0.17	< 0.02	2.85	1985
	1× 0.9		height	14	grass	0.32	0.05	< 0.02	0.39	1984/10464
				21	grass	0.17	0.03	< 0.02	0.22	
				28	grass	0.09	< 0.02	< 0.02	0.13	
				32	hay	0.48	0.03	< 0.02	0.53	
n.r., Germany	150 g/L	400	15–20 cm	0	grass	24.59	4.33	0.04	28.69	Fuchs, A
1984 (n.r.)	SC		plant	7	grass	0.28	3.27	0.04	3.38	1985,
	1× 0.9		height	14	grass	0.15	1.17	< 0.02	1.27	1984/10463
				21	grass	0.04	0.94	< 0.02	0.94	
				28	grass	< 0.02	< 0.02	< 0.02	< 0.06	
				28	hay	0.22	1.39	0.03	1.55	
n.r., Germany	200 g/L	400	15 cm	0	grass	371	7.8	0.59	379	Anonymous
1980/81 (n.r.)	n.r.			215	grass	0.28	< 0.02	< 0.02	0.32	1981
	1× 1.2			222	grass	0.37	< 0.02	< 0.02	0.41	1981/10438
				229	grass	0.12	< 0.02	< 0.02	0.16	
				240	hay	0.16	< 0.02	< 0.02	0.20	
n.r., Germany	200 g/L	330	15 cm	0	grass	49.0	5.98	< 0.02	54.6	Anonymous
1980/81 (n.r.)	n.r.			217	grass	2.52	0.35	< 0.02	2.87	1981,
	1× 1.2			224	grass	0.89	< 0.02	< 0.02	0.93	1981/10437
				231	grass	0.62	< 0.02	< 0.02	0.66	
				231	hay	1.02	< 0.02	< 0.02	1.06	
n.r., Germany	200 g/L	600	15 cm	0	grass	84.0	0.87	< 0.02	84.8	Anonymous
1980/81 (n.r.)	n.r.			173	grass	2.12	< 0.02	< 0.02	2.16	1981
	1× 1.2			180	grass	1.26	< 0.02	< 0.02	1.30	1981/10436
				187	grass	< 0.02	< 0.02	< 0.02	< 0.06	
				189	hay	< 0.02	< 0.02	< 0.02	< 0.06	

^a At application

n.r. = Not reported

FATE OF RESIDUES IN STORAGE AND PROCESSING

Information and Data from Trials on Stored Products

Bentazone is not used in stored products.

Information and Data from Residues in Processed Commodities

The Meeting received five processing studies on soya beans, maize, rice, linseed and peanuts.

During the 1991 growing season, two field trials in soya beans were conducted in representative growing areas in the USA (Iowa and Illinois) (Stewart, J 1992, 1992/5169). Bentazone

was applied at an exaggerated rate of five times 2.25 kg ai/ha and the spray volume used was approximately 190 L/ha. The application was done at growth stage BBCH 12–89. Specimens of soya bean samples (RAC seeds) as well as processed fractions thereof were collected at harvest (BBCH 89). The soya bean samples were processed according commercial standards into hulls, meal, crude oil, refined oil and soapstock. The specimens were analysed for bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone with BASF Method No. 19A which quantifies the relevant residues with a limit of quantitation (LOQ) of 0.05 mg/kg. The results are summarized in Table 99.

Table 99 Summary of total residues in process fractions and processing factors

Portion Analysed	Residue Bentazone, Parent (mg/kg)		Residue Bentazone, Total (mg/kg)		Processing Factor ^a Bentazone, Parent			Processing Factor ^a Bentazone, Total		
	1	2	1	2	1	2	Mean	1	2	Mean
Trial ^a										
seeds (RAC)	< 0.05	< 0.05	< 0.15	< 0.15	–	–	–	–	–	–
hulls	< 0.05	< 0.05	< 0.15	< 0.15						
meal	0.055	< 0.05	0.2	0.17	1.1		> 1.1	1.33	1.13	> 1.23
crude oil	0.072	0.118	0.17	0.21	1.44	2.36	> 1.9	1.13	1.4	> 1.27
refined oil	< 0.05	< 0.05	< 0.15	< 0.15						
soapstock	< 0.05	< 0.05	< 0.15	< 0.15						

^a Trial 1: RCN 91016, Trial 2: RCN 91017

During the 1991 growing season, two field trials were conducted in representative maize growing areas in the United States to determine the residue level of bentazone in or on raw agricultural commodities (RAC) and processing products (Stewart, J, 1992, 1992/5168). Bentazone was foliar applied an exaggerated five times at rates of 2.24 kg ai/ha to maize. Maize grain specimens were harvested at maturity (BBCH 89), 69–70 days after the last application (DALA). The samples were processed using a small-scale wet-milling procedure according to commercial standards into starch, crude oil and refined oil. Maize grain samples were also processed using a small-scale dry-milling procedure into grits, meal, flour, crude oil and refined oil according to commercial standards. The results are summarized in Table 100.

Table 100 Summary of total residues in process fractions and processing factors

Portion Analysed	Residue Bentazone, Parent (mg/kg)		Residue Bentazone, Total (mg/kg)		Processing Factor ^a Bentazone, Parent			Processing Factor ^a Bentazone, Total		
	1	2	1	2	1	2	Mean	3	4	Mean
Trial ^b										
maize grain (RAC)	< 0.05	< 0.05	0.154	< 0.15	–	–	–	–	–	–
grits	< 0.05	< 0.05	< 0.15	< 0.15	N/A	N/A		< 0.97	N/A	
meal	< 0.05	< 0.05	< 0.15	< 0.15	N/A	N/A		< 0.97	N/A	
flour	< 0.05	< 0.05	< 0.15	< 0.15	N/A	N/A		< 0.97	N/A	
starch	< 0.05	< 0.05	< 0.15	< 0.15	N/A	N/A		< 0.97	N/A	
crude oil, dry processing	< 0.05	< 0.05	< 0.15	< 0.15	N/A	N/A		< 0.97	N/A	
refined oil, dry processing	< 0.05	< 0.05	< 0.15	< 0.15	N/A	N/A		< 0.97	N/A	
crude oil, wet processing	< 0.05	< 0.05	< 0.15	< 0.15	N/A	N/A		< 0.97	N/A	
refined oil, wet processing	< 0.05	< 0.05	< 0.15	< 0.15	N/A	N/A		< 0.97	N/A	

^a Trial 1: RCN 91012, Trial 2: RCN 91013

N/A = not applicable since residues in RAC and processed products were < LOQ

During the 1991 growing season, two field trials were conducted in representative rice growing areas in the United States to determine the residue level of bentazone in or on raw agricultural commodities (RAC) and processing products (Stewart, J, 1992, 1992/5170). Bentazone was applied an exaggerated five times at rates of 2.24 kg ai/ha to rice. Rice grain specimens were harvested at maturity (BBCH 89), 15–17 days after the last application (DALA). Rice grain samples were processed into hulls, polished rice and bran using a small-scale procedure to simulate commercial practices. The results are summarized in Table 101.

Table 101 Summary of total residues in process fractions and transfer factors

Portion Analysed	Residue Bentazone, Parent (mg/kg)		Residue Bentazone, Total (mg/kg)		Processing Factor ^a Bentazone, Parent			Processing Factor ^a Bentazone, Total		
	1	2	1	2	1	2	Mean	3	4	Mean
Trial ^b										
rice grain (RAC)	0.43 ^c	1.48	2.27	4.77	—	—	—	—	—	—
hulls	6.89 ^c	2.50 ^c	10.2	16.7	16	1.7	8.9	4.5	3.5	4.0
bran	0.08	0.82	1.65	4.94	0.19	0.55	0.37	0.73	1.0	0.87
polished rice	< 0.05	< 0.05	0.22	0.37	< 0.12	< 0.03	< 0.08	0.50	0.08	0.29

^a Transfer factor = residue in processed fraction / residue in RAC

^b Trial 1: RCN 91014, Trial 2: RCN 91015

^c Average of two analyses

During the 1989 growing season, one field trial was conducted in representative linseed growing area in the United States (Minnesota) to determine the residue level of bentazone in or on raw agricultural commodities (RAC) and processing products (Single, Y, 1992, 1992/5124). Bentazone was applied by ground equipment an exaggerated three times at rates of 1.69 kg ai/ha to linseed. Linseed specimens were harvested at maturity (BBCH 89), 30 days after the last application (DALA) and processed in a manner designed to simulate the commercial procedure. The results are summarized in Table 102.

Table 102 Summary of total residues in process fractions and transfer factors

Portion Analysed	Residue Bentazone, Parent (mg/kg)		Residue Bentazone, Total (mg/kg)		Processing Factor ^a Bentazone, Parent			Processing Factor ^a Bentazone, Total		
	1	2	1	2	1	2	Mean	3	4	Mean
seed (RAC)	0.49		1.24		—	—	—	—	—	—
meal	0.31		0.84		0.63			0.68		

^a Transfer factor = residue in processed fraction / residue in RAC

During the 1975 growing season, a field trial was conducted in the United States to determine the residue level of bentazone in or on raw agricultural commodities (RAC) and processing products (Horton, WE, 1973, 1975/5056). Bentazone was applied once at a rate of either 2.24 or 4.48 kg ai/ha to peanuts at the four-leaf stage (BBCH 14) at 10 inch plant height. Peanut specimens were harvested 65 days after the last application. Samples were processed into crude oil, refined oil, meal and soapstock. None of them contained detectable residues. Since the residues in peanut were not determined processing factors cannot be calculated.

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

Dairy goats

A lactating goat feeding study was conducted to determine the magnitude of residues of bentazone and its metabolites 6-hydroxy bentazone in milk and animal tissues (Keller, W, 1981, 1981/10068). Seven crossbred lactating female goats, 3 to 6 years of age, were orally dosed for 21 consecutive days with the diets containing test compound. Observations were continued for a further 14 days. The dose levels in the dry food were for bentazone 15 mg/kg and 75 mg/kg and for 6-hydroxybentazone 75 mg/kg and 150 mg/kg on the basis of an individual feed intake of 3 kg of feed per animal per day and incorporating an allowance for the difference in dry matter percentage between the type of diet offered (cereal/protein concentrate feed and hay) and fresh herbage, respectively. Milk samples from day 1, 7, 14, 21, 28 and 35 were analysed. The results are shown in the tables 103 and 104. Tissues

such as loin muscle, leg muscle, back fat, omental fat, liver and kidney were not analysed. The results are shown in Table 105 and Table 106.

Table 103 Summary of group mean residues in milk—bentazone

	Group Mean (and Maximum Individual) Residues for Bentazone in Milk (mg/kg)		
Study Day	Group 1 (control)	Group 2 (low level)	Group 3 (high level)
1	n.r.	< 0.02 (< 0.02)	< 0.02 (< 0.02)
7	n.r.	< 0.02 (< 0.02)	< 0.02 (< 0.02)
14	n.r.	< 0.02 (< 0.02)	< 0.02 (< 0.02)
21	n.r.	< 0.02 (< 0.02)	< 0.02 (< 0.02)
28 (7 days after last dose)	n.r.	< 0.02 (< 0.02) ^a	< 0.02 (< 0.02) ^a
35 (14 days after last dose)	n.r.	< 0.02 ^b	< 0.02 ^b

n.r. = Not reported

^a results of two goats

^b results of one goat

Table 104 Summary of group mean residues in milk—6-OH-bentazone (Keller, W, 1981, 1981/10068)

	Group Mean (and Maximum Individual) Residues for 6-OH-Bentazone in Milk (mg/kg)		
Study Day	Group 1 (control)	Group 2 (low level)	Group 3 (high level)
1	n.r.	0.02 (0.03)	0.02 (0.03)
7	n.r.	< 0.02 (0.02)	0.03 (0.06)
14	n.r.	< 0.02 (< 0.02)	0.03 (0.07)
21	n.r.	< 0.02 (< 0.02)	0.03 (0.05)
28 (7 days after last dose)	n.r.	< 0.02 (< 0.02) ^a	< 0.02 (< 0.02) ^a
35 (14 days after last dose)	n.r.	< 0.02 ^b	< 0.02 ^b

n.r. = Not reported

^a Results of two cows

^b Results of one cow

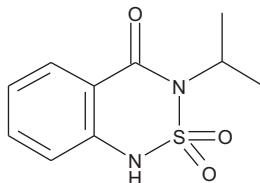
APPRAISAL

Bentazone, a post-emergence herbicide, was originally evaluated by the JMPR in 1991 and re-evaluated for residues and toxicity several times up to 2004. It was reviewed as part of the periodic re-evaluation programme of CCPR on toxicity in 2012 JMPR. Bentazone is a selective herbicide applied as a post emergence treatment to control dicotyledonous weeds in agriculture, horticulture, ornamentals and amenity grasslands. The mode of action is based primarily on an irreversible blockage of photosynthetic electron transport and in further consequence the inhibition of photosynthesis at photosystem II. As a result of this reaction, CO₂ assimilation is suppressed and after a short period of growth stagnation, the plant dies.

At the 43rd Session of the CCPR (REP 12/PR, Appendix VIII), bentazone was scheduled for periodic review of residues by the 2013 JMPR. The Meeting received information on physical and chemical properties, metabolism, environmental fate, analytical methods and freezer storage stability, national registered use patterns, as well as supervised trials, processing studies and livestock feeding studies.

The 2012 JMPR established an ADI for bentazone of 0–0.09 mg/kg bw/day and reaffirmed its previous conclusion that no ARfD is necessary.

Bentazone is 3-isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one 2,2-dioxide.



The chemical structures and names of metabolites discussed in this appraisal are:

6-OH-bentazone (M351H001) 3-Isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one-6-hydroxy-2,2-dioxide	
8-OH-bentazone (M351H002) 3-Isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one-8-hydroxy-2,2-dioxide	
Bentazone-6-O-glucoside (M351H013)	
Bentazone-8-O-glucoside (M351H017)	
Bentazone-N-glucuronide (Metabolite A, M351H004) 3-isopropyl-1-methyl-2,2-dioxo-2,1,3-benzothiadiazin-4-one	
M351H014 and isomers: M351H015-016, -018-019, -022	

Animal metabolism

Information was available on metabolism of bentazone in lactating goats and laying hens.

Laboratory animals

Metabolism in laboratory animals was summarized and evaluated by JMPR in 2012. Studies on toxicokinetics showed that elimination was almost exclusively via the urine (approximately 91% within 24 hours). Five days after dosing, less than 2% was found in faeces and less than 0.02% in expired air. Biliary excretion of radioactivity was minimal. No significant differences were found in absorption and elimination among the different species investigated (rat, rabbit and mouse). Bentazone is minimally metabolized in vivo, with the parent compound being the predominant excretion product. Only small amounts of 6-hydroxybentazone (up to approximately 6% of the dose) and minimal amounts of 8-hydroxybentazone (less than approximately 0.2% of the dose) were detected in urine.

Lactating goats

Lactating goats were administered orally with uniformly ring-labelled [^{14}C]-bentazone for 5 or 8 consecutive days at 3 and 50 mg/kg bw, 97.3% and 99.1% TAR was recovered respectively. Most of the administered dose was eliminated in the urine (91.4% and 80.6% TAR). TRR levels in tissues ranged from 0.017 mg eq/kg for muscle to 0.91 mg eq/kg in fat for the low dosed goat and from 1.2 mg eq/kg in muscle to 54 mg eq/kg in kidney for the high dosed goat. The parent bentazone was the major residue component and constituted about 71–96% (0.034 mg/kg and 0.39 mg/kg) of TRR in milk, 71–97% (0.010 mg/kg and 1.2 mg/kg) in muscle, 94–98% (1.6 mg/kg and 2.8 mg/kg) in fat, 91–98% (0.55 mg/kg and 49 mg/kg) in kidney, 83–84% (0.033 mg/kg and 3.1 mg/kg) in liver. The liver in high dosed goat contained bentazone-N-glucuronide (11.1% TRR, 0.40 mg/kg) in addition to the parent compound. Two unidentified minor metabolites at a concentration of 0.002 mg/kg bentazone equivalents were found in milk from the goat dosed at 3 mg/kg bw.

The metabolism studies with [^{14}C]-6-hydroxy-bentazone and [^{14}C]-8-hydroxy-bentazone were conducted separately at two dose levels of 2 mg/kg bw and 40 mg/kg bw for 5 or 6 consecutive days, respectively. Residue were rapidly excreted 70–86% TAR for 6-hydroxy-bentazone and 83–91% TAR for 8-hydroxy-bentazone. The major residue component in edible tissues was unchanged 6-hydroxy-bentazone constituted >43% TRR and main metabolite was sulphate conjugate of 6-hydroxybentazone (43% of the TRR) in milk. The unchanged 8-hydroxybentazone (29–95% TRR) was the major residue component in the milk and edible tissues. In all three studies unidentified metabolites in milk or edible tissues amounted less than 10% of the TRR.

Laying hens

[^{14}C]-bentazone, [^{14}C]-6-hydroxybentazone and [^{14}C]-8-hydroxybentazone were each administered orally to separate groups of 10 laying hens once daily for 5 days. The doses were 10 mg/hen/day, equivalent to feed containing about 100 ppm. The excretion of radioactivity was rapid. The mean proportions of the total cumulative dose recovered 6 hours after the final dose were 94% from the bentazone group, 90% from the 6-hydroxybentazone group and 93% from the 8-hydroxybentazone group. The mean concentrations of radioactivity were highest in the kidneys in all groups (3.9, 0.66, 1.6 mg eq/kg), followed by muscle (0.39, 0.32, 0.23 mg eq/kg), and liver (1.1, 0.13, 0.23 mg eq/kg). After the administration of bentazone, the parent compound was the major radioactive component in extracts of liver (0.91 mg/kg, 84% TRR) and was exclusively found in muscle (0.29 mg/kg, 100% TRR), fat (0.056 mg/kg, 100% TRR) and eggs (0.13 mg/kg, 100% TRR).

In summary, bentazone is the major residue in the animals tissues, milk and eggs (> 70% TRR).

Plant metabolism

The Meeting received plant metabolism studies with bentazone on soya bean, rice, maize, green beans, potatoes and wheat.

Soya beans

Soya beans were treated with [^{14}C] bentazone once at 2.24 kg ai/ha or twice at 1.68 and 1.12 kg ai/ha. Forage at long and short pre-harvest intervals, hay and bean samples were collected. The residues from single treated forage were 19 mg eq/kg and 7.0 mg eq/kg at 9 DAT and 36 DAT and from the double treated forage were 17 mg eq/kg and 24 mg eq/kg at 9 days after the first treatment and 11 days after the second treatment. In hay, residues for the single treated forage were 21 mg eq/kg at 93 days after treatment and for the double treatment 80 mg eq/kg at 48 days after the second treatment. The residues of bentazone, 6-hydroxy and 8-hydroxy bentazone in the double treated forage, 11 days after the second treatment, were 5.0 mg/kg (21% TRR), 1.8 mg/kg (3.3% TRR) and 2.3 mg/kg (9.6% TRR), respectively. The residues in seed were too low for further analysis.

Rice

Rice plants were treated by foliar application with 1 kg ai/ha of [^{14}C] bentazone and radioactive residues were determined in whole plants, grain and straw. At day 0, only bentazone (72% TRR) and 6-hydroxy-bentazone (6.5% TRR) were detected. At day 26 bentazone decreased to 24% of the TRR and 6-hydroxy-bentazone in free form increased to 17% of the TRR. At 63 days, 15% bentazone (7.8 mg/kg) and 4.0% 6-hydroxy-bentazone (2.1 mg/kg) were found in straw. In grain samples 63 days after treatment only 6.6% of the TRR was extracted and 93% remained in the insoluble fraction. It was shown that the terminal ^{14}C residue consisted predominantly of recycled fragments of bentazone and 6-hydroxy-bentazone taken up into glucose, polysaccharides and lignin. Minor residues of bentazone were observed in rice grains (1.5% TRR, 0.007 mg/kg) and were below the limit of detection (0.02 mg/kg).

Maize

The metabolism of bentazone was investigated in maize grown in outdoor plots and sprayed with an aqueous solution of the sodium salt of [^{14}C] bentazone at a rate equivalent of 1.68 kg ai/ha. In forage only bentazone and 6-hydroxy-bentazone were found in the methanol extract. The levels were 0.12 mg eq/kg and 1.2 mg eq/kg after one week and declined to < 0.05 mg eq/kg and 0.09 mg eq/kg after 9 weeks, respectively. Analysis of the final harvested grain, cobs, husk and stover showed no residues of bentazone or 6-hydroxy- or 8-hydroxy-bentazone (< 0.05 mg/kg).

Green beans

The magnitude of the residues in green beans were determined after one application of [^{14}C] bentazone at 2.24 kg ai/ha or two at 1.68 and 1.12 kg ai/ha. The total radioactive residues in forage (4.1–22% TAR, 5.0–45 mg eq/kg), succulent bean (0.1–0.6% TAR, 0.13–1.9 mg eq/kg) and seed (0.02–0.04% TAR, 0.61–1.3 mg eq/kg) were not further identified.

Potatoes

The metabolism in potato plants was studied after two foliar spray applications of 1.12 kg ai/ha [^{14}C] bentazone. Potato tubers were harvested 41 days after the final treatment. TRR levels found in the whole tuber (0.14 mg eq/kg) were mainly located in the pulp (0.1 mg eq/kg), while the peel contained lower residues (0.037 mg eq/kg). The identified extractable residues were bentazone (3.7% TRR, 0.005 mg/kg) and conjugates of 6-hydroxy-bentazone (about 25% TRR, 0.034 mg/kg). Most of the radioactivity (56% of the TRR) was incorporated into starch.

Wheat

A wheat metabolism study was performed with [^{14}C] bentazone. The active substance was applied once at a rate of 1 kg ai/ha. Samples of wheat forage and hay were collected at BBCH 39 (20 days after application) and samples of grain, chaff and straw were sampled at BBCH 89 (83 days after application). The total radioactive residues (TRR) for wheat forage accounted for 4.46 mg eq/kg. Wheat hay showed the highest residue level of all matrices at 31 mg eq/kg, followed by wheat straw with residue levels of 17 mg eq/kg. In wheat chaff the residues amounted to 1.6 mg eq/kg while

lowest residue levels were found in wheat grain at 1.1 mg eq/kg. The parent compound was found to be moderately metabolized until harvest. Portions between approximately 39% and 56% of the TRR were still present as unchanged bentazone in forage, hay and straw. The major metabolite in quantitative terms was an O-monosaccharide conjugate of a 6-hydroxylated derivative of parent compound. Other metabolites identified represented less than 4.7% of the TRR each. In the grain the major part of the radioactivity was characterized as carbohydrates (58% of the TRR).

In summary, the metabolism of bentazone in six different crops was similar and considered comparable. The main residue components were parent bentazone and 6-hydroxy-bentazone in soya bean forage and hay, rice hay and straw and grain, maize forage, potato tuber and wheat hay and straw. However, the parent compound was quite low in grains or seeds and confirmed by the supervised trials.

Environmental fate in soil

The Meeting received information on the environmental fate of bentazone in soil, including studies on aerobic soil metabolism, degradation in water/sediment system soil photolysis and crop rotational studies.

Aerobic soil metabolism

The aerobic soil metabolism of bentazone was investigated with [^{14}C -phenyl]-bentazone at a nominal rate of 2.0 and 2.7 mg per kg dry soil. The majority of radioactivity in the extracts was always unchanged compound. At the end of incubation, bentazone was detected in amounts of 2.3–19% TAR. None of metabolites exceeded 5% TAR. Metabolites were formed only in minor amounts of which the most prominent metabolite (max. 2.8% TAR) was identified as N-methyl-bentazone. The half-lives were calculated to be 31 to 45 days. Mineralization to ^{14}C - CO_2 reached a total of 9.0% to 21% TAR. No other volatile compounds were detected. In summary, bentazone was not persistent in soil.

Water/sediment dissipation

The degradation of [^{14}C] bentazone was investigated in two different water/sediment systems (sandy loam/sand) under aerobic conditions over a period of 100 days at 0.34 mg/kg in water. The major residue component was parent bentazone which accounted for more than 60% of the TAR after 100 days. Methyl-bentazone was observed only in the water phase with the maximum concentration less than 13% of the TAR after 100 days. The half-lives in the total system were calculated to be greater than 500 days. Bentazone is stable in the water/sediment system.

Soil Photolysis

The photolytic degradation of ^{14}C -labelled bentazone was investigated on a sandy clay loam soil. The overall results for the material balances in the photolysis and the dark control samples were in the range of 95–100% TAR. Carbon dioxide was the only volatile degradation product trapped (8.1% TAR) after 15 days in the photolysis test and 1.8% TAR in the dark control. The concentration of bentazone decreased to 49% TAR in the course of the photolysis study and to 77% in the dark control samples. No degradation products of $\geq 4\%$ TAR occurred in the photolysis samples or in the dark controls. The half-lives for bentazone in the test systems were calculated to be 13 days under continuous irradiation and 42 days in the dark.

Confined rotational crop

The metabolism of bentazone in succeeding crops was investigated in wheat, radish and lettuce cultivated at three different replant intervals for all crops (30, 120 and 365 DAT). Significant translocation of radioactive residues from soil into the plants was observed for the plant back interval of 30 DAT which decreased rapidly after longer aging periods of 120 and 365 days. The residue concentration in the top soil layer after aging and ploughing decreased slightly with increasing plant

back intervals. The total radioactive residues (TRR) in lettuce (immature and mature samples) did not exceed 0.13 mg eq/kg for all plant back intervals. The TRR in white radish tops was 0.17 mg/kg at a plant back interval of 30 DAT, 0.019 mg eq/kg after 120 DAT and to 0.003 mg eq/kg (TRR combusted) after 365 DAT. The total radioactive residues in radish roots of mature crop decreased from 0.13 mg eq/kg (30 DAT), to 0.012 mg eq/kg (120 DAT) and finally to 0.001 mg eq/kg (365 DAT, TRR combusted). In spring wheat, the highest residue levels were measured in hay (declining from 1.6 to 0.07 mg eq/kg, for 30 DAT and 365 DAT, respectively) and straw (declining from 1.1 to 0.049 mg eq/kg, for 30 DAT and 365 DAT, respectively). The total radioactive residues in grain accounted 0.71 to 0.041 mg eq/kg after 30 to 365 days.

Bentazone and/or its soil metabolites were taken up and transformed in the rotational crops primarily into sugars (glucose, fructose and sucrose and further components of similar polarity) which were without exception the most abundant components in all matrices examined. The unchanged parent molecule was found as minor component in samples of immature (30 DAT) and mature lettuce (30 and 120 DAT) in concentrations of < 0.0013 mg/kg and 1.2% TRR only. Additional medium polar degradation products were detected in minor concentrations. The results of this study indicated that potential for uptake of parent bentazone residues from the soil by the succeeding crops is low.

Methods of analysis

The Meeting received descriptions and validation data for analytical methods for residues of bentazone in raw agricultural commodities, feed commodities and animal commodities.

The methods for crop and animal matrices typically use an initial extraction and hydrolysis step, either with acid, base or enzymatic treatment to hydrolyse any sugar conjugates in plant or animal matrices. After a $\text{Ca}(\text{OH})_2$ -precipitation step to remove acidic plant constituents, a reversed phase C_{18} -column clean-up is performed. The analytes are then methylated with diazomethane and their derivatives are purified using a silica gel-column. The final determination of the residues of bentazone and its OH-metabolites is performed by GC-MS or LC-MS/MS. Bentazone residues can be measured in most matrices to an LOQ of 0.01 mg/kg. All methods are considered sufficiently validated for the determination of bentazone, 6-OH-bentazone and 8-OH-bentazone including conjugates thereof. No multi-residue method was provided.

Stability of residues in stored analytical samples

The Meeting received information on the freezer storage stability of residues of bentazone in plant and animal commodities.

Storage stability studies indicated that the residues are stable over a period of two years maize (green plant, grain and straw), pea (seed), flax (seed) and potato (tuber). Analytical results demonstrated that bentazone and its metabolites 6-OH-bentazone and 8-OH-bentazone as glucoside derivatives, were stable in the different plant matrices over the test period of two years.

No storage stability study on bentazone in animal matrices was provided to the Meeting.

Definition of the residue

The composition of the residue in the metabolism studies, the available residue data in the supervised trials, the toxicological significance of metabolites, the capabilities of enforcement analytical methods and the national residue definitions already operating all influence the decision on residue definitions.

Animal metabolism studies showed that the parent bentazone was a major component of the residue, representing 84–100% of the TRR in poultry matrices and 71–98% of the TRR in goats. No 6-hydroxy and 8-hydroxy bentazone were found in milk and tissues in goat metabolism studies. Analytical methods are suitable for the determination of bentazone. The Meeting decided that for animal commodities, parent bentazone is the appropriate residue of concern for MRL enforcement and for dietary risk assessment.

The maximum octanol-water partition coefficient of bentazone ($\log K_{ow} = -0.94$ at pH 7) implied that bentazone may not be fat-soluble. Noting that bentazone residues in goat fat were

artificial and TRRs in poultry fat were much less than those in muscle the Meeting agreed that bentazone residue is not fat-soluble.

Metabolism studies on plants and supervised trials showed that the main residues in food or feed of plant origin were bentazone and one or both of its conjugated metabolites, 6-hydroxy- and 8-hydroxy-bentazone. However, the two hydroxy-bentazones were less toxic compared with parent bentazone and only existed in feed commodities. Therefore the Meeting decided that for plant commodities, parent bentazone is the appropriate residue of concern for MRL enforcement and for dietary risk assessment.

Definition of the residue (for compliance with the MRL and for estimation of dietary intake for animal and plant commodities): *bentazone*.

The residue is considered to be not fat-soluble.

Results of supervised residue trials on crops

The Meeting received supervised trials data in bulb onions, cucumbers, sweet corn, green peas, green beans, dried beans, soya beans, potatoes, barley, oats, maize, rice, sorghum, wheat, linseed, peanuts, herbs, alfalfa, clover, sugar beet and grass.

Onion, bulb

The critical GAP for bentazone on bulb onions was from Turkey (one foliar application at 0.96 kg ai/ha with a PHI of 30 days). Eight trials were available from southern Europe on bulb onions matching Turkish GAP from which residues were < 0.01 (7) and 0.02 mg/kg.

The Meeting estimated an STMR of 0.01 mg/kg and a maximum residue level of 0.04 mg/kg for bulb onion to replace the previous recommendation of 0.1 mg/kg.

Spring onion

The critical GAP for bentazone on spring onions was from the Netherlands (one spray application of 0.72 kg ai/ha, at least 10 cm height). Two trials were available from the Northern Europe on spring onion matching Dutch GAP with residues of < 0.01 and 0.04 mg/kg. Two trials from the Southern Europe were reported at a rate of 0.96 kg ai/ha treated at later growth stage. The residues of bentazone in spring onion from these trials were < 0.01(2) mg/kg.

Noting that the residues from the Northern and Southern Europe's trials were similar, the Meeting agreed to combine Northern and Southern Europe dataset to estimate an STMR 0.01 mg/kg, and a maximum residue level of 0.08 mg/kg for spring onion.

Cucumber

The critical GAP for bentazone on cucumber is from Sweden (one spray application of 1.0 kg ai/ha with a PHI of 42 days). Four trials were available from Canada on cucumber matching Swedish GAP from which residues were < 0.02(4) mg/kg.

Four trials from Canada on cucumber were not considered sufficient for the estimation of a maximum residue level.

Sweet corn (corn-on-the-cob)

The critical GAP for bentazone on sweet corn is from Canada (one spray application of 1.08 kg ai/ha, at 1 to 5-leaf stage) and in France (one spray application of 1.2 kg ai/ha with a PHI of 28 days). Two trials were available from Canada on sweet corn complying with Canadian GAP with residues of < 0.02 (2) mg/kg and one 2× trial treated at a later growth stage with a residue of < 0.02 mg/kg. Two trials were available from France on sweet corn matching French GAP with residues of < 0.01(2) mg/kg. Ten trials were available from Europe on maize cobs w/o husks against French GAP with residues in immature corn of < 0.01(10) mg/kg.

As the residues from the European trials were considered similar, the Meeting decided to combine them and estimated an STMR 0.01 mg/kg, and maximum residue level of 0.01* mg/kg for sweet corn (corn-on-the-cob) respectively.

Peas (pods and succulent = immature seeds)

The critical GAP for bentazone on peas is from the USA (two applications of 1.12 kg ai/ha with a PHI of 10 days). Ten trials were available from the USA on peas matching US GAP, residues found in peas (pods and succulent immature seeds) were < 0.05(6), 0.05, 0.06, 0.46 and 0.74 mg/kg.

The Meeting estimated an STMR 0.05 mg/kg, and maximum residue level of 1.5 mg/kg for peas (pods and succulent immature seeds) and agreed to withdraw the previous recommendation of 0.2 mg/kg for garden pea (young pods) (= succulent, immature seeds).

Beans, except broad bean and soya bean

The critical GAP for bentazone on beans, except broad beans and soya beans was from France (one application at 1.22 kg ai/ha with a PHI of 42 days). From eight trials in Northern Europe and six trials in Southern Europe on green beans with pods matching French GAP at a shorter PHI (35days) residues were < 0.01 (14) mg/kg.

The Meeting estimated an STMR 0.01 mg/kg, and maximum residue level of 0.01* mg/kg for beans, except broad bean and soya bean (green pods and/or immature seeds) and agreed to withdraw the previous recommendations of 0.2 mg/kg for common bean (pods and /or immature seeds) and 0.05 mg/kg for lima bean (pods and /or immature seeds).

Beans, shelled

Five trials from the Northern Europe and seven trials from the Southern Europe on green beans (immature seeds) (green beans without pods) matching French GAP at a shorter PHI (35 days) gave residues of < 0.01 (11) and 0.02 mg/kg.

The Meeting estimated an STMR 0 mg/kg, and maximum residue level of 0.01* mg/kg for beans, shelled (succulent = immature seeds), respectively.

Peas (dry)

The critical GAP for bentazone on peas in the USA, is two applications at 1.12 kg ai/ha with a PHI of 30 days. Three trials were available from the USA on peas matching US GAP resulting in residues of < 0.05(2) mg/kg.

Three trials on peas (dry) were not considered sufficient for the estimation of a maximum residue level. The Meeting agreed to withdraw the previous recommendation of 1 mg/kg for field pea (dry).

Beans (dry)

The critical GAP for bentazone on beans (dry) in Poland, is one application at 1.44 kg ai/ha, at 6–12 cm plant height. From seven southern European trials on beans matching Polish GAP residues were < 0.02(6) and 0.021 mg/kg. Two trials were available from northern Europe on beans matching the GAP of Poland with residues of < 0.02(2) mg/kg.

As residues from the Southern and Northern European trials were similar, the Meeting decided to combine the two datasets and estimated an STMR 0.02 mg/kg, and maximum residue level of 0.04 mg/kg for beans (dry) to replace the previous recommendation of 0.05 mg/kg.

Soya beans (dry)

The critical GAP for bentazone on soya beans (dry) is from Spain (one application of 1.0 kg ai/ha, 1st and 3rd trifoliolate leaf); The GAP in Germany is for one application of 0.96 kg ai/ha, emergence to 10 cm height; and the GAP in the USA, two applications of 1.12 kg ai/ha with no PHI. Twelve trials

were available from southern Europe on soya bean matching Spanish GAP with some trials treated at later growth stage. Residues found were < 0.01(12) mg/kg. Two trials were available from northern Europe on soya beans matching German GAP with one trial treated at a later growth stage with residues of < 0.01(2) mg/kg. Six trials were available from the USA on soya beans matching US GAP with residues of < 0.05(6) mg/kg. Two exaggerated rate trials from the US resulted in residues of < 0.05(2) mg/kg.

The Meeting estimated an STMR 0.01 mg/kg, and maximum residue level of 0.01* mg/kg for soya bean (dry) on the basis of European dataset replacing its previous recommendation of 0.1 mg/kg.

Potatoes

The GAP for bentazone on potatoes in Ireland is for one application of 1.44 kg ai/ha, before shoots exceed 15 cm in height. The GAP in Spain is for one application of 1.0 kg ai/ha, from post-emergence to the fourth leaf growth stage. Eight trials were available from southern Europe on potato matching Spanish GAP from which residues found were < 0.01(4), 0.01, 0.02(2) and 0.06 mg/kg. Twenty five trials were available from northern Europe on potato matching Irish GAP from which residues found were < 0.02(24) and 0.04 mg/kg.

Noting that Southern European trials resulted in higher residue, the Meeting estimated an STMR 0.01 mg/kg, and a maximum residue level of 0.1 mg/kg for potato confirming the previous recommendations.

Cereals grains

Barley, oats and wheat

The GAP for bentazone on cereal grains in Finland is for one application of 1.48 kg ai/ha, 2–3 leaf stage (BBCH 12–13). Five trials were available from southern Europe on barley matching the Finnish application rate but treated at later growth stage. Residues found were < 0.02(5) mg/kg. One trial was available from Canada on barley matching the Finnish application rate and treated at later growth stage with a residue of < 0.02 mg/kg.

The residue found from one trial on oats from Germany, at higher application rate than that of the Finnish GAP and treated at later growth stage, was below the LOQ (0.05 mg/kg).

Three trials were available from southern Europe on wheat matching the Finnish application rate and treated at later growth stage with residues of < 0.02 (3) mg/kg.

Maize

The GAP for bentazone on cereal grains in Italy is one application of 1.48 kg ai/ha with no PHI; the GAP in the Netherlands is for one application of 1.44 kg/ha, at 5-leaf stage. Thirteen trials were available from southern Europe on maize matching the Italian application rate with some trials treated at later growth stages. Residues found were < 0.01(5) and < 0.02(8) mg/kg. Seven trials were available from northern Europe on maize matching the Dutch application rate with some trials treated at later growth stages. Residues found were < 0.01(5) and < 0.02(2) mg/kg.

The ranked order of concentrations of parent compound, median underlined, was < 0.01(10) and < 0.02(10) mg/kg.

Rice

The GAP for bentazone on rice in China is one application of 1.44 kg ai/ha, no PHI; the GAP in Greece is one application of 1.44 kg ai/ha, BBCH 12–21; the GAP in Japan is one application of 2.8 kg ai/ha, applied up to 60 days before harvest.

Two trials were available from China on rice matching Chinese GAP with residues of < 0.02(2) mg/kg. Two trials were available from China on rice at about 1.5× maximum Chinese GAP rate with residues of < 0.02(2) mg/kg.

Two trials were available from Japan on rice matching Japanese GAP with residues of < 0.01(2) mg/kg. Two trials were available from Japan on rice at about 1.5× maximum Japanese GAP rate with residues of < 0.01(2) mg/kg.

Two trials were available from Portugal on rice matching Greek GAP with two trials treated at later growth stage with residues of < 0.02(2) mg/kg.

One trial was available from France on rice against about 1.3× maximum Greek GAP with residues of < 0.02 mg/kg.

All 11 trials in Asia and Europe were treated at maximum rate or 1.3–1.6× the maximum rate and resulted in non-detectable residues in rice or brown rice.

Sorghum

The critical GAP for bentazone on sorghum is from Luxembourg (one application of 1.2 kg ai/ha, from emergence to 6-leaf stage (BBCH 16)). Six trials were available from France on sorghum matching the GAP of Luxembourg with residues of < 0.05(6) mg/kg.

The Meeting noted that no residues above LOQ (0.01–0.05 mg/kg) were observed in the samples of barley, oats, wheat, maize, rice and sorghum from 47 supervised trials in various countries following treatment at early growth stages. The Meeting agreed to estimate a maximum residue level 0.01 mg/kg and an STMR 0.01 mg/kg for cereal grains and to withdraw the previous recommendations of 0.1 mg/kg for barley, oat, rice, rye, sorghum and wheat and 0.2 mg/kg for maize.

Oilseeds

Linseed

The critical GAP for bentazone on linseed in France is for one application of 1.2 kg ai/ha with a PHI of 70 days. Three trials were available from France on linseed matching the French application rate. Residues found were < 0.02(3) mg/kg. Three trials were available from Canada on linseed matching French GAP showed residues of < 0.02(3) mg/kg.

Considering residues from the French and Canadian trials were similar, the Meeting decided to combine the two dataset and estimated an STMR of 0.02 mg/kg, and maximum residue level of 0.02* mg/kg for linseed, respectively.

Peanuts

The critical GAP for bentazone on peanuts in the USA is for two applications of 1.12 kg ai/ha, up to 28 days after ground crack stage for the second application. Six trials were available from USA on peanut matching the application rate of the US GAP with residues of < 0.05(6) mg/kg. Two trials were available from USA on peanuts with exaggerated application rates resulting in residues of < 0.05(2) mg/kg.

The Meeting estimated a maximum residue level and an STMR value for peanut of 0.05* and 0 mg/kg and replaced the previous maximum residue level recommendation of 0.05 mg/kg.

Herbs

The GAP for bentazone on herbs in Germany is for one application of 0.96 kg ai/ha with a PHI of 42 days; in France the GAP consists of one application at 1.13 kg ai/ha with a PHI of 28 days. Two trials were available from Germany on peppermint matching German GAP with residues of < 0.05(2) mg/kg. Two trials were available from France on melissa (lemon balm) matching French GAP with residues of < 0.02 and 0.037 mg/kg.

As the residues from the European trials were considered similar, the Meeting decided to combine the data and estimated a maximum residue level and an STMR value for herbs, except dry hops, of 0.1 and 0.0435 mg/kg, respectively.

Sugar beet

One trial from USA on sugar beet was received however as no associated GAP was provided the Meeting could not estimate a maximum residue level.

*Animal feedstuffs**Pea vines (green)*

The critical GAP for bentazone on peas in USA is two applications of 1.12 kg ai/ha with a PHI of 10 days. Ten trials were available from USA on peas matching US GAP from which residues found, median underlined, were: 0.11, 0.12, 0.17, 0.19, 0.22(2), 0.31, 1.05, 7.05 and 13.1 mg/kg.

The Meeting estimated a median and highest residue for bentazone in pea vines (green) of 0.22 and 13.1 mg/kg.

Pea hay

The critical GAP for bentazone on peas in USA is for two applications of 1.12 kg ai/ha with a PHI of 10 days. Three trials were available from USA on peas matching US GAP from which residues found were: 0.48, 1.45 and 1.99 mg/kg.

Three trials on peas hay (dry) were considered insufficient for maximum residue level estimation.

Bean forage (green)

The critical GAP for bentazone on beans, except broad bean and soya bean in France is for one application of 1.22 kg ai/ha with a PHI of 42 days. Five trials were available from Southern Europe on green beans matching French GAP with residues found in forage of < 0.01(3), 0.01 and 0.02 mg/kg. Three trials were available from Northern Europe on green beans against French GAP with residues in forage of < 0.01 and 0.01(2) mg/kg.

As the residues from the European trials were considered similar, the Meeting decided to that the data may be combined, median underlined, < 0.01(4), 0.01(3) and 0.02 mg/kg. The Meeting estimated median and highest residue for bentazone in green beans forage of 0.01 and 0.02 mg/kg.

Soya bean forage (green)

The GAP for bentazone on soya beans (dry) in the USA is for two applications of 1.12 kg ai/ha, with no grazing or cutting for forage or hay for at least 30 days after the last treatment. Four trials were available from USA on soya bean forage matching US GAP with residues of < 0.05, 0.06, 0.12 and 0.15 mg/kg.

The Meeting considered four trials an insufficient number for the estimation of median and the highest residue levels for soya bean forage.

Soya bean straw and fodder

The critical GAP for bentazone on soya beans (dry) in USA, two applications of 1.12 kg ai/ha, not graze or cut for forage or hay for at least 30 days after the last treatment. Four trials were available from USA on soya bean hay against the GAP of the USA with residues of < 0.05, 0.10, 0.45 and 0.62 mg/kg.

The Meeting considered four trials an insufficient number for the estimation of median and the highest residue levels for soya bean straw and fodder.

Alfalfa forage (green)

The critical GAP for bentazone on legume animal feeds in France is one application of 0.6 kg ai/ha, BBCH 12 or 1 trifoliate leaf; in the Netherlands the GAP is one application of 1.44 kg ai/ha, 1–2 trifoliate (true) leaves. Four trials were available from Southern Europe on alfalfa forage matching

French GAP with residues of 0.01(2) and 0.03(2) mg/kg. Two trials were available from Northern Europe on alfalfa forage matching French GAP with residues of 0.06 and 0.07 mg/kg.

Considering residues from European trials were comparable, the Meeting decided they could be combined. The combined residues, in rank order, were: 0.01(2), 0.03(2), 0.06 and 0.07 mg/kg. The Meeting estimated a median of 0.03 mg/kg and the highest residue of 0.07 mg/kg, respectively.

Alfalfa fodder

The critical GAP for bentazone on legume animal feeds in France is one application of 0.6 kg ai/ha, BBCH 12 or 1 trifoliolate leaf; the GAP of the Netherlands is one application of 1.44 kg ai/ha, 1–2 trifoliolate (true) leaves. Four trials were available from Southern Europe on alfalfa hay matching French GAP with residues of 0.04, 0.07, 0.08 and 0.12 mg/kg. Two trials were available from Northern Europe on alfalfa hay matching French GAP with residues of 0.10 and 0.23 mg/kg.

As the residues from the European trials were considered parable, the Meeting decided to they could be combined. The residues in rank order were: 0.04, 0.07, 0.08, 0.10, 0.12 and 0.23 mg/kg. Noting the residues from European trials were consistent and based on an average dry-mass of 89% residues in alfalfa fodder (dry weight) were: 0.04, 0.08, 0.09, 0.11, 0.13 and 0.26 mg/kg. The Meeting estimated a median of 0.09 mg/kg, the highest residue of 0.23 mg/kg and a maximum residue level of 0.5 mg/kg for alfalfa fodder (dry), respectively.

Clover forage

The critical GAP for bentazone on clover in the US is one application of 1.12 kg ai/ha with a PHI of 50 days (for grazing of forage or hay). Two trials were available from the US on clover forage against US GAP with residues of < 0.05 and 0.06 mg/kg.

The Meeting considered two trials an insufficient number for the estimation of median and the highest residue levels for clover forage.

Clover hay or fodder

The critical GAP for bentazone on clover in US is one application of 1.12 kg ai/ha with a PHI of 50 days (for grazing of forage or hay). Two trials were available from the USA on clover forage against US GAP with residues of < 0.05 and 0.07 mg/kg.

The Meeting considered two trials an insufficient number for the estimation of STMR and a maximum residue levels for clover hay.

Peanut fodder

The critical GAP for bentazone on peanuts in the US is two application of 1.12 kg ai/ha, up to 28 days after ground crack stage for the second application. Noting that no trials were in line with US GAP the Meeting agreed that the maximum residue level for peanut fodder could not be recommended.

Grass forage

The critical GAP for bentazone on grasses in Sweden is one application of 1.0 kg ai/ha with a PHI of 21 days. Thirteen trials were available from Northern Europe on grass forage matching Swedish GAP from which residues found were: 0.04(2), 0.12, 0.17(2), 0.20 and 0.22 mg/kg.

The Meeting estimated a median and the highest residue for bentazone in grass forage of 0.17 and 0.37 mg/kg, respectively.

Hay or fodder (dry) of grasses

The critical GAP for bentazone on grasses in Sweden is one application of 1.0 kg ai/ha with a PHI of 21 days. Ten trials were available from Northern Europe on grass hay matching Swedish GAP with residues of < 0.02, 0.03, 0.07, 0.08, 0.16, 0.22, 0.39, 0.48, 0.61 and 1.02 mg/kg.

Based on an average dry-mass of 88% residues in grass hay (dry weight) were: < 0.02, 0.03, 0.08, 0.09, 0.18, 0.25, 0.44, 0.55, 0.69 and 1.16 mg/kg.

The Meeting estimated a maximum residue level, an STMR and the highest residue for bentazone in grass hay of 2 mg/kg (DM based), 0.215 mg/kg and 1.16 mg/kg (air dry), respectively.

Straw and fodder (dry) of cereal grain

Barley, millet, oats, rye, triticale, and wheat straw and fodder, dry

The critical GAP for bentazone on cereal grains in Finland is one application of 1.48 kg ai/ha, 2–3 leaf stage. Five trials were available from southern Europe on barley matching Finnish GAP with residues of 0.04(2), 0.06(2) and 0.14 mg/kg.

Residue from one German oat trial, at higher application rate than that of the Finnish GAP, was below the LOQ (0.05 mg/kg).

Three trials were available from southern Europe on wheat matching Finnish GAP with residues of 0.03(2) and 0.04 mg/kg.

As the residues from the Southern and Northern European trials were comparable, the Meeting decided to combine these datasets. The residues from the combined European residue trials in rank order, median underlined, were: 0.03(2), 0.04(3), < 0.05, 0.06(2) and 0.14 mg/kg.

Based on an average dry-mass of 88% residues in grass hay (dry weight) were: 0.03(2), 0.04(3), < 0.06, 0.07(2) and 0.16 mg/kg.

The Meeting estimated a maximum residue level, an STMR and a highest residue for bentazone in barley, millet, oats, rye, triticale, and wheat straw and fodder (dry) of 0.3 mg/kg (DM based), 0.05 mg/kg and 0.16 mg/kg (air dry), respectively.

Maize fodder

The critical GAP for bentazone on cereal grains in Italy is one application of 1.48 kg ai/ha, at the 2–4 true leaf growth stage for dicotyledonous weeds. The GAP of the Netherlands is one application of 1.44 kg/ha, (at the 5-leaf stage). Thirteen trials were available from southern Europe on maize straw matching Italian GAP with residues of < 0.01, 0.01, < 0.02(6), 0.04, 0.05, 0.13, 0.14 and 0.24 mg/kg. Seven trials were available from northern Europe on maize straw against Dutch GAP with residues of 0.01, < 0.02(2), 0.03(2), 0.06 and 0.08 mg/kg.

As the residues from the southern and northern European trials were comparable, the Meeting decided to combine the two datasets. The residues from the combined European residue trials in rank order, were: < 0.01, 0.01(2), < 0.02(8), 0.03(2), 0.04, 0.05, 0.06, 0.08, 0.13, 0.14 and 0.24 mg/kg.

Based on an average dry-mass of 83% residues in maize fodder (dry weight) were: < 0.01, 0.01(2), < 0.02(8), 0.04(2), 0.05, 0.06, 0.07, 0.10, 0.16, 0.17 and 0.29 mg/kg.

The Meeting agreed to estimate a median of 0.02 mg/kg, the highest residue 0.24 mg/kg and a maximum residue level of 0.4 mg/kg for maize fodder replacing its previous recommendation of 0.2 mg/kg.

Rice straw, dry

The critical GAP for bentazone on rice in China is one application of 1.44 kg ai/ha, no PHI; The GAP in Greece is one application of 1.44 kg ai/ha, BBCH 12–21. The GAP in Japan is one application of 2.80 kg ai/ha, up to 60 days before harvest. Two trials were available from China on rice straw against Chinese GAP with residues of < 0.02(2) mg/kg. Two trials were available from Japan on rice straw against Japanese GAP with residues of 0.06 and 0.07 mg/kg.

The Meeting considered the number of trials insufficient for the estimation of a maximum residue level for rice straw.

Fate of residues during processing

The Meeting received information on the fate of bentazone residues during the food processing of rice.

Portion Analysed	Mean Processing Factor	STMR (mg/kg)	STMR-P (mg/kg)
Rice hulls	8.9	0.01	0.089
bran	0.37		0.0037
polished rice	0.08		0.0008

Residues in animal commodities***Estimated maximum and mean dietary burdens of farm animals***

Dietary burden calculations for beef cattle, dairy cattle, broilers and layers are provided in Annex 6. The calculations were made according to the animal diets from US-Canada, EU, Australia and Japan in the OECD Feed Table 2009.

The calculations are then summarized and the highest dietary burdens are selected for MRL and STMR estimates on animal commodities.

	Animal dietary burden, bentazone, ppm of dry matter diet							
	US-Canada		EU		Australia		Japan	
	max	mean	max	mean	max	mean	max	mean
Beef cattle	0.24	0.06	11.3	0.54	32 ^a	0.8 ^b	0.57	0.14
Dairy cattle	5.94	0.41	11.4	0.60	22 ^c	0.76 ^d	1.0	0.24
Poultry—broiler	0.0091	0.0091	0.013	0.013	0.019	0.0019	0.018	0.012
Poultry—layer	0.091	0.091	5.4 ^e	0.17 ^f	0.019	0.019	0.01	0.01

^a Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian meat.

^b Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat.

^c Highest maximum dairy cattle dietary burden suitable for MRL estimates for mammalian milk.

^d Highest mean dairy cattle dietary burden suitable for STMR estimates for mammalian milk.

^e Highest maximum poultry dietary burden suitable for MRL estimates for poultry meat and eggs.

^f Highest mean poultry dietary burden suitable for STMR estimates for meat and eggs.

Lactating goats were orally administered bentazone at the equivalent to 15 ppm and 75 ppm on the basis of an individual feed intake of 3 kg of feed per animal per day and incorporating an allowance for the difference in dry matter percentage between the type of diet offered (cereal/protein concentrate feed and hay) and fresh herbage, respectively. Residues of bentazone in the whole milk of goats in the 15 and 75 ppm groups were < 0.02 mg/kg and < 0.02 mg/kg respectively, goat tissues were not analysed.

Since no analysis of tissues was carried out in the goats feeding study, the Meeting decided that no recommendations could be made on the basis of this study.

In the animal metabolism study on lactating goats, residues in fat were significantly higher than that in muscle. However, it is not expected that bentazone, with a log P_{ow} of -0.45, would accumulate in fat. The Meeting decided not to estimate maximum residue levels for animal tissues on the basis of this study.

Residues in poultry tissues and eggs are estimated using the data from the poultry metabolism study in which the dose rate was 100 ppm and the highest and mean residues in tissues and eggs were determined.

Estimation of residues in poultry tissues and eggs

	Feed level	Residues	Feed level	Residues (mg/kg) in

	(ppm) for egg residues	(mg/kg) in egg	(ppm) for tissue residues	Muscle	Liver	Fat
Maximum residue level broiler or layer poultry						
Feeding study ^a	100	0.15	100	0.42	1.1	0.11
Dietary burden and residue estimate	5.4	0.008	5.4	0.023	0.059	0.006
STMR broiler or layer poultry						
Feeding study ^b	100	0.15	100	0.42	1.1	0.11
Dietary burden and residue estimate	0.17	0.0003	0.17	0.0007	0.002	0.0002

^a Highest residue for tissues and mean residue for egg

^b Mean residues for tissue and egg

The Meeting noted that the LOQ of the analytical method was 0.01 mg/kg, and agreed to estimate maximum residue level of 0.03 mg/kg for poultry meat (fat) and estimate maximum residue level of 0.01* for eggs and estimated a maximum residue level of 0.07 mg/kg for poultry edible offal. The Meeting estimated STMRs of 0 mg/kg for poultry meat (fat), edible offal and for eggs.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue concentrations listed below are suitable for establishing MRLs and for assessing IEDIs and/or IESTIs.

Definition of the residue (for compliance with the MRL and for estimation of dietary intake for animal and plant commodities): *bentazone*.

CCN	Commodity	MRL, mg/kg		STMR or STMR-P, mg/kg	highest residue mg/kg
		new	previous		
AL 1021	Alfalfa fodder	0.5	—	0.09	0.23
GC 0640	Barley	W	0.1		
AS 0640	Barley straw and fodder, dry	0.3	—	0.04	0.14
VD 0071	Beans, dry	0.04	0.05*	0.02	—
VP 0061	Beans, except broad bean and soya beans (green pods and immature seeds)	0.01*	—	0.01	
VP 062	Beans, shelled (succulent = immature seeds)	0.01*		0.01	
VD 0526	Common bean (pods and/or immature seeds)	W	0.2		
GC 0080	Cereal grains	0.01*		0.01	—
PE 0112	Egg	0.01*	0.05*—	0	—
VD 0561	Field pea (dry)	W	1		
VP 0528	Garden pea (young pods)(= succulent, immature seeds)	W	0.2		
AS 0162	Hay of fodder (dry) of grass	2	—	0.215	1.16

CCN	Commodity	MRL, mg/kg		STMR or STMR-P, mg/kg	highest residue mg/kg
		new	previous		
HH 0720	Herbs except hops, dry	0.1	—	0.0435	—
VP 0534	Lima bean (young pods and /or immature beans)	W	0.05		
SO 0693	Linseed	0.02*	0.1	0.02	—
GC 0645	Maize	W	0.2		
AS 0645	Maize straw and fodder, dry	0.4	0.2	0.02	0.24
MM 0095	Meat (from mammals other than marine mammals)	W	0.05*-		
ML 0106	Milks	0.01*	0.05*	0	—
AS	Millet straw and fodder, dry	0.3	0.2	0.04	0.14
GC 0647	Oats	W	0.1		
AF 0647	Oat straw and fodder, dry	0.3	0.1	0.04	0.14
VA 0385	Onion, bulb	0.04	0.1	0.01	—
SO 0697	Peanut	0.05*	0.05	0	—
VP 0063	Pea (pods and succulent = immature seeds)	1.5		0.05	—
VR 0589	Potato	0.1	0.1	0.01	—
PM 0110	Poultry meat (fat)	0.03	—	0	—
PO 0110	Poultry, Edible offal of	0.07	—	0	—
GC 0649	Rice	W	0.1		
GC 0650	Rye	W	0.1		
AF 0650	Rye straw and fodder, dry	0.3	—	0.04	0.14
GC 0651	Sorghum	W	0.1		
VD 0541	Soy bean, dry	0.01*	0.1	0.01	—
VA 0389	Spring onion	0.08	—	0.01	—
VO 0447	Sweet corn (corn-on-the-cob)	0.01*	—	0.01	—
AS 0653	Triticale straw and fodder, dry	0.3	—	0.04	0.14
GC 0654	Wheat	W	0.1		
AF 0654	Wheat straw and fodder, dry	0.3	—	0.04	0.14

Animal commodities and processed foods for which no maximum residue levels were recommended

CCN		Commodity	STMR or STMR-P (mg/kg)	highest residue (mg/kg)
AF	1020	Alfalfa forage (green)	0.03	0.07
AF		Pea vines	0.22	13.1
AF		Grass, forage	0.17	0.22
AF		Bean forage (green)	0.01	0.02

CCN		Commodity	STMR or STMR-P (mg/kg)	highest residue (mg/kg)
		Rice hulls	0.089	
CM	1206	Rice bran	0.0037	

DIETARY RISK ASSESSMENT

Long term intake

The evaluation of bentazone resulted in recommendations for MRLs and STMR values for raw and processed commodities. Data on consumption were available for 17 food commodities and were used to calculate dietary intake. The results are shown in Annex 3 of the 2013 Report.

The International Estimated Daily Intakes (IEDIs) of bentazone, based on the STMRs estimated, were 0% of the maximum ADI of 0.09 mg/kg bw for the thirteen GEMS/Food cluster diets. The Meeting concluded that the long-term intake of residues of bentazone resulting from its uses that have been considered by JMPR is unlikely present a public health concern.

Short-term intake

The 2012 Meeting decided that an ARfD for bentazone is unnecessary and concluded that the short-term intake of residues resulting from the use of bentazone is unlikely to present a public health

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1992/12126	Anonymous	1993	Bentazone: Residus de produits phytosanitaires donnees sur l'essai H 826/92/312 facteur 2—Residus sorgho. INRA—Institut National de la Recherche Agronomique, Montfavet, France. 1992/12126, Not GLP; Unpublished.
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1976/10557	Anonymous	1977	Bentazone: Pesticide residue analysis—BAS 351 07 H (Basagran): Residues cucumber. BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed. Rep. 1976/10557, Not GLP, studies were conducted prior to the implementation of GLP but are scientifically valid; Unpublished.
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1977/10275	Anonymous	1977	Bentazone: Pesticide residue analysis—Sweet corn. BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed. Rep. 1977/10275, Not GLP, studies were conducted prior to the implementation of GLP but are scientifically valid; Unpublished.
1977/10274	Anonymous	1977	Bentazone: Pesticide residue analysis—Sweet corn. BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed. Rep. 1977/10274, Not GLP, studies were conducted prior to the implementation of GLP but are scientifically valid; Unpublished.
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1975/5059	Anonymous	1976	Bentazone: Determination of Bentazon and 6- and 8-hydroxy Bentazon in peanuts from Bethel, North Carolina. Cannon Laboratories Inc., Reading PA, United States of America. 1975/5059, Not GLP, studies were conducted prior to the implementation of GLP but are scientifically valid; Unpublished.

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2008/1055036	Oxspring, S	2008	Bentazone: Final report amendment number 1: Study on the residue behaviour of Bentazone in corn (maize) and sweet corn after treatment with BAS 351 40 H under field conditions in Northern and Southern Europe during 2007. Agrisearch UK Ltd., Melbourne Derbyshire DE73 8AG, United Kingdom. 2008/1055036, GLP; Unpublished.
2011/1059497	Oxspring, S	2011	Bentazone: Study on the behaviour of Bentazone in wheat after treatment with BAS 351 32 H in Northern Europe during 2010. Eurofins Agrosience Services, Melbourne Derbyshire DE73 8AG, United Kingdom. 2011/1059497, GLP; Unpublished.
2009/1091211	Penning, H	2009	Bentazone: Validation of analytical method L0136/01 for the LC-MS/MS determination of BAS 351 H (Bentazon) and its metabolite BH 351-N-Me (Reg.No. 79520) in soil and sediment. BASF SE, Limburgerhof, Germany Fed.Rep. 2009/1091211, GLP; Unpublished.
2009/1076476	Penning, H	2009	Bentazone: Validation of analytical method L0141/01 for the LC-MS/MS determination of BAS 351 H (Bentazon) in surface water and groundwater. BASF SE, Limburgerhof, Germany Fed.Rep. 2009/1076476, GLP; Unpublished.
2010/1062115	Rabe, U & Kloeppner, U	2011	Metabolism of BAS 351 H in wheat. BASF SE, Limburgerhof, Germany Fed.Rep. 2010/1062115, GLP; Unpublished.
2010/1062115	Rabe, U & Kloeppner, U	2011	Bentazone: Metabolism of BAS 351 H in wheat. BASF SE, Limburgerhof, Germany Fed.Rep. 2010/1062115, GLP; Unpublished.
2010/1143715	Radzom, M <i>et al.</i>	2011	Bentazone: Confined rotational crop study with BAS 351 H. BASF SE, Limburgerhof, Germany Fed.Rep. 2010/1143715, GLP; Unpublished.
2005/1034455	Reichert, N	2006	Bentazone: Study on the residue behaviour of Bentazone and Terbutylazine in corn after treatment with BAS 600 00 H under field conditions in Germany and the Netherlands, 2005. SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep. 2005/1034455, GLP; Unpublished.
2006/1024264	Reichert, N	2006	Bentazone: 1 Amendment: Study on the residue behaviour of Bentazone and Terbutylazine in corn after treatment with BAS 600 00 H under field

Code	Author	Year	Title, Institute, Report reference
			conditions in Germany and the Netherlands, 2005. SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep. 2006/1024264, GLP; Unpublished.
1976/10602	Resnick, H & Adato, I	1976	Bentzone: Residues of Basagran in peanuts. Ministry of Agriculture, Bet-Dagan, Israel. 1976/10602, No GLP, studies were conducted prior to the implementation of GLP but are scientifically valid; Unpublished.
1995/5159	Riley, ME <i>et al.</i>	1995	Bentazone: The magnitude of Bentazon residues in green peas. BASF Corp., Research Triangle Park NC, United States of America. 1995/5159, GLP; Unpublished.
2002/1008779	Sasturain, J <i>et al.</i>	2002	Bentazone: Investigation of the stability of residues of Bentazone and its metabolites 6-OH-Bentazone and 8-OH-Bentazone as glucoside derivatives in plant matrices under normal storage conditions. BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed. Rep. 2002/1008779, GLP; Unpublished.
2010/1164276	Schroth, E & Martin, T	2010	Bentazone: Study on the residue behavior of BAS 351 H (Bentazone) in bulb onions after the application of BAS 351 45 H under field conditions in France (South), Greece, Italy and Spain, 2009. Agrologia SL, Utrera, Spain. 2010/1164276, GLP; Unpublished.
2010/1164274	Schroth, E & Martin, T	2010	Bentazone: Study on the residue behavior of BAS 351 H (Bentazone) in spring onion after the application of BAS 351 45 H under field conditions in Germany, Netherlands, Greece and Spain, 2009. Agrologia SL, Utrera, Spain. 2010/1164274, GLP; Unpublished.
2009/1123296	Schroth, E & Martin, T	2010	Bentazone: Study on the residue behavior of BAS 351 H (Bentazone) in bean after the application of BAS 351 45 H under field conditions in Germany, Netherlands, Greece, France (South), Italy and Spain, 2009. Agrologia SL, Utrera, Spain. 2009/1123296, GLP; Unpublished.
2011/1059498	Schroth, E & Martin, T	2011	Bentazone: Study on the residue behavior of BAS 351 H (Bentazone) in broad bean (<i>Vicia faba</i>) after the application of BAS 351 45 H under field conditions in France (South) and Spain, 2009–2010. Agrologia SL, Utrera, Spain. 2011/1059498, GLP; Unpublished.
2010/1144246	Schroth, E & Martin, T	2010	Bentazone: Study on the residue behavior of BAS 351 H (Bentazone) in potato after the application of BAS 351 45 H under field conditions in France (South), Greece, Italy and Spain, 2009. Agrologia SL, Utrera, Spain.. 2010/1144246, GLP; Unpublished.
2010/1164275	Schroth, E & Martin, T	2010	Bentazone: Study on the residue behavior of BAS 351 H (Bentazone) in soya beans/soya bean after the application of BAS 351 45 H under field conditions in Germany, Greece, France (South), Italy and Spain, 2009. Agrologia SL, Utrera, Spain. 2010/1164275, GLP; Unpublished.
2009/1024806	Schulz, H	2009	Bentazone: Study on the residue behaviour of Bentazone in green beans after treatment with BAS 351 45 H under field conditions in United Kingdom, Northern France, Southern France and Spain, 2008. SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep. 2009/1024806, GLP; Unpublished.
2002/1006296	Schulz, H	2002	Bentazone: Determination of the residues of BAS 351 H in beans following treatment with BAS 351 32 H (Basagran) under field conditions in Southern France and Spain 2000. Institut Fresenius Chemische und Biologische Laboratorien AG, Taunusstein, Germany Fed. Rep. 2002/1006296, GLP; Unpublished.
2001/1000919	Schulz, H	2001	Bentazone: Determination of the residues of Reg.No. 271 272 and Bentazone in maize following treatment with BAS 635 00 H, BAS 351 40 H and BAS 152 00 S under field conditions in France 1999. Institut Fresenius Chemische und Biologische Laboratorien GmbH, Taunusstein, Germany Fed. Rep. 2001/1000919, GLP; Unpublished.
2007/1013926	Schulz, H & Meyer, M	2007	Bentazone: Determination of Bentazone, 6-OH-Bentazone and 8-OH-Bentazone in plant matrices—Independent laboratory validation of the analytical method No. 438/2. SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep. 2007/1013926, GLP; Unpublished.
2007/1013927	Schulz, H & Meyer, M	2007	Bentazone: Determination of Bentazone, 6-OH-Bentazone and 8-OH-Bentazone in animal matrices—Independent laboratory validation of the analytical method. No. 438/2. SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep. 2007/1013927, GLP; Unpublished.
2011/7002318	Singh, M	2011	Bentazone: Aqueous photolysis of [¹⁴ C]-BAS 351 H. BASF Agricultural Research Center, Research Triangle Park NC, United States of America, 2011/7002318, GLP; Unpublished.
1989/5046	Single, YH	1989	Bentazone: Magnitude of the residues of Bentazon and its metabolites in dry peas and pea hay. EN-CAS Analytical Laboratories, Winston-Salem NC, United States of America. 1989/5046, Not GLP; Unpublished.
1989/5045	Single, YH	1989	Magnitude of the residues of Bentazon and its metabolites in soya beans, soya

Code	Author	Year	Title, Institute, Report reference
1992/5123	Single, YH	1992	bean seed, forage, hay, and fodder. EN-CAS Analytical Laboratories, Winston-Salem NC, United States of America. 1989/5045, Not GLP; Unpublished. Bentazone: Magnitude of the residue of Bentazon, the active ingredient in Basagran herbicide, and its metabolites in flax seed and straw. BASF Corp. Agricultural Products Center, Research Triangle Park NC, United States of America. 1992/5123, GLP; Unpublished.
1992/5124	Single, YH & Zehr, RD	1992	Bentazone: Magnitude of the residue of Bentazon (BAS 351 H), the active ingredient in Basagran herbicide, and its metabolites in processed flax seed. BASF Corp., Research Triangle Park NC, United States of America. 1992/5124, Not GLP, Unpublished.
2002/1011918	Smelt, JH	2003	Bentazone: Laboratory studies on the degradation rates of Bentazone in Dutch soil profiles. BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed.Rep. 2002/1011918, GLP; Unpublished.
2010/1057318	Staudenmaier, H & Kuhnke, G	2010	Bentazone: Aerobic soil metabolism of [¹⁴ C] Bentazone. BASF SE, Limburgerhof, Germany Fed.Rep. 2010/1057318, GLP; Unpublished.
1992/5169	Stewart, J	1992	Bentazone: Magnitude of the residues of Bentazon and its metabolites in processing fractions of soya beans, soya bean seed following treatment with Basagran herbicide. BASF Corp. Agricultural Products Center, Research Triangle Park NC, United States of America. 1992/5169, GLP; Unpublished.
1992/5168	Stewart, J	1992	Bentazone: Magnitude of the residues of Bentazon and its metabolites in processing fractions of field corn grain following treatment with Basagran herbicide. BASF Corp. Agricultural Products Center, Research Triangle Park NC, United States of America. 1992/5168, GLP; Unpublished.
1992/5169	Stewart, J	1992	Bentazone: Magnitude of the residues of Bentazon and its metabolites in processing fractions of soya beans, soya bean seed following treatment with Basagran herbicide. BASF Corp. Agricultural Products Center, Research Triangle Park NC, United States of America. 1992/5169, GLP; Unpublished.
1992/5168	Stewart, J	1992	Bentazone: Magnitude of the residues of Bentazon and its metabolites in processing fractions of field corn grain following treatment with Basagran herbicide. BASF Corp. Agricultural Products Center, Research Triangle Park NC, United States of America. 1992/5168, GLP; Unpublished.
1992/5170	Stewart, J.	1992	Bentazone: Magnitude of the residues of Bentazon and its metabolites in processing fractions of rice grain following treatment with Basagran herbicide. BASF Corp. Agricultural Products Center, Research Triangle Park NC, United States of America. 1992/5170, GLP; Unpublished.
2000/1014883	Stroemel, C <i>et al.</i>	2000	Bentazone: Study on the residue behavior of Bentazone in beans (PHSVN) after treatment with BAS 351 32 H under field conditions in Germany, 1999. Agro-Check, Lentzke, Germany Fed. Rep. 2000/1014883, GLP; Unpublished.
1986/10849	Tianxi, L	1986	Bentazone: Basagran (Bentazon)—Residue analysis trials in rice. China National Rice Research Institute, Hangzhou, China. 1986/10849, Not GLP, studies were conducted prior to the implementation of GLP but are scientifically valid; Unpublished.
1986/10850	Tianxi, L <i>et al.</i>	1986	Bentazone: Pesticide residue analysis—Residues rice. China National Rice Research Institute, Hangzhou, China. 1986/10850, Not GLP, studies were conducted prior to the implementation of GLP but are scientifically valid; Unpublished.
1975/5057	Tiller, H & Thompson, J	1976	Bentazone: Determination of Bentazon (BAS 351 H) and 6- and 8-hydroxy Bentazon residues in peanut forage, hay, nuts, hulls, nut plus hull samples from Sumter, South Carolina. Cannon Laboratories Inc., Reading PA, United States of America. 1975/5057, Not GLP, studies were conducted prior to the implementation of GLP but are scientifically valid; Unpublished.
2011/1000621	Tornisielo, A & Sacchi, RR	2011	Bentazone: Rate of degradation of BAS 351 H in European soils under aerobic conditions. BASF SA, Guaratingueta, Brazil. 2011/1000621, GLP; Unpublished.
1994/11115	Tuerk, W	1994	Bentazone: Determination of the appearance, the melting point and thermal conversions of Bentazone (Reg.No. 051 929) (PAI). BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed. Rep. 1994/11115, GLP; Unpublished.
1994/11193	Tuerk, W	1994	Bentazone: Determination of the odour of Bentazone (Reg.No. 051 929) (PAI). BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed. Rep. 1994/11193, GLP; Unpublished.
1994/11112	Tuerk, W	1994	Bentazone: Spectra of Bentazone Reg.No. 051 929 (PAI). BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed. Rep. 1994/11112, GLP; Unpublished.
2002/1008886	van de Veen, JR	2003	Bentazone: Kinetic evaluation of the degradation rates of Bentazone in 5 soil profiles. BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany

Code	Author	Year	Title, Institute, Report reference
2000/5188	Versoi, PL & Abdel-Baky, S	2000	Fed.Rep. 2002/1008886, Not GLP; Unpublished. Bentazone: The magnitude of Bentazon residues in low linoleic acid flax. BASF Corp. Agricultural Products Center, Research Triangle Park NC, United States of America. 2000/5188, GLP; Unpublished.

BIXAFEN (262)

First draft was prepared by Mr Christian Sieke, the Federal Institute for Risk Assessment, Berlin,, Germany

EXPLANATION

Bixafen (ISO common name) is a pyrazole-carboxamide fungicide used to control diseases on rape plants and cereals. Bixafen inhibits fungal respiration by binding to mitochondrial respiratory complex II. It was considered for the first time by the 2013 JMPR for toxicology and residues.

IDENTITY

ISO common name Bixafen

Chemical name

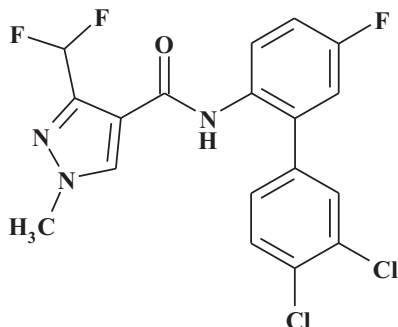
IUPAC N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide

CA 1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluoro[1,1'-biphenyl]-2-yl)-3-(difluoromethyl)-1-methyl-

CIPAC No. 819

CAS No. 581809-46-3

Structural formula



Molecular formula $C_{18}H_{12}Cl_2F_3N_3O$

Molecular mass 414.21 g/mol

Specifications

Specifications for bixafen are not yet developed by FAO.

PHYSICAL AND CHEMICAL PROPERTIES

Property	Results	Method (test material)	Reference
Melting point	The melting point of pure bixafen (purity 98.9%) at atmospheric pressure is 146.6 °C The melting point of bixafen technical (purity 95.8%) at atmospheric pressure is 142.9 °C	EC A.1, OECD 102 batch 1 + batch 2	Smeykal, H 2007, BIXAFEN_001 & Smeykal, H 2007, BIXAFEN_002

Property	Results	Method (test material)	Reference
Boiling point & temperature of decomposition	No boiling before decomposition at approx. 250 °C observed	EC A.2, OECD 103 + OECD 113 batch 1 + batch 2	Smeykal, H 2007, BIXAFEN_001 & Smeykal, H 2007, BIXAFEN_002
Relative density	Bixafen, pure (purity 98.9%): $D_4^{20} = 1.43$ Bixafen, technical (purity 95.8%): $D_4^{20} = 1.51$	EC A.3, OECD 109 batch 1 + batch 2	Bogdoll, B and Strunk, B 2007, BIXAFEN_003
Vapour pressure	Extrapolated: 4.6×10^{-8} Pa at 20 °C 1.1×10^{-7} Pa at 25 °C 5.9×10^{-6} Pa at 50 °C	EC A.4, OECD 104 batch 3 (purity 98.8%)	Smeykal, H 2006, BIXAFEN_004
Henry's Law Coefficient	Henry's law constant at 20 °C (calculated): 3.89×10^{-5} Pa m ³ mol ⁻¹	Calculation	Bogdoll, B and Lemke, G 2007, BIXAFEN_005
Physical state, colour	Active substance, pure: no noticeable odour Active substance as manufactured: no noticeable odour	OPPTS 830.6302 OPPTS 830.6303 batch 1 (purity 98.9%) + batch 2 (purity 95.8%)	Bogdoll, B and Strunk, B 2007, BIXAFEN_006
Odour	Active substance, pure: white powder Active substance as manufactured: light brown powder		
Solubility in water including effect of pH	0.49 mg/L at 20 °C Investigation on different pH is not necessary, because bixafen has no acidic or basic properties in the range of pH 1 to pH 12.	EC A.6, OECD 105 batch 4 (purity 99.2%)	Jungheim, R, 2005, BIXAFEN_007 & Bogdoll, B 2008, BIXAFEN_008
Solubility in organic solvents	[g/L at 20 °C] n-heptane 0.056 dichloromethane 102 methanol 32 toluene 16 acetone > 250 ethylacetate 82 dimethylsulfoxide > 250	CIPAC MT 157 based on EC A.6, OECD 105 batch 1 (purity 98.9%) + batch 3 (purity 98.8%)	Bogdoll, B and Eyrich, U, 2007, BIXAFEN_009
Dissociation constant	No dissociation constant of bixafen was found in the pH range of pH 1–pH 12. This result is in line with the chemical structure of bixafen which does not contain an acidic or a basic group.	OECD 112 batch 3 (purity 98.8%)	Bogdoll, B and Wiche, A 2007, BIXAFEN_010
Partition coefficient n-octanol / water	Determination of the partition coefficient of Bixafen in 1-octanol / water (HPLC column 40 °C) P _{ow} 2046	EC A.8, OECD 117 (HPLC-method)	Bogdoll, B and Lemke, G 2005, BIXAFEN_011

Property	Results	Method (test material)	Reference
	log P _{ow} 3.3	batch 3 (purity 98.8%)	
Hydrolysis rate	Pyrazole-[¹⁴ C] Bixafen had shown no hydrolytic breakdown at pH 4, 7 and 9 over 5 days (120 hours) at 50 °C.	EPA 161-1, OECD 111, EC C.7 batch 5 (purity 99.2%)	Oddy, AM 2005, BIXAFEN_012
Photochemical degradation	In sterile aqueous buffer solution at 25 °C under artificial sunlight exposure ($\lambda > 290$ nm) the calculated experimental half-life was 82 days of intensive continuous irradiation (791 W/m ² in the wavelength range 300–800 nm).	EPA 161-2 batch 6	Muehmel, T and Fliege, R 2006, BIXAFEN_013

Hydrolysis of bixafen

A hydrolysis study was carried out by Oddy, AM (2005, BIXAFEN_012). Pyrazole-¹⁴C-bixafen at concentrations of 0.25 mg/L was investigated in aqueous buffer solutions at three pH values at 50 °C for up to 120 h.

Duplicate samples were analysed after 2.4, 48 and 120 hours by HPLC-LSC and TLC for confirmation purposes.

A summary of the results is presented in the following table:

Table 1 Summary of radioactive residues in sterile buffer solutions fortified with [¹⁴C] pyrazole labelled bixafen at a concentration of 0.25 mg/L

Time (hours)	pH 4		pH 7		pH 9	
	% TRR recovered	% recovered as bixafen in mg eq/kg	% TRR recovered	TRR recovered as bixafen in mg eq/kg	% TRR recovered	TRR recovered as bixafen in mg eq/kg
0	97 101	100 100	101.49	100 100	103 103	100 100
2.4	96 93	100 100	97 96	100 100	93 96	100 100
48	100 95	100 100	99 90	100 100	99 101	100 100
120	97 94	100 100	99 93	100 100	95 92	100 100

The hydrolysis of bixafen under processing conditions is described under fate of residues in storage and processing.

Formulations

Bixafen is registered as the following EC formulations:

Table 2 Formulations registered containing bixafen as active ingredient

Formulation	Content of active ingredients
EC 125	125 g/L bixafen
EC 190	40 g/L bixafen 50 g/L fluoxastrobin 100 g/L prothioconazole

Formulation	Content of active ingredients
EC 216	50 g/L bixafen 166 g/L tebuconazole
EC 225	75 g/L bixafen 150 g/L prothioconazole
EC 235	75 g/L bixafen 160 g/L prothioconazole
EC 260	60 g/L bixafen 200 g/L prothioconazole
EC 275	75 g/L bixafen 100 g/L prothioconazole 100 g/L tebuconazole
EC 275	75 g/L bixafen 110 g/L prothioconazole 90 g/L tebuconazole
EC 285	75 g/L bixafen 110 g/L prothioconazole 100 g/L tebuconazole
EC 400	50 g/L bixafen 250 g/L spiroxamine 100 g/L prothioconazole

METABOLISM AND ENVIRONMENTAL FATE

Metabolism studies were conducted using [^{14}C -5-pyrazole]-bixafen (pyrazole-label) and [^{14}C -dichlorophenyl-UL]-bixafen (dichlorophenyl-label). The position of the label for both substances is presented in the following figures:

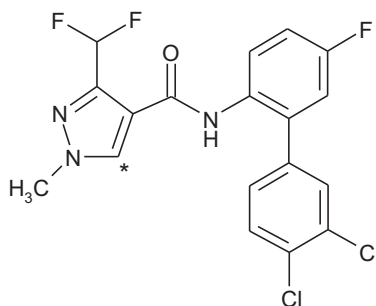


Figure 1 [pyrazole-5- ^{14}C]-bixafen

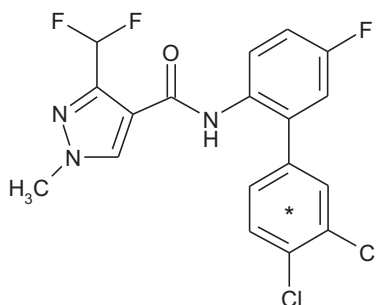
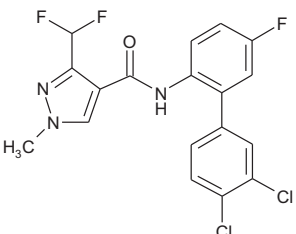
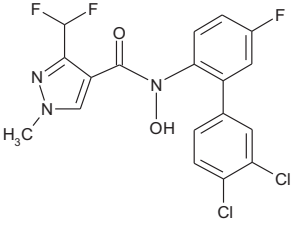
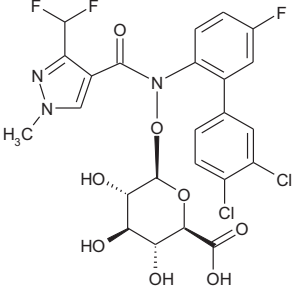
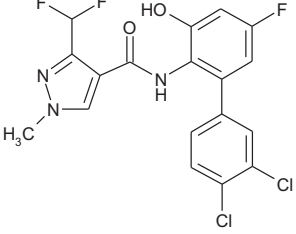


Figure 2 [dichlorophenyl-UL- ^{14}C] bixafen

Chemical names, structures and code names of metabolites and degradation products of bixafen are shown in Table 3.

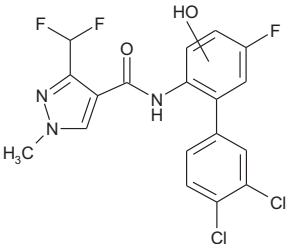
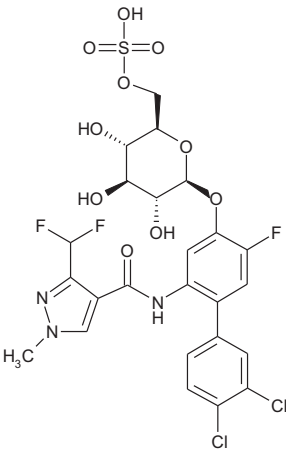
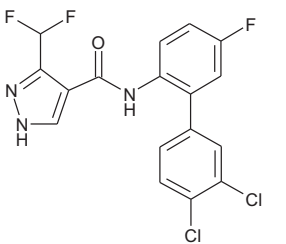
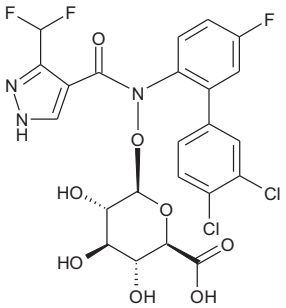
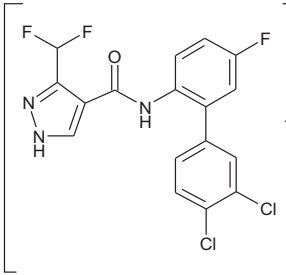
Table 3 Known metabolites of bixafen

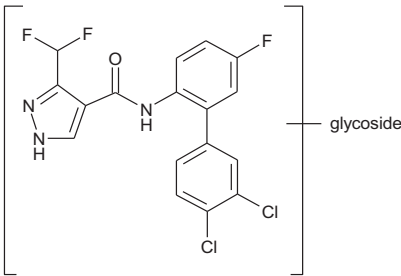
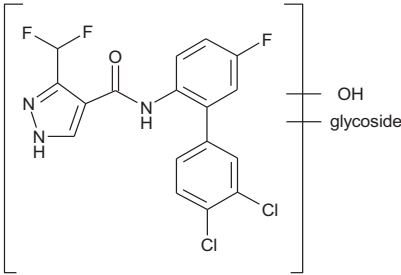
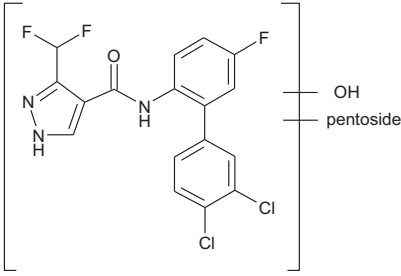
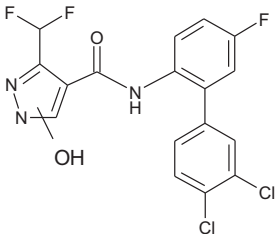
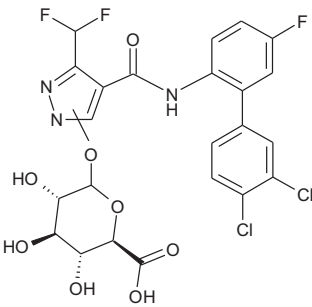
Code Names	Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass	Structure	Where found
bixafen (parent substance) BYF 00587 (“ai”)	N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) 1H-Pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluoro[1,1'-biphenyl]-2-yl)-3-(difluoromethyl)-1-methyl- (CAS) [CAS No.: 581809-46-3] $C_{18}H_{12}Cl_2F_3N_3O$ 414.2 g/mol		All matrices
M01 BYF 00587-N-hydroxy	N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-N-hydroxy-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) $C_{18}H_{12}Cl_2F_3N_3O_2$ 430.2 g/mol		Rat
M02 BYF 00587-N-O-glucuronide	tbd1-O-((3',4'-dichloro-5-fluorobiphenyl-2-yl){[3-(difluoromethyl)-1-methyl-1H-pyrazol-4-yl]carbonyl}amino)-beta-L-glucopyranuronic acid (IUPAC) $C_{24}H_{20}Cl_2F_3N_3O_8$ 606.3 g/mol		Rat
M03 BYF 00587-3-hydroxyphenyl	N-(3',4'-dichloro-5-fluoro-3-hydroxybiphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) $C_{18}H_{12}Cl_2F_3N_3O_2$ 430.2 g/mol		Rat

Code Names	Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass	Structure	Where found
M04 BYF 00587-3-hydroxyphenyl-glucuronide	3',4'-dichloro-2-({[3-(difluoromethyl)-1-methyl-1H-pyrazol-4-yl]carbonyl}amino)-5-fluorobiphenyl-3-yl beta-L-glucopyranosiduronic acid (IUPAC) $C_{24}H_{20}Cl_2F_3N_3O_8$ 606.3 g/mol		Rat
M05 BYF 00587-4-hydroxyphenyl	N-(3',4'-dichloro-5-fluoro-4-hydroxybiphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) $C_{18}H_{12}Cl_2F_3N_3O_2$ 430.2 g/mol		Rat
M06 BYF 00587-4-hydroxyphenyl-glucuronide	3',4'-dichloro-2-({[3-(difluoromethyl)-1-methyl-1H-pyrazol-4-yl]carbonyl}amino)-5-fluorobiphenyl-4-yl beta-L-glucopyranosiduronic acid (IUPAC) $C_{24}H_{20}Cl_2F_3N_3O_8$ 606.3 g/mol		Rat
M07 BYF 00587-6-hydroxyphenyl (&BYF 00587-5-hydroxyphenyl due to F/OH substitution)	N-(3',4'-dichloro-5-fluoro-6-hydroxybiphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) $C_{18}H_{12}Cl_2F_3N_3O_2$ 430.2 g/mol		Rat (postulated intermediate)
M08 BYF 00587-6-hydroxyphenyl-glucuronide	3',4'-dichloro-6-({[3-(difluoromethyl)-1-methyl-1H-pyrazol-4-yl]carbonyl}amino)-3-fluorobiphenyl-2-yl beta-L-glucopyranosiduronic acid (IUPAC) $C_{24}H_{20}Cl_2F_3N_3O_8$ 606.3 g/mol		Rat

Code Names	Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass	Structure	Where found
M09 BYF 00587-4-fluoro-5-hydroxyphenyl	N-(3',4'-dichloro-4-fluoro-5-hydroxybiphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) C ₁₈ H ₁₂ Cl ₂ F ₃ N ₃ O ₂ 430.2 g/mol		Rat
M10 BYF 00587-4-fluoro-5-hydroxyphenyl-glucuronide	3',4'-dichloro-6-({[3-(difluoromethyl)-1-methyl-1H-pyrazol-4-yl]carbonyl}amino)-4-fluorobiphenyl-3-yl beta-L-glucopyranosiduronic acid (IUPAC) C ₂₄ H ₂₀ Cl ₂ F ₃ N ₃ O ₈ 606.3 g/mol		Rat
M11 BYF 00587-6-fluoro-5-hydroxyphenyl	N-(3',4'-dichloro-6-fluoro-5-hydroxybiphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) C ₁₈ H ₁₂ Cl ₂ F ₃ N ₃ O ₂ 430.2 g/mol		Rat
M12 BYF 00587-5-hydroxyphenyl	N-(3',4'-dichloro-5-hydroxybiphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) C ₁₈ H ₁₃ Cl ₂ F ₂ N ₃ O ₂ 412.2 g/mol		Rat
M13 BYF 00587-5-hydroxyphenyl-6-glutathionyl	gamma-glutamyl-S-[3',4'-dichloro-6-({[3-(difluoromethyl)-1-methyl-1H-pyrazol-4-yl]carbonyl}amino)-3-hydroxybiphenyl-2-yl]cysteinylglycine (IUPAC) C ₂₈ H ₂₈ Cl ₂ F ₂ N ₆ O ₈ S 717.5 g/mol		Goat, hen (postulated intermediate)

Code Names	Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass	Structure	Where found
M14 BYF 00587-5-hydroxyphenyl-6-cysteiny	S-[3',4'-dichloro-6-({[3-(difluoromethyl)-1-methyl-1H-pyrazol-4-yl]carbonyl}amino)-3-hydroxybiphenyl-2-yl]cysteine (IUPAC) C ₂₁ H ₁₈ Cl ₂ F ₂ N ₄ O ₄ S 531.4 g/mol		Goat, hen, rat
M15 BYF 00587-5-hydroxyphenyl-6-thiol-acetaldehyde	N-{3',4'-dichloro-5-hydroxy-6-[(2-oxoethyl)thio]biphenyl-2-yl}-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) C ₂₀ H ₁₅ Cl ₂ F ₂ N ₃ O ₃ S 486.3 g/mol		Rat
M16 BYF 00587-5-hydroxyphenyl-6-(methylsulfinyl)	N-[3',4'-dichloro-5-hydroxy-6-(methylsulfinyl)biphenyl-2-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) C ₁₉ H ₁₅ Cl ₂ F ₂ N ₃ O ₃ S 474.3 g/mol		Rat
M17 BYF 00587-5-hydroxyphenyl-6-(methylthio)	N-[3',4'-dichloro-5-hydroxy-6-(methylthio)biphenyl-2-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC) C ₁₉ H ₁₅ Cl ₂ F ₂ N ₃ O ₂ S 458.3 g/mol		Rat
M18 BYF 00587-5-hydroxyphenyl-6-(methylthio)-glucuronide	3',4'-dichloro-6-({[3-(difluoromethyl)-1-methyl-1H-pyrazol-4-yl]carbonyl}amino)-2-(methylthio)biphenyl-3-yl beta-L-glucopyranosiduronic acid (IUPAC) C ₂₅ H ₂₃ Cl ₂ F ₂ N ₃ O ₈ S 634.4 g/mol		Hen

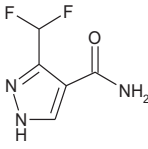
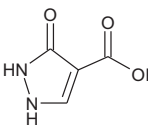
Code Names	Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass	Structure	Where found
M19 BYF 00587-hydroxy	not possible—position of hydroxy group not specified $C_{18}H_{12}Cl_2F_3N_3O_2$ 430.2 g/mol		Rotational crops (postulated intermediate)
M20 BYF 00587-hydroxy-glycoside-sulfate	not possible—position of hydroxy group not specified $C_{24}H_{22}Cl_2F_3N_3O_{10}S$ 672.4 g/mol	 or isomer	Rotational crops (Swiss chard)
M21 Bixafen-desmethyl BYF 00587-desmethyl	N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1H-pyrazole-4-carboxamide (IUPAC) $C_{17}H_{10}Cl_2F_3N_3O$ 400.2 g/mol		Goat, hen, rat, rotational crops, soya bean, wheat, soil
M22 BYF 00587-desmethyl-N-O-glucuronide	1-O-((3',4'-dichloro-5-fluorobiphenyl-2-yl){[3-(difluoromethyl)-1H-pyrazol-4-yl]carbonyl}amino)-beta-L-glucopyranuronic acid (IUPAC) $C_{23}H_{18}Cl_2F_3N_3O_8$ 592.3 g/mol		Rat
M23 BYF 00587-desmethyl-N-glucuronide (isomer 1 and isomer 2)	structure not specified $C_{23}H_{18}Cl_2F_3N_3O_7$ 576.3 g/mol	 glucuronide	Goat, rat

Code Names	Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass	Structure	Where found
M24 BYF 00587-desmethyl-glycoside	structure not specified $C_{23}H_{20}Cl_2F_3N_3O_6$ 562.3 g/mol		Hen
M25 BYF 00587-desmethyl-hydroxy-glycoside	structure not specified $C_{23}H_{20}Cl_2F_3N_3O_7$ 578.3 g/mol		Hen
M26 BYF 00587-desmethyl-hydroxy-pentoside	structure not specified $C_{22}H_{18}Cl_2F_3N_3O_6$ 548.3 g/mol		Hen
M27 BYF 00587-desmethyl-hydroxypyrazole	structure not specified $C_{17}H_{10}Cl_2F_3N_3O_2$ 416.2 g/mol		Hen, rat
M28 BYF 00587-desmethyl-hydroxypyrazole-glucuronide	structure not specified $C_{23}H_{18}Cl_2F_3N_3O_8$ 592.3 g/mol		Rat

Code Names	Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass	Structure	Where found
M29 BYF 00587- desmethyl-3- hydroxyphenyl	N-(3',4'-dichloro-5-fluoro-3-hydroxybiphenyl-2-yl)-3-(difluoromethyl)-1H-pyrazole-4-carboxamide (IUPAC) C ₁₇ H ₁₀ Cl ₂ F ₃ N ₃ O ₂ 416.2 g/mol		Rat
M30 BYF 00587- desmethyl-4- fluoro-5- hydroxyphenyl	N-(3',4'-dichloro-4-fluoro-5-hydroxybiphenyl-2-yl)-3-(difluoromethyl)-1H-pyrazole-4-carboxamide (IUPAC) C ₁₇ H ₁₀ Cl ₂ F ₃ N ₃ O ₂ 416.2 g/mol		Rat
M31 BYF 00587- desmethyl-6- fluoro-5- hydroxyphenyl	N-(3',4'-dichloro-6-fluoro-5-hydroxybiphenyl-2-yl)-3-(difluoromethyl)-1H-pyrazole-4-carboxamide (IUPAC) C ₁₇ H ₁₀ Cl ₂ F ₃ N ₃ O ₂ 416.2 g/mol		Rat
M32 BYF 00587- desmethyl-5- hydroxyphenyl	N-(3',4'-dichloro-5-hydroxybiphenyl-2-yl)-3-(difluoromethyl)-1H-pyrazole-4-carboxamide (IUPAC) C ₁₇ H ₁₁ Cl ₂ F ₂ N ₃ O ₂ 398.2 g/mol		Rat
M33 BYF 00587- desmethyl-5- hydroxyphenyl-6- (glutathionyl- glutamic acid)	N-(1,3-dicarboxypropyl)-alpha-glutaminyI-S-[3',4'-dichloro-6-({[3-(difluoromethyl)-1H-pyrazol-4-yl]carbonyl}amino)-3-hydroxybiphenyl-2-yl]cysteinylglycine (IUPAC) C ₃₂ H ₃₃ Cl ₂ F ₂ N ₇ O ₁₁ S 832.6 g/mol		Rat

Code Names	Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass	Structure	Where found
M34 BYF 00587-desmethyl-5-hydroxyphenyl-6-glutathionyl	structure not specified $C_{27}H_{26}Cl_2F_2N_6O_9S$ 719.5 g/mol		Rat
M35 BYF 00587-desmethyl-5-hydroxyphenyl-6-glutathionyl	$C_{27}H_{26}Cl_2F_2N_6O_8S$ 703.5 g/mol		Rat
M36 BYF 00587-desmethyl-5-hydroxyphenyl-6-cysteiny-glucuronide	structure not specified $C_{26}H_{24}Cl_2F_2N_4O_{10}S$ 693.5 g/mol		Rat
M37 BYF 00587-desmethyl-5-hydroxyphenyl-6-cysteinyl	S-[3',4'-dichloro-6-({[3-(difluoromethyl)-1H-pyrazol-4-yl]carbonyl}amino)-3-hydroxybiphenyl-2-yl]cysteine (IUPAC) $C_{20}H_{16}Cl_2F_2N_4O_4S$ 517.3 g/mol		Hen, rat
M38 BYF 00587-desmethyl-5-hydroxyphenyl-6-(methylsulfinyl)	N-[3',4'-dichloro-5-hydroxy-6-(methylsulfinyl)biphenyl-2-yl]-3-(difluoromethyl)-1H-pyrazole-4-carboxamide (IUPAC) $C_{18}H_{13}Cl_2F_2N_3O_3S$ 460.3 g/mol		Rat

Code Names	Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass	Structure	Where found
M39 BYF 00587- desmethyl-5- hydroxyphenyl-6- (methylthio)	N-[3',4'-dichloro-5- hydroxy-6- (methylthio)biphenyl-2- yl]-3-(difluoromethyl)-1H- pyrazole-4-carboxamide (IUPAC) C ₁₈ H ₁₃ Cl ₂ F ₂ N ₃ O ₂ S 444.3 g/mol		Rat
M40 BYF 00587- desmethyl-5- hydroxyphenyl- deschloro- (methylthio)	structure not specified C ₁₈ H ₁₄ Cl F ₂ N ₃ O ₂ S 409.8 g/mol		Rat
M41 BYF 00587- desmethyl-6'- hydroxy	N-(4',5'-dichloro-5-fluoro- 2'-hydroxybiphenyl-2-yl)- 3-(difluoromethyl)-1H- pyrazole-4-carboxamide (IUPAC) C ₁₇ H ₁₀ Cl ₂ F ₃ N ₃ O ₂ 416.2 g/mol		Rat
M42 BYF 00587- pyrazole-4- carboxylic acid AE 1954999	3-(difluoromethyl)-1- methyl-1H-pyrazole-4- carboxylic acid (IUPAC) C ₆ H ₆ F ₂ N ₂ O ₂ 176.1 g/mol		Goat, rat, rotational crops, soil
M43 BYF 00587- pyrazole-4- carboxamide	3-(difluoromethyl)-1- methyl-1H-pyrazole-4- carboxamide (IUPAC) C ₆ H ₇ F ₂ N ₃ O 175.1 g/mol		Rat, rotational crops
M44 BYF 00587- desmethyl- pyrazole-4- carboxylic acid (tautomer 1)	3-(difluoromethyl)-1H- pyrazole-4-carboxylic acid (IUPAC) C ₅ H ₄ F ₂ N ₂ O ₂ 162.1 g/mol		Rotational crops, soya bean, soil
M45 BYF 00587- desmethyl- pyrazole-4- carboxylic acid (tautomer 2)	5-(difluoromethyl)-1H- pyrazole-4-carboxylic acid (IUPAC) C ₅ H ₄ F ₂ N ₂ O ₂ 162.1 g/mol		Rotational crops, soya bean,

Code Names	Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass	Structure	Where found
M46 BYF 00587- desmethyl- pyrazole-4- carboxamide	3-(difluoromethyl)-1H-pyrazole-4-carboxamide (IUPAC) C ₅ H ₅ F ₂ N ₃ O 161.1 g/mol		Rat
M47 BYF 00587- pyrazolone-4- carboxylic acid	3-hydroxy-1H-pyrazole-4-carboxylic acid (IUPAC) C ₄ H ₄ N ₂ O ₃ 128.1 g/mol		Rotational crops, soya bean

Animal metabolism

The Meeting received metabolism studies on laboratory animals, poultry and lactating goats using the pyrazole- and the dichlorophenyl-label of bixafen.

The metabolism of bixafen in livestock animals was limited, showing unchanged parent bixafen as main residue in all matrices except liver. Besides the unchanged parent substance the metabolite M21 (bixafen-desmethyl) was found as major residue in all tissues, and represented the main residue in liver following exhaustive extraction involving hydrolysis. The sum of parent and M21 represented more than 50% of the total residue in all samples of animal origin, often more than 80% TRR. The only other major metabolites present at > 10% of the TRR were the two isomers of M23 in goat livers and kidneys.

The most important metabolic reaction was the demethylation of the pyrazole ring resulting in bixafen-desmethyl. Further biochemical reactions included substitution of the fluorine atom by a hydroxy group and an adjacent glutathione conjugation, an unspecified hydroxylation of an aromatic ring and conjugation with various sugar molecules, and hydroxylation of the pyrazole ring.

In general the metabolic pathway of bixafen was comparable between ruminants and hens. All metabolites identified in goats were also found in rats. The metabolites M26, M25 and M18 found in eggs and poultry liver were not directly identified in the rat.

Laboratory animals

Rats

In rats given (dichlorophenyl-U-¹⁴C)-labelled bixafen orally by gavage, absorption was rapid and accounted for at least 83% of the total administered radioactivity after a single low dose (2 mg/kg bw). The maximum plasma concentrations of radioactivity were reached approximately 2–4 and 8 hours after administration of the low and high doses (2 and 50 mg/kg bw), respectively. Radioactivity was widely distributed throughout the body. Elimination of the radioactivity was mainly via faeces (≥ 91%), whereas elimination via urine accounted for 1–3% of the administered dose. In bile duct-cannulated rats, extensive biliary excretion (up to 83%) was demonstrated. Elimination of the radioactivity from the body was rapid, with a half-life in plasma of 8–9 hours and a mean residence time of 13–19 hours (for the low dose). Residues in tissues at 72 hours after a single oral dose as well as after repeated oral dosing accounted for 0.1–3% of the administered radioactivity, with liver and kidneys containing the highest concentrations of residues.

Metabolism of bixafen in rats was extensive, and more than 30 metabolites were identified. The main metabolic routes included demethylation, hydroxylation of the parent and bixafen-desmethyl, and conjugation with glucuronic acid or glutathione. A minor metabolic reaction was the cleavage of the amide bridge of bixafen.

Lactating goats

The kinetic behaviour and the metabolism of [pyrazole-5-¹⁴C]-bixafen was investigated in the lactating goat by Spiegel, K and Koester, J (2007, BIXAFEN_014). One goat (41 kg bw) was dosed orally five times in 24 h intervals with 2.0 mg radiolabelled bixafen per kg body weight per day (equivalent to 34.7 ppm in the diet). The goat was sacrificed about 24 hours after the last dose. Milk, plasma, urine and faeces were collected during the whole dosing period. After sacrifice liver, kidney, muscle and fat were sampled.

Analysis of the total radioactive residues (TRR) was carried out using combustion and liquid scintillation counting (LSC).

Milk pools, muscle and kidney were extracted with acetonitrile/water mixtures. The resulting extracts were degreased by a clean-up step using a C₁₈-SPE cartridge. Milk sugar was removed in a second clean-up step using an XAD-4 cartridge.

Liver was extracted analogously to muscle and kidney but the solids after conventional extraction were additionally subjected to four exhaustive extraction steps at increased temperature with microwave assistance. In the third and fourth step formic acid and hydrochloric acid, respectively were added to the acetonitrile/water mixtures. These extracts were also degreased by a clean-up step using a C₁₈-SPE cartridge in the same way as the conventional extracts.

An aliquot of the fat composite was extracted subsequently with hexane and acetonitrile. The hexane phases were partitioned with acetonitrile and vice versa. The acetonitrile phases were combined, concentrated and analysed.

The radioactivity in all extracts was determined by LSC. Aliquots were concentrated and analysed by radio-HPLC and UV detection (254 nm) using a reversed phase column and an acidic acetonitrile/water gradient. The identification of metabolites was conducted either by comparison with reference substances and/or confirmation by LC-MS/MS.

At the end of the dosing period most of the administered radioactivity was excreted via the urine (5.42% AR) and the faeces (82.088% AR).

The total radioactive residues (TRR) found were highest in liver with 1.178 mg eq/kg, followed by fat (perirenal: 0.318 mg eq/kg, omental: 0.544 mg eq/kg), kidney (0.203 mg eq/kg) and muscle (round muscle: 0.057 mg eq/kg, loin muscle: 0.063 mg eq/kg). In milk the TRR increased from 0.003 mg eq/kg directly after the first administration up to a plateau of 0.153 mg eq/kg after three days. The TRR levels found are summarized in Table 5. The radioactivity in milk and plasma are presented in Tables 5 and 6.

Table 4 TRR in goats milk and tissues after administration of pyrazole-¹⁴C-bixafen at 2.0 mg/kg bw and day (34.7 ppm in the diet)

Matrix	% of total dose administered	TRR [mg eq/kg]
Liver	0.278	1.18
Kidney	0.007	0.203
Round muscle	–	0.057
Loin muscle	–	0.063
Total body muscle ^a	0.17	0.057
Perirenal fat	–	0.318
Omental fat	–	0.544
Total body fat ^a	0.55	0.466
Total in organs and tissues	1.01	–
Milk, 0–120 h	0.28	0.092
Urine, 0–120 h	5.42	2.38
Faeces, 0–120 h	82.08	13.5
Total excreted in milk, urine and faeces	87.78	–
Total Recovery	88.78	–

^a % of total dose assuming 30% of the body weight for total body muscle and 12% for total body fat

Table 5 Time course of total radioactive residues in milk and plasma after administration of pyrazole-¹⁴C-bixafen at 2.0 mg/kg bw and day (34.7 ppm in the diet)

Time after first administration [h]	administration no.	TRR [mg eq/kg] plasma	TRR [mg eq/kg] milk
0.5	1	0.003	–
2		0.039	–
4		0.066	–
6		0.081	–
8		0.081	0.109
24	2	0.065	0.054
32		0.144	0.219
48	3	0.044	0.041
56		0.153	0.205
72	4	0.066	0.055
80		0.144	0.197
96	5	0.042	0.039
104		0.108	0.143
120		0.041	0.040

Samples of tissues and milk were further analysed for the composition of the radioactivity. Extraction rates using acetonitrile/water were generally > 90%, except for liver, which required additional exhaustive extraction including hydrolysis. Parent bixafen was the major residue in milk (73.8% TRR, 0.127 mg eq/kg), muscle (55.8% TRR, 0.032 mg eq/kg), fat (88.5% TRR, 0.413 mg eq/kg) and kidney (44.1% TRR, 0.089 mg eq/kg). In liver bixafen was more strongly degraded being present at levels of 17.6% of the TRR (0.207 mg eq/kg).

Besides the parent compound M21 (bixafen-desmethyl) was a major metabolite in all matrices investigated: 17.6% TRR in milk (0.03 mg eq/kg), 43.2% TRR in muscle (0.025 mg eq/kg), 10.6% TRR in fat (0.05 mg eq/kg) and 37.9% TRR in kidney (0.077 mg eq/kg). In liver, the conventional and exhaustive extraction released a total of 33.6% of the TRR (0.397 mg eq/kg) as bixafen-desmethyl.

The only other major metabolite found was M23 in milk, liver and kidney. The sum of both isomers reached levels of 13.8% of the TRR in liver (isomer 1: 8.6% TRR, 0.102 mg eq/kg; isomer 2: 5.2% TRR, 0.062 mg eq/kg) and of 14.5% of the TRR in kidney (isomer 1: 4.3% TRR, 0.009 mg eq/kg; isomer 2: 10.2% TRR, 0.021 mg eq/kg). In milk M23 was present in lower amounts (isomer 2 only: 1.4% TRR, 0.002 mg eq/kg)

In the following table the extraction rates and the metabolites identified are summarised.

Table 6 Characterisation and identification of compounds in milk and tissues of the lactating goats after administration of pyrazole-¹⁴C-bixafen at 2.0 mg/kg bw and day (34.7 ppm in the diet)

Compound / Fraction	Milk % TRR	mg eq/kg	Muscle % TRR	mg eq/kg	Fat % TRR	mg eq/kg	Liver % TRR	mg eq/kg	Kidney % TRR	mg eq/kg
TRR [mg/kg]		0.172		0.057		0.466		1.178		0.203
Conventional extraction										
Bixafen	73.8	0.127	55.8	0.032	88.5	0.413	17.6	0.207	44.1	0.089
M14	–	–	–	–	–	–	2.2	0.026	–	–
M23	–	–	–	–	–	–	8.6	0.102	4.3	0.009
M23	1.4	0.002	–	–	–	–	5.2	0.062	10.2	0.021
M21 (bixafen-desmethyl)	17.6	0.030	43.2	0.025	10.6	0.050	21.0	0.248	37.9	0.077
Subtotal identified	92.9	0.159	99.0	0.057	99.1	0.462	54.7	0.644	96.5	0.196
Exhaustive extraction										
M42	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	7.8	0.091	n.a.	n.a.
M21 (BYF 00587-desmethyl)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	12.6	0.149	n.a.	n.a.

Compound / Fraction	Milk % TRR	mg eq/kg	Muscle % TRR	mg eq/kg	Fat % TRR	mg eq/kg	Liver % TRR	mg eq/kg	Kidney % TRR	mg eq/kg
Subtotal identified	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	20.4	0.240	n.a.	n.a.
Total identified	92.9	0.159	99.0	0.057	99.1	0.462	75.0	0.884	96.5	0.196
Total characterised by HPLC, but unidentified	—	—	—	—	—	—	23.5	0.277	—	—
Fractions not analysed	6.8	0.012	—	—	—	—	1.1	0.013	—	—
Total extracted	99.7	0.064	99.0	0.057	99.1	0.462	99.6	1.174	96.5	0.196
Not extracted	0.3	0.001	1.0	0.001	0.9	0.004	0.4	0.005	3.5	0.007
Accountability	100.0	0.172	100.0	0.057	100.0	0.466	100.0	1.178	100.0	0.203

n.a. = Not analysed

In a second study by Spiegel, K and Koester, J (2007, BIXAFEN_015) the metabolism of [dichlorophenyl-UL-¹⁴C]-bixafen was investigated in one lactating goat. The goat (39 kg bw) was dosed orally five times in 24 h intervals with 2.0 mg radiolabelled BYF 00587 per kg body weight per day. This amount corresponded to 46.08 ppm in the diet. The goat was sacrificed about 24 hours after the last dose.

Analysis of the total radioactive residues and the extraction of samples collected was conducted as described in the metabolism in goats study using [pyrazole-5-¹⁴C]-bixafen by Spiegel, K and Koester, J (2007, BIXAFEN_014).

From the total dose administered approximated 1.75% of the AR was excreted via the urine and 71.88% via the faeces. The total radioactive residues (TRR) found were highest in liver with 0.737 mg eq/kg, followed by fat (0.611 mg eq/kg), kidney (0.143 mg eq/kg) and muscle (0.047 mg eq/kg). In milk the TRR increased from 0.03 mg eq/kg after the first administration up to a plateau of 0.126 mg eq/kg after four days. The TRR levels found are summarized in Table 7. The radioactivity in milk and plasma are presented in Tables 8 and 9.

Table 7 TRR in goats milk and tissues after administration of dichlorophenyl-¹⁴C-bixafen at 2.0 mg/kg bw and day (46.08 ppm in the diet)

Matrix	% of total dose administered	TRR [mg eq/kg]
Liver	0.166	0.737
Kidney	0.004	0.143
Round muscle	0.13	0.047
Fat (composite sample perirenal and omental)	0.70	0.611
Total in organs and tissues	1.0	—
Milk, 0–120 h	0.09	0.039
Urine, 0–120 h	1.75	0.717
Faeces, 0–120 h	71.88	17.631
Total excreted in milk, urine and faeces	73.72	—
Total Recovery	74.73	—

Table 8 Time course of total radioactive residues in milk and plasma after administration of dichlorophenyl-¹⁴C-bixafen at 2.0 mg/kg bw and day (46.08 ppm in the diet)

Time after first administration [h]	administration no.	TRR [mg eq/kg] plasma	TRR [mg eq/kg] milk
0.25	1	0.001	—
0.5		0.004	—
1		0.015	—
2		0.045	—
3		0.052	—
4		0.042	—
6		0.028	—
8		0.022	0.030

Time after first administration [h]	administration no.	TRR [mg eq/kg] plasma	TRR [mg eq/kg] milk
24	2	0.008	0.009
32		0.030	0.043
48	3	0.008	0.009
56		0.032	0.056
72	4	0.023	0.029
80		0.065	0.126
96	5	0.037	0.050
104		0.048	0.071
120		0.029	0.037

Samples of tissues and milk were further analysed for the composition of the radioactivity. Extraction rates using acetonitrile/water were generally > 90%, except for liver, which required additional exhaustive extraction including hydrolysis. Parent bixafen was the major residue in milk (77.2% TRR, 0.05 mg eq/kg), muscle (65.6% TRR, 0.031 mg eq/kg), fat (89.4% TRR, 0.547 mg eq/kg) and kidney (46.3% TRR, 0.066 mg eq/kg). In liver bixafen was more strongly degraded being present at levels of 22.8% of the TRR (0.168 mg eq/kg) in the conventional extract plus 3.7% of the TRR (0.027 mg eq/kg) in the exhaustive extract for a total of 26.5% of the TRR (0.195 mg eq/kg).

Besides the parent compound M21 (bixafen-desmethyl) was a major metabolite in all matrices investigated: 15.6% TRR in milk (0.001 mg eq/kg), 34.4% TRR in muscle (0.016 mg eq/kg), 10.4% TRR in fat (0.064 mg eq/kg) and 36.5% TRR in kidney (0.052 mg eq/kg). In liver, the conventional and exhaustive extraction released a total of 38.7% of the TRR (0.286 mg eq/kg) as bixafen-desmethyl.

The only other metabolite found was M23 in milk, liver and kidney. The sum of both isomers reached levels of 2.3% of the TRR in milk (isomer 1: 0.8% TRR, < 0.001 mg eq/kg; isomer 2: 1.5% TRR, 0.001 mg eq/kg), 18.9% of the TRR in liver (isomer 1: 13.1% TRR, 0.097 mg eq/kg; isomer 2: 5.8% TRR, 0.043 mg eq/kg) and of 9.3% of the TRR in kidney (isomer 1: 2.8% TRR, 0.004 mg eq/kg; isomer 2: 6.5% TRR, 0.009 mg eq/kg).

In the following table the extraction rates and the metabolites identified are summarised:

Table 9 Characterisation and identification of compounds in milk and tissues of the lactating goats after administration of dichlorophenyl-¹⁴C-bixafen at 2.0 mg/kg bw and day (46.08 ppm in the diet)

Compound / Fraction	Milk		Muscle		Fat		Liver		Kidney	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR [mg/kg]	100	0.064	100	0.047	100	0.611	100	0.737	100	0.143
Conventional extraction										
Bixafen	77.2	0.050	65.6	0.031	89.4	0.547	22.8	0.168	46.3	0.066
M23	0.8	< 0.001	—	—	—	—	13.1	0.097	2.8	0.004
M23	1.5	0.001	—	—	—	—	5.8	0.043	6.5	0.009
M21 (bixafen-desmethyl)	15.6	0.010	34.4	0.016	10.4	0.064	18.7	0.138	36.5	0.052
Subtotal identified	95.1	0.061	100.0	0.047	99.8	0.610	60.4	0.445	92.0	0.132
Exhaustive extraction										
Bixafen	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	3.7	0.027	n.a.	n.a.
M21 (bixafen-desmethyl)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	20.0	0.148	n.a.	n.a.
Subtotal identified	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	23.8	0.175	n.a.	n.a.
Total identified	95.1	0.061	100.0	0.047	99.8	0.610	84.2	0.620	92.0	0.132
Total characterised by HPLC without identification	2.4	0.002	—	—	—	—	5.4	0.040	5.4	0.008
Fractions not analysed	2.2	0.001	—	—	—	—	1.6	0.012	—	—

	Milk		Muscle		Fat		Liver		Kidney	
Compound / Fraction	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Total extracted	99.7	0.064	100.0	0.047	99.8	0.610	91.2	0.672	97.4	0.139
Not extracted	0.3	< 0.001	—	—	0.2	0.001	8.8	0.065	2.6	0.004
Accountability	100.0	0.064	100.0	0.047	100.0	0.611	100.0	0.737	100.0	0.143

n.a. = Not analysed

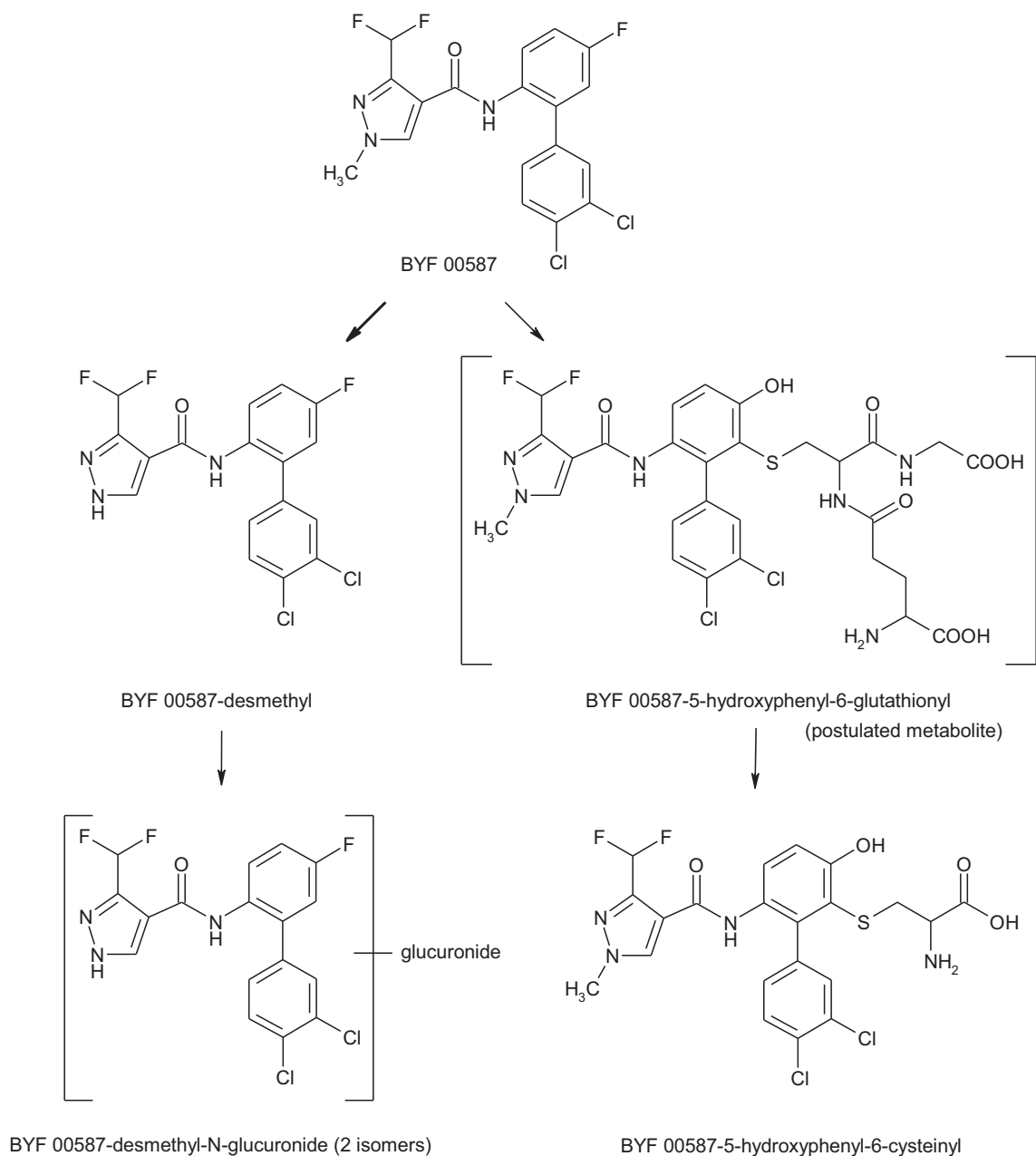


Figure 3 Proposed metabolic pathway of bixafen in lactating goats

Laying hens

The metabolism of [pyrazole-5-¹⁴C]-bixafen was investigated in laying hens by Koester, J (2007, BIXAFEN_016). Six hens were orally dosed 14 times in intervals of 24 h with 2.04 mg radiolabelled bixafen per kg body weight per day (corresponding to 25.75 ppm in the diet). The animals were sacrificed about 24 hours after the last dose. The total radioactivity was measured daily in the excreta and in eggs, and at sacrifice in the dissected tissues muscle, liver, fat and skin.

Analysis of the total radioactive residues (TRR) was carried out using combustion and liquid scintillation counting (LSC).

For metabolism investigations, composite samples of muscle (leg and breast), liver, subcutaneous fat and eggs (day 1 to 6 and day 7 to 14) of all animals were used. Aliquots of egg pools, muscle, liver and excreta were extracted with acetonitrile/water mixtures. The solids obtained by conventional extraction of liver were further extracted at increased temperature (approx. +120 °C) under microwave conditions. The fat sample was extracted with acetonitrile/n-hexane mixtures and partitioned into an acetonitrile and n-hexane phase. The acetonitrile extract was concentrated and analysed.

All samples were analysed by radio-HPLC using a reversed phase column and an acidic acetonitrile/water gradient. The identity of the major components was confirmed by LC-MS/MS in the egg. The identification of parent compound and metabolites in other matrices of the laying hen was achieved by co-chromatography of original extracts with isolated metabolites or radiolabelled reference items or by comparison of known metabolic profiles.

After the dosing period a total of 88.33% of the applied radioactivity was excreted. The total radioactive residues (TRR) found were highest in eggs with up to 1.019 mg eq/kg after 13 days of dosing. A plateau of the total radioactivity in eggs was observed after approximately one week. In tissues liver contained the highest TRR (0.641 mg eq/kg), followed by fat (0.227 mg eq/kg), kidney (0.193 mg eq/kg) and muscle (0.032 mg eq/kg). The TRR levels found are summarized in Table . The time course of radioactivity in eggs is presented in Table and Table .

Table 10 TRR in laying hen eggs and tissues after administration of pyrazole-¹⁴C-bixafen at 2.04 mg/kg bw and day (25.75 ppm in the diet)

Matrix	% of total dose administered (cumulative value)	TRR [mg eq/kg]
Liver	0.05	0.641
Kidney	< 0.01	0.193
Eggs from ovary/oviduct	0.16	1.464
Total body muscle	0.05	0.032
Total body skin	0.01	0.072
Total body fat (subcutaneous)	0.10	0.227
Total of organs/tissues	0.37	–
Eggs, day 1–14	1.15	0.776
Excreta, day 1–14	88.33	12.989
Total Recovery	89.95	–

Table 11 Time course of total radioactive residues in excreta after administration of pyrazole-¹⁴C-bixafen at 2.04 mg/kg bw and day (25.75 ppm in the diet) to laying hens (mean of six animals)

Time after first administration [h]	administration no.	Excretion per day [% of total dose]	Cumulative excretion [% of total dose]
0	1	no excreta collected	–
1	2	5.65	12.391
2	3	12.04	14.030
3	4	18.54	13.397
4	5	24.92	13.637
5	6	31.41	17.885
6	7	38.34	17.040
7	8	45.40	16.462
8	9	50.96	10.314
9	10	57.09	11.834
10	11	63.46	12.627
11	12	70.03	12.382
12	13	76.30	12.268
13	14	82.53	11.617
14	-	88.33	10.202
Mean			12.989

Table 12 Time course of total radioactive residues in eggs after administration of pyrazole-¹⁴C-bixafen at 2.04 mg/kg bw and day (25.75 ppm in the diet, mean of six animals)

Time after first administration [h]	administration no.	Cumulative secretion [% of the total dose]	TRR in eggs [mg eq/kg]
0	1	no egg collected	–
1	2	0.02	0.205
2	3	0.05	0.359
3	4	0.12	0.546
4	5	0.19	0.701
5	6	0.27	0.842
6	7	0.36	0.906
7	8	0.44	0.875
8	9	0.54	0.790
9	10	0.62	0.872
10	11	0.74	0.997
11	12	0.84	0.908
12	13	0.96	0.955
13	14	1.05	1.019
14	–	1.15	0.857
Mean			0.776

Samples of tissues and eggs were further analysed for the composition of the radioactivity. Extraction rates using acetonitrile/water were generally > 90%, except for liver, which required additional exhaustive extraction including hydrolysis.

Parent bixafen was the major residue in eggs found at levels of 68.6% of the TRR after 1–6 days (0.416 mg eq/kg) and 55.4% of the TRR after 7–14 days (0.498 mg eq/kg). Besides the parent compound M21 (bixafen-desmethyl) was a major metabolite being present at levels of 26% TRR after 1–6 days (0.157 mg eq/kg) and 35.4% TRR (0.318 mg eq/kg) after 7–14 days. M24 and M26 were also detected in eggs (7–14 days only) with 0.6% TRR (0.006 mg eq/kg) and 1.0% TRR (0.009 mg eq/kg), respectively.

Fat mainly contained unchanged parent as major residue (79.6% TRR, 0.181 mg eq/kg). M21 (bixafen-desmethyl) was the only other metabolite with 19.9% TRR (0.045 mg eq/kg).

In muscle M21 (bixafen-desmethyl) gave the highest residue (35.4% of the TRR, 0.011 mg eq/kg). The unchanged parent substance was the only other substance identified at levels of 23.4% of the TRR (0.008 mg eq/kg).

In liver a total of 42.3% of the TRR were identified as bixafen-desmethyl (conventional extract: 24.1% TRR, 0.155 mg eq/kg; exhaustive extract: 18.2% TRR, 0.116 mg eq/kg). The unchanged parent was present mainly in conjugated form cleaved by hydrolysis, resulting in a total of 0.14 mg eq/kg or 21.9% of the TRR (conventional extraction: 4.5% TRR, 0.029 mg eq/kg; exhaustive extraction: 17.4% TRR as conjugate, 0.111 mg eq/kg). Besides parent bixafen and M21 liver contained several minor metabolites all being present at levels below 10% of the TRR. M14 and M18 represented 2.3% TRR (0.015 mg eq/kg) and 1.5% TRR (0.01 mg eq/kg), respectively. In addition hydroxylated and conjugated metabolites following bixafen-desmethyl were identified: M24 with 1.8% TRR (0.012 mg eq/kg), M25 with 1.0% TRR (0.007 mg eq/kg), M26 with 8.8% TRR (0.057 mg eq/kg), M27 with 4.6% TRR (0.029 mg eq/kg) and M37 with 2.7% TRR (0.017 mg eq/kg).

In the following table the extraction rates and the metabolites identified are summarised:

Table 13 Characterisation and identification of compounds in eggs and tissues of the laying hens after administration of pyrazole-¹⁴C-bixafen at 2.04 mg/kg bw and day (25.75 ppm in the diet)

Compound / Fraction	Eggs day 1–6		Eggs day 7–14		Muscle		Fat		Liver	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR [mg/kg]	100	0.606	100	0.900	100	0.032	100	0.227	100	0.641
Conventional extraction										
Bixafen	68.6	0.416	55.4	0.498	23.4	0.008	79.6	0.181	4.5	0.029
M14	–	–	–	–	–	–	–	–	2.3	0.015
M18	–	–	–	–	–	–	–	–	1.5	0.010
M21 (bixafen-desmethyl)	26.0	0.157	35.4	0.318	35.4	0.011	19.9	0.045	24.1	0.155
M24	–	–	0.6	0.006	–	–	–	–	1.8	0.012
M25	–	–	–	–	–	–	–	–	1.0	0.007
M26	–	–	1.0	0.009	–	–	–	–	8.8	0.057
M27	–	–	0.5	0.005	–	–	–	–	4.6	0.029
M37	–	–	–	–	–	–	–	–	2.7	0.017
Exhaustive extraction of solids of liver										
M21 (bixafen-desmethyl)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	18.2	0.116
Bixafen-conjugate ^a	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	17.4	0.111
Total identified	94.6	0.573	92.8	0.835	58.7	0.019	99.5	0.226	87.0	0.557
Total characterised by HPLC without identification	3.4	0.020	3.2	0.029	34.9	0.011	–	–	4.2	0.027
Total extracted	98.0	0.593	96.0	0.864	93.6	0.030	99.5	0.226	91.2	0.584
Unextracted	2.0	0.012	4.0	0.036	6.4	0.002	0.5	0.001	8.8	0.056
Accountability	100	0.606	100	0.900	100	0.032	100	0.227	100	0.641

^a Cleaved conjugate during exhaustive extraction. Type of conjugate not identified.

In a second study on laying hens conducted by Koester, J (2007, BIXAFEN_017) [dichlorophenyl-UL-¹⁴C]-bixafen was administered to five hens orally for 14 days with 2.03 mg radiolabelled bixafen per kg body weight per day (corresponding to 32.42 ppm in the diet). The animals were sacrificed about 24 hours after the last dose. The total radioactivity was measured daily in the excreta and in eggs, and at sacrifice in the dissected tissues muscle, liver, fat and skin.

Analysis of the total radioactive residues and the extraction of samples collected was conducted as described in the metabolism in laying hens study using [pyrazole-5-¹⁴C]-bixafen by Koester, J (2007, BIXAFEN_016).

At the end of the dosing period approximately 92.54% of the administered doses were excreted. The total radioactive residues (TRR) found were highest in eggs with up to 0.826 mg eq/kg

after 7 days of dosing. A plateau of the total radioactivity in eggs was observed after approximately one week. In tissues liver contained the highest TRR (0.807 mg eq/kg), followed by fat (0.365 mg eq/kg), kidney (0.331 mg eq/kg) and muscle (0.037 mg eq/kg). The TRR levels found are summarized in Table . The time course of radioactivity in eggs and excreta is presented in Table and

Table .

Table 14 TRR in laying hen eggs and tissues after administration of dichlorophenyl-¹⁴C-bixafen at 2.03 mg/kg bw and day (32.42 ppm in the diet)

Matrix	% of total dose administered (cumulative value)	TRR [mg eq/kg]
Liver	0.06	0.807
Kidney	0.01	0.331
Eggs from ovary/oviduct	0.10	1.449
Total body muscle	0.05	0.037
Total body skin	0.01	0.070
Total body fat (subcutaneous)	0.03	0.365
Total of organs/tissues	0.25	–
Eggs, day 1–14	0.98	0.640
Excreta, day 1–14	92.54	18.605
Total Recovery	93.77	–

Table 15 Time course of total radioactive residues in excreta after administration of dichlorophenyl-¹⁴C-bixafen at 2.03 mg/kg bw and day (32.42 ppm in the diet) to laying hens (mean of five animals)

Time after first administration [h]	administration no.	Excretion per day [% of total dose]	Cumulative excretion [% of total dose]
0	1	no excreta collected	–
1	2	5.50	17.272
2	3	12.43	21.039
3	4	19.02	16.638
4	5	25.59	19.990
5	6	32.75	21.211
6	7	38.72	18.312
7	8	46.79	20.532
8	9	52.57	17.556
9	10	59.74	19.665
10	11	66.43	18.724
11	12	73.15	20.322
12	13	79.37	18.059
13	14	85.57	15.919
14	–	92.54	17.338
Mean			18.605

Table 16 Time course of total radioactive residues in eggs after administration of dichlorophenyl-¹⁴C-bixafen at 2.03 mg/kg bw and day (32.42 ppm in the diet, mean of five animals)

Time after first administration [h]	administration no.	Cumulative secretion [% of the total dose]	TRR in eggs [mg eq/kg]
0	1	no egg collected	–
1	2	0.039	0.301
2	3	0.053	0.347
3	4	0.100	0.442
4	5	0.158	0.545
5	6	0.222	0.607
6	7	0.289	0.650
7	8	0.375	0.826
8	9	0.454	0.752
9	10	0.530	0.807
10	11	0.615	0.816

Time after first administration [h]	administration no.	Cumulative secretion [% of the total dose]	TRR in eggs [mg eq/kg]
11	12	0.683	0.804
12	13	0.763	0.759
13	14	0.843	0.767
14	—	0.976	0.788
Mean			0.640

Samples of tissues and eggs were further analysed for the composition of the radioactivity. Extraction rates using acetonitrile/water were generally > 90%, except for liver, which required additional exhaustive extraction including hydrolysis.

Parent bixafen was the major residue in eggs found at levels of 62.3% of the TRR after 1–7 days (0.327 mg eq/kg) and 51.1% of the TRR after 8–14 days (0.405 mg eq/kg). Besides the parent compound M21 (bixafen-desmethyl) was a major metabolite being present at levels of 33.2% TRR after 1–6 days (0.174 mg eq/kg) and 39.1% TRR (0.31 mg eq/kg) after 8–14 days. M24 and M26 were also detected in eggs with 0.9% TRR (0.007 mg eq/kg, 8–14 days only) and 0.9 to 1.2% TRR (0.005 to 0.009 mg eq/kg), respectively.

Fat mainly contained unchanged parent as major residue (80.3% TRR, 0.305 mg eq/kg). M21 (bixafen-desmethyl) was the only other metabolite with 18.6% TRR (0.071 mg eq/kg).

In muscle M21 (bixafen-desmethyl) gave the highest residue (50.8% of the TRR, 0.019 mg eq/kg). The unchanged parent substance was the only other substance identified at levels of 40.8% of the TRR (0.015 mg eq/kg).

In liver a total of 45.7% of the TRR were identified as bixafen-desmethyl (conventional extract: 25.7% TRR, 0.207 mg eq/kg; exhaustive extract: 20% TRR, 0.161 mg eq/kg). The unchanged parent was present mainly in conjugated form cleaved by hydrolysis, resulting in a total of 0.27 mg eq/kg or 31.5% of the TRR (conventional extraction: 6.7% TRR, 0.054 mg eq/kg; exhaustive extraction: 26.8% TRR as conjugate, 0.216 mg eq/kg). Besides parent bixafen and M21 liver contained several minor metabolites all being present at levels below 10% of the TRR. M14 represented M14 (bixafen-5-hydroxyphenyl-6-cysteinyl) was found with 3.5% TRR (0.029 mg eq/kg). In addition hydroxylated and conjugated metabolites following bixafen-desmethyl were identified: M24 with 3.1% TRR (0.025 mg eq/kg), M26 with 8.4% TRR (0.067 mg eq/kg) and M27 with 5.1% TRR (0.041 mg eq/kg).

In the following table the extraction rates and the metabolites identified are summarised.

Table 17 Characterisation and identification of compounds in eggs and tissues of the laying hens after administration of dichlorophenyl-¹⁴C-bixafen at 2.03 mg/kg bw and day (32.42 ppm in the diet)

[illegible]

Compound / Fraction	Eggs day 1–7		Eggs day 8–14		Muscle		Fat		Liver	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Total identified	96.4	0.506	92.9	0.736	91.6	0.034	98.9	0.376	99.4	0.801
Total characterised by HPLC without identification	—	—	1.9	0.015	—	—	—	—	—	—
Total extracted	96.4	0.506	94.9	0.751	91.6	0.034	98.9	0.376	99.4	0.801
Unextracted	3.6	0.019	5.1	0.041	8.4	0.003	1.1	0.004	0.6	0.005
Accountability	100	0.525	100	0.791	100	0.037	100	0.380	100	0.806

^a Cleaved conjugate during exhaustive extraction. Type of conjugate not identified.

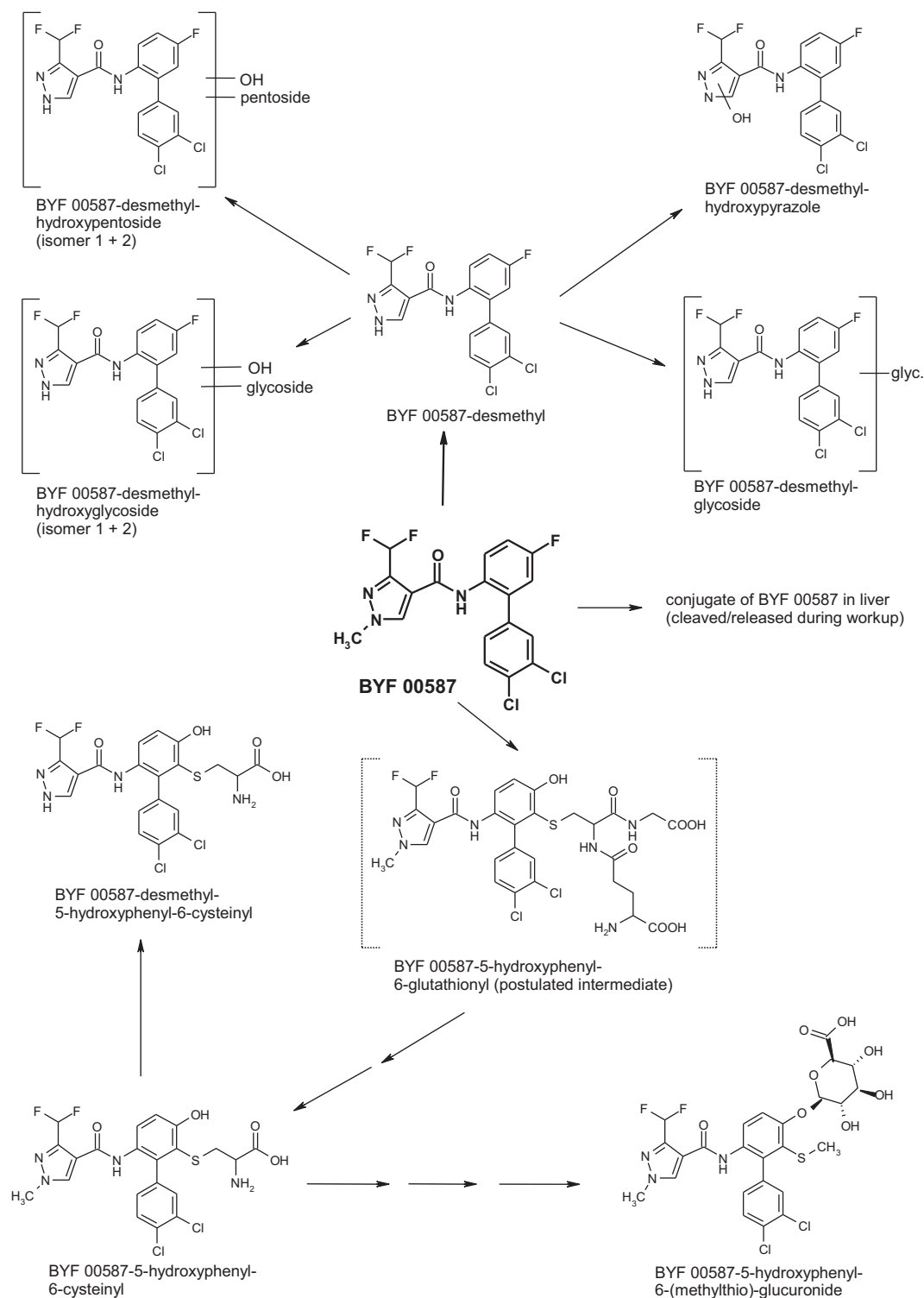


Figure 4 Proposed metabolic pathway of bixafen in laying hens

Plant metabolism

The fate of bixafen in plants was investigated following foliar application of ^{14}C -radiolabelled active substance to soya beans and wheat. In all samples unchanged bixafen was the major residue, normally

amounting nearly 90% of the TRR or more. Except for soya bean seeds, the only other metabolite found was M21 (bixafen-desmethyl), however its levels were below 3% of the TRR in all samples.

In soya bean seeds, which were not directly affected by the spray solution, parent bixafen was still the main residue but represented only 29.5% of the TRR. In addition the tautomers M44 & M45 (BYF 00587-desmethyl-pyrazole-4-carboxylic acid, 18.8% TRR, 0.004 mg eq/kg) and M47 (pyrazolone-4-carboxylic acid, 12.1% TRR, 0.003 mg eq/kg) were identified. No M21 (bixafen-desmethyl) was found in soya bean seeds.

Soya beans

The metabolism of bixafen was investigated (Spiegel, K 2007, BIXAFEN_018) in soya beans (var. Merlin) after three spray applications with [pyrazole-5-¹⁴C]-bixafen formulated as an EC 125. The first application was performed when the first flowers opened (BBCH 60), the second at the end of flowering (BBCH 69) and the third when approximately 80% of the pods were ripe (BBCH 88). Each application was conducted with a nominal amount of 0.06 kg ai/ha, however a total amount of 0.188 kg ai/ha was actually applied. The plants were grown in a greenhouse.

Forage was harvested at growth stage BBCH 70–71 (5 days after the 2nd application), hay at growth stage BBCH 75 (29 days after the 2nd application), and straw and seeds at maturity (BBCH 96, 26 days after the 3rd application).

The samples were homogenised with liquid nitrogen and extracted three times with a mixture of acetonitrile/water (4/1, v/v) using an Ultra-Turrax homogeniser. After each extraction step, the extracts were separated from the solids by centrifugation. The radioactivity of each extract was determined by LS measurement. The extracts were combined, diluted or, if necessary concentrated, for HPLC analysis. The remaining solids were lyophilised, and the radioactivity was determined by combustion followed by LSC. The TRR was calculated as the sum of the radioactivity determined in the extracts and in the solids.

For seeds, a subsequent exhaustive extraction was conducted with acetonitrile/water 4/1 (v/v) and with acetonitrile/acetic acid 4/1 (v/v) with microwave assistance, both at 80 °C. The microwave extracts were concentrated to the aqueous remainder and partitioned three times with heptane. The heptane phase contained only negligible amounts of radioactivity and was discarded. The aqueous phase was concentrated and analysed by HPLC.

Parent compound and metabolites were identified by HPLC and TLC co-chromatography (by spiking) or HPLC and TLC comparison with reference compounds (peak retention times, comparison of chromatographed zones).

The TRRs found in the samples collected amounted 5.32 mg eq/kg in forage, 4.0 mg eq/kg in hay, 12.9 mg eq/kg in straw, and 0.024 mg eq/kg in the seed. In forage, hay and straw unchanged bixafen was the major residue being present at levels > 89.9% of the TRR. The only other metabolite present was M21 (bixafen-desmethyl) found at 0.5% to 2.6% of the TRR.

In the seeds parent bixafen was also identified as major residue; however, the levels of 29.7% of the TRR (0.007 mg eq/kg) were lower compared to other plant parts. Besides the parent substance the tautomers M44 & M45 (BYF 00587-desmethyl-pyrazole-4-carboxylic acid, 18.8% TRR, 0.004 mg eq/kg) and M47 (pyrazolone-4-carboxylic acid, 12.1% TRR, 0.003 mg eq/kg) were found as major metabolites. M21 (bixafen-desmethyl) was not present in soya bean seeds.

An overview of the TRR levels found in the collected samples and the composition of the residue is presented in the following table.

Table 18 Total radioactive residues and their composition after application of [pyrazole-5-¹⁴C]-bixafen to soya beans

Metabolite Fraction	Forage (5 d after 2 nd application)		Hay (29 d after 2 nd application)		Straw (26 d after 3 rd application)		Seeds (26 d after 3 rd application)	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
TRR	100	5.32	100	4.00	100	12.9	100	0.024
Bixafen	95.8	5.10	91.8	3.67	89.9	11.59	29.7	0.007
M44 & M45	—	—	—	—	—	—	18.8	0.004
M47	—	—	—	—	—	—	12.1	0.003
M21 (bixafen-desmethyl)	1.5	0.08	2.6	0.10	0.5	0.06	—	—
Total identified	97.4	5.18	94.4	3.78	90.4	11.66	60.6	0.014
Total characterised	0.6	0.03	0.7	0.03	0.6	0.08	16.2	0.004
Fractions not analysed	—	—	—	—	—	—	0.7	< 0.001
Total extracted	98.0	5.21	95.1	3.80	91.0	11.74	77.5	0.018
Unextracted	2.0	0.11	4.9	0.20	9.0	1.16	22.5	0.005
Accountability	100.0	5.32	100.0	4.00	100.0	12.90	100.0	0.024

A second study investigating the metabolism of bixafen in soya beans was conducted by Spiegel, K (2007, BIXAFEN_019). [Dichlorophenyl-UL-¹⁴C]-bixafen was formulated as an EC 125. The first application was performed when the first flowers opened (BBCH 60), the second at the end of flowering (BBCH 69) and the third when approximately 80% of the pods were ripe (BBCH 88). Each application was conducted with a nominal amount of 0.06 kg ai/ha, however a total amount of 0.187 kg ai/ha was actually applied. The plants were grown in a greenhouse.

Forage was harvested at growth stage BBCH 70–71 (5 days after the 2nd application), hay at growth stage BBCH 75 (29 days after the 2nd application), and straw and seeds at maturity (BBCH 96, 26 days after the 3rd application).

The samples were homogenised with liquid nitrogen and extracted three times with a mixture of acetonitrile/water (4/1, v/v) using an Ultra-Turrax homogeniser. After each extraction step, the extracts were separated from the solids by centrifugation. The radioactivity of each extract was determined by LS measurement. The extracts were combined, diluted or, if necessary concentrated, for HPLC analysis. The remaining solids were lyophilised, and the radioactivity was determined by combustion followed by LSC. The TRR was calculated as the sum of the radioactivity determined in the extracts and in the solids.

Parent compound and metabolites were identified by HPLC and TLC co-chromatography (by spiking) or HPLC and TLC comparison with reference compounds (peak retention times, comparison of chromatographed zones).

The TRRs found in the samples collected amounted 3.98 mg eq/kg in forage, 2.81 mg eq/kg in hay, 9.52 mg eq/kg in straw, and 0.005 mg eq/kg in the seed. In forage, hay and straw unchanged bixafen was the major residue being present at levels > 91.8% of the TRR. The only other metabolite present was M21 (bixafen-desmethyl) found at 0.6% to 1.9% of the TRR.

In the seeds total radioactive residues were too low for identification. The described extraction methods released 53% of the TRR.

An overview of the TRR levels found in the collected samples and the composition of the residue is presented in the following table.

Table 19 Total radioactive residues and their composition after application of [dichlorophenyl-UL-¹⁴C]-bixafen to soya beans

Metabolite Fraction	Forage (5 d after 2 nd application)		Hay (29 d after 2 nd application)		Straw (26 d after 3 rd application)		Seeds (26 d after 3 rd application)	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
TRR	100	3.98	100	2.81	100	9.52	100	0.005
Bixafen	97.7	3.89	91.8	2.58	92.3	8.79	n.a.	n.a.
M21 (bixafen-desmethyl)	1.1	0.04	1.9	0.05	0.6	0.06	n.a.	n.a.

Metabolite Fraction	Forage (5 d after 2 nd application)		Hay (29 d after 2 nd application)		Straw (26 d after 3 rd application)		Seeds (26 d after 3 rd application)	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
Total identified	98.8	3.93	93.7	2.63	92.9	8.84	n.a.	n.a.
Total extracted	98.8	3.93	93.7	2.63	92.9	8.84	53.0	0.002
Unextracted	1.2	0.05	6.3	0.18	7.1	0.67	47.0	0.002
Accountability	100.0	3.98	100.0	2.81	100.0	9.52	100.0	0.005

n.a. = Not analysed

Wheat

The metabolism of bixafen in wheat (var. Thassos) was investigated by Miebach, D and Bongartz, R (2007, BIXAFEN_020) after two spray applications with [pyrazole-5-¹⁴C]-bixafen formulated as an EC 200. The first application with 0.125 kg ai/ha (actual 132 g ai/ha) was performed at the end of tillering / beginning of stem elongation (BBCH 29–31), and the second with 0.15 kg ai/ha (actual 154 g ai/ha) at the end of flowering (BBCH 69). Plants were grown in plastic containers under natural temperature and light conditions in Monheim, Germany. The glass roof of the vegetation area was open during the sunshine periods and was automatically closed during rainfall. Plants were irrigated as needed.

Forage was harvested at growth stage BBCH 38 (9 days after 1st application), hay at growth stage BBCH 77 (9 days after 2nd application), and straw and grain at maturity (BBCH 89, 50 days after 2nd application).

The homogenised samples were extracted three times with a mixture of acetonitrile/water (4/1, v/v) and once with acetonitrile using an Ultra-Turrax homogeniser. The extracts were separated from the solids by suction through a filter. The ¹⁴C-radioactivity of liquid samples was determined by liquid scintillation counting (LSC). The remaining solids were air dried. Solid samples were combusted and the released ¹⁴CO₂ was absorbed in an alkaline scintillation cocktail and radio-assayed by LSC. The TRR of each RAC was determined by summation of the radioactivity in the combined extracts and in the solids.

The corresponding extracts of wheat RAC were combined and concentrated to a volume suitable for HPLC chromatography. Parent compound and metabolites were quantified by HPLC. The TRRs and the quantified amounts of compounds were expressed as mg bixafen-equivalents per kg sample material.

Parent compound in the extracts of straw and grain was identified by LC-MS-spectroscopy. Metabolites in straw and grain were identified by HPLC co-chromatography with radiolabelled reference compounds. Parent compound and metabolites in forage and hay were assigned by comparison of the metabolite patterns obtained for straw and grain.

The TRRs found in the samples collected amounted 1.67 mg eq/kg in forage, 6.57 mg eq/kg in hay, 24.27 mg eq/kg in straw, and 0.162 mg eq/kg in grain. In all samples unchanged bixafen was the major residue being present at levels > 89.5% of the TRR. The only other metabolite present was M21 (bixafen-desmethyl) found at 0.8% to 2.4% of the TRR.

In the samples one further analyte (BYF 00587-4'-deschloro) was identified, which was also found at levels of 1% to 1.3% of the active ingredient in the spray solution, suggesting impurities of the tank-mix used.

An overview of the TRR levels found in the collected samples and the composition of the residue is presented in the following table.

Table 20 Total radioactive residues and their composition after application of [pyrazole-5-¹⁴C]-bixafen to wheat

Compound	Forage (9 d after 1 st application)		Hay (9 d after 2 nd application)		Straw (50 d after 2 nd application)		Grain (50 d after 2 nd application)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	100	1.67	100	6.57	100	24.27	100	0.162
Bixafen	92.9	1.55	91.9	6.04	92.6	22.47	89.5	0.145
M21 (bixafen-desmethyl)	0.8	0.01	2.3	0.15	1.8	0.43	2.4	0.004
Total identified	93.7	1.57	94.2	6.19	94.4	22.90	91.8	0.148
Total characterised ^a	1.6	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BYF 00587-4'-deschloro ^b	3.5	0.06	2.2	0.14	1.4	0.35	2.0	0.003
Total extractable (combined extracts)	98.7	1.65	96.4	6.33	95.8	23.25	93.8	0.152
Unextracted	1.3	0.02	3.6	0.24	4.2	1.02	6.2	0.010

^a Extracted and characterised by chromatographic behaviour

^b Impurity in spraying solution

An additional plant metabolism study on wheat (var. Thassos) using [dichlorophenyl-UL-¹⁴C]-bixafen was conducted by Miebach, D and Bongartz, R (2007, BIXAFEN_021). The active ingredient was formulated as an EC 200. The first application with 0.125 kg ai/ha (actual 128 g ai/ha) was performed at the end of tillering / beginning of stem elongation (BBCH 29–31), and the second with 0.15 kg ai/ha (actual 158 g ai/ha) at the end of flowering (BBCH 69). Plants were grown in plastic containers under natural temperature and light conditions in Monheim, Germany. The glass roof of the vegetation area was open during the sunshine periods and was automatically closed during rainfall. Plants were irrigated as needed.

Forage was harvested at growth stage BBCH 38 (9 days after 1st application), hay at growth stage BBCH 77 (9 days after 2nd application), and straw and grain at maturity (BBCH 89, 50 days after 2nd application).

All samples were analysed according to the procedures described for the wheat metabolism study conducted with [pyrazole-5-¹⁴C]-bixafen by Miebach, D and Bongartz, R (2007, BIXAFEN_020).

The TRRs found in the samples collected amounted 1.57 mg eq/kg in forage, 7.64 mg eq/kg in hay, 22.85 mg eq/kg in straw, and 0.229 mg eq/kg in grain. In all samples unchanged bixafen was the major residue being present at levels > 91.7% of the TRR. The only other metabolite present was M21 (bixafen-desmethyl) found at 0.8% to 2.1% of the TRR.

In the samples one further analyte (BYF 00587-4'-deschloro) was identified, which was also found at levels of 1% to 1.3% of the active ingredient in the spray solution, suggesting impurities of the tank-mix used.

An overview of the TRR levels found in the collected samples and the composition of the residue is presented in the following table.

Table 21 Total radioactive residues and their composition after application of [dichlorophenyl-UL-¹⁴C]-bixafen to wheat

Compound	Forage (9 d after 1 st application)		Hay (9 d after 2 nd application)		Straw (50 d after 2 nd application)		Grain (50 d after 2 nd application)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	100	1.57	100	7.64	100	22.85	100	0.229
Bixafen	97.1	1.53	91.7	7.01	93.2	21.29	92.9	0.213
M21 (bixafen-desmethyl)	0.8	0.01	2.1	0.16	1.7	0.39	2.1	0.005
Total identified	97.9	1.54	93.8	7.17	94.9	21.68	95.0	0.218

Compound	Forage (9 d after 1 st application)		Hay (9 d after 2 nd application)		Straw (50 d after 2 nd application)		Grain (50 d after 2 nd application)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
BYF 00587-4'-deschloro ^a	1.1	0.02	1.7	0.13	1.2	0.27	2.0	0.005
Total extractable (combined extracts)	99.0	1.56	95.5	7.30	96.1	21.95	97.0	0.222
Unextracted	1.0	0.02	4.5	0.34	3.9	0.90	3.0	0.007

^a Impurity in spraying solution

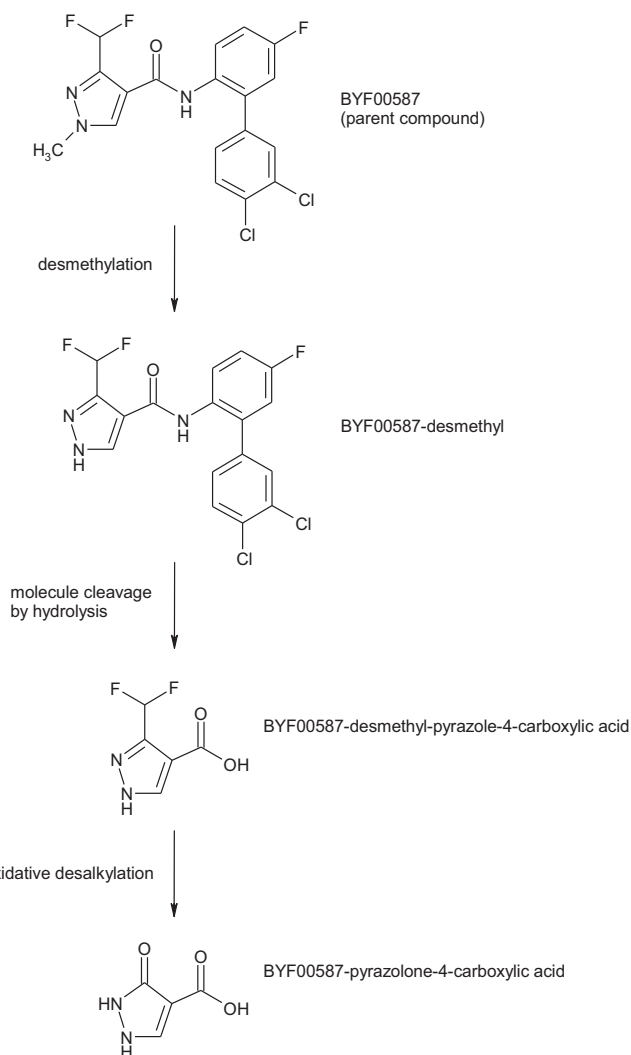


Figure 5 Proposed metabolic pathway of bixafen in plants

Environmental fate in soil

For the investigation of the environmental fate of bixafen the Meeting received studies on photolysis on soil, the aerobic soil metabolism, the behaviour in confined and field rotational crops and short- and long-term field dissipation studies.

Soil photolysis of bixafen was not observed. In the soil bixafen is highly persistent, showing about 80–90% of the applied dose remaining after 120 days observed in aerobic soil metabolism

studies. The only metabolites found in minor proportions were M44 (BYF 00587-desmethyl-pyrazole-4-carboxylic acid) and M21 (Bixafen-desmethyl), the tautomers M44 & M45 later in soil of below mentioned confined rotational crop studies.

In confined rotational crop studies conducted at rates equivalent to 0.785 and 0.847 kg ai/ha bixafen and M21 (bixafen-desmethyl) were the major residue. After application of the [pyrazole-5-¹⁴C]-labelled active substance, the labelled cleavage products M43 (BYF 00587-pyrazole-4-carboxamide), M44 (BYF 00587-desmethyl-pyrazole-4-carboxylic acid (tautomer 1)) and M45 (BYF 00587-desmethyl-pyrazole-4-carboxylic acid (tautomer 2)) were also identified as major metabolites.

In field rotational crop studies conducted on four locations in Europe, residues of bixafen and M21 were mostly below the LOQs of 0.01 mg/kg, except for two single detects in wheat straw (0.03 mg/kg total residue) and lettuce of pre-mature growth stage (0.06 mg/kg total residue).

Field dissipation studies confirmed the slow degradation of bixafen in the soil observed in aerobic metabolism studies. Over 5 years of annual treatment the bixafen peak concentrations in soil under field conditions still represented approximately 32–47% of the total dose applied within these years. Most of the residue was present as unchanged parent substance.

Photolysis on soil

The photodegradation of [¹⁴C] bixafen (pyrazole and dichlorophenyl labels) on the soil surface was investigated under artificial sunlight (Muehmel, T and Fliege, R 2007, BIXAFEN_022). The two labels of the test item were individually applied to a 3 mm thick layer of soils (see Table) on glass dishes at a rate equivalent to 0.25 kg ai/ha. The 8 days of irradiation corresponded to about 30 days of midsummer sunlight at Phoenix, Arizona (USA).

The soil moisture was maintained at 75% field capacity at a temperature of 20 °C. Irradiated and dark control samples were taken at a range of intervals during the 8 days irradiation/incubation periods.

Table 22 Soil characteristics used in soil photolysis experiments

	Dichlorophenyl label test	Pyrazole label test
Soil ID	‘Laacher Hof AXxa’	‘Laacher Hof Wurmwiase’
Texture Class (USDA)	Sandy Loam	Sandy Loam
Sand [50 µm–2 mm]	73%	53%
Silt [2 µm–50 µm]	20%	28%
Clay [< 2 µm]	7%	19%
pH in 0.01 M CaCl ₂ (1:1)	6.2	5.6
pH in 1 N KCl (1:1)	6.2	5.2
pH in Water (1:1)	6.6	5.9
pH in Water (Saturated Paste)	6.7	6.0
Organic Matter [%OM]	4.0%	2.4%
Organic Carbon [%OC]	2.3%	1.4%
Soil Microbial Biomass	day 0, untreated: 785 mg C/kg soil	day 0, untreated: 550 mg C/kg soil
Cation Exchange Capacity [CEC]	11.4 meq/100 g	10.3 meq/100 g
Water Holding Capacity at 0.33 bar [1/3 bar WHC]	20.6 g/100 g	20.1 g/100 g
Maximum Water Holding Capacity [MWHC]	55.7 g/100 g	59.1 g/100 g

In irradiated samples no degradation of bixafen was observed. A summary of the metabolic spectrum of irradiated and dark samples is presented in the following tables.

Table 23 Photodegradation of [dichlorophenyl-¹⁴C]-labelled bixafen on soil

	Amount (% of applied radioactivity) at days after treatment								
	irradiated samples						dark samples		
	0	1	2	4	6	8	1	4	8
Bixafen	98.9	95.9	96.8	94.6	94.4	91.8	97.5	97.8	98.6
Unidentified radioactivity (sum)	1.9	2.7	2.8	3.0	4.4	4.3	1.8	1.5	1.6
Greatest single peak	0.6	0.9	0.9	1.1	1.4	1.4	0.6	0.7	0.6
Total extracted residue	> 99	99	99	98	98	96	> 99	99	99
¹⁴ CO ₂	n.m.	n.m.	n.m.	n.m.	n.m.	0.4	n.m.	n.m.	0.1
Volatile organic radioactivity	n.m.	n.m.	n.m.	n.m.	n.m.	< 0.1	n.m.	n.m.	0.1
Unextracted residue	0.1	1.2	1.3	1.7	2.0	3.3	0.6	1.0	1.5
Total recovery	100.9	99.8	100.9	99.3	100.9	99.9	99.6	100.3	101.5

n.m. = Not measured

Table 24 Photodegradation of [pyrazole-¹⁴C]-labelled bixafen on soil

	Amount (% of applied radioactivity) at days after treatment							
	AXXa (air dried)				Wurmwiese (moist)			
	irradiated			dark	irradiated			dark
	0	4	8	8	0	4	8	8
Bixafen	99.2	94.6	89.9	98.5	98.7	94.5	92.2	96.7
Unidentified radioact. (sum)	1.7	3.5	6.7	1.7	1.8	2.7	4.4	1.5
Greatest single peak	0.7	1.1	1.6	0.7	0.8	0.9	1.2	0.6
Total extracted residue	101	99.6	99.5	100.7	100.6	99.3	99.8	100.3
Unextracted residue	0.1	1.5	2.9	0.5	0.1	2.1	3.2	2.1
Total recovery	100.0	99.6	99.5	100.7	100.6	99.3	99.8	100.3

¹⁴CO₂ and volatile organic radioactivity not measured*Soil metabolism**Aerobic soil metabolism*

The aerobic soil metabolism of bixafen was investigated in several soil types using [pyrazole]- and [dichlorophenyl]-¹⁴C-bixafen.

In the study conducted by Sneikus, J and Koehn, D (2005, BIXAFEN_023) soil samples were extracted several times by shaking at ambient temperature and microwave extraction with acetonitrile/water (80/20, v/v), and the bixafen residues were analysed by TLC. HPLC was used as confirmation method. The identity of the test item was confirmed by co-chromatography using non-labelled reference item. Identification of transformation products was performed by LC/MS/MS.

Table 25 Distribution of radioactive residues after incubation of 0.7 mg/kg [pyrazole]-¹⁴C-bixafen in soil "Laacherhof AXXa" (sandy loam, 55% MWHC, 1.3% OC, pH 6.6)

	Residues (% of applied radioactivity) at days after treatment									
	0	1	3	7	14	21	38	62	90	120
Bixafen	94.8	96.2	93.6	93.4	95.2	92.4	93.0	91.2	90.8	89.8
M44 & M45	n.d.	n.d.	n.d.	n.d.	0.2	0.3	0.5	0.3	0.4	0.4
Unidentified radioactivity	< 0.1	0.5	0.6	0.5	0.6	0.3	0.3	0.2	0.3	0.2
Total extracted	94.8	96.7	94.2	93.9	96.0	93.0	93.9	91.7	91.5	90.3
¹⁴ CO ₂	n.a.	0.1	0.1	0.1	0.1	0.2	0.3	0.4	0.5	0.7
Volatile organic radioactivity	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted residue	5.2	5.7	6.9	6.7	6.9	6.5	8.3	7.7	8.7	8.9
Total recovery	100.0	102.5	101.2	100.7	103.0	99.6	102.4	99.8	100.8	99.9

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

Table 26 Distribution of radioactive residues after incubation of 0.7 mg/kg [dichlorophenyl]-¹⁴C-bixafen in soil “Laacherhof AXXa” (sandy loam, 55% MWHC, 1.3% OC, pH 6.6)

	Residues (% of applied radioactivity) at days after treatment									
	0	1	3	7	14	21	38	62	90	120
Bixafen	95.7	95.2	94.2	94.4	92.7	92.3	91.9	93.7	90.8	91.6
Unidentified radioactivity	< 0.1	0.3	0.3	0.3	0.3	0.2	0.3	0.2	0.4	0.2
Total extracted	95.7	95.6	94.6	94.8	93.0	92.5	92.2	93.9	91.3	91.9
¹⁴ CO ₂	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	0.1	0.1	0.1	0.1	0.2
Volatile organic radioactivity	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted residue	4.3	5.2	6.0	6.3	6.2	5.3	7.6	7.1	8.2	9.0
Total recovery	100.0	100.8	100.6	101.1	99.2	97.9	99.9	101.1	99.6	101.1

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

Table 27 Distribution of radioactive residues after incubation of 0.7 mg/kg [pyrazole]-¹⁴C-bixafen in soil “Laacherhof AIIla” (silt loam, 55% MWHC, 1.1% OC, pH 6.9)

	Residues (% of applied radioactivity) at days after treatment									
	0	1	3	7	14	21	38	62	90	120
Bixafen	94.3	95.1	94.2	92.9	88.5	90.0	89.3	88.9	87.2	86.6
M44 & M45	n.d.	n.d.	n.d.	n.d.	0.6	0.9	0.8	1.5	2.1	2.9
Unidentified radioactivity	< 0.1	0.7	0.5	0.8	0.5	0.3	0.3	0.2	0.4	0.2
Total extracted	94.3	95.8	94.7	93.7	89.6	91.2	90.5	90.7	89.7	89.7
¹⁴ CO ₂	n.a.	0.1	0.1	0.1	0.2	0.2	0.1	0.4	0.6	0.8
Volatile organic radioactivity	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted residue	5.7	4.7	5.5	6.2	5.6	7.1	7.5	7.5	8.9	10.4
Total recovery	100.0	100.5	100.3	100.0	95.4	98.5	98.0	98.6	99.3	101.0

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

Table 28 Distribution of radioactive residues after incubation of 0.7 mg/kg [dichlorophenyl]-¹⁴C-bixafen in soil “Laacherhof AIIla” (silt loam, 55% MWHC, 1.1% OC, pH 6.9)

	Residues (% of applied radioactivity) at days after treatment									
	0	1	3	7	14	21	38	62	90	120
Bixafen	94.2	95.8	94.4	93.9	92.4	92.6	89.8	90.8	88.7	86.4
Unidentified radioactivity	< 0.1	0.2	0.3	0.9	0.5	0.2	0.6	0.3	0.7	0.6
Total extracted	94.2	96.0	94.7	94.7	92.9	92.9	90.4	91.1	89.4	87.0
¹⁴ CO ₂	n.a.	< 0.1	< 0.1	< 0.1	0.1	0.1	0.2	0.2	0.3	0.4
Volatile organic radioactivity	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted residue	5.8	4.4	5.9	6.0	6.2	7.5	9.0	8.2	9.9	12.0
Total recovery	100.0	100.5	100.6	100.7	99.2	100.4	99.6	99.4	99.6	99.5

MWHC = Maximum water holding capacity

OC = organic carbon

n.a. = Not analysed

n.d. = Not detected

Table 29 Distribution of radioactive residues after incubation of 0.7 mg/kg [pyrazole]-¹⁴C-bixafen in soil “Laacherhof Wurmwiese” (loam, 55% MWHC, 2.07% OC, pH 6.0)

	Residues (% of applied radioactivity) at days after treatment									
	0	1	3	7	14	21	38	62	90	120
Bixafen	89.2	92.9	91.1	92.1	89.8	92.6	90.3	90.3	88.0	86.8
M44 & M45	n.d.	n.d.	n.d.	< 0.1	0.2	0.1	0.3	0.3	0.4	0.4
Unidentified radioactivity	4.6	0.5	0.4	0.4	0.3	0.3	0.6	0.3	1.4	0.6
Total extracted	93.8	93.4	91.5	92.5	90.3	93.0	91.3	90.9	89.8	87.8
¹⁴ CO ₂	n.a.	< 0.1	0.1	0.1	0.3	0.5	0.7	1.1	1.3	1.5
Volatile organic radioactivity	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted residue	6.2	5.3	6.5	6.2	5.3	6.6	7.9	7.0	7.6	7.7
Total recovery	100.0	98.7	98.1	98.8	95.9	100.1	99.9	99.1	98.7	97.0

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

Table 30 Distribution of radioactive residues after incubation of 0.7 mg/kg [dichlorophenyl]-¹⁴C-bixafen in soil “Laacherhof Wurmwiese” (loam, 55% MWHC, 2.07% OC, pH 6.0)

	Residues (% of applied radioactivity) at days after treatment									
	0	1	3	7	14	21	38	62	90	120
Bixafen	94.4	93.0	90.7	92.9	90.5	90.3	89.7	87.2	88.1	87.3
Unidentified radioactivity	0.4	0.2	0.2	0.3	0.2	0.3	0.5	0.3	0.9	0.6
Total extracted	94.8	93.2	90.9	93.3	90.8	90.6	90.2	87.5	89.0	88.0
¹⁴ CO ₂	n.a.	< 0.1	< 0.1	< 0.1	0.1	0.1	0.1	0.1	0.2	< 0.1
Volatile organic radioactivity	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted residue	5.2	5.0	5.2	6.2	6.1	6.8	7.2	7.0	8.9	9.0
Total recovery	100.0	98.1	96.1	99.5	96.9	97.5	97.5	94.6	98.0	96.9

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

Table 31 Distribution of radioactive residues after incubation of 0.7 mg/kg [pyrazole]-¹⁴C-bixafen in soil “Hoefchen am Hohenseh” (silt loam, 55% MWHC, 2.62% OC, pH 6.7)

	Residues (% of applied radioactivity) at days after treatment									
	0	1	3	7	14	21	38	62	90	120
Bixafen	91.2	96.4	93.3	94.2	92.2	91.1	92.3	89.8	89.3	89.1
M44 & M45	n.d.	n.d.	n.d.	< 0.1	0.2	0.2	0.2	0.5	0.6	0.6
Unidentified radioactivity	2.1	0.4	0.7	0.5	0.3	0.2	0.3	0.3	0.9	0.5
Total extracted	93.3	96.8	94.0	94.7	92.7	91.5	92.9	90.6	90.8	90.2
¹⁴ CO ₂	n.a.	< 0.1	0.1	0.1	0.2	0.3	0.5	0.8	1.1	1.6
Volatile organic radioactivity	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted residue	6.7	5.6	7.1	6.9	6.7	7.0	7.6	7.7	7.9	7.5
Total recovery	100.0	102.4	101.1	101.7	99.6	98.8	101.0	99.1	99.8	99.3

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

Table 32 Distribution of radioactive residues after incubation of 0.7 mg/kg [dichlorophenyl]-¹⁴C-bixafen in soil “Hoefchen am Hohenseh” (silt loam, 55% MWHC, 2.62% OC, pH 6.7)

	Residues (% of applied radioactivity) at days after treatment									
	0	1	3	7	14	21	38	62	90	120
Bixafen	94.5	93.6	91.0	92.1	91.1	89.9	90.7	88.5	90.8	88.7
Unidentified radioactivity	0.3	0.2	0.1	0.4	0.2	0.1	0.2	0.2	0.6	0.2
Total extracted	94.7	93.8	91.1	92.5	91.3	90.0	90.9	88.7	91.3	89.0
¹⁴ CO ₂	n.a.	< 0.1	< 0.1	< 0.1	0.1	0.1	0.1	0.1	0.2	0.3
Volatile organic radioactivity	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted residue	5.3	5.2	6.1	6.2	6.9	6.9	7.2	7.1	8.5	9.0
Total recovery	100.0	99.1	97.2	98.7	98.3	97.0	98.2	96.0	100.1	98.3

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

In addition to the study presented, De Souza, TJT (2011, BIXAFEN_024) investigated the aerobic degradation of [pyrazole]-¹⁴C-bixafen in four Brazilian soils. Microbial viable soil samples were collected freshly from the field and treated with a rate of 0.4909 mg ai/kg soil.

The soils were extracted with methanol/water. The quantification was performed by high pressure liquid chromatography (HPLC) with radioactivity detector. Unextracted residues were determined by combustion. The liberated ¹⁴CO₂ was absorbed in an appropriate scintillation cocktail and measured by LS counting.

Table 33 Distribution of radioactive residues after incubation of 0.49 mg/kg [pyrazole]-¹⁴C-bixafen in soil “Argissolo” (clay, 50% MWHC, 3.0% OC, pH 5.9)

	Residues (% of applied radioactivity) at days after treatment						
	0	7	14	28	64	92	120
Bixafen	99.1	94.0	100.2	93.1	90.3	83.2	81.1
M44 & M45	n.d.	n.d.	n.d.	2.8	3.1	0.53	0.86
Total extracted	99.1	98.3	100.2	95.9	93.4	84.2	83.5
¹⁴ CO ₂	n.a.	0.2	0.6	1.3	4.4	6.3	8.2
Volatile organic radioactivity	n.a.	< 0.13	< 0.13	< 0.13	< 0.13	< 0.13	< 0.13
Unextracted residue	1.6	3.4	4.4	6.0	8.1	8.0	9.2
Total recovery	100.7	101.9	105.2	103.2	105.9	98.5	100.9

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

Table 34 Distribution of radioactive residues after incubation of 0.49 mg/kg [pyrazole]-¹⁴C-bixafen in soil “Latossolo” (clay, 50% MWHC, 1.4% OC, pH 4.9)

	Residues (% of applied radioactivity) at days after treatment						
	0	7	14	28	64	92	120
Bixafen	101.7	95.1	97.9	91.4	92.0	92.7	84.3
M44 & M45	n.d.	n.d.	0.76	3.06	1.07	0.61	2.39
Total extracted	102.2	97.2	98.3	93.0	92.6	96.4	90.0
¹⁴ CO ₂	n.a.	< 0.13	0.4	1.0	3.4	3.9	4.7
Volatile organic radioactivity	n.a.	< 0.13	< 0.13	< 0.13	0.1	0.2	0.2

	Residues (% of applied radioactivity) at days after treatment						
	0	7	14	28	64	92	120
Unextracted residue	0.9	2.0	3.6	6.0	6.6	3.3	5.4
Total recovery	103.0	99.2	102.3	100.0	102.7	103.8	100.2

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

Table 35 Distribution of radioactive residues after incubation of 0.49 mg/kg [pyrazole]-¹⁴C-bixafen in soil “Neossolo” (clay, 50% MWHC, 0.5% OC, pH 5.6)

	Residues (% of applied radioactivity) at days after treatment						
	0	7	14	28	64	92	120
Bixafen	107.7	108.4	103.5	101.9	96.1	92.9	92.0
M44 (BYF 00587-desmethyl-pyrazole-4-carboxylic acid)	n.d.	n.d.	n.d.	n.d.	1.16	2.84	1.25
Total extracted	107.7	109.3	103.4	101.9	97.2	95.7	95.1
¹⁴ CO ₂	n.a.	< 0.13	< 0.13	0.3	1.6	1.9	2.5
Volatile organic radioactivity	n.a.	< 0.13	< 0.13	< 0.13	< 0.13	< 0.13	< 0.13
Unextracted residue	< 0.13	0.4	0.7	1.0	2.1	2.0	3.0
Total recovery	107.7	109.8	104.2	103.2	100.9	99.6	100.6

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

Table 36 Distribution of radioactive residues after incubation of 0.49 mg/kg [pyrazole]-¹⁴C-bixafen in soil “Gleissolo” (clay, 50% MWHC, 5.5% OC, pH 4.4)

	Residues (% of applied radioactivity) at days after treatment						
	0	7	14	28	64	92	120
Bixafen	97.9	86.6	89.2	88.9	82.8	84.0	84.0
M44 & M45	n.d.	n.d.	n.d.	n.d.	n.d.	0.43	0.42
Total extracted	97.9	92.0	89.3	88.9	82.8	84.7	85.1
¹⁴ CO ₂	n.a.	< 0.13	< 0.13	0.2	1.0	1.2	1.3
Volatile organic radioactivity	n.a.	< 0.13	< 0.13	< 0.13	< 0.13	< 0.13	< 0.13
Unextracted residue	3.1	5.4	5.6	8.6	8.6	10.8	10.5
Total recovery	101.1	97.4	95.0	97.6	92.4	96.7	96.9

MWHC = Maximum water holding capacity

OC = Organic carbon

n.a. = Not analysed

n.d. = Not detected

A third study investigating the aerobic soil metabolism of bixafen was presented by Menke, U (2008, BIXAFEN_025). In this study soils (0–15 cm depth) obtained from a confined rotational crop metabolism study involving application of [pyrazole]- and [dichlorophenyl]-¹⁴C-bixafen at target rates of 0.75 kg ai/ha.

Aliquots of acetonitrile/water extracts were analysed and radioactivity quantified by HPLC (¹⁴C-radio- and UV-detector). The limit of quantification (LOQ) was 0.4% TRR. TLC was used as a method to confirm formation of metabolites. Unextracted residues were determined by combustion followed by LSC and were not characterised further.

Table 37 Distribution of radioactive residues in soil from rotational crop metabolism studies after application of 0.75 kg ai/ha [pyrazole-¹⁴C]-bixafen (sandy loam, 38.4% MWHC, 1.36% OC, pH 7.3)

	Residues (% of applied radioactivity) at days after treatment			
	30	138	285	418
Bixafen	85.3	83.5	77.1	73.6
M21 (bixafen-desmethyl)	0.5	1.2	2.2	1.9
Unidentified	2.3	1.5	1.0	0.6
Total extracted	88.1	86.2	80.3	76.1
Unextracted residue	4.9	7.4	9.8	15.6
Total recovery	93.0	93.7	90.0	91.7

MWHC = Maximum water holding capacity

OC = Organic carbon

Table 38 Distribution of radioactive residues in soil from rotational crop metabolism studies after application of 0.75 kg ai/ha [dichlorophenyl-¹⁴C]-bixafen (sandy loam, 38.4% MWHC, 1.36% OC, pH 7.3)

	Residues (% of applied radioactivity) at days after treatment			
	30	138	285	418
Bixafen	104.9	90.7	80.5	84.4
M21 (bixafen-desmethyl)	0.6	1.1	1.6	2.7
Unidentified	2.3	1.0	0.2	0.4
Total extracted	107.7	92.8	83.0	81.7
Unextracted residue	5.3	8.3	10.4	16.7
Total recovery	113.0	101.1	93.4	104.1

MWHC = Maximum water holding capacity

OC = Organic carbon

Confined rotational crop studies

The metabolism of [pyrazole-5-¹⁴C]-bixafen was investigated by Weber, E, Spiegel, K and Koehn, D (2007, BIXAFEN_029) in the rotational crops wheat, Swiss chard and turnips from three consecutive rotations. The active ingredient was applied uniformly to the soil of a planting container by spray application (day 0) at a rate of 0.785 kg ai/ha. Crops of the first, second and third rotation were sown at day 30, day 138 and day 285. Immature samples investigated were wheat forage and hay. Wheat straw and grain, Swiss chard, turnip leaves and roots were harvested at maturity. Residues in soil were reported in the aerobic metabolism section by Menke, U (2008, BIXAFEN_025).

The samples were extracted with acetonitrile/water (4/1, v/v) subjected to a clean-up step using a C₁₈-SPE cartridge (conventional extraction). For the exhaustive extraction (only conducted for hay and straw), the solids were extracted in a first step with acetonitrile/water (4/1, v/v) and in a second step with acetonitrile/acetic acid (4/1, v/v), both with microwave assistance at increased temperature (80 °C). Each microwave extract was purified using a C₁₈-SPE cartridge. The purified fractions were combined, evaporated and the aqueous remainder was partitioned with dichloromethane.

The total radioactivity was determined by LSC (LOQ: 0.01 mg eq/kg, LOD: 0.001–0.009 mg eq/kg based on background noise level). The extracts were analysed by HPLC. Major metabolites were identified by HPLC and TLC co-chromatography using authentic reference compounds. The conventional extract of Swiss chard of the first rotation showed nearly all metabolites of the other RACs and was used to isolate the polar metabolites which were identified by HPLC-MS/MS. The metabolites in all other samples were assigned by comparison of the HPLC profiles.

In the following table the TRR found in plant samples are summarized.

Table 39 Total radioactive residues in confined rotational crops (three rotations) after application of [pyrazole-5-¹⁴C]-bixafen onto soil at a rate of 0.785 kg ai/ha

	TRR (mg eq/kg)						
	wheat				Swiss	turnip	
	forage	Hay	straw	grain	chard	leaves	roots
first rotation (PBI 30 days)	0.045	0.288	0.434	< 0.01	0.064	0.077	0.047
second rotation (PBI 138 days)	0.058	0.176	0.337	< 0.01	0.059	0.027	0.012
third rotation (PBI 285 days)	0.025	0.153	0.217	n.e.	0.040	0.021	0.015

n.e. = Not extracted

The identification of the radioactive residues revealed the parent substance and seven other metabolites, most of them cleavage products characteristic for the radiolabelled side of the parent molecule. In Table –42 the extracted and identified radioactivity is presented. In wheat grain the TRR was too low for an identification of the residue.

Table 40 Identification and characterisation of radioactive residues in rotational crops (1st rotation, 30 d) following one soil application of [pyrazole-5-¹⁴C]-bixafen at a total field rate of 0.785 kg ai/ha

Metabolite Fraction	Wheat forage (DAT 71)		Wheat hay (DAT 99)		Wheat grain ^a (DAT 138)		Wheat straw (DAT 138)		Swiss chard (DAT 84)		Turnip leaves (DAT 104)		Turnip roots (DAT 104)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	100	0.045	100	0.288	100	0.008	100	0.434	100	0.064	100	0.077	100	0.047
Bixafen	18.5	0.008	32.3	0.093			22.9	0.100	25.5	0.016	36.7	0.028	59.2	0.028
M20	–	–	–	–			–	–	14.6	0.009	–	–	–	–
M21	31.2	0.014	32.0	0.092			43.6	0.189	–	–	6.2	0.005	13.9	0.007
M42	19.8	0.009	–	–			2.4	0.011	1.9	0.001	8.5	0.007	4.3	0.002
M43	11.0	0.005	7.7	0.022			4.7	0.020	13.8	0.009	11.5	0.009	3.1	0.001
M44	–	–	–	–			0.3	0.001	15.2	0.010	5.3	0.004	–	–
M45	6.8	0.003	–	–			3.6	0.016	22.9	0.015	3.4	0.003	3.1	0.001
M47	5.9	0.003	–	–			–	–	4.0	0.003	5.5	0.004	4.3	0.002
Total identified	93.2	0.042	72.0	0.207			77.6	0.337	97.8	0.062	77.1	0.059	87.8	0.041
Total characterised without identification	–	–	12.5	0.036			7.2	0.031	–	–	20.4	0.016	10.9	0.005
Fractions not analysed	–	–	5.5	0.016	45.6	0.004	10.3	0.045	–	–	–	–	–	–
Total extracted	93.2	0.042	90.1	0.259	45.6	0.004	95.1	0.413	97.8	0.062	97.5	0.075	98.7	0.047
Total unextracted	6.8	0.003	10.0	0.029	54.4	0.004	4.9	0.022	2.2	0.001	2.5	0.002	1.3	0.001

DAT = Days after treatment

^a The TRR found in wheat grain was too low for further analysis

Table 41 Identification and characterisation of radioactive residues in rotational crops (2nd rotation, 138 d) following one soil application of [pyrazole-5-¹⁴C]-bixafen at a total field rate of 0.785 kg ai/ha

Metabolite Fraction	Wheat forage (DAT 187)		Wheat hay (DAT 236)		Wheat grain ^a (DAT 285)		Wheat straw (DAT 285)		Swiss chard (DAT 198)		Turnip leaves (DAT 212)		Turnip roots (DAT 212)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	100	0.058	100	0.176	100	0.007	100	0.337	100	0.059	100	0.027	100	0.012
Bixafen	18.1	0.011	11.7	0.021			13.9	0.047	36.7	0.022	21.8	0.006	68.8	0.008
M20	–	–	–	–			–	–	19.8	0.012	–	–	–	–
M21	51.0	0.030	48.7	0.086			62.3	0.210	3.4	0.002	6.1	0.002	19.3	0.002
M42	2.9	0.002	7.2	0.013			–	–	–	–	3.5	0.001	4.3	0.001
M43	3.2	0.002	14.0	0.025			3.5	0.012	7.1	0.004	5.6	0.002	–	–
M44	–	–	–	–			2.0	0.007	19.2	0.011	36.9	0.010	–	–
M45	–	–	–	–			1.8	0.006	7.6	0.005	12.3	0.003	–	–
M47	3.1	0.002	–	–			–	–	2.6	0.002	4.8	0.001	3.0	< 0.001
Total identified	78.4	0.046	81.7	0.144			83.5	0.281	96.3	0.057	91.1	0.025	95.5	0.011
Total characterised without identification	10.3	0.006	5.0	0.009			1.2	0.004	–	–	4.6	0.001	–	–
Fractions not analysed	–	–	8.4	0.015	22.2	0.001	7.9	0.026	–	–	–	–	–	–
Total extracted	88.7	0.052	95.1	0.167	22.2	0.001	92.5	0.311	96.3	0.057	95.7	0.026	95.5	0.011
Total unextracted	11.3	0.007	5.0	0.009	77.8	0.005	7.5	0.025	3.7	0.002	4.3	0.001	4.5	0.001

DAT = days after treatment

^a The TRR found in wheat grain was too low for further analysis

Table 42 Identification and characterisation of radioactive residues in rotational crops (3rd rotation, 285 d) following one soil application of [pyrazole-5-¹⁴C]-bixafen at a total field rate of 0.785 kg ai/ha

Metabolite Fraction	Wheat forage (DAT 330)		Wheat hay (DAT 380)		Wheat straw (DAT 418)		Swiss chard (DAT 348)		Turnip leaves (DAT 357)		Turnip roots (DAT 357)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	100	0.025	100	0.153	100	0.217	100	0.040	100	0.021	100	0.015
Bixafen	11.3	0.003	18.8	0.029	16.6	0.036	34.9	0.014	28.0	0.006	62.9	0.009
M20	–	–	–	–	–	–	18.4	0.007	–	–	–	–
M21	45.8	0.011	50.4	0.077	53.5	0.116	2.5	0.001	7.6	0.002	26.8	0.004
M42	–	–	4.1	0.006	–	–	–	–	6.7	0.001	4.0	0.001
M43	15.0	0.004	14.0	0.021	4.9	0.011	9.9	0.004	14.1	0.003	–	–
M44	–	–	–	–	–	–	14.8	0.006	–	–	–	–
M45	–	–	–	–	–	–	4.9	0.002	16.1	0.003	–	–
M47	–	–	–	–	–	–	–	–	4.9	0.001	3.9	0.001
Total identified	72.0	0.018	87.3	0.133	74.9	0.162	85.4	0.034	77.3	0.016	97.6	0.014
Total characterised without identification	16.9	0.004	–	–	13.9	0.030	9.0	0.004	19.0	0.004	–	–
Fractions not analysed	–	–	7.0	0.011	7.0	0.015	–	–	–	–	–	–

Metabolite Fraction	Wheat forage (DAT 330)		Wheat hay (DAT 380)		Wheat straw (DAT 418)		Swiss chard (DAT 348)		Turnip leaves (DAT 357)		Turnip roots (DAT 357)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Total extracted	88.9	0.022	94.3	0.144	95.8	0.208	94.4	0.038	96.3	0.020	97.6	0.014
Total unextracted	11.1	0.003	5.7	0.009	4.2	0.009	5.6	0.002	3.7	0.001	2.4	< 0.001

DAT = Days after treatment

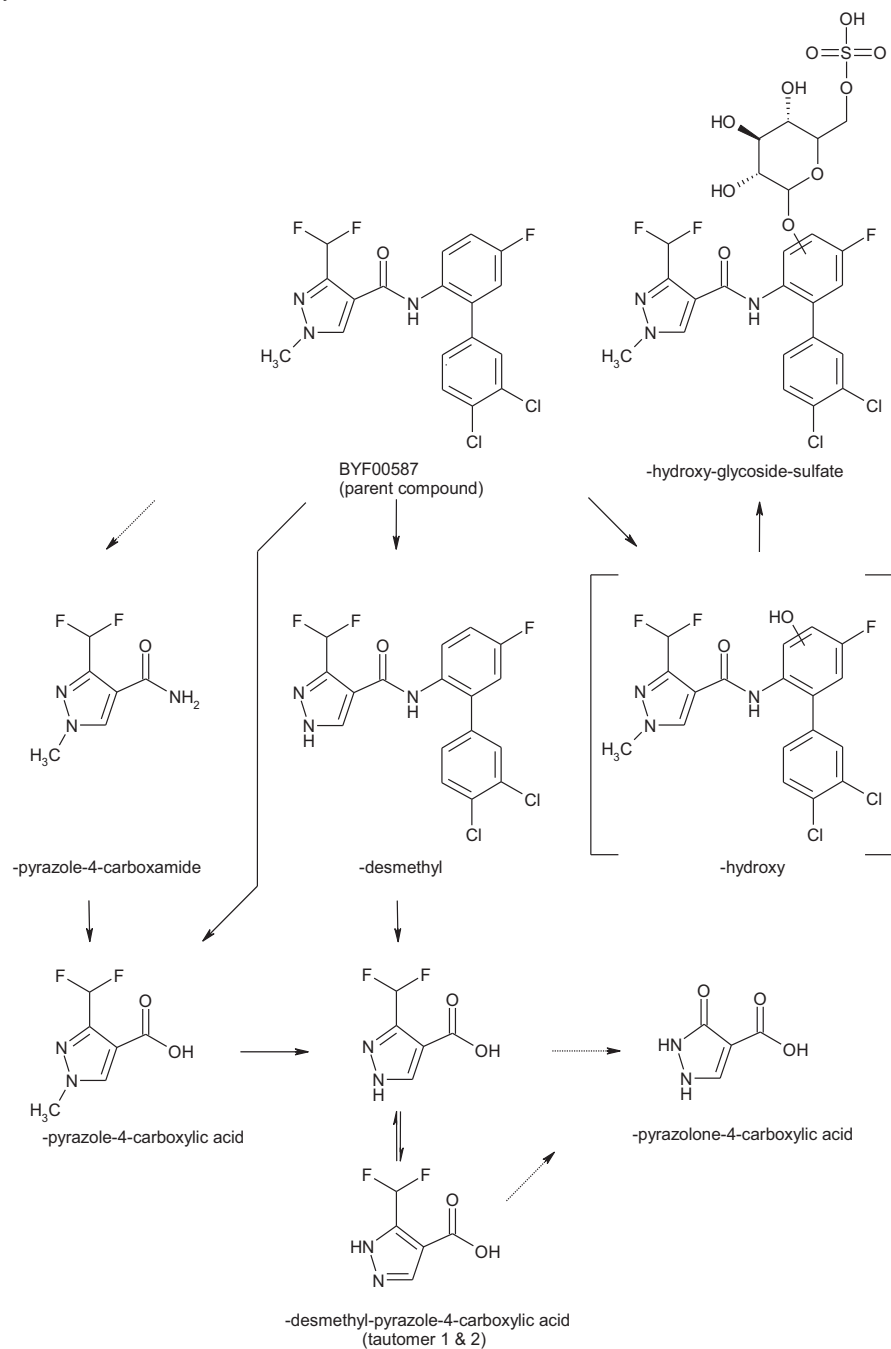


Figure 6 Proposed metabolic pathway of bixafen in rotational crops following application of [pyrazole-5-¹⁴C]-bixafen

For [dichlorophenyl-UL-¹⁴C]-bixafen the metabolism was investigated in the rotational crops wheat, Swiss chard and turnips from three consecutive rotations by Kuhnke, G, Weber, E., and Koehn, D (2007, BIXAFEN_028). The active ingredient was applied uniformly to the soil of a planting container by spray application (day 0) at a rate of 847 g ai/ha. Crops of the first, second and third rotation were sown at day 30, day 138 and day 285. Immature samples investigated were wheat forage and hay. Wheat straw and grain, Swiss chard, turnip leaves and roots were harvested at maturity. No residues in soil were reported.

The samples were extracted with acetonitrile/water (4/1, v/v) subjected to a clean-up step using a C₁₈-SPE cartridge (conventional extraction). For the exhaustive extraction (only conducted for hay and straw), the solids were extracted in a first step with acetonitrile/water (4/1, v/v) and in a second step with acetonitrile/acetic acid (4/1, v/v), both with microwave assistance at increased temperature (80 °C). Each microwave extract was purified using a C₁₈-SPE cartridge. The purified fractions were combined, evaporated and the aqueous remainder was partitioned with dichloromethane.

The total radioactivity was determined by LSC (LOQ: 0.01 mg eq/kg, LOD: 0.001–0.009 mg eq/kg based on background noise level). The extracts were analysed by HPLC. Major metabolites were identified by HPLC and TLC co-chromatography using authentic reference compounds.

In the following table the TRR found in plant samples are summarized:

Table 43 Total radioactive residues in confined rotational crops (three rotations) after application of [dichlorophenyl-UL-¹⁴C]-bixafen at a total field rate of 0.847 kg ai/ha

	TRR (mg eq/kg)						
	wheat				Swiss	turnip	
	forage	Hay	straw	grain	chard	leaves	roots
first rotation (PBI 30 days)	0.020	0.195	0.492	0.001	0.033	0.025	0.033
second rotation (PBI 138 days)	0.035	0.193	0.269	0.002	0.041	0.013	0.012
third rotation (PBI 285 days)	0.013	0.129	0.241	n.a.	0.027	0.007	0.011

n.a. = Not analysed

The identification of the radioactive residues revealed the parent substance, M20 (BYF 00587-hydroxy-glycoside-sulfate) and M21 (bixafen-desmethyl) as major metabolites. Further degradation or breakdown products were not identified. In Table –46 the extracted and identified radioactivity is presented. In wheat grain the TRR was too low for an identification of the residue.

Table 44 Identification and characterisation of radioactive residues in rotational crops (1st rotation, 30 d) following one soil application of [dichlorophenyl-UL-¹⁴C]-bixafen at a total field rate of 0.847 kg ai/ha

Metabolite Fraction	Wheat forage (DAT 70)		Wheat hay (DAT 98)		Wheat grain ^a (DAT 137)		Wheat straw (DAT 137)		Swiss chard (DAT 83)		Turnip leaves (DAT 103)		Turnip roots (DAT 103)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	100	0.020	100	0.195	100	0.001	100	0.492	100	0.033	100	0.025	100	0.033
Bixafen	27.0	0.006	43.0	0.084			36.9	0.181	70.5	0.023	62.7	0.016	77.8	0.026
M20	–	–	–	–			–	–	27.6	0.009	–	–	–	–
M21	61.7	0.013	45.4	0.089			57.2	0.281	–	–	20.4	0.005	20.3	0.007
Total identified	88.7	0.018	88.4	0.172			94.1	0.462	70.5	0.032	83.1	0.021	98.2	0.033
Total characterised without identification	–	–	–	–			–	–	–	–	12.6	0.003	–	–
Fractions not	–	–	4.4	0.009	39.5	< 0.001	1.3	0.006	–	–	–	–	–	–

Metabolite Fraction	Wheat forage (DAT 70)		Wheat hay (DAT 98)		Wheat grain ^a (DAT 137)		Wheat straw (DAT 137)		Swiss chard (DAT 83)		Turnip leaves (DAT 103)		Turnip roots (DAT 103)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
analysed														
Total extracted	88.7	0.018	92.8	0.181	39.5	< 0.001	95.3	0.469	98.1	0.032	95.7	0.024	98.2	0.033
Total unextracted	11.3	0.002	7.2	0.014	60.5	0.001	4.7	0.023	1.9	0.001	4.3	0.001	1.8	0.001

DAT = Days after treatment

^a The TRR found in wheat grain was too low for further analysis

Table 45 Identification and characterisation of radioactive residues in rotational crops (2nd rotation, 138 d) following one soil application of [dichlorophenyl-UL-¹⁴C]-bixafen at a total field rate of 0.847 kg ai/ha

Metabolite Fraction	Wheat forage (DAT 186)		Wheat hay (DAT 235)		Wheat grain ^a (DAT 284)		Wheat straw (DAT 284)		Swiss chard (DAT 197)		Turnip leaves (DAT 211)		Turnip roots (DAT 211)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	100	0.035	100	0.193	100	0.002	100	0.269	100	0.041	100	0.013	100	0.012
Bixafen	20.7	0.007	37.8	0.073			13.8	0.037	51.7	0.021	41.9	0.005	74.9	0.009
M20	—	—	—	—			—	—	38.3	0.016	—	—	—	—
M21	61.9	0.022	55.3	0.107			72.1	0.194	5.0	0.002	14.6	0.002	21.2	0.003
Total identified	82.7	0.029	93.1	0.180			85.9	0.231	95.0	0.039	56.5	0.007	96.1	0.012
Total characterised without identification	—	—	1.9	0.004			5.8	0.016	—	—	33.6	0.004	—	—
Fractions not analysed	—	—	1.9	0.004	10.7	< 0.001	5.8	0.016	—	—	—	—	—	—
Total extracted	82.7	0.029	95.1	0.184	10.7	< 0.001	91.7	0.247	95.0	0.039	90.0	0.012	96.1	0.012
Total unextracted	17.3	0.006	4.9	0.010	89.3	0.001	8.4	0.023	5.0	0.002	10.0	0.001	3.9	< 0.001

DAT = Days after treatment

^a The TRR found in wheat grain was too low for further analysis

Table 46 Identification and characterisation of radioactive residues in rotational crops (3rd rotation, 285 d) following one soil application of [dichlorophenyl-UL-¹⁴C]-bixafen at a total field rate of 0.847 kg ai/ha

Metabolite Fraction	Wheat forage (DAT 329)		Wheat hay (DAT 379)		Wheat straw (DAT 417)		Swiss chard (DAT 347)		Turnip leaves (DAT 356)		Turnip roots (DAT 356)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	100	0.013	100	0.129	100	0.241	100	0.027	100	0.007	100	0.011
Bixafen	17.2	0.002	32.8	0.042	22.0	0.053	56.4	0.015	59.3	0.004	72.7	0.008
M20	—	—	—	—	—	—	24.7	0.007	—	—	—	—
M21	65.9	0.009	58.2	0.075	72.8	0.175	3.1	0.001	18.1	0.001	24.2	0.003
Total identified	83.1	0.011	90.9	0.117	94.8	0.228	84.3	0.022	77.3	0.006	96.9	0.011
Total characterised without identification	—	—	2.5	0.003	1.5	0.004	10.7	0.003	17.1	0.001	—	—
Fractions not analysed	—	—	2.5	0.003	1.5	0.004	—	—	—	—	—	—
Total extracted	83.1	0.011	93.5	0.121	96.3	0.232	95.0	0.025	94.4	0.007	96.9	0.011
Total	16.9	0.002	6.5	0.009	3.7	0.009	5.0	0.001	5.6	< 0.001	3.1	< 0.001

DAT = Days after treatment



Field crop rotation studies

Four rotational crop studies (limited field studies) were carried out on bixafen during the 2006 and 2007 season. Two studies were performed in Germany and one study each in northern France and Spain.

For investigation of the residue levels that may arise in succeeding crops after a short plant back interval simulating crop failure (30 days), the bixafen was applied once as a spray application at a rate of 0.281 kg ai/ha to bare soil. For longer rotations split spray applications to barley as primary crops were carried out. At all locations, the first spray application on barley was performed at a rate of 0.156 kg ai/ha at growth stage of BBCH 47 (“flag leaf sheath opening”). The second application was carried out at a rate of 0.125 kg ai/ha at growth stage BBCH 69 (“end of flowering”). The grain was harvested normally and the straw was left on the field and ploughed. Until plating/sowing of succeeding crops, no other crop was cultivated.

In all plots turnips/carrots, lettuce and wheat were planted as succeeding crops with plant back intervals of 30, 60–180 and 270–365 days.

In the following table an overview of the studies, involved plots and cultivated crops is presented.

Table 47 Overview of field crop rotation studies for bixafen

Study Report, Location, Reference	Succeeding crop, plant back interval		
Rotation 1: 0.281 kg ai/ha to bare soil			
RA-2143/06, Northern France, Fresnoy les Roye, Schoening, R and Erler, S (2008, BIXAFEN 031)	Turnip, 30 days	Lettuce, 30 days	Wheat, 30 days
RA-2145/06, Spain, Llorona, Schoening, R and Erler, S (2008, BIXAFEN 033)	Carrot, 32 days	Lettuce, 32 days	Wheat, 32 days
RA-2144/06, Germany, Monheim, Schoening, R and Erler, S (2008, BIXAFEN 032)	Turnip, 30 days	Lettuce, 27 days	Wheat, 28 days
RA-2139/06, Germany, Burscheid, Schoening, R and Erler, S (2008, BIXAFEN 030)	Turnip, 30 days	Lettuce, 27 days	Wheat, 30 days
Rotation 2: primary crop: barley; 0.156 kg ai/ha at BBCH 47 plus 0.125 kg ai/ha at BBCH 69 (RA-2145/06 at BBCH 71)			
RA-2143/06, Northern France, Fresnoy les Roye, Schoening, R and Erler, S (2008, BIXAFEN 031)	Turnip/carrot, 60 days	Lettuce, 60 days	Wheat, 120 days
RA-2145/06, Spain, Llorona, Schoening, R and Erler, S (2008, BIXAFEN 033)	Turnip/carrot, 70 days	Lettuce, 70 days	Wheat, 184 days
RA-2144/06, Germany, Monheim, Schoening, R and Erler, S (2008, BIXAFEN 032)	Turnip/carrot, 60 days	Lettuce, 60 days	Wheat, 136 days
RA-2139/06, Germany, Burscheid, Schoening, R and Erler, S (2008, BIXAFEN 030)	Turnip/carrot, 61 days	Lettuce, 61 days	Wheat, 140 days
Rotation 3: primary crop: barley; 0.156 kg ai/ha at BBCH 47 plus 0.125 kg ai/ha at BBCH 69 (RA-2145/06 at BBCH 71)			
RA-2143/06, Northern France, Fresnoy les Roye, Schoening, R and Erler, S (2008, BIXAFEN 031)	Turnip/carrot, 331 days	Lettuce, 298 days	Wheat, 298 days
RA-2145/06, Spain, Llorona, Schoening, R and Erler, S (2008, BIXAFEN 033)	Turnip/carrot, 302 days	Lettuce, 302 days	Wheat, 278 days
RA-2144/06, Germany, Monheim, Schoening, R and Erler, S (2008, BIXAFEN 032)	not sampled—damaged by animals	Lettuce, 331 days	Wheat, 304 days
RA-2139/06, Germany, Burscheid, Schoening, R and Erler, S (2008, BIXAFEN 030)	Turnip/carrot, 314 days	Lettuce, 328 days	Wheat, 300 days

Sampling was done as follows: Samples of lettuce, turnip body and leaf (northern Europe) or carrot root and leaf (southern Europe) were taken 14 days prior to harvest date and at commercial harvest following all plant back-intervals. Wheat green material was sampled at growth stage BBCH 29/30, while samples of grain and straw were collected at full maturity of the crop (BBCH 89) from all rotations.

Samples of plant material were analysed for bixafen and M21 (bixafen-desmethyl) using method no. 01012 (see analytical methods).

In nearly all samples collected not residues of bixafen or its metabolite M21 (bixafen-desmethyl) above the LOQ of 0.01 mg/kg for each analyte were found. The only exceptions were residues 0.05 mg/kg for bixafen in lettuce (early growth stage, BBCH 46) grown in Burscheid, Germany (1st rotation, sampled 60 days after treatment) and of 0.02 mg/kg for M21 in wheat straw grown Llorona, Spain (1st rotation, sampled 262 days after treatment). In the following table a summary of all residue data is presented:

Rotation	Crop, variety	Treatment	Portion analysed	DALT (d)	Bixafen (mg/kg)	M21 (mg/kg)	Total (mg/kg)
RA-2143/06, Northern France, Fresnoy les Roye, Schoening, R and Erler, S (2008, BIXAFEN_031)							
1 st	Turnip, BI.6I Collet Violet	1 × 0.281 kg ai/ha	leaf	78	< 0.01	< 0.01	< 0.02
			body	93	< 0.01	< 0.01	< 0.02
				78	< 0.01	< 0.01	< 0.02
				93	< 0.01	< 0.01	< 0.02
	Lettuce, Beurre-Hardy		head	61	< 0.01	< 0.01	< 0.02
				75	< 0.01	< 0.01	< 0.02
	Winter wheat, Perfector		forage	204	< 0.01	< 0.01	< 0.02
			straw	336	< 0.01	< 0.01	< 0.02
			grain	336	< 0.01	< 0.01	< 0.02
2 nd	Turnip, Collet Violett	1 × 0.156 kg ai/ha + 1 × 0.125 kg ai/ha	leaf	111	< 0.01	< 0.01	< 0.02
			body	125	< 0.01	< 0.01	< 0.02
				111	< 0.01	< 0.01	< 0.02
				125	< 0.01	< 0.01	< 0.02
	Lettuce, Beurre Hardy, Butterhead variety		head	90	< 0.01	< 0.01	< 0.02
				104	< 0.01	< 0.01	< 0.02
	Winter wheat, Isengrain		forage	293	< 0.01	< 0.01	< 0.02
			straw	419	< 0.01	< 0.01	< 0.02
			grain	419	< 0.01	< 0.01	< 0.02
3 rd	Turnip, Collet Violett	1 × 0.156 kg ai/ha + 1 × 0.125 kg ai/ha	leaf	406	< 0.01	< 0.01	< 0.02
			body	421	< 0.01	< 0.01	< 0.02
				406	< 0.01	< 0.01	< 0.02
				421	< 0.01	< 0.01	< 0.02
	Lettuce, Madras, Loose leaf		head	344	< 0.01	< 0.01	< 0.02
				358	< 0.01	< 0.01	< 0.02
	Spring wheat, Lona		grain	453	< 0.01	< 0.01	< 0.02
			straw	453	< 0.01	< 0.01	< 0.02
RA-2145/06, Spain, Llorona, Schoening, R and Erler, S (2008, BIXAFEN_033)							
1 st	Carrot, Touchon	1 × 0.281 kg ai/ha	leaf	179	< 0.01	< 0.01	< 0.02
			body	193	< 0.01	< 0.01	< 0.02
				179	< 0.01	< 0.01	< 0.02
				193	< 0.01	< 0.01	< 0.02
	Lettuce, Batavia, Butterhead variety		head	70	< 0.01	< 0.01	< 0.02
				83	< 0.01	< 0.01	< 0.02
	Winter wheat		forage	155	< 0.01	< 0.01	< 0.02
			straw	262	< 0.01	0.02	0.03
			grain	262	< 0.01	< 0.01	< 0.02
2 nd	Carrot	1 × 0.156 kg ai/ha + 1 × 0.125 kg ai/ha	leaf	173	< 0.01	< 0.01	< 0.02
			body	187	< 0.01	< 0.01	< 0.02
				173	< 0.01	< 0.01	< 0.02
				187	< 0.01	< 0.01	< 0.02

Rotation	Crop, variety	Treatment	Portion analysed	DALT (d)	Bixafen (mg/kg)	M21 (mg/kg)	Total (mg/kg)
	Lettuce		head	97 110	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02
	Winter wheat		forage straw grain	307 394 394	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02
3 rd	Carrot	1 × 0.156 kg ai/ha + 1 × 0.125 kg ai/ha	leaf body	421 435 421 435	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02
	Lettuce		head	358 371	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02
	Winter wheat		forage straw grain	371 442 442	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02
RA-2144/06, Germany, Monheim, Schoening, R and Erler, S (2008, BIXAFEN_032)							
1 st	Turnip, Rondo	1 × 0.281 kg ai/ha	leaf body	86 100 86 100	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02
	Lettuce		head	59 73	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02
	Winter wheat, Skater		forage straw grain	216 304 304	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02
2 nd	Turnip, Rondo	1 × 0.156 kg ai/ha + 1 × 0.125 kg ai/ha	leaf body	122 136 122 136	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02
	Lettuce, Gisela		head	94 108	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02
	Winter wheat, Skater		forage straw grain	324 412 412	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02
3 rd	Lettuce, Gisela	1 × 0.156 kg ai/ha + 1 × 0.125 kg ai/ha	head	354 368	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02
	Spring wheat, Thasos		forage straw grain	368 448 448	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02
RA-2139/06, Germany, Burscheid, Schoening, R and Erler, S (2008, BIXAFEN_030)							
1 st	Turnip, Rondo	1 × 0.281 kg ai/ha	leaf body	90 104 90 104	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02
	Lettuce		head	60 74	0.05 < 0.01	< 0.01 < 0.01	0.06 < 0.02
	Winter wheat, Tommy		forage straw grain	190 314 314	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02
2 nd	Turnip, Rondo	1 × 0.156 kg ai/ha + 1 × 0.125 kg ai/ha	leaf body	151 135 121 135	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02
	Lettuce, Gisela		head	97 111	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02
	Winter wheat, Tommy		forage straw grain	302 426 426	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02
3 rd	Turnip, Mairuebe	1 × 0.156 kg ai/ha + 1 ×	leaf body	421 435 421	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02

Rotation	Crop, variety	Treatment	Portion analysed	DALT (d)	Bixafen (mg/kg)	M21 (mg/kg)	Total (mg/kg)
		0.125 kg ai/ha		435	< 0.01	< 0.01	< 0.02
	Lettuce, Gisela		head	359	< 0.01	< 0.01	< 0.02
				373	< 0.01	< 0.01	< 0.02
	Winter wheat, Tommy		forage	350	< 0.01	< 0.01	< 0.02
			straw	446	< 0.01	< 0.01	< 0.02
			grain	446	< 0.01	< 0.01	< 0.02

Field dissipation studies

The dissipation of bixafen in soil was investigated at six sites under European field conditions (Heinemann, O, 2007, BIXAFEN_026). The active ingredient was applied at nominal rates of 0.125 kg ai/ha as a 450 SC formulation onto the ground in Burscheid (Germany), Little Shelford (Great Britain), Esloe (Sweden), Vatteville (Northern France), Vilobi d'Onyar (Spain) and Albaro (Italy).

Soil samples were taken at day 0 to approximately 730 days post application at a maximum depth of 50 cm. The samples were extracted in a microwave extractor using acetonitrile/water (4/1, v/v). Identification and quantitation of the analytes was achieved by high performance liquid chromatography using MS/MS detection in the Multiple Reaction Monitoring mode. The limit of quantitation (LOQ) of the method was 5.0 µg/kg for bixafen and bixafen-desmethyl. The limit of detection (LOD) of the method was 1.5 µg/kg for both analytes.

In the soil only the first 0–10 cm contained significant residues above the LOQ. Other layers are not summarized. The soil characteristics investigated are summarized in Table .

Table 48 Soil characteristics (0–30 cm depth) used for bixafen soil dissipation studies

Soil		Burscheid, Germany	Little Shelford, Great Britain	Esloe, Sweden	Vatteville, Northern France	Vilobi d'Onyar, Spain	Albaro, Italy
Soil type (USDA)	Dim	silt loam	sandy loam	silt loam	silt loam	loam	silt loam
Clay (< 0.002 mm)	[%]	22.9	15.6	27.4	16.5	14.8	20.7
Silt (0.002-0.050 mm)	[%]	70.5	20.8	50.2	66.0	37.8	53.5
Sand (0.050-2.00 mm)	[%]	6.6	63.6	22.4	17.5	47.4	25.8
CEC	[meq/100 g]	12.9	16.1	29.9	12.5	7.4	20.0
Chalk	[% CaCO ₃]	< 0.1	10.8	3.0	< 0.1	< 0.1	12.9
Organic carbon	[% Carbon]	1.01	1.21	3.48	0.80	0.68	1.14
pH (CaCl ₂)		6.3	7.4	7.4	6.7	6.1	7.5
pH (H ₂ O)		6.9	8.0	8.1	7.3	6.7	8.3
Wk max	[g/100 g]	45.6	43.2	52.5	43.3	36.2	48.8
Wk pF 2	[Vol%]	45.5	30.5	43.5	42.1	26.3	41.3

For M21 (bixafen-desmethyl) no residues above the LOQ were found in the samples investigated. In the following tables the bixafen residue found in soil and the percent remaining are summarized.

Table 49 Residues of bixafen found in different soils treated with nominal rates of 0.125 kg ai/ha after 0–740 days

Burscheid, Germany		Little Shelford, Great Britain		Esloe, Sweden		Vatteville, North. France		Vilobi d'Onyar, Spain		Albaro, Italy	
DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg
0	97.4	0	107.8	0	132	0	89.9	0	85.1	0	92.3

Burscheid, Germany		Little Shelford, Great Britain		Esloe, Sweden		Vatteville, North. France		Vilobi d'Onyar, Spain		Albaro, Italy	
DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg
12	83.1	13	71.3	14	79.6	14	60.2	13	56.7	14	53.8
25	85.1	27	72.6	28	94.0	28	58.7	27	64.0	27	44.4
56	52.4	55	59.2	56	67.5	56	45.6	55	65.8	57	23.4
104	45.8	102	65.8	100	63.0	107	56.7	100	36.0	100	48.6
151	47.6	146	53.5	150	66.3	153	46.7	154	24.8	150	22.3
201	54.9	211	49.5	209	60.7	210	43.6	223	21.1	209	32.6
266	40.4	270	44.7	276	66.5	267	50.4	273	34.7	272	42.5
363	51.6	365	52.2	365	65.6	364	36.8	377	26.5	366	19.9
481	47.2	481	40.7	480	60.3	484	35.2	504	24.8	479	12.4
592	49.5	613	34.8	578	57.1	607	36.7	603	26.6	601	18.3
726	46.1	740	31.0	724	52.1	734	37.2	729	18.3	730	15.9

Table 50 Percent bixafen remaining in different soils treated with nominal rates of 0.125 kg ai/ha after 0–740 days

Burscheid, Germany		Little Shelford, Great Britain		Esloe, Sweden		Vatteville, North. France		Vilobi d'Onyar, Spain		Albaro, Italy	
DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg	DAT [days]	µg/kg
0	100.0	0	100.0	0	100.0	0	100.0	0	100.0	0	100.0
12	85.3	13	66.1	14	60.3	14	67.0	13	66.6	14	58.3
25	87.4	27	67.3	28	71.2	28	65.3	27	75.2	27	48.1
56	53.8	55	54.9	56	51.1	56	50.7	55	77.3	57	25.4
104	47.0	102	61.0	100	47.7	107	63.1	100	42.3	100	52.7
151	48.9	146	49.6	150	50.2	153	51.9	154	29.1	150	24.2
201	56.4	211	45.9	209	46.0	210	48.5	223	24.8	209	35.3
266	41.5	270	41.5	276	50.4	267	56.1	273	40.8	272	46.0
363	53.0	365	48.4	365	49.7	364	40.9	377	31.1	366	21.6
481	48.5	481	37.8	480	45.7	484	39.2	504	29.1	479	13.4
592	50.8	613	32.3	578	43.3	607	40.8	603	31.3	601	19.8
726	47.3	740	28.8	724	39.5	734	41.4	729	21.5	730	17.2

Long-term soil accumulation

The possibility of the accumulation of bixafen and M21 (bixafen-desmethyl) in soil under European field conditions was investigated after annual applications of bixafen on bare soil plots at two sites in Monheim am Rhein (Germany) and Tarascon (France) by Heinemann, O and Weuthen, M (2013, BIXAFEN_027). The sites were located in the Monheim, Germany and Les Cayades, Southern France. Each plot received annual treatments to bare soil equivalent to 0.138 kg ai/ha. During the year grass was sown on these plots and incorporated before the next application.

Table 51 Soil properties for the long-term soil dissipation study with bixafen

		Depth (cm)			
		Monheim		Les Cayades	
Soil property	Units	0–30	30–50	0–30	30–50
Soil type (USDA)		sandy loam	sandy loam	silt loam	silt loam
lay (< 0.002 mm)	[%]	10.5	8.5	19.5	27.1
Silt (0.002–0.050 mm)	[%]	18.2	21.3	62.8	53.9
Sand (0.050–2.00 mm)	[%]	71.3	70.2	17.7	19.0
CEC	[meq/100 g]	7.1	3.8	12.1	12.8
Chalk	[% CaCO ₃]	< 0.1	< 0.1	40.6	38.6
Organic carbon	[% Carbon]	1.28	0.43	0.74	0.89
pH (CaCl ₂)		6.3	6.6	7.5	7.7

		Depth (cm)			
		Monheim		Les Cayades	
Soil property	Units	0–30	30–50	0–30	30–50
pH (H ₂ O)		6.9	7.3	8.4	8.7
Max water capacity	[g/100 g]	39.7	33.8	40.3	42.7
pF 2	[Vol%]	26.9	23.5	36.4	35.9

Since 2005 soil samples were collected and analysed for residues of bixafen and M21. Soil samples were extracted with acetonitrile/water (4/1, v/v). Identification and quantitation of the analytes was done by high performance liquid chromatography using MS/MS detection in the Multiple Reaction Monitoring mode. The limit of quantitation (LOQ) of the method was 5.0 µg/kg, the limit of detection (LOD) was 1.5 µg/kg for both analytes.

Following the 1st application in spring 2005, the experiments were either terminated when a plateau concentration was reached (France in autumn 2010), or due to technical reasons (Germany in autumn 2012).

Following eight consecutive annual treatments in Germany, the total soil residue of Bixafen was degraded to 47% (based on a nominal concentration of 734 µg/kg resulting from eight applications of 137.7 g/ha each and the highest peak concentration of 347.5 µg/kg soil). However, a plateau in the soil concentration of bixafen was not observed.

Following six consecutive annual treatments in France, the total soil residue of Bixafen in autumn, i.e. prior to winter dormancy, was degraded to 32.5% (based on a nominal concentration of 551 µg/kg resulting from six applications of 137.7 g/ha each and the highest peak concentration of 179.2 µg/kg soil). A plateau was reached at the end of the study.

At both sites, the residues of M21 were low and represented less than 5% of the nominal Bixafen concentration applied until the respective sampling point in time.

In the following tables the residues of bixafen and M21 (bixafen-desmethyl) in soil over 2720 days are summarized. Although soil samples up to a depth of 100 cm were collected, residues are only presented for soil layers containing detectable residues.

Bixafen

Table 52 Residues of bixafen and bixafen-desmethyl after annual application in Monheim, Germany at rates of 0.138 kg ai/ha

Days & appl.	Bixafen in µg/kg soil															
	0 ^a	0	194	353	354	565	710	711	914	1082	1082	1284	1460	1460	1460	1665
Layer	0 ^a	0	194	353	354	565	710	711	914	1082	1082	1284	1460	1460	1460	1665
in cm	/1 st	/1 st	/2 nd	/2 nd	/2 nd	/2 nd	/2 nd	/3 rd	/3 rd	/4 th	/4 th	/4 th	/6 th	/6 th	/7 th	/8 th
Bixafen																
0–10	n.d.	81.5	51.8	59.9	115.6	101	90.3	144	146.1	137.6	n.d.	161.2	159.3	239.8	226.9	223.5
10–20	n.d.	<5	<5	<5	<5	<5	<5	<5	7.09	18.27	12.97	8.68	16.81	12.27	21.5	24.7
20–30	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<5	<5	<5	<5	<5	<5	<5	<5	5.5	5.1
30–40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<5	<5	<5	<5	<5	<5	<5
40–50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<5	<5	<5
50–60	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<5	<5
60–70	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<5
70–80	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<5
80–90	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	<5
90–100	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	<5
M21 (bixafen-desmethyl)																
0–10	n.d.	n.d.	n.d.	n.d.	<5	<5	<5	<5	5.2	5.3	5.2	6.2	7.5	7.6	9.0	10.2
10–20	n.d.	n.d.	n.d.	n.d.	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
20–30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.a. = Not analysed

n.d. = Not detected (LOD: 1.5 µg/kg soil)

Table 53 Residues of bixafen and bixafen-desmethyl after annual application in Les Cayades, Southern France at rates of 0.138 kg ai/ha

Days & appl.	Bixafen in µg/kg soil														
	0 ^a	0/1 st	215	334	335	570	697	698	913	1062	1063	1293	1426	1427	1655
Layer in cm	Bixafen														
0–10	n.d.	79.5	27.1	34.5	120.8	52.3	54.5	132.3	93.3	91.2	140.4	73.6	106.4	154.6	91.5
10–20	n.d.	n.d.	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	6.3	< 5	< 5	6.2	< 5
20–30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	n.d.	< 5	< 5	< 5	< 5	< 5	< 5
30–40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	< 5	< 5
40–50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	< 5	n.d.
50–60	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	< 5	n.a.
	M21 (bixafen-desmethyl)														
0–10	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	< 5	< 5	< 5	< 5	< 5	< 5	5.6	< 5	< 5
10–20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

n.a. = Not analysed

n.d. = Not detected (LOD: 1.5 µg/kg soil)

RESIDUE ANALYSIS

Analytical methods

For bixafen and M21 bixafen-desmethyl analytical method were provided following a comparable pattern. The samples (plant, animal and soil) are extracted using acetonitrile/water (4/1, v/v) or in case of fatty matrices n-hexane (saturated with acetonitrile). For some matrices the extraction is supported by using microwaves. After filtration and a clean-up with C18 SPE the residue is measured by HPLC-MS/MS with two specific mass transitions for each analyte. All methods were validated with an LOQ of 0.01 mg/kg.

The applicability of multi residue methods was investigated for the DFG S19; however, the results did not confirm sufficient applicability.

Table 54 Overview of analytical methods for bixafen

Method	Matrix	Extraction	Clean-Up	Detection, LOQ
Method 00983	Plants (high acid, high, starch, high oil, high water)	acetonitrile/water (4/1, v/v), using microwaves	filtration	HPLC-MS/MS Bixafen: m/z 414 → 394 and m/z 414 → 266 LOQ: 0.01 mg/kg
Method 01063	Animals (eggs, milk, muscle, kidney, fat, liver)	eggs, muscle, kidney and milk: acetonitrile/water (4/1, v/v) liver: acetonitrile/water (4/1, v/v), using microwaves fat: n-hexane (saturated with acetonitrile), partitioning with acetone (saturated with n-hexane)	filtration & C18 SPE	HPLC-MS/MS Bixafen: m/z 414 → 394 and m/z 414 → 266 LOQ: 0.01 mg/kg M21: m/z 398 → 378 and m/z 398 → 358 LOQ: 0.01 mg/kg
Method 00959 & Method 00959/M001	Soil	acetonitrile/water (4/1, v/v), using microwaves	centrifugation	HPLC-MS/MS Bixafen: m/z 414 → 394 and m/z 414 → 266 LOQ: 5 µg/kg M21: m/z 398 → 378 and m/z 398 → 358 LOQ: 5 µg/kg
Method 01012	Plants (high, starch, high water)	acetonitrile/water (4/1, v/v), using microwaves	filtration	HPLC-MS/MS with isotopically-labelled ISTD Bixafen: m/z 414 → 394 and m/z 414 → 266 LOQ: 0.01 mg/kg M21: m/z 398 → 378 and m/z 398 → 358 LOQ: 0.01 mg/kg
Method 01013	Plants (high acid, high, starch, high oil, high water)	acetonitrile/water (4/1, v/v) containing cysteine hydrochloride	filtration	HPLC-MS/MS with isotopically-labelled ISTD Bixafen: m/z 414 → 394 and m/z 414 → 266 LOQ: 0.01 mg/kg M21: m/z 398 → 378 and

Method	Matrix	Extraction	Clean-Up	Detection, LOQ
				m/z 398→ 358 LOQ: 0.01 mg/kg
Method 01036	Animals (eggs, milk, muscle, kidney, fat, liver)	eggs, muscle, kidney and milk: acetonitrile/water (4/1, v/v) liver: acetonitrile/water (4/1, v/v), using microwaves fat and milk cream: n-hexane (saturated with acetonitrile), partitioning with acetone (saturated with n-hexane)	filtration & C18 SPE	HPLC-MS/MS with isotopically-labelled ISTD Bixafen: m/z 414 → 394 and m/z 414→ 266 LOQ: 0.01 mg/kg M21: m/z 398 → 378 and m/z 398→ 358 LOQ: 0.01 mg/kg

ISDT = Internal standard

Plant materials

For plant materials a suitable enforcement method (method 00983) was developed by Bardel, P and Schoening, R (2006, BIXAFEN_034). The residues are extracted from 5 g of plant material with acetonitrile/water (4/1, v/v), using microwaves. After filtration and dilution, the solution was analysed by HPLC-MS/MS (m/z 414 → 394 and m/z 414→ 266). Residues were quantified against external bracketing matrix-matched standards.

The applicability of the method was confirmed in an independent laboratory by Ballesteros C and Portet, M (2007, BIXAFEN_035). In both laboratories parent bixafen was analysed with a validated LOQ of 0.01 mg/kg (see Table).

The applicability of the DFG method S 19 multi-residue method was investigated by Class, T (2006, BIXAFEN_036). However, even though GC gave acceptable peak shapes for bixafen, it was assessed that the DFG method S 19 used in combination with GC/MS is not applicable as a multi-residue enforcement method due to a lack of sensitivity, even when the most prominent fragment ion observed was monitored, and a lack of specificity, as no other ions were observed with sufficient sensitivity to serve as confirmatory ions. Thus, it was shown that DFG method S 19 is not suitable for the determination of bixafen residues.

Table 55 Recovery data for the determination of bixafen in plant commodities

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Wheat grain	0.01	5	98–102	101	1.7	Bixafen,
	0.1	5	87–100	95	5.2	Bardel, P and Schoening, R
Wheat, green material	0.01	5	80–100	90	9.6	(2006, BIXAFEN_034)
	0.1	5	90–103	96	4.8	m/z 414 → 394
Orange, fruit	0.01	5	88–98	93	4.9	
	0.1	5	78–95	86	8.0	
Rape, seed	0.01	5	86–978	92	5.0	
	0.1	5	92–95	93	1.2	
Wheat grain	0.01	5	94–107	102	4.9	Bixafen,
	0.1	5	81–101	94	8.3	Bardel, P and Schoening, R
Wheat, green material	0.01	5	81–105	94	12.1	(2006, BIXAFEN_034)
	0.1	5	88–99	96	4.8	m/z 414 → 266 (confirmation)
Orange, fruit	0.01	5	85–998	92	7.0	
	0.1	5	77–90	84	6.9	
Rape, seed	0.01	5	91–101	95	4.9	

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
	0.1	5	93–97	95	1.9	
Wheat grain	0.01	5	89–98	93	3.6	Bixafen,
	0.1	5	98–101	99	1.1	Ballesteros, C and Portet, M
Orange, fruit	0.01	5	93–97	94	2.3	(2007, BIXAFEN_035)
	0.1	5	99–106	101	2.8	m/z 414 → 394
Rape, seed	0.01	5	86–93	88	3.1	Independent laboratory validation
	0.1	5	89	89	0	

Animal materials

For the enforcement of bixafen and M21 (bixafen-desmethyl) in animal commodities method 01063 was developed by Billian, P and Druskus, M (2007, BIXAFEN_037). The residues were extracted from 5 g of milk, muscle, liver, kidney and egg with acetonitrile/water (4/1, v/v) using an ultra-turax (for liver with microwave assistance).

The extraction of fat samples was performed with n-hexane (saturated with acetonitrile) in a blender. After filtration, addition of acetonitrile (saturated with n-hexane) and subsequent shaking, the acetonitrile phase was separated.

The solutions were cleaned up on a C18 cartridge, made up to volume, diluted, and subjected to reversed phase HPLC-MS/MS in positive (parent compound, M21 bixafen-desmethyl) or negative (bixafen-desmethyl) ion modes. Two MRM transitions were monitored for bixafen (m/z 414 → 394 and m/z 414 → 266) and M21 (bixafen-desmethyl, m/z 398 → 378 and m/z 398 → 358). Residues were quantified against matrix-matched standards (without using the ISTD signal for calculation of the results).

The applicability of the method was confirmed in an independent laboratory by Ballesteros, C (2007, BIXAFEN_038). In both laboratories parent bixafen and M21 (bixafen-desmethyl) were validated with a LOQ of 0.01 mg/kg (see Table & Table).

Table 56 Recovery data for the determination of bixafen in animal commodities

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Egg (without shell)	0.01	5	80–103	92	9.4	Bixafen,
	0.1	5	91–101	96	4.1	Billian, P and Druskus, M
Milk	0.01	5	85–98	91	5.9	(2007, BIXAFEN_037)
	0.1	5	86–98	91	6.4	m/z 414 → 394
Muscle	0.01	5	90–105	97	6.1	
	0.1	5	92–100	95	3.6	
Kidney	0.01	5	83–98	93	6.4	
	0.1	5	95–113	103	7.4	
Fat	0.01	5	90–99	95	3.5	
	0.1	5	93–104	98	4.6	
Liver	0.01	5	88–100	95	4.5	
	0.1	5	98–104	101	2.8	
Egg (without shell)	0.01	5	84–104	93	8.5	Bixafen,
	0.1	5	91–100	96	3.6	Billian, P and Druskus, M
Milk	0.01	5	86–99	92	5.8	(2007, BIXAFEN_037)
	0.1	5	85–99	91	7.0	m/z 414 → 266 (confirmation)
Muscle	0.01	5	90–105	96	5.8	
	0.1	5	92–100	95	3.8	
Kidney	0.01	5	84–96	93	5.4	
	0.1	5	94–113	102	7.6	
Fat	0.01	5	90–96	93	2.6	
	0.1	5	91–102	96	4.8	
Liver	0.01	5	89–100	96	4.5	
	0.1	5	98–103	100	2.3	

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Egg (without shell)	0.01	5	89–97	94	3.9	Bixafen,
	0.1	5	88–95	92	3.2	Ballesteros C
Milk	0.01	5	111–123	115	4.2	(2007, BIXAFEN_038)
	0.1	5	106–114	110	3.3	m/z 414 → 394
Fat	0.01	5	101–106	103	1.8	Independent laboratory validation
	0.1	5	93–100	95	3.2	
Liver	0.01	5	80–100	92	8.1	
	0.1	5	84–116	97	13.6	
Egg (without shell)	0.01	5	92–97	94	2.4	Bixafen,
	0.1	5	87–94	91	3.2	Ballesteros C
Milk	0.01	5	106–121	113	5.1	(2007, BIXAFEN_038)
	0.1	5	104–113	108	3.6	m/z 414 → 266 (confirmation)
Fat	0.01	5	100–104	102	2.0	Independent laboratory validation
	0.1	5	91–97	93	2.8	
Liver	0.01	5	81–98	93	7.6	
	0.1	5	82–115	95	13.7	

Table 57 Recovery data for the determination of M21 (bixafen-desmethyl) in animal commodities

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Egg (without shell)	0.01	5	78–104	90	11.1	M21 (bixafen-desmethyl),
	0.1	5	90–97	94	3.2	Billian, P and Druskus, M
Milk	0.01	5	90–101	94	4.9	(2007, BIXAFEN_037)
	0.1	5	88–108	97	9.0	m/z 398 → 378
Muscle	0.01	5	88–95	92	3.0	
	0.1	5	90–102	95	4.8	
Kidney	0.01	5	76–101	91	10.8	
	0.1	5	74–87	80	7.3	
Fat	0.01	5	84–92	89	3.5	
	0.1	5	96–111	103	5.8	
Liver	0.01	5	93–99	96	2.7	
	0.1	5	95–101	98	2.4	
Egg (without shell)	0.01	5	77–102	89	10.5	M21 (bixafen-desmethyl),
	0.1	5	89–97	94	3.6	Billian, P and Druskus, M
Milk	0.01	5	88–100	92	5.3	(2007, BIXAFEN_037)
	0.1	5	89–108	98	8.9	m/z 398 → 358 (confirmation)
Muscle	0.01	5	88–93	90	2.4	
	0.1	5	90–102	95	4.7	
Kidney	0.01	5	76–98	91	9.4	
	0.1	5	73–87	80	7.2	
Fat	0.01	5	83–93	89	4.4	
	0.1	5	97–111	103	5.5	
Liver	0.01	5	91–99	95	3.2	
	0.1	5	96–102	99	2.4	
Egg (without shell)	0.01	5	89–99	94	3.9	M21 (bixafen-desmethyl),
	0.1	5	91–98	94	3.3	Ballesteros C
Milk	0.01	5	95–107	99	4.8	(2007, BIXAFEN_038)
	0.1	5	105–116	112	3.9	m/z 398 → 378
Fat	0.01	5	92–101	97	3.4	Independent laboratory validation
	0.1	5	95–103	99	3.4	
Liver	0.01	4	102–108	106	2.7	
	0.1	5	106–114	112	2.9	
Egg (without shell)	0.01	5	90–97	94	2.7	M21 (bixafen-desmethyl),
	0.1	5	91–99	94	3.3	Ballesteros C
Milk	0.01	5	94–111	101	6.5	(2007, BIXAFEN_038)
	0.1	5	104–119	113	5.0	m/z 398 → 358 (confirmation)
Fat	0.01	5	94–102	98	3.8	Independent laboratory validation
	0.1	5	96–104	100	3.3	

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Liver	0.01	4	104–112	109	3.1	
	0.1	5	109–116	113	2.4	

Soil

For the analysis of bixafen in soil method 00959 was developed by Brumhard, B and Freitag, T (2006, BIXAFEN_039). Residues of bixafen are extracted from approx. 20 g of soil in a microwave extractor with 40 mL of a mixture of acetonitrile/water (4+1, v+v). Then a subsample is centrifuged to remove fine particles of the soil.

Identification and quantitation of the test items is done by high performance liquid chromatography using MS/MS detection in the Multiple Reaction Monitoring mode (MRM). The first MRM transition of bixafen is the quantification ion with the mass 394 [m/z 414 → 394] and the second MRM transition is the confirmatory ion with the mass 266 [m/z 414 → 266]. The analytical method was successfully validated with a LOQ of 5 µg/kg soil.

An extension of this method for the determination of the metabolite M21 (bixafen-desmethyl) was reported by Brumhard, B and Koch, V (2008, BIXAFEN_048). The extraction of the residue is identical to the methodology described for parent bixafen. For the HPLC-MS/MS measurement the following mass transitions are used for bixafen-desmethyl: m/z 398 → 378 and m/z 398 → 358.

Table 58 Recovery data for analytical method 00959 measuring bixafen in soil

Matrix	Fortification level (µg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Soil "Höfchen"	5	15	79–108	97	7.2	Bixafen,
	50	15	69–101	82	11.5	Brumhard, B and Freitag, T
Soil "Laacher Hof"	5	10	79–103	87	8.1	(2006, BIXAFEN_039)
	50	10	68–94	79	9.8	m/z 414 → 394
Soil "Höfchen"	5	15	84–109	98	7.6	Bixafen,
	50	15	69–100	82	11.5	Brumhard, B and Freitag, T
Soil "Laacher Hof"	5	10	82–113	89	10.3	(2006, BIXAFEN_039)
	50	10	68–94	79	10.2	m/z 414 → 266 (confirmation)

Table 59 Recovery data for analytical method 00959/M001 measuring M21 (bixafen-desmethyl) in soil

Matrix	Fortification level (µg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Soil "Höfchen"	5	5	89–100	95	4.3	Bixafen,
	50	5	90–95	94	2.3	Brumhard, B and Koch, V
Soil "Laacher Hof"	5	5	86–97	91	4.9	(2008, BIXAFEN_48)
	50	5	91–96	93	1.9	m/z 398 → 378
Soil "Höfchen"	5	5	93–98	95	2.6	Bixafen,
	50	5	92–96	93	1.6	Brumhard, B and Koch, V
Soil "Laacher Hof"	5	5	94–99	97	2.4	(2008, BIXAFEN_48)
	50	5	89–94	92	2.2	m/z 398 → 358 (confirmation)

Specialised methods

For the data generation in supervised field trials and processing studies method 01012 was developed by Schoening, R (2006, BIXAFEN_040). Residues were extracted from 5 g of plant material with acetonitrile/water (4/1, v/v), using microwaves. After filtration of the extract, the stable isotopically-labelled analytes were added as internal standards (ISTD). The solution was made up to volume, diluted and subjected to reversed phase HPLC-MS/MS in positive (bixafen, bixafen-desmethyl) or negative (bixafen-desmethyl) ion modes without further clean-up. Two MRM transitions for

quantitation and confirmation were monitored for each analyte and in each matrix tested (bixafen: m/z 414→394 and 414→266; bixafen-desmethyl: m/z 398→378 and 398→358).

The extraction efficiency of method 01012 was investigated on wheat samples from the [dichlorophenyl-UL-¹⁴C]-wheat metabolism study (Sur, R and Kuhnke, G, 2007, BIXAFEN_041) and on samples from the confined rotational crop study (Justus, K and Kuhnke, G, 2007, BIXAFEN_042). In summary method 01012 was validated with an LOQ of 0.01 mg/kg for each analyte. Validation data and the extraction efficiencies are summarised in Table

Table 60 Recovery data for analytical method 01012 measuring bixafen in plant matrices

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Wheat, grain	0.01	5	93–97	95	1.4	Bixafen,
	0.1	5	94–95	95	0.3	Schoening, R
Wheat, straw	0.01	5	87–92	89	1.9	(2006, BIXAFEN_040)
	0.1	5	83–90	87	3.3	m/z 414 → 394
Wheat, green material	0.01	5	88–99	92	4.9	
	0.1	5	88–93	90	2.2	
Lettuce, head	0.01	5	96–99	98	1.5	
	0.1	5	95–98	96	1.5	
Turnip, body	0.01	5	94–96	95	1.3	
	0.1	5	94–96	95	0.6	
Wheat, grain	0.01	5	96–99	98	1.1	Bixafen,
	0.1	5	95–96	96	0.6	Schoening, R
Wheat, straw	0.01	5	85–90	88	2.5	(2006, BIXAFEN_040)
	0.1	5	84–90	87	2.8	m/z 414 → 266 (confirmation)
Wheat, green material	0.01	5	87–95	90	4.1	
	0.1	5	86–94	90	3.5	
Lettuce, head	0.01	5	91–95	93	1.9	
	0.1	5	88–100	95	5.7	
Turnip, body	0.01	5	92–100	95	3.4	
	0.1	5	94–99	96	1.8	

Table 61 Recovery data for analytical method 01012 measuring M21 (bixafen-desmethyl) in plant matrices

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Wheat, grain	0.01	5	93–100	96	2.9	M21 (bixafen-desmethyl),
	0.1	5	94–99	97	1.8	Schoening, R
Wheat, straw	0.01	5	84–90	86	2.8	(2006, BIXAFEN_040)
	0.1	5	81–88	86	3.0	m/z 398 → 378
Wheat, green material	0.01	5	86–93	90	2.9	
	0.1	5	88–92	90	1.8	
Lettuce, head	0.01	5	90–95	92	2.2	
	0.1	5	94–98	96	1.3	
Turnip, body	0.01	5	92–98	95	2.5	
	0.1	5	94–97	96	1.5	
Wheat, grain	0.01	5	92–97	94	1.9	M21 (bixafen-desmethyl),
	0.1	5	89–95	92	2.3	Schoening, R
Wheat, straw	0.01	5	86–92	90	2.6	(2006, BIXAFEN_040)
	0.1	5	82–87	85	2.5	m/z 398 → 358 (confirmation)
Wheat, green material	0.01	5	87–93	89	3.2	
	0.1	5	88–93	90	1.9	
Lettuce, head	0.01	5	93–97	95	1.6	
	0.1	5	92–95	94	1.2	
Turnip, body	0.01	5	95–103	98	3.1	

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
	0.1	5	96–100	97	1.6	

Table 62 Extraction efficiency of method 01012

Matrix	Reference	Method	% of TRR (mg/kg)					
			TRR	combined extracts	unextracted	bixafen	M21 (bixafen-desmethyl)	Total ^a
Wheat, forage (from wheat metabolism)	Sur, R and Kuhnke, G, 2007, BIXAFEN_041	metabolism study	100 (1.57)	99.0 (1.56)	1.0 (0.02)	97.1 (1.53)	0.8 (0.01)	97.9 (1.54)
		method 01012	100 (1.53)	97.7 (1.50)	2.3 (0.04)	96.1 (1.47)	0.9 (0.01)	96.9 (1.49)
Wheat, grain (from wheat metabolism)	Sur, R and Kuhnke, G, 2007, BIXAFEN_041	metabolism study	100 (0.229)	97.0 (0.222)	3.0 (0.007)	92.9 (0.213)	2.1 (0.005)	95.0 (0.218)
		method 01012	100 (0.174)	95.1 (0.166)	4.9 (0.009)	91.7 (0.160)	1.6 (0.003)	93.3 (0.163)
Wheat, straw (from wheat metabolism)	Sur, R and Kuhnke, G, 2007, BIXAFEN_041	metabolism study	100 (22.85)	96.1 (21.95)	3.9 (0.90)	93.2 (21.29)	1.7 (0.39)	94.9 (21.68)
		method 01012	100 (32.23)	95.3 (30.73)	4.7 (1.50)	92.2 (29.71)	1.9 (0.62)	94.1 (30.34)
Wheat, straw (from confined rotation crops study)	Justus, K and Kuhnke, G, 2007, BIXAFEN_042	metabolism study	100 (0.492)	95.3 (0.469)	4.7 (0.023)	36.9 (0.181)	57.2 (0.281)	94.1 (0.462)
		method 01012	100 (0.536)	68.0 (0.365)	32.0 (0.171)	28.2 (0.151)	39.8 (0.213)	68.0 (0.365)
Wheat, forage (from confined rotation crops study)	Justus, K and Kuhnke, G, 2007, BIXAFEN_042	metabolism study	100 (0.035)	82.7 (0.029)	17.3 (0.006)	20.7 (0.007)	61.9 (0.022)	82.7 (0.029)
		method 01012	100 (0.037)	72.6 (0.027)	27.4 (0.010)	19.6 (0.007)	53.0 (0.020)	72.6 (0.027)

^a Sum of bixafen and M21 (bixafen-desmethyl), expressed as bixafen equivalents

For plant commodities a second study used in supervised field trials was conducted by Brumhard, B and Stuke, S (2008, BIXAFEN_043). Multi method 01013 was developed for the determination of residues of bixafen, prothioconazole, tebuconazole, trifloxystrobin and their metabolites bixafen-desmethyl, prothioconazole-desthio and CGA321113 in/on plant material (citrus fruit, pea green seed, wheat grain, rape seed and corn green material). All analytes are extracted from plant materials using a mixture of acetonitrile/water (4/1; v/v) containing cysteine hydrochloride by using a blender. After filtration of the extract, the stable isotopically labelled analytes were added. The solution was made up to volume, diluted and subjected to reversed phase HPLC-MS/MS without a further clean-up step.

Bixafen was detected using electrospray ionization in the positive ion mode (ESI+), while M21 (bixafen-desmethyl) was detected using electrospray ionization in the negative ion mode (ESI-). Two MRM transitions for quantitation and confirmation were monitored for each analyte and in each matrix tested (bixafen: m/z 414→ 394 and 414→ 266; bixafen-desmethyl: m/z 398→ 378 and 398→ 358). Residues were quantified using internal stable-labelled standards.

In the following tables the validation data for bixafen and M21 (bixafen-desmethyl) are summarised. The analytical method was successfully validated with LOQs of 0.01 mg/kg for bixafen and M21 (bixafen-desmethyl).

Table 63 Recovery data for analytical method 01013 measuring bixafen in plant matrices

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Citrus fruit	0.01	5	95–114	105	6.5	Bixafen,
	0.1	5	90–100	97	4.4	Brumhard, B and Stuke, S
Pea, green seed	0.01	5	97–106	101	3.5	(2008, BIXAFEN_043)
	0.1	5	98–101	99	1.2	m/z 414 → 394
Rape, seed	0.01	5	101–117	106	6.2	
	0.1	5	96–103	100	3.1	
Wheat, grain	0.01	5	100–104	102	1.6	
	0.1	5	96–102	99	2.3	
Maize, green material	0.01	5	104–114	109	3.5	
	0.1	5	100–110	105	4.0	
Citrus fruit	0.01	5	96–113	106	6.0	Bixafen,
	0.1	5	96–108	104	4.6	Brumhard, B and Stuke, S
Pea, green seed	0.01	5	80–95	85	7.1	(2008, BIXAFEN_043)
	0.1	5	90–101	96	4.5	m/z 414 → 266 (confirmation)
Rape, seed	0.01	5	95–104	101	4.1	
	0.1	5	95–100	97	2.2	
Wheat, grain	0.01	5	97–108	103	4.8	
	0.1	5	91–100	94	4.5	
Maize, green material	0.01	5	101–118	110	6.4	
	0.1	5	102–114	107	4.4	

Table 64 Recovery data for analytical method 01013 measuring M21 (bixafen-desmethyl) in plant matrices

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Citrus fruit	0.01	5	98–107	103	3.2	M21 (bixafen-desmethyl),
	0.1	5	91–102	98	4.8	Brumhard, B and Stuke, S
Pea, green seed	0.01	5	92–106	99	5.3	(2008, BIXAFEN_043)
	0.1	5	94–103	98	3.4	m/z 398 → 378
Rape, seed	0.01	5	100–110	104	4.1	
	0.1	5	98–107	101	3.9	
Wheat, grain	0.01	5	96–103	100	2.7	
	0.1	5	97–101	99	1.8	
Maize, green material	0.01	5	103–115	111	4.3	
	0.1	5	100–109	104	3.5	
Citrus fruit	0.01	5	98–108	103	4.1	M21 (bixafen-desmethyl),
	0.1	5	90–102	97	4.6	Brumhard, B and Stuke, S

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Pea, green seed	0.01	5	91–102	97	5.2	(2008, BIXAFEN_043)
	0.1	5	92–102	99	4.2	m/z 398 → 358 (confirmation)
Rape, seed	0.01	5	98–112	103	5.6	
	0.1	5	93–102	97	3.5	
Wheat, grain	0.01	5	97–103	99	2.6	
	0.1	5	96–102	99	2.4	
Maize, green material	0.01	5	102–114	110	4.6	
	0.1	5	101–111	106	4.4	

In the livestock animal feeding study the analytical method 01036 was used, which was described by Schoening, R and Willmes, J (2008, BIXAFEN_044).

Skim milk and cream first were separated by using a centrifuge. The residues were extracted from 5 g of whole milk, skim milk, muscle, kidney, and egg with acetonitrile/water (4/1, v/v) using an ultra-turax. After filtration and clean-up on a C18 Cartridge the stable labelled internal standards were added to the extracts.

Residues in fat and milk cream were extracted from 5 g sample material with n-hexane (saturated with acetonitrile) first in an ultra-turax. After filtration and clean-up through a syringe tube, acetonitrile (saturated with n-hexane) was added, and, after shaking, the acetonitrile phase was separated. Subsequently the stable isotopically labelled standards were added.

Residues in liver were extracted from 5 g sample material with acetonitrile/water (4/1, v/v), either directly by using a microwave (cattle liver) or for chicken liver by using a blender first and a subsequent microwave extraction of the solids with acetonitrile/water (7/3, v/v). After filtration and clean-up on a C18 cartridge, the stable isotopically labelled standards were added to the extracts.

The solutions were made up to volume, diluted, filtered through a membrane filter and subjected to reversed phase HPLC-MS/MS in positive (parent compound, BYF00587-desmethyl) or negative (BYF00587-desmethyl) ion modes. Two MRM transitions for quantitation and confirmation were monitored for each analyte and in each matrix tested (bixafen: m/z 414 → 394 and 414 → 266; bixafen-desmethyl: m/z 398 → 378 and 398 → 358). Residues were quantified using internal stable-labelled standards.

In the following tables the validation data for bixafen and M21 (bixafen-desmethyl) are summarised. The analytical method was successfully validated with LOQs of 0.01 mg/kg for bixafen and M21 (bixafen-desmethyl).

Table 65 Recovery data for analytical method 01036 measuring bixafen in animal matrices

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Egg (without shell)	0.01	5	97–107	102	3.6	Bixafen,
	0.1	5	98–104	101	2.3	Schoening, R and Willmes, J
Egg yolk	0.01	3	91–98	95	3.8	(2008, BIXAFEN_044)
	0.1	3	101–102	101	0.6	m/z 414 → 394
Egg white	0.01	3	91–105	99	7.3	
	0.1	3	100–105	102	2.5	
Milk, whole	0.01	5	87–105	98	6.8	

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
	0.1	5	99–104	101	2.1	
Skim milk	0.01	3	91–104	97	6.8	
	0.1	3	97–102	100	2.9	
Milk cream	0.01	3	93–95	94	1.1	
	0.1	3	94–95	94	0.6	
Muscle	0.01	5	92–105	98	5.4	
	0.1	5	89–100	96	4.4	
Kidney	0.01	5	91–99	94	3.3	
	0.1	5	97–99	98	0.7	
Poultry liver	0.01	5	95–100	91	4.8	
	0.1	5	96–100	97	2.1	
Cattle liver	0.01	5	96–102	99	2.9	
	0.1	5	96–100	97	1.7	
Fat	0.01	5	83–101	92	7.8	
	0.1	5	93–99	96	2.6	
Egg (without shell)	0.01	5	92–99	95	3.2	Bixafen,
	0.1	5	99–104	101	1.9	Schoening, R and Willmes, J
Egg yolk	0.01	3	80–99	91	11.0	(2008, BIXAFEN_044)
	0.1	3	95–98	96	1.6	m/z 414 → 266 (confirmation)
Egg white	0.01	3	96–115	104	9.7	
	0.1	3	100–104	102	2.0	
Milk, whole	0.01	5	97–113	103	6.3	
	0.1	5	105–111	107	2.1	
Skim milk	0.01	3	103–119	110	7.4	
	0.1	3	96–102	99	3.0	
Milk cream	0.01	3	69–103	99	3.6	
	0.1	3	94–96	95	1.1	
Muscle	0.01	5	93–104	100	5.0	
	0.1	5	95–108	103	5.1	
Kidney	0.01	5	86–103	97	6.8	
	0.1	5	95–98	97	1.3	
Poultry liver	0.01	5	85–96	90	4.9	
	0.1	5	98–103	100	2.1	
Cattle liver	0.01	5	73–104	90	12.7	
	0.1	5	95–97	96	0.9	
Fat	0.01	5	84–108	99	9.3	
	0.1	5	96–104	101	3.2	

Table 66 Recovery data for analytical method 01036 measuring M21 (bixafen-desmethyl) in animal matrices

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Egg (without shell)	0.01	5	91–102	97	4.1	M21 (bixafen-desmethyl), Schoening, R and Willmes, J (2008, BIXAFEN 044)
	0.1	5	94–101	97	2.7	
Egg yolk	0.01	3	85–103	95	9.6	m/z 398 → 378
	0.1	3	94–103	99	4.6	
Egg white	0.01	3	102–105	103	1.7	
	0.1	3	103–107	105	2.0	
Milk, whole	0.01	5	94–104	99	4.0	
	0.1	5	96–102	99	2.4	
Skim milk	0.01	3	91–104	98	6.7	
	0.1	3	97–101	99	2.0	
Milk cream	0.01	3	91–99	94	4.6	
	0.1	3	98–102	100	2.0	
Muscle	0.01	5	95–109	101	5.1	
	0.1	5	89–98	96	4.0	
Kidney	0.01	5	89–100	95	5.2	
	0.1	5	94–97	95	1.4	
Poultry liver	0.01	5	83–100	93	7.5	
	0.1	5	93–96	94	1.5	
Cattle liver	0.01	5	92–99	94	3.1	
	0.1	5	94–96	95	1.4	
Fat	0.01	5	84–100	94	5.6	
	0.1	5	88–98	93	4.0	
Egg (without shell)	0.01	5	89–102	96	6.1	M21 (bixafen-desmethyl), Schoening, R and Willmes, J (2008, BIXAFEN 044)
	0.1	5	91–96	94	2.8	
Egg yolk	0.01	3	90–102	98	6.8	m/z 398 → 358 (confirmation)
	0.1	3	97–103	99	3.2	
Egg white	0.01	3	99–109	103	5.0	
	0.1	3	100–104	102	2.0	
Milk, whole	0.01	5	90–104	99	5.8	
	0.1	5	93–99	97	2.6	
Skim milk	0.01	3	91–110	99	9.9	
	0.1	3	92–97	94	2.7	
Milk cream	0.01	3	93–95	94	1.2	
	0.1	3	86–92	89	3.4	
Muscle	0.01	5	93–112	100	7.3	
	0.1	5	88–99	95	4.8	
Kidney	0.01	5	90–102	98	5.0	
	0.1	5	97–105	102	3.1	
Poultry liver	0.01	5	87–96	91	3.9	
	0.1	5	93–96	95	1.2	
Cattle liver	0.01	5	88–100	94	5.3	
	0.1	5	93–97	95	1.6	
Fat	0.01	5	81–101	90	8.1	
	0.1	5	90–99	94	4.1	

Stability of pesticides in stored analytical samples

The storage stability of bixafen and M21 (bixafen-desmethyl) has been investigated in wheat grain, wheat straw, wheat green material, lettuce head, potato tuber, rape seed and soil for a storage period of up to 24 months. No significant degradation of the residues was observed.

For animal matrices no storage stability data were provided. Samples in livestock metabolism or feeding studies were analysed within one month.

The storage stability of bixafen and its primary metabolite M21 (bixafen-desmethyl) was investigated in plant matrices (wheat grain, wheat straw, wheat green material, lettuce head, potato tuber and rape seed) for up to 24 months by Schoening, R and Billian, P (2009, BIXAFEN_045).

Homogenised samples were weighed into glass bottles and fortified individually at levels of 0.1 mg/kg for each analyte. After fortification, the solvent was allowed to evaporate. In addition, untreated samples of each sample material were prepared for control and recovery experiments. Subsequently the bottles were closed and stored deep frozen until analysis (except for the day 0 samples). At each sampling interval, three fortified and three control samples were removed from the deep-freezer. Subsequently, two of the control samples of each sample material were freshly fortified with a mixture of the test items to determine the concurrent recoveries. Fortification levels were at the same magnitude as the spiked storage samples. Bixafen and desmethyl-bixafen were spiked separately to separate control material.

The analytical method 01012 was used for the determination of bixafen and its metabolite desmethyl-bixafen in/on plant material. The analytes were extracted with acetonitrile/water (4/1, v/v) using a microwave. After filtration of the extract, the stable isotopically-labelled analytes were added as internal standards. The solution was made up to volume, diluted and subjected to reversed phase HPLC-MS/MS in positive and negative ion modes without further clean-up. Residues were quantified using internal stable-labelled standards. The LOQ was 0.01 mg/kg for all matrices and for both analytes investigated.

In the following table the recovered residues in stored samples are summarised:

Table 67 Storage stability of bixafen and M21 (bixafen-desmethyl) in plant commodities fortified at levels of 0.1 mg/kg

Matrix	Analyte	Storage period (months)	Residue level in stored samples (% nominal level)			Procedural recovery (% nominal level)	
			Individual values	Mean	RSD (%)	Individual values	Mean
Wheat, grain	bixafen	0	97, 94, 93, 96, 92	94	2.2	—	—
		1	87, 100, 92	93	7.1	99, 99	99
		2	101, 91, 101	98	5.9	94, 95	95
		3	74, 88, 90	84	10.4	97, 104	101
		6	100, 101, 103	101	1.5	98, 107	103
		12	84, 84, 86	85	1.4	95, 98	97
		18	92, 100, 101	98	5.1	97, 105	101
		24	100, 98, 99	99	1.0	95, 96	96
	M21 (bixafen-desmethyl)	0	88, 86, 90, 89, 86	88	2.0	—	—
		1	120, 123, 129	124	3.7	98, 98	98
		2	115, 116, 117	116	0.9	98, 96	97
		3	118, 118, 127	121	4.3	100, 98	99
		6	115, 119, 124	119	3.8	113, 97	105
		12	111, 112, 111	111	0.5	98, 97	98
		18	118, 118, 114	117	2.0	104, 109	107
		24	99, 104, 102	102	2.5	89, 86	88
Wheat, green material	bixafen	0	93, 86, 94, 96, 95	93	4.3	—	—
		1	101, 103, 100	101	1.5	102, 103	103
		2	101, 102, 99	101	1.5	98, 100	99
		3	105, 108, 111	108	2.8	101, 103	102
		6	95, 100, 102	99	3.6	102, 98	100
		12	91, 94, 94	93	1.9	93, 96	95
		18	99, 99, 101	100	1.2	96, 98	97
		24	96, 96, 102	98	3.5	97, 102	100
	M21 (bixafen-desmethyl)	0	87, 87, 89, 87, 83	87	2.5	—	—
		1	112, 114, 116	114	1.8	98, 98	98

Matrix	Analyte	Storage period (months)	Residue level in stored samples (% nominal level)			Procedural recovery (% nominal level)	
			Individual values	Mean	RSD (%)	Individual values	Mean
		2	113, 120, 121	118	3.7	95, 97	96
		3	115, 120, 121	119	2.7	103, 101	102
		6	110, 110, 111	110	0.5	96, 100	98
		12	106, 113, 117	112	5.0	101, 99	100
		18	108, 105, 108	107	1.6	98, 93	96
		24	96, 93, 97	95	2.2	81, 84	83
Wheat, straw	bixafen	0	93, 95, 98, 95, 96	95	1.9	–	–
		1	89, 92, 92	91	1.9	87, 88	88
		2	86, 90, 93	90	3.9	84, 85	85
		3	90, 91, 93	91	1.7	108, 104	106
		6	104, 104, 105	104	0.6	95, 97	96
		12	84, 87, 88	86	2.4	87, 85	86
		18	96, 96, 96	96	0.0	93, 93	93
		24	98, 93, 93	95	3.1	90, 88	89
	M21 (bixafen-desmethyl)	0	85, 90, 86, 84, 88	87	2.8	–	–
		1	104, 106, 107	106	1.4	85, 88	87
		2	102, 103, 105	103	1.5	86, 85	86
		3	115, 116, 118	116	1.3	103, 109	106
		6	98, 101, 103	101	2.5	87, 87	87
		12	104, 104, 104	104	0.0	90, 91	91
		18	107, 117, 112	112	4.5	93, 95	94
		24	100, 98, 100	99	1.2	78, 80	79
Potato, tuber	bixafen	0	90, 92, 91, 91, 91	91	0.8	–	–
		1	104, 105, 104	104	0.6	102, 107	105
		2	74, 76, 76	75	1.5	75, 73	74
		3	129, 129, 129	129	0.0	100, 100	100
		6	102, 104, 104	103	1.1	102, 103	103
		12	95, 94, 96	95	1.1	97, 93	95
		18	102, 103, 100	102	1.5	113, 96	105
		24	93, 94, 95	94	0.6	96, 94	95
	M21 (bixafen-desmethyl)	0	87, 89, 93, 90, 92	90	2.6	–	–
		1	124, 125, 126	125	0.8	98, 106	102
		2	94, 97, 95	95	1.6	80, 76	78
		3	125, 130, 135	130	3.8	99, 97	98
		6	118, 123, 121	121	2.1	96, 100	98
		12	113, 113, 113	113	0.0	96, 95	96
		18	114, 114, 114	114	0.0	111, 93	102
		24	106, 107, 106	106	0.5	84, 83	84
Lettuce, head	bixafen	0	95, 96, 97, 103, 97	98	3.2	–	–
		1	103, 104, 102	103	1.0	99, 100	100
		2	101, 105, 111	106	4.8	99, 104	102
		3	112, 114, 115	114	1.3	97, 103	100
		6	104, 104, 117	108	6.9	114, 100	107
		12	100, 98, 100	99	1.2	94, 100	97
		18	99, 100, 101	100	1.0	97, 99	98
		24	101, 100, 101	101	0.6	93, 94	94
	M21 (bixafen-desmethyl)	0	91, 93, 96, 93, 89	92	2.8	–	–
		1	62, 75, 76	71	11.0	101, 103	102
		2	100, 101, 104	102	2.0	95, 100	98
		3	84, 81, 85	83	2.5	103, 106	105
		6	79, 84, 90	84	6.5	99, 113	106
		12	92, 93, 95	93	1.6	96, 93	95
		18	92, 92, 93	92	0.6	95, 92	94
		24	97, 99, 93	96	3.2	91, 87	89
Rape, seed	bixafen	0	87, 87, 91, 89, 89	89	1.9	–	–
		1	91, 90, 93	91	1.7	100, 99	100
		2	63, 66, 67	65	3.2	69, 69	69

Matrix	Analyte	Storage period (months)	Residue level in stored samples (% nominal level)			Procedural recovery (% nominal level)	
			Individual values	Mean	RSD (%)	Individual values	Mean
		3	109, 113, 114	112	2.4	100, 101	101
		6	94, 89, 88	90	3.6	98, 99	99
		12	77, 89, 92	86	9.2	92, 92	92
		18	103, 96, 95	98	4.5	93, 93	93
		24	93, 91, 91	92	1.3	89, 90	90
	M21 (bixafen-desmethyl)	0	90, 89, 86, 91, 91	89	2.3	–	–
		1	123, 123, 122	123	0.5	103, 100	102
		2	86, 86, 86	86	0.0	71, 74	73
		3	114, 120, 121	118	3.2	90, 98	94
		6	111, 112, 113	112	0.9	96, 95	96
		12	117, 117, 117	117	0.0	96, 96	96
		18	113, 113, 121	116	4.0	89, 89	89
		24	105, 104, 104	104	0.6	84, 89	87

In addition to plant matrices the storage stability of bixafen (Brumhard, B and Freitag, T, 2008, BIXAFEN_046) and bixafen-desmethyl (Freitag, T and Hoffmann, M, 2009, BIXAFEN_047) in stored soil samples was investigated.

Untreated soil from Laacher Hof, Germany (sandy loam) and Höfchen, Germany (silt loam) was used for the storage stability study and individually fortified at levels of 50 µg/kg with both analytes. After 273/279, 456 and 587 days for bixafen and 134, 183, and 721 days for M21 (bixafen-desmethyl) samples were analysed for the remaining residue.

Soil samples were analysed for bixafen according to method 00952. The residue of M21 (bixafen-desmethyl) in soil was measured with the modified version 00950/M001. The LOQ for both methods was 5 µg/kg soil (see analytical methods).

Table 68 Storage stability of bixafen and M21 (bixafen-desmethyl) in soil fortified at levels of 50 µg/kg

Soil	Analyte, Reference	Storage period (days)	Residue level in stored samples (% nominal level)			Procedural recovery (% nominal level)	
			Individual values	Mean	RSD (%)	Individual values	Mean
Laacher Hof	bixafen, Brumhard, B and Freitag, T 2008, BIXAFEN_046	0	95, 98, 97, 94	96	1.7	–	–
		273	92, 93, 95, 94	93	1.3	91.9	–
		456	94, 94, 93, 94	94	0.6	97.4	–
		587	104, 95, 97, 96	98	3.8	92.2	–
	M21 (bixafen-desmethyl) Freitag, T and Hoffmann, M, 2009, BIXAFEN_047	0	95, 96, 95, 96	96	0.8	–	–
		134	92, 98, 107, 96	98	6.2	102	–
		183	112, 111, 107, 102	108	4.4	107	–
		721	97, 95, 99, 91	96	3.6	101	–
Höfchen	bixafen, Brumhard, B and Freitag, T 2008, BIXAFEN_046	0	96, 99, 100, 97	98	1.9	–	–
		279	97, 98, 97, 98	97	0.6	100	–
		456	93, 95, 97, 94	95	1.7	97.8	–
		587	100, 96, 97, 97	98	2.0	100	–
	M21 (bixafen-desmethyl) Freitag, T and Hoffmann, M, 2009, BIXAFEN_047	0	94, 92, 94, 95	94	1.5	–	–
		134	100, 99, 107, 103	102	3.7	98	–
		183	99, 107, 113, 103	105	5.7	105	–
		721	95, 98, 102, 98	98	3.0	105	–

USE PATTERN

Bixafen is a protectant fungicide. The Meeting received uses involving foliar spray applications in the field to rape plants and cereal grains.

Table 69 List of uses of bixafen

Crop	Country	Application detail					
		Form	Type	kg ai/ha	Growth stage at last treatment	No.	Pre harvest interval (PHI) in days
Oilseeds							
Oilseed rape	United Kingdom	EC	spraying	0.075	—	2	56
Cereals							
Barley	Austria	EC	spraying	0.075	BBCH 69	2	35
Barley	Belgium	EC	spraying	0.075	BBCH 49	2	not established—covered by growth stage
Barley	Estonia	EC	spraying	0.075	BBCH 61	2	35
Barley	France	EC	spraying	0.075	BBCH 61	1	35
Barley	Germany	EC	spraying	0.075	BBCH 61	2	not established—covered by growth stage
Barley	Hungary	EC	spraying	0.075	flowering	2	35
Barley	Ireland	EC	spraying	0.06	BBCH 61	2	not established—covered by growth stage
Barley	Latvia	EC	spraying	0.06	BBCH 61	2	35
Barley	Lithuania	EC	spraying	0.06	BBCH 61	2	35
Barley	Netherlands	EC	spraying	0.075	BBCH 61	2	not established—covered by growth stage
Barley	Romania	EC	spraying	0.05	BBCH 59	2	35
Barley	Switzerland	EC	spraying	0.075	BBCH 51	1	not established—covered by growth stage
Barley	United Kingdom	EC	spraying	0.125	BBCH 61	2	not established—covered by growth stage
Oats	Belgium	EC	spraying	0.075	BBCH 59	2	not established—covered by growth stage
Oats	Estonia	EC	spraying	0.075	BBCH 61	2	35
Oats	France	EC	spraying	0.094	BBCH 61	1	35
Oats	Hungary	EC	spraying	0.075	flowering	2	35
Oats	Ireland	EC	spraying	0.06	BBCH 61	2	not established—covered by growth stage
Oats	Netherlands	EC	spraying	0.075	BBCH 61	2	not established—covered by growth stage
Oats	United Kingdom	EC	spraying	0.125	BBCH 61	2	not established—covered by growth stage
Rye	Austria	EC	spraying	0.094	BBCH 69	2	35
Rye	Belgium	EC	spraying	0.094	BBCH 59	2	covered by growth stage
Rye	Estonia	EC	spraying	0.075	BBCH 69	2	35
Rye	France	EC	spraying	0.094	BBCH 69	1	35
Rye	Germany	EC	spraying	0.094	BBCH 69	2	covered by growth stage
Rye	Hungary	EC	spraying	0.075	flowering	2	35
Rye	Ireland	EC	spraying	0.094	BBCH 73	2	not established—covered by growth stage
Rye	Latvia	EC	spraying	0.06	BBCH 69	2	35
Rye	Lithuania	EC	spraying	0.06	BBCH 69	2	35
Rye	Netherlands	EC	spraying	0.094	BBCH 69	2	not established—covered by growth stage
Rye	Switzerland	EC	spraying	0.094	BBCH 61	1	not established—covered by growth stage
Rye	United Kingdom	EC	spraying	0.125	BBCH 73	2	not established—covered by growth stage
Spelt	Belgium	EC	spraying	0.094	BBCH 65	2	not established—covered by growth stage
Spelt	Netherlands	EC	spraying	0.094	BBCH 69	2	not established—covered by growth

Crop	Country	Application detail					
		Form	Type	kg ai/ha	Growth stage at last treatment	No.	Pre harvest interval (PHI) in days
							stage
Spelt	Switzerland	EC	spraying	0.075	BBCH 61	1	not established—covered by growth stage
Triticale	Austria	EC	spraying	0.094	BBCH 69	2	35
Triticale	Belgium	EC	spraying	0.094	BBCH 65	2	covered by growth stage
Triticale	Estonia	EC	spraying	0.075	BBCH 69	2	35
Triticale	France	EC	spraying	0.094	BBCH 69	1	35
Triticale	Germany	EC	spraying	0.094	BBCH 69	2	covered by growth stage
Triticale	Hungary	EC	spraying	0.075	flowering	2	35
Triticale	Ireland	EC	spraying	0.094	BBCH 73	2	not established—covered by growth stage
Triticale	Latvia	EC	spraying	0.06	BBCH 69	2	35
Triticale	Lithuania	EC	spraying	0.06	BBCH 69	2	35
Triticale	Netherlands	EC	spraying	0.094	BBCH 69	2	not established—covered by growth stage
Triticale	Switzerland	EC	spraying	0.094	BBCH 61	1	not established—covered by growth stage
Triticale	United Kingdom	EC	spraying	0.125	BBCH 73	2	not established—covered by growth stage
Wheat	Austria	EC	spraying	0.094	BBCH 69	2	35
Wheat	Belgium	EC	spraying	0.094	BBCH 65	2	covered by growth stage
Wheat	Estonia	EC	spraying	0.075	BBCH 69	2	35
Wheat	France	EC	spraying	0.094	BBCH 69	1	35
Wheat	Germany	EC	spraying	0.094	BBCH 69	2	covered by growth stage
Wheat	Hungary	EC	spraying	0.075	flowering	2	35
Wheat	Ireland	EC	spraying	0.094	BBCH 73	2	not established—covered by growth stage
Wheat	Latvia	EC	spraying	0.06	BBCH 69	2	35
Wheat	Lithuania	EC	spraying	0.06	BBCH 69	2	35
Wheat	Netherlands	EC	spraying	0.094	BBCH 69	2	not established—covered by growth stage
Wheat	Romania	EC	spraying	0.06	BBCH 69	2	35
Wheat	Switzerland	EC	spraying	0.094	BBCH 61	1	not established—covered by growth stage
Wheat	United Kingdom	EC	spraying	0.125	BBCH 73	2	not established—covered by growth stage

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

Residue levels were reported as measured. Application rates were always reported as bixafen equivalents. When residues were not detected they are shown as below the LOQ, e.g., < 0.01 mg/kg. Application rates and spray concentrations have generally been rounded to two significant figures. HR and STMR values from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels. These results are underlined.

Laboratory reports included method validation including batch recoveries with spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analyses or duration of residue sample storage were also provided. Field reports provided data on the sprayers used and their calibration, plot size, residue sample size and sampling date. Although trials included control plots, no control data are recorded in the tables except where residues in control samples exceeded the LOQ. Residue data are recorded unadjusted for % recovery.

Bixafen—supervised residue trials

Commodity	Indoor/Outdoor	Treatment	Countries	Table
Rape seed	outdoor	foliar	Belgium, France, Germany, Italy, Spain,	Table 70

Commodity	Indoor/Outdoor	Treatment	Countries	Table
			The Netherlands, United Kingdom	
Barley	outdoor	foliar	Belgium, France, Germany, Italy, Portugal, Spain, Sweden, United Kingdom	Table 71
Wheat	outdoor	foliar	France, Germany, Greece, Italy, Portugal, Spain, Sweden, United Kingdom	Table 72Table
Rape forage	outdoor	foliar	Belgium, France, Germany, Italy, Spain, The Netherlands, United Kingdom	Table 73
Barley, forage	outdoor	foliar	Belgium, France, Germany, Italy, Portugal, Spain, Sweden, United Kingdom	Table 74
Wheat, forage	outdoor	foliar	France, Germany, Greece, Italy, Portugal, Spain, Sweden, United Kingdom	Table 75
Barley, straw	outdoor	foliar	Belgium, France, Germany, Italy, Portugal, Spain, Sweden, United Kingdom	Table 76
Wheat, straw	outdoor	foliar	France, Germany, Greece, Italy, Portugal, Spain, Sweden, United Kingdom	Table 77

Table 70 Residues of bixafen and M21 (bixafen-desmethyl) in rape seeds following foliar spray with an EC formulation

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
cGAP UK	2	0.075	0.025–0.075	100–300	n.s.						
France (North), Braslou	2	0.075	0.025	300	63	pod seed	42	0.02	0.01	0.03	08-2116-01 BIXAFEN_057
2008 (Grizzly)		0.075	0.025	300	67		55	<u>0.01</u>	< 0.01	<u>0.02</u>	
The Netherlands, Hoofddorp	2	0.075	0.038	200	64	seed	64	< <u>0.01</u>	< 0.01	< <u>0.02</u>	08-2116-02 BIXAFEN_057
2008 (Maximus)		0.075	0.038	200	69						Processing trial
Belgium, Cortil-Noirmont	2	0.075	0.038	200	64	pod seed	42	0.09	0.09	0.18	08-2116-03 BIXAFEN_057
2008 (Exocet)		0.075	0.038	200	73		56	< <u>0.01</u>	0.01	<u>0.02</u>	
Germany, Werl	2	0.075	0.038	200	65	seed	56	<u>0.01</u>	0.01	<u>0.02</u>	08-2116-04 BIXAFEN_057
2008 (Astrid)		0.075	0.038	200	69						
The Netherlands, Nieuw Beerta	2	0.075	0.025	300	69	seed	49	< <u>0.01</u>	< 0.01	< <u>0.02</u>	09-2053-02 BIXAFEN_058
2009 (not specified)		0.075	0.025	300	77						
Belgium, Cortil-Noirmont	2	0.075	0.038	200	65	pod	30	0.20	0.03	0.23	09-2053-03 BIXAFEN_058
		0.075	0.038	200	73		42	0.14	0.03	0.17	
						seed	55	< <u>0.01</u>	< 0.01	< <u>0.02</u>	

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
2009 (Monalisa)											
France (North), Lignieres les Roye	2	0.075 0.075	0.025 0.025	300 300	67 79	seed	55	< 0.01	< 0.01	< 0.02	09-2053-04 BIXAFEN_058
2009 (Kador)											
United Kingdom, Bishop Burton	2	0.075 0.075	0.039 0.038	192 200	65 69	pod	30 42	0.19 0.05	0.05 0.02	0.24 0.07	09-2244-01 Bixafen_059
2009 (Castille)						seed	56	< 0.01	< 0.01	< 0.02	
Germany, Burscheid	2	0.06 0.06	0.02 0.02	300 300	71 78	pod	31	0.18	0.11	0.29	11-2013-03 BIXAFEN_060
2011 (Elektra)						seed	50	0.017	0.011	0.028	
France (North), Cahmbourg sur Indre	2	0.06 0.06	0.02 0.02	300 300	76 80	pod	21	0.24	0.04	0.28	08-2112-01 BIXAFEN_066
2008 (Flash)						seed	33	< 0.01	< 0.01	< 0.02	
Germany, Burscheid	2	0.06 0.06	0.02 0.02	300 300	69 73	seed	35	0.02	< 0.01	0.03	08-2112-02 BIXAFEN_066
2008 (Titan)											Processing trial
Belgium, Cortil-Noirmont	2	0.06 0.06	0.02 0.02	300 300	77 80	pod	21	0.32	0.09	0.41	08-2112-03 BIXAFEN_066
2008 (Exocet)						seed	28	< 0.01	< 0.01	< 0.02	
Germany, Werl	2	0.06 0.06	0.02 0.02	300 300	75 78	seed	30	0.02	< 0.01	0.03	08-2112-04 BIXAFEN_066
2008 (Astrid)											
United Kingdom, Bishop Burton	2	0.06 0.06	0.03 0.03	200 200	67 75	pod	29	< 0.01	< 0.01	< 0.02	09-2245-01 BIXAFEN_067
2009 (Castille)						seed	44	0.01	< 0.01	0.02	Processing trial
United Kingdom, Banbury	2	0.06 0.06	0.03 0.03	200 200	80 83	Seed	28	0.052	< 0.01	0.062	11-2137-01 BIXAFEN_073
2011 (D.K. Cabernet)											
Spain, Les Franqueses del Valles	2	0.063 0.06	0.02 0.02	315 300	74 78	pod	(14) 21	– < 0.01	– < 0.01	– < 0.02	11-2013-01 BIXAFEN_060
						seed	30	0.017	< 0.01	0.027	

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
2011 (Pacific)											
France (South), Bouloc	2	0.06 0.06	0.02 0.02	300 300	72 79	seed	30	< 0.01	< 0.01	< 0.02	11-2013-02 BIXAFEN_060
2011 (NK Alamir)											
Italy, Tarquinia	2	0.06 0.06	0.02 0.02	300 300	73 75	pod	14 21	0.48 0.51	0.063 0.087	0.543 0.597	11-2013-04 BIXAFEN_060
2011 (Hybristar)						seed	30	< 0.01	< 0.01	< 0.02	
Spain, La Luisiana	2	0.06 0.069	0.02 0.02	300 344	77 82	seed	31	< 0.01	< 0.01	< 0.02	11-2013-05 BIXAFEN_060
2011 (Eswilliams)											
France (South), Velleron	2	0.06 0.06	0.02 0.02	300 300	79 80	seed	30	< 0.01	< 0.01	< 0.02	11-2013-06 BIXAFEN_060
2011 (Hybrilux)											

^a Expressed as bixafen

DALT = Days after last treatment

BBCH 63 = 30% of flowers on main raceme open

BBCH 64 = 40% of flowers on main raceme open

BBCH 65 = Full flowering: 50% of flowers on main raceme open

BBCH 67 = Flowering declining: majority of petals fallen

BBCH 69 = End of flowering

BBCH 71–78 = 10% to 80% of pods have reached final size

BBCH 79 = Nearly all pods have reached final size

BBCH 82 = 20% of pods ripe, seeds dark and hard

Table 71 Residues of bixafen and M21 (bixafen-desmethyl) in barley grain following foliar spray with an EC formulation

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
France (North), St. Cyr en Arthies	2	0.125 0.125	0.042 0.042	300 300	37 61	grain	34	<u>0.04</u>	< 0.01	<u>0.05</u>	R 2006 0432/7 BIXAFEN_049
2006 (Carafe)											
France (North), Chambourg sur Indre	2	0.125 0.125	0.042 0.042	300 300	37 61	grain	49	<u>0.08</u>	0.02	<u>0.10</u>	R 2006 0433/5 BIXAFEN_049
2006 (Vanessa)											
Sweden, Staffanstorp	2	0.125 0.125	0.042 0.042	300 300	37 61	grain	36 45	<u>0.09</u> 0.06	0.02 0.01	<u>0.11</u> 0.07	R 2006 0434/3 BIXAFEN_049

Location, Year (variety)	Application					Residues, mg/kg					Trial No.,	
	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference	
Spain, Llerona 2006 (Graphic)	2	0.125 0.125	0.042 0.042	300 300	37 61	grain	35 48	<u>0.08</u> 0.06	0.02 0.02	<u>0.10</u> 0.08	R 2006 0441/6 BIXAFEN_051	
Portugal, Azambuja 2006 (Prestige)	2	0.125 0.125	0.042 0.042	300 300	37 61	grain	35 57	0.02 <u>0.03</u>	< 0.01 < 0.01	0.03 <u>0.04</u>	R 2006 0442/4 BIXAFEN_051	
France (South), Villeneuve Lés Bouloc 2007 (Prestige)	2	0.125 0.125	0.042 0.042	300 300	37 61	ear grain	34 60	0.17 <u>0.06</u>	0.07 0.02	0.24 <u>0.08</u>	R 2007 0083/0 BIXAFEN_052	
Italy, Bologna 2007 (Tunica)	2	0.125 0.125	0.042 0.042	300 300	39 61	grain	39 56	<u>0.06</u> 0.06	0.02 0.02	<u>0.08</u> 0.08	R 2007 0084/9 BIXAFEN_052	
Spain, Caldes de Montbui 2007 (Grafit)	2	0.125 0.125	0.042 0.042	300 300	37 61	grain	35 40	<u>0.25</u> 0.25	0.04 0.04	<u>0.29</u> 0.29	R 2007 0085/7 BIXAFEN_052	
France (South), Cherves 2007 (Scarlett)	2	0.125 0.125	0.042 0.042	300 300	37 61	ear grain	35 50	0.08 <u>0.04</u>	0.04 < 0.01	0.12 <u>0.05</u>	R 2007 0158/6 BIXAFEN_052	
Italy, Senetica di Bondeno 2007 (Tunica)	2	0.125 0.125	0.042 0.042	300 300	37 61	grain	35	<u>0.34</u>	0.04	<u>0.38</u>	R 2007 0159/4 BIXAFEN_052	
Sweden, Staffanstorp 2006 (Prestige)	2	0.25 0.25	0.084 0.084	300 300	37 61	grain	40	0.23	0.03	0.26	R 2006 0444/0 BIXAFEN_062 processing trial	
Germany, Swisttal- Heimerzheim 2006 (Class)	2	0.25 0.25	0.084 0.084	300 300	37 61	grain	35	0.13	0.02	0.15	R 2006 0445/9 BIXAFEN_062 processing trial	
France (North), Fresnoy les Roye 2006 (Scarlet)	2	0.25 0.25	0.084 0.084	300 300	37 61	grain	46	0.20	0.02	0.22	R 2006 0446/7 BIXAFEN_062 processing trial	
Germany, Burscheid 2006 (Barke)	2	0.25 0.25	0.084 0.084	300 300	37 61	grain	43	0.03	< 0.01	0.04	R 2006 0447/5 BIXAFEN_062 processing trial	

^a Expressed as bixafen

DALT = Days after last treatment

BBCH 37 = Flag leaf just visible, still rolled

BBCH 39 = Flag leaf stage: flag leaf fully unrolled, ligule just visible

BBCH 41 = Early boot stage: flag leaf sheath extending

BBCH 61 = Beginning of flowering: first anthers visible

BBCH 69 = End of flowering: all spikelets have completed flowering but some dehydrated anthers may remain

BBCH 71 = Watery ripe: first grains have reached half their final size

Table 72 Residues of bixafen and M21 (bixafen-desmethyl) in wheat grain following foliar spray with an EC formulation

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
France (North), Chambourg sur Indre 2006 (Tecnico)	2	0.125 0.125	0.042 0.042	300 300	47 69	grain	34	<u>0.01</u>	< 0.01	<u>0.02</u>	R 2006 0421/1 BIXAFEN_053
France (North), Chaussy 2006 (Isengrain)	2	0.125 0.125	0.042 0.042	300 300	47 69	grain	37	< <u>0.01</u>	< 0.01	< <u>0.02</u>	R 2006 0423/8 BIXAFEN_053
Sweden, Staffanstorp 2006 (Vinjett)	2	0.125 0.125	0.042 0.042	300 300	47 69	grain	35 47	< <u>0.01</u> < 0.01	< 0.01 < 0.01	< <u>0.02</u> < 0.02	R 2006 0424/6 BIXAFEN_053
United Kingdom, Thetford 2006 (Paragon)	2	0.125 0.125	0.042 0.042	300 300	47 69	grain	34 38	<u>0.03</u> 0.01	< 0.01 < 0.01	<u>0.04</u> 0.02	R 2006 0425/4 BIXAFEN_053
Germany, Leverkusen 2006 (Batis)	2	0.125 0.125	0.042 0.042	300 300	47 69	grain	35	<u>0.01</u>	< 0.01	<u>0.02</u>	R 2006 0426/2 BIXAFEN_053
France (North), Braslou 2007 (Mendel)	2	0.125 0.125	0.042 0.042	300 300	47 69	ear grain	35 44	0.17 < <u>0.01</u>	0.12 < 0.01	0.29 < <u>0.02</u>	R 2007 0091/1 BIXAFEN_054
United Kingdom, Diss 2007 (Belvoir)	2	0.125 0.125	0.039 0.042	318 300	47 69	ear grain	35 73	0.06 < <u>0.01</u>	0.05 < 0.01	0.11 < <u>0.02</u>	R 2007 0093/8 BIXAFEN_054
France (North), Chambourg sur Indre 2007	2	0.125 0.125	0.042 0.042	300 300	47 69	ear grain	35 56	0.14 < <u>0.01</u>	0.10 < 0.01	0.24 < <u>0.02</u>	R 2007 0094/6 BIXAFEN_054

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
(Apache)											
Sweden, Staffanstorp	2	0.125 0.125	0.042 0.042	300 300	47 69	ear	35	0.18	0.17	0.35	R 2007 0095/4 BIXAFEN_054
2007 (Vinjett)						grain	69	< 0.01	< 0.01	< 0.02	
Germany, Burscheid	2	0.125 0.125	0.042 0.042	300 300	47 69	grain	35 56	0.03 < 0.01	0.01 < 0.01	0.04 < 0.02	R 2007 0155/1 BIXAFEN_054
2007 (Thasos)											
Greece, Thiva	2	0.125 0.125	0.042 0.042	300 300	47 69	grain	35 43	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	R 2006 0427/0 BIXAFEN_055
2006 (Claudio)											
Italy, Palidoro Fiumicino	2	0.125 0.125	0.042 0.042	300 300	47 69	grain	35 52	0.01 < 0.01	< 0.01 < 0.01	0.02 < 0.02	R 2006 0428/9 BIXAFEN_055
2006 (Claudio)											
France (South), Lagardelle/Lèze	2	0.125 0.125	0.042 0.042	300 300	47 69	grain	35	< 0.01	< 0.01	< 0.02	R 2006 0429/7 BIXAFEN_055
2006 (not specified)											
Spain, Paradas Sevilla	2	0.125 0.125	0.042 0.042	300 300	53 69	grain	35 47	0.03 0.02	< 0.01 < 0.01	0.04 0.03	R 2006 0430/0 BIXAFEN_055
2006 (Italo)											
France (South), Vouille	2	0.125 0.125	0.042 0.042	300 300	47 69	grain	35 35	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	R 2006 0431/9 BIXAFEN_055
2006 (Technico)											
France (South), Villeneuve lès Bouloc	2	0.125 0.125	0.042 0.042	300 300	47 69	ear	35	0.37	0.24	0.61	R 2007 0086/5 BIXAFEN_056
2007 (Panifor)						grain	35	< 0.01	< 0.01	< 0.02	
Italy, Spinazzola	2	0.125 0.125	0.042 0.042	300 300	47 69	ear	35	0.61	0.15	0.76	R 2007 0087/3 BIXAFEN_056
2007 (Simeto)						grain	44	0.02	< 0.01	0.03	
France (South), Les Chères	2	0.125 0.125	0.042 0.042	300 300	52 69	ear	35	0.14	0.17	0.31	R 2007 0088/1 BIXAFEN_056
2007 (Autan)						grain	44	< 0.01	< 0.01	< 0.02	
Spain, Alcala de Guadaira	2	0.125 0.125	0.045 0.042	279 300	47 69	ear	36	0.38	0.13	0.51	R 2007 0090/3 BIXAFEN_056
						grain	54	0.02	< 0.01	0.03	

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
Sevilla											
2007 (Bolido R1)											
Portugal, Ereira	2	0.125 0.125	0.042 0.042	300 300	47 69	ear	35	0.47	0.25	0.72	R 2007 0157/8 BIXAFEN_056
2007 (Galeira)						grain	53	< 0.01	< 0.01	< 0.02	
United Kingdom, Bury St. Edmunds	2	0.23 0.25	0.082 0.083	279 300	47 69	grain	40	0.05	< 0.01	0.06	R 2006 0527/7 BIXAFEN_064 processing trial
2006 (Cordiale)											
Sweden, Staffanstorps	2	0.25 0.25	0.083 0.083	300 300	47 61	grain	75	0.03	0.01	0.04	R 2006 0528/5 BIXAFEN_064 processing trial
2006 (Tommi)											
France (North), Fresnoy les Roye	2	0.25 0.25	0.083 0.083	300 300	47 69	grain	53	0.02	0.01	0.03	R 2006 0529/3 BIXAFEN_064 processing trial
2006 (Chango)											
France (North), Chambourg sur Indre	2	0.25 0.25	0.083 0.083	300 300	47 69	grain	39	0.04	< 0.01	0.05	R 2006 0530/7 BIXAFEN_064 processing trial
2006 (Apache)											

^a Expressed as bixafen

DALT = Days after last treatment

BBCH 47 = Flag leaf sheath opening

BBCH 52 = 20% of inflorescence emerged

BBCH 53 = 30% of inflorescence emerged

BBCH 69 = End of flowering: all spikelets have completed flowering but some dehydrated anthers may remain

Table 73 Residues of bixafen and M21 (bixafen-desmethyl) in rape forage following foliar spray with an EC formulation

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
France (North), Braslou	2	0.075 0.075	0.025 0.025	300 300	63 67	forage	–0 0	0.44 1.5	0.04 0.04	0.48 1.54	08-2116-01 BIXAFEN_057
2008 (Grizzly)						rest of plant	42	0.08	0.02	0.10	
The Netherlands,	2	0.075 0.075	0.038 0.038	200 200	64 69	forage	–0 0	0.19 2.5	0.03 0.03	0.22 2.53	08-2116-02 BIXAFEN_057

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
Hoofddorp 2008 (Maximus)											Processing trial
Belgium, Cortil- Noirmont 2008 (Exocet)	2	0.075 0.075	0.038 0.038	200 200	64 73	forage rest of plant	−0 0 42	0.17 1.3 0.07	0.05 0.05 0.02	0.22 1.35 0.09	08-2116-03 BIXAFEN_057
Germany, Werl 2008 (Astrid)	2	0.075 0.075	0.038 0.038	200 200	65 69	forage	−0 0	0.27 1.5	0.04 0.04	0.31 1.54	08-2116-04 BIXAFEN_057
The Netherlands, Nieuw Beerta 2009 (not specified)	2	0.075 0.075	0.025 0.025	300 300	69 77	forage	−0 0	0.17 0.99	0.03 0.02	0.20 1.01	09-2053-02 BIXAFEN_058
Belgium, Cortil- Noirmont 2009 (Monalisa)	2	0.075 0.075	0.038 0.038	200 200	65 73	forage rest of plant	−0 0 30 42	0.17 1.0 0.31 0.19	0.01 0.01 0.02 0.02	0.18 1.01 0.33 0.21	09-2053-03 BIXAFEN_058
France (North), Lignieres les Roya 2009 (Kador)	2	0.075 0.075	0.025 0.025	300 300	67 79	forage	−0 0	0.11 0.74	0.01 0.02	0.12 0.76	09-2053-04 BIXAFEN_058
United Kingdom, Bishop Burton 2009 (Castille)	2	0.075 0.075	0.039 0.038	192 200	65 69	forage rest of plant	−0 0 30 42	0.28 1.7 0.09 0.18	0.03 0.03 0.02 0.02	0.31 1.73 0.11 0.20	09-2244-01 Bixafen_059
Germany, Burscheid 2011 (Elektra)	2	0.06 0.06	0.02 0.02	300 300	71 78	forage	−0 0	0.23 1.1	0.028 0.028	0.258 1.128	11-2013-03 BIXAFEN_060
France (North), Cahmbourg sur Indre 2008 (Flash)	2	0.06 0.06	0.02 0.02	300 300	76 80	forage rest of plant	−0 0 21	0.23 1.3 0.29	0.02 0.02 0.02	0.25 1.35 0.31	08-2112-01 BIXAFEN_066
Germany,	2	0.06	0.02	300	69	forage	−0	0.14	0.01	0.15	08-2112-02

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
Burscheid 2008 (Titan)		0.06	0.02	300	73		0	1.3	0.02	1.32	BIXAFEN_066 Processing trial
Belgium, Cortil- Noirmont 2008 (Exocet)	2	0.06 0.06	0.02 0.02	300 300	77 80	forage rest of plant	-0 0 21	0.23 0.88 0.25	0.02 0.02 0.04	0.25 0.90 0.29	08-2112-03 BIXAFEN_066
Germany, Werl 2008 (Astrid)	2	0.06 0.06	0.02 0.02	300 300	75 78	forage	-0 0	0.27 1.5	0.03 0.03	0.30 1.53	08-2112-04 BIXAFEN_066
United Kingdom, Bishop Burton 2009 (Castille)	2	0.06 0.06	0.03 0.03	200 200	67 75	forage rest of plant	-0 0 29	0.17 0.69 0.06	0.01 0.01 0.01	0.18 0.70 0.07	09-2245-01 BIXAFEN_067 Processing trial
United Kingdom, Banbury 2011 (D.K. Cabernet)	2	0.06 0.06	0.03 0.03	200 200	80 83	Forage	-0 0	0.54 1.7	0.03 0.029	0.57 1.7	11-2137-01 BIXAFEN_073
Spain, Les Franqueses del Valles 2011 (Pacific)	2	0.063 0.06	0.02 0.02	315 300	74 78	forage rest of plant	-0 0 14 21	0.12 0.26 0.087 < 0.01	0.012 0.017 < 0.01 < 0.01	0.132 0.277 0.097 < 0.02	11-2013-01 BIXAFEN_060
France (South), Bouloc 2011 (NK Alamir)	2	0.06 0.06	0.02 0.02	300 300	72 79	forage	-0 0	0.39 1.8	0.065 0.074	0.455 1.874	11-2013-02 BIXAFEN_060
Italy, Tarquinia 2011 (Hybristar)	2	0.06 0.06	0.02 0.02	300 300	73 75	forage rest of plant	-0 0 14 21	0.22 0.87 0.20 0.18	0.013 0.01 < 0.01 0.01	0.233 0.88 0.21 0.19	11-2013-04 BIXAFEN_060
Spain, La Luisiana 2011 (Eswilliams)	2	0.06 0.069	0.02 0.02	300 344	77 82	forage	-0 0	0.47 2.1	0.093 0.077	0.563 2.177	11-2013-05 BIXAFEN_060
France (South), Velleron	2	0.06 0.06	0.02 0.02	300 300	79 80	forage	-0 0	0.31 1.1	0.035 0.041	0.345 1.141	11-2013-06 BIXAFEN_060

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
2011 (Hybrilux)											

–0 = Sampling directly before last treatment

^a Expressed as bixafen

DALT = Days after last treatment

BBCH 63 = 30% of flowers on main raceme open

BBCH 64 = 40% of flowers on main raceme open

BBCH 65 = Full flowering: 50% of flowers on main raceme open

BBCH 67 = Flowering declining: majority of petals fallen

BBCH 69 = End of flowering

BBCH 71–78 = 10% to 80% of pods have reached final size

BBCH 79 = Nearly all pods have reached final size

BBCH 82 = 20% of pods ripe, seeds dark and hard

Table 74 Residues of bixafen and M21 (bixafen-desmethyl) in barley forage following foliar spray with an EC formulation

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
France (North), St. Cyr en Arthies 2006 (Carafe)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage	–0 0	1.4 <u>4.4</u>	0.08 0.08	1.48 <u>4.48</u>	R 2006 0432/7 BIXAFEN_049
France (North), Chambourg sur Indre 2006 (Vanessa)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage	–0 0	1.0 <u>3.9</u>	0.03 0.04	1.03 <u>3.94</u>	R 2006 0433/5 BIXAFEN_049
Sweden, Staffanstorp 2006 (Pasadena)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage	–0 0 7 14 28	1.7 <u>7.0</u> 4.1 3.7 4.6	0.23 0.25 0.51 0.60 0.49	1.93 <u>7.25</u> 4.61 4.3 5.09	R 2006 0434/3 BIXAFEN_049
United Kingdom, Hoxne 2006 (Sequel)	2	0.125 0.125	0.042 0.042	300 300	39 61	forage	–0 0 8 14 28	0.42 <u>2.1</u> 0.80 0.59 0.38	0.03 0.04 0.05 0.06 0.04	0.45 <u>2.14</u> 0.85 0.65 0.42	R 2006 0435/1 BIXAFEN_049
Germany, Swisttal- Heimerzheim 2006 (Class)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage	–0 0 7 13 28	0.88 <u>3.9</u> 2.0 2.7 2.8	0.11 0.10 0.12 0.21 0.20	0.99 <u>4.0</u> 2.12 2.91 3.0	R 2006 0437/8 BIXAFEN_049

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 a	Total ^a	Reference
France (North), St. Cyr en Arthies 2007 (Heinley)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage rest of plant	–0 0 7 14 28 34	0.47 <u>3.4</u> 2.1 1.5 0.41 0.54	0.07 0.07 0.13 0.14 0.08 0.11	0.54 <u>3.47</u> 2.23 1.64 0.49 0.64	R 2007 0081/4 BIXAFEN_050
France (North), Carrépuis 2007 (Prestige)	2	0.125 0.125	0.042 0.042	300 300	41 61	forage rest of plant	–0 0 35	1.5 <u>4.3</u> 0.66	0.09 0.10 0.09	1.59 <u>4.4</u> 0.75	R 2007 0082/0 BIXAFEN_050
Germany, Vechta- Lanförden 2007 (Tocada)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage rest of plant	–0 0 7 14 28 35	0.37 <u>2.5</u> 1.5 0.90 1.1 0.66	0.08 0.07 0.11 0.09 0.07 0.09	0.45 <u>2.57</u> 1.61 0.99 1.17 0.75	R 2007 0160/8 BIXAFEN_050
United Kingdom, Sandringham 2007 (Tippel)	2	0.125 0.125	0.042 0.042	300 300	39 69	forage rest of plant	–0 0 8 14 28 35	0.36 <u>2.4</u> 1.3 0.84 0.39 0.66	0.07 0.07 0.08 0.11 0.09 0.09	0.43 <u>2.47</u> 1.38 0.95 0.48 0.75	R 2007 0161/6 BIXAFEN_050
Belgium, Villers- Perwin 2007 (Beatrix)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage rest of plant	–0 0 35	0.18 <u>2.8</u> 0.66	0.07 0.09 0.09	0.25 <u>2.89</u> 0.75	R 2007 0162/4 BIXAFEN_050
France (South), Villeneuve lés Boulac 2006 (Prestige)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage rest of plant	–0 0 35	0.84 <u>3.6</u> 0.66	0.12 0.10 0.09	0.96 <u>3.7</u> 0.75	R 2006 0438/6 BIXAFEN_051
Italy, Bologna 2006 (Federal)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage rest of plant	–0 0 35	0.58 <u>3.4</u> 0.66	0.01 0.01 0.09	0.59 <u>3.41</u> 0.75	R 2006 0439/4 BIXAFEN_051
France (South), Quincieux 2006 (Scarlett)	2	0.125 0.125	0.042 0.042	300 300	37 71	forage rest of plant	–0 0 7 14 27 35	0.89 3.8 2.5 1.6 2.2 0.66	0.21 0.20 0.34 0.28 0.26 0.09	1.1 4.0 2.84 1.88 2.46 0.75	R 2006 0440/8 BIXAFEN_051
Spain, Llerona 2006 (Graphic)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage rest of plant	–0 0 7 14 28 35	1.2 <u>3.3</u> 2.8 2.1 2.0 0.66	0.10 0.11 0.16 0.18 0.27 0.09	1.3 <u>3.41</u> 2.96 2.28 2.27 0.75	R 2006 0441/6 BIXAFEN_051
Portugal,	2	0.125	0.042	300	37	forage	–0	1.1	0.08	1.18	R 2006 0442/4

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 a	Total ^a	Reference
Azambuja 2006 (Prestige)		0.125	0.042	300	61		0 7 14 28	<u>2.6</u> 1.5 1.4 1.1	0.09 0.11 0.15 0.11	<u>2.69</u> 1.61 1.55 1.21	BIXAFEN_051
France (South), Villeneuve Lés Bouloc 2007 (Prestige)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage rest of plant	−0 0 7 13 27 34	0.85 <u>3.1</u> 1.4 0.96 0.51 0.17	0.12 0.14 0.16 0.18 0.16 0.07	0.96 <u>3.24</u> 1.56 1.14 0.67 0.24	R 2007 0083/0 BIXAFEN_052
Italy, Bologna 2007 (Tunica)	2	0.125 0.125	0.042 0.042	300 300	39 61	forage	−0 0	0.46 <u>3.6</u>	0.22 0.20	0.68 <u>3.8</u>	R 2007 0084/9 BIXAFEN_052
Spain, Caldes de Montbui 2007 (Grafitt)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage	−0 0 7 13 28	0.13 <u>3.0</u> 1.8 1.5 2.1	0.03 0.04 0.11 0.17 0.20	0.16 <u>3.04</u> 1.91 1.67 2.3	R 2007 0085/7 BIXAFEN_052
France (South), Cherves 2007 (Scarlett)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage rest of plant	−0 0 7 14 28 35	0.91 <u>4.2</u> 2.8 1.4 0.50 	0.06 0.07 0.14 0.15 0.08 	0.97 <u>4.27</u> 2.94 1.55 0.58 	R 2007 0158/6 BIXAFEN_052
Italy, Senetica di Bondeno 2007 (Tunica)	2	0.125 0.125	0.042 0.042	300 300	37 61	forage	−0 0	0.69 <u>5.8</u>	0.18 0.17	0.87 <u>5.97</u>	R 2007 0159/4 BIXAFEN_052
Sweden, Staffanstorp 2006 (Prestige)	2	0.25 0.25	0.084 0.084	300 300	37 61	forage	0	9.1	0.18	9.28	R 2006 0444/0 BIXAFEN_062 processing trial
Germany, Swisttal- Heimerzheim 2006 (Class)	2	0.25 0.25	0.084 0.084	300 300	37 61	forage	0	6.1	0.18	6.28	R 2006 0445/9 BIXAFEN_062 processing trial
France (North), Fresnoy les Roye 2006 (Scarlet)	2	0.25 0.25	0.084 0.084	300 300	37 61	forage	0	7.8	0.17	7.97	R 2006 0446/7 BIXAFEN_062 processing trial
Germany,	2	0.25	0.084	300	37	forage	0	6.3	0.07	6.37	R 2006 0447/5

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
Burscheid 2006 (Barke)		0.25	0.084	300	61						BIXAFEN_062 processing trial

–0 = Sampling directly before last treatment

^a Expressed as bixafen

DALT = Days after last treatment

BBCH 37 = Flag leaf just visible, still rolled

BBCH 39 = Flag leaf stage: flag leaf fully unrolled, ligule just visible

BBCH 41 = Early boot stage: flag leaf sheath extending

BBCH 61 = Beginning of flowering: first anthers visible

BBCH 69 = End of flowering: all spikelets have completed flowering but some dehydrated anthers may remain

BBCH 71 = Watery ripe: first grains have reached half their final size

Table 75 Residues of bixafen and M21 (bixafen-desmethyl) in wheat forage following foliar spray with an EC formulation

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
France (North), Chambourg sur Indre 2006 (Tecnico)	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0	1.9 <u>7.1</u>	0.19 0.21	2.09 <u>7.31</u>	R 2006 0421/1 BIXAFEN_053
France (North), Chaussy 2006 (Isengrain)	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0	1.1 <u>3.0</u>	0.09 0.09	1.19 <u>3.09</u>	R 2006 0423/8 BIXAFEN_053
Sweden, Staffanstorp 2006 (Vinjett)	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0 7 14 28	1.8 <u>4.6</u> 4.1 3.2 3.2	0.12 0.13 0.36 0.39 0.50	1.92 <u>4.73</u> 4.46 3.59 3.7	R 2006 0424/6 BIXAFEN_053
United Kingdom, Thetford 2006 (Paragon)	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0 7 14 28	0.83 <u>2.7</u> 2.1 1.8 1.8	0.07 0.08 0.13 0.13 0.13	0.90 <u>2.78</u> 2.23 1.93 1.93	R 2006 0425/4 BIXAFEN_053
Germany, Leverkusen 2006 (Batis)	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0 7 14 28	0.31 <u>2.2</u> 1.3 0.92 0.59	0.05 0.05 0.06 0.10 0.11	0.36 <u>2.25</u> 1.36 1.02 0.70	R 2006 0426/2 BIXAFEN_053
France (North), Braslou	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0 7 14	2.6 <u>1.4</u> 0.88 0.65	0.09 0.14 0.18 0.26	2.69 <u>1.54</u> 1.06 0.91	R 2007 0091/1 BIXAFEN_054

Location,		Application				Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
2007 (Mendel)						rest of plant	28 35	0.45 0.97	0.09 0.33	0.54 1.3	
United Kingdom, Diss	2	0.125 0.125	0.039 0.042	318 300	47 69	forage	–0 0	0.57 <u>2.7</u>	0.16 0.17	0.73 <u>2.87</u>	R 2007 0093/8 BIXAFEN_054
2007 (Belvoir)						rest of plant	35	0.36	0.25	0.61	
France (North), Chambourg sur Indre	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0 7 14 28	0.70 <u>3.6</u> 1.8 1.2 1.1	0.16 0.19 0.25 0.28 0.45	0.86 <u>3.79</u> 2.05 1.48 1.55	R 2007 0094/6 BIXAFEN_054
2007 (Apache)						rest of plant	35	1.5	0.63	2.13	
Sweden, Staffanstorp	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0	2.8 <u>3.2</u>	0.14 0.15	2.94 <u>3.35</u>	R 2007 0095/4 BIXAFEN_054
2007 (Vinjett)						rest of plant	35	1.4	0.70	2.1	
Germany, Burscheid	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0 7 14 28	1.5 <u>4.5</u> 2.0 1.4 1.0	0.24 0.26 0.29 0.30 0.31	1.74 <u>4.76</u> 2.29 1.7 1.31	R 2007 0155/1 BIXAFEN_054
2007 (Thasos)											
Greece, Thiva	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0	1.0 <u>3.8</u>	0.07 0.07	1.07 <u>3.87</u>	R 2006 0427/0 BIXAFEN_055
2006 (Claudio)											
Italy, Palidoro Fiumicino	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0	0.48 <u>2.5</u>	0.09 0.08	0.57 <u>2.58</u>	R 2006 0428/9 BIXAFEN_055
2006 (Claudio)											
France (South), Lagardelle/ Lèze	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0 7 14 28	1.2 <u>5.3</u> 2.7 2.9 3.4	0.13 0.15 0.18 0.24 0.34	1.33 <u>5.45</u> 2.88 3.14 3.74	R 2006 0429/7 BIXAFEN_055
2006 (not specified)											
Spain, Paradas Sevilla	2	0.125 0.125	0.042 0.042	300 300	53 69	forage	–0 0 7 14 28	1.0 <u>2.8</u> 1.6 1.1 1.7	0.08 0.07 0.09 0.09 0.17	1.08 <u>2.87</u> 1.69 1.19 1.87	R 2006 0430/0 BIXAFEN_055
2006 (Italo)											
France (South), Vouille	2	0.125 0.125	0.042 0.042	300 300	47 69	forage	–0 0 7 14	1.2 <u>5.1</u> 3.6 3.0	0.07 0.09 0.22 0.31	1.27 <u>5.19</u> 3.82 3.31	R 2006 0431/9 BIXAFEN_055

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
France (North), Chambourg sur Indre 2006 (Apache)	2	0.25 0.25	0.083 0.083	300 300	47 66	forage	0	5.8	0.13	5.93	R 2006 0530/7 BIXAFEN_064 processing trial

–0 = Sampling directly before last treatment

^a expressed as bixafen

DALT = Days after last treatment

BBCH 47 = Flag leaf sheath opening

BBCH 52 = 20% of inflorescence emerged

BBCH 53 = 30% of inflorescence emerged

BBCH 69 = End of flowering: all spikelets have completed flowering but some dehydrated anthers may remain

Table 76 Residues of bixafen and M21 (bixafen-desmethyl) in barley straw following foliar spray with an EC formulation

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 ^a	Total ^a	Reference
France (North), St. Cyr en Arthies 2006 (Carafe)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	34	<u>5.4</u>	0.18	<u>5.58</u>	R 2006 0432/7 BIXAFEN_049
France (North), Chambourg sur Indre 2006 (Vanessa)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	49	<u>3.7</u>	0.20	<u>3.9</u>	R 2006 0433/5 BIXAFEN_049
Sweden, Staffanstorp 2006 (Pasadena)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	36 45	<u>10</u> 4.3	1.4 0.66	<u>11.4</u> 4.96	R 2006 0434/3 BIXAFEN_049
United Kingdom, Hoxne 2006 (Sequel)	2	0.125 0.125	0.042 0.042	300 300	39 61	straw	62	<u>1.1</u>	0.08	<u>1.18</u>	R 2006 0435/1 BIXAFEN_049
Germany, Swisttal-Heimerzheim 2006 (Class)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	35	<u>4.8</u>	0.37	<u>5.17</u>	R 2006 0437/8 BIXAFEN_049
France (North),	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	58	<u>0.64</u>	0.08	<u>0.72</u>	R 2007 0081/4 BIXAFEN_050

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 _a	Total _a	Reference
St. Cyr en Arthies 2007 (Heinley)											
France (North), Carrépuis 2007 (Prestige)	2	0.125 0.125	0.042 0.042	300 300	41 61	straw	60	<u>0.77</u>	0.08	<u>0.85</u>	R 2007 0082/0 BIXAFEN_050
Germany, Vechta-Lanförden 2007 (Tocada)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	35	<u>0.70</u>	0.04	<u>0.74</u>	R 2007 0160/8 BIXAFEN_050
United Kingdom, Sandringham 2007 (Tippel)	2	0.125 0.125	0.042 0.042	300 300	39 69	straw	35 66	0.45 <u>1.1</u>	0.13 0.14	0.58 <u>1.24</u>	R 2007 0161/6 BIXAFEN_050
Belgium, Villers-Perwin 2007 (Beatrix)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	34 51	0.68 <u>0.86</u>	0.17 0.14	0.85 <u>1.0</u>	R 2007 0162/4 BIXAFEN_050
France (South), Villeneuve lés Bouloc 2006 (Prestige)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	35	<u>5.2</u>	0.40	<u>5.6</u>	R 2006 0438/6 BIXAFEN_051
Italy, Bologna 2006 (Federal)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	35 46	<u>0.46</u> 0.32	0.04 0.03	<u>0.50</u> 0.35	R 2006 0439/4 BIXAFEN_051
France (South), Quincieux 2006 (Scarlett)	2	0.125 0.125	0.042 0.042	300 300	37 71	straw	35	3.7	0.37	4.07	R 2006 0440/8 BIXAFEN_051
Spain, Llerona 2006 (Graphic)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	35 48	4.2 <u>5.7</u>	0.41 0.42	4.61 <u>6.12</u>	R 2006 0441/6 BIXAFEN_051
Portugal, Azambuja 2006 (Prestige)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	35 57	1.4 <u>1.5</u>	0.11 0.14	1.51 <u>1.64</u>	R 2006 0442/4 BIXAFEN_051

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 _a	Total _a	Reference
France (South), Villeneuve Lés Bouloc 2007 (Prestige)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	60	<u>1.2</u>	0.10	<u>1.3</u>	R 2007 0083/0 BIXAFEN_052
Italy, Bologna 2007 (Tunica)	2	0.125 0.125	0.042 0.042	300 300	39 61	straw	39 56	0.75 <u>0.76</u>	0.25 0.25	1.0 <u>1.01</u>	R 2007 0084/9 BIXAFEN_052
Spain, Caldes de Montbui 2007 (Grafit)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	35 40	<u>3.1</u> 2.5	0.22 0.18	<u>3.32</u> 2.68	R 2007 0085/7 BIXAFEN_052
France (South), Cherves 2007 (Scarlett)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	50	<u>1.9</u>	0.23	<u>2.13</u>	R 2007 0158/6 BIXAFEN_052
Italy, Senetica di Bondeno 2007 (Tunica)	2	0.125 0.125	0.042 0.042	300 300	37 61	straw	35	<u>6.2</u>	0.48	<u>6.68</u>	R 2007 0159/4 BIXAFEN_052

a Expressed as bixafen

DALT = Days after last treatment

BBCH 37 = Flag leaf just visible, still rolled

BBCH 39 = Flag leaf stage: flag leaf fully unrolled, ligule just visible

BBCH 41 = Early boot stage: flag leaf sheath extending

BBCH 61 = Beginning of flowering: first anthers visible

BBCH 69 = End of flowering: all spikelets have completed flowering but some dehydrated anthers may remain

BBCH 71 = Watery ripe: first grains have reached half their final size

Table 77 Residues of bixafen and M21 (bixafen-desmethyl) in wheat straw following foliar spray with an EC formulation

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 _a	Total _a	Reference
France (North), Chambourg sur Indre 2006 (Tecnico)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	34	<u>10</u>	0.78	<u>10.78</u>	R 2006 0421/1 BIXAFEN_053

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 _a	Total _a	Reference
France (North), Chaussy 2006 (Isengrain)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	37	<u>1.8</u>	0.27	<u>2.07</u>	R 2006 0423/8 BIXAFEN_053
Sweden, Staffanstorp 2006 (Vinjett)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	35 47	<u>8.4</u> 7.8	1.2 1.3	<u>9.6</u> 9.1	R 2006 0424/6 BIXAFEN_053
United Kingdom, Thetford 2006 (Paragon)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	34 38	<u>3.6</u> 3.1	0.26 0.18	<u>3.86</u> 3.28	R 2006 0425/4 BIXAFEN_053
Germany, Leverkusen 2006 (Batis)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	35	<u>1.3</u>	0.20	<u>1.5</u>	R 2006 0426/2 BIXAFEN_053
France (North), Braslou 2007 (Mendel)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	44	<u>0.95</u>	0.35	<u>1.3</u>	R 2007 0091/1 BIXAFEN_054
United Kingdom, Diss 2007 (Belvoir)	2	0.125 0.125	0.039 0.042	318 300	47 69	straw	73	<u>0.52</u>	0.26	<u>0.78</u>	R 2007 0093/8 BIXAFEN_054
France (North), Chambourg sur Indre 2007 (Apache)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	56	<u>1.9</u>	0.6	<u>2.5</u>	R 2007 0094/6 BIXAFEN_054
Sweden, Staffanstorp 2007 (Vinjett)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	69	<u>0.93</u>	0.31	<u>1.24</u>	R 2007 0095/4 BIXAFEN_054
Germany, Burscheid 2007 (Thasos)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	35 56	<u>4.1</u> 0.55	0.30 0.21	<u>4.4</u> 0.76	R 2007 0155/1 BIXAFEN_054
Greece, Thiva 2006	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	35 43	2.6 <u>3.2</u>	0.47 0.50	3.07 <u>3.7</u>	R 2006 0427/0 BIXAFEN_055

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 _a	Total _a	Reference
(Claudio)											
Italy, Palidoro Fiumicino 2006 (Claudio)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	35 52	0.90 <u>1.8</u>	0.27 0.37	1.17 <u>2.17</u>	R 2006 0428/9 BIXAFEN_055
France (South), Lagardelle/ Lèze 2006 (not specified)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	35	<u>5.7</u>	0.52	<u>6.22</u>	R 2006 0429/7 BIXAFEN_055
Spain, Paradas Sevilla 2006 (Italo)	2	0.125 0.125	0.042 0.042	300 300	53 69	straw	35 47	<u>1.7</u> 1.5	0.18 0.21	<u>1.88</u> 1.71	R 2006 0430/0 BIXAFEN_055
France (South), Vouille 2006 (Technico)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	35 35	<u>5.4</u> 4.9	0.59 0.60	<u>5.99</u> 5.5	R 2006 0431/9 BIXAFEN_055
France (South), Villeneuve lès Bouloc 2007 (Panifor)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	45	<u>1.4</u>	0.51	<u>1.91</u>	R 2007 0086/5 BIXAFEN_056
Italy, Spinazzola 2007 (Simeto)	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	44	<u>3.6</u>	0.45	<u>4.05</u>	R 2007 0087/3 BIXAFEN_056
France (South), Les Chères 2007 (Autan)	2	0.125 0.125	0.042 0.042	300 300	52 69	straw	44	<u>0.79</u>	0.36	<u>1.15</u>	R 2007 0088/1 BIXAFEN_056
Spain, Alcala de Guadaira Sevilla 2007 (Bolido R1)	2	0.125 0.125	0.045 0.042	279 300	47 69	straw	54	<u>2.6</u>	0.64	<u>3.24</u>	R 2007 0090/3 BIXAFEN_056
Portugal, Ereira 2007	2	0.125 0.125	0.042 0.042	300 300	47 69	straw	53	<u>3.3</u>	0.61	<u>3.91</u>	R 2007 0157/8 BIXAFEN_056

Location,	Application					Residues, mg/kg					Trial No.,
Year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	BBCH	Sample	DALT	Bixafen	M21 _a	Total _a	Reference
(Galeira)											

a Expressed as bixafen

DALT = Days after last treatment

BBCH 47 = Flag leaf sheath opening

BBCH 52 = 20% of inflorescence emerged

BBCH 53 = 30% of inflorescence emerged

BBCH 69 = End of flowering: all spikelets have completed flowering but some dehydrated anthers may remain

FATE OF RESIDUES IN STORAGE AND PROCESSING

Nature of residue during processing

The hydrolysis of bixafen under processing conditions was investigated by Justus, K and Kuhnke, G (2008, BIXAFEN_061). [Pyrazole-5-¹⁴C]-bixafen was diluted in buffered drinking water at 0.25 mg ai/L, which corresponds to approximately 50% of the water solubility. The test solutions contained 0.7% acetonitrile. Incubation was done at three representative sets of hydrolysis conditions: 90 °C, pH 4 for 20 minutes (pasteurisation); 100 °C, pH 5 for 60 minutes (baking, brewing and boiling) and 120 °C, pH 6 for 20 minutes (sterilisation).

Parent compound and potential hydrolysis products were identified and quantified by HPLC. Thin layer chromatography was used for confirmation of the identity of the test item by co-chromatography with the non-labelled reference item. Material balances were established for each set of hydrolysis conditions.

In the following table the recovered radioactivity and its composition is summarised:

Table 78 Hydrolysis of bixafen under simulated processing conditions

Hydrolysis conditions	Incubation time (min)	Bixafen	
		mg/L	% applied radioactivity
pH 4, 90 °C	0	0.240	100
	20	0.236	98.2
pH 5, 100 °C	0	0.222	100
	60	0.222	100
pH 6, 120 °C	0	0.245	100
	20	0.240	98.0

Residues after processing

The fate of bixafen and its metabolite M21 (bixafen-desmethyl) during processing of raw agricultural commodity (RAC) was investigated in rapeseeds, barley grain and wheat grain using important processing procedures. As a measure of the transfer of residues into processed products, a processing factor (PF) was used, which is defined as:

$$PF = \frac{\text{Total residue in processed product (mg kg}^{-1}\text{)}}{\text{Total residue in raw agricultural commodity (mg kg}^{-1}\text{)}}$$

If residues in the RAC were below the LOQ, no processing factor could be derived. In case of residues below the LOQ, but above the LOD in the processed product, the numeric value of the LOQ

was used for the calculation. If residues in the processed product were below the LOD, the numeric value of the LOQ was used for the calculation but the PF was expressed as “less than” (e.g. < 0.5).

A summary of all processing factors for bixafen relevant for the estimation of maximum residue levels of the dietary intake is given in Table 79.

Rape seed

For the processing of oilseed, rape seed collected from three locations in Northern Europe (Freitag, T, Reineke, A and Krusell, L, 2010, BIXAFEN_057; Freitag, T, Reineke, A and Krusell, L, 2010, BIXAFEN_066 and Noss, G and Teubner, L, 2010, BIXAFEN_067) were processed into pomace, meal and different oils simulating the industrial practice at a laboratory scale (Freitag, T and Hoffmann, M, 2011, BIXAFEN_68; Freitag, T and Hoffmann, M, 2011, BIXAFEN_69 and Hoffmann, M and Teubner, L, 2012, BIXAFEN_70). The treatment program consisted of two spray applications at 0.06 or 0.075 kg ai/ha for each treatment. The first treatment was carried out at the growth stage BBCH 64 to 69 (end of flowering), and the second one at BBCH 69 to 75. The sampling dates were 35, 44 or 64 days after the final application was carried out.

The rape seeds were dried and cleaned using a sieve. The conditioned and cleaned rape seeds were pressed in a screw press yielding oil, screw-pressed and pomace.

An aliquot of the pomace was milled and then extracted with addition of n-hexane. In the rotary evaporator the n-hexane was removed, yielding oil, solvent extracted. The solvent-extracted meal was sampled after storing at room temperature or drying.

The oil fractions (screw-pressed oil and solvent extracted oil) were mixed yielding the sample of crude oil. The crude oil was filtered or hydrated and deslimed by adding water and phosphorus acid, heating and stirring, yielding the sample crude oil, preclarified.

The oily phase was heated while stirring and a sodium hydroxide solution was added. Water was added and the phases were allowed to separate. After phase separation the watery phase was removed. Crude oil, neutralised was sampled.

For bleaching, the oil was heated up to 90–100 °C while stirring. After addition of 1% pod sol the oil was bleached for 5 min without vacuum and 20 min with vacuum. Afterwards the pod sol was removed (filtration).

The oil was heated under vacuum up to 160 °C while stirring. After reaching 160 °C, steam was transferred through the oil for deodorization. After cooling to 160 °C the steam supply was stopped and then the oil was dried under vacuum until a temperature of ≤ 80 °C was reached. The refined oil was sampled.

All samples were analysed for bixafen and M21 (bixafen-desmethyl) according to method 01013. The limit of quantification (LOQ) was 0.01 mg/kg for the individual analytes, and consequently 0.02 mg/kg for the sum of both in all matrices. In the following table the residues found in the processed products are summarised:

Table 79 Residues of bixafen and M21 (bixafen-desmethyl) in processed rape commodities and calculation of processing factors

Location, year, reference (variety)	No.	kg ai/ha	BBCH	Sample	DALT	Bixafen		M21 (bixafen-desmethyl)		Total	
						mg/kg	PF	mg/kg	PF	mg/kg	PF
The Netherlands, Hoofddorp 2008 (Maximus)	2	0.075 0.075	64 69	seed	64	< 0.01	–	< 0.01	–	< 0.01	–
				oil, screw-pressed	64	< 0.01	–	< 0.01	–	< 0.01	–
				pomace	64	< 0.01	–	< 0.01	–	< 0.01	–

Location, year, reference (variety)	No.	kg ai/ha	BBCH	Sample	DALT	Bixafen		M21 (bixafen-desmethyl)		Total	
						mg/kg	PF	mg/kg	PF	mg/kg	PF
08-2116-02				meal	64	< 0.01	—	< 0.01	—	< 0.01	—
Field part: BIXAFEN_057				oil, solv. extracted	64	< 0.01	—	< 0.01	—	< 0.01	—
Processing part: BIXAFEN_068				oil, crude	64	< 0.01	—	< 0.01	—	< 0.01	—
				crude oil, preclarified	64	< 0.01	—	< 0.01	—	< 0.01	—
				crude oil, neutralised	64	< 0.01	—	< 0.01	—	< 0.01	—
				oil, refined	64	< 0.01	—	< 0.01	—	< 0.01	—
Germany, Burscheid	2	0.06 0.06	69 73	seed	35	0.02	—	< 0.01	—	0.03	—
2008 (Titan)				oil, screw-pressed	35	< 0.01	< 0.5	< 0.01	—	< 0.02	< 0.66
08-2112-02				pomace	35	0.01	0.5	0.01	—	0.02	0.66
Field part: BIXAFEN_056				meal	35	< 0.01	< 0.5	0.01	—	0.02	0.66
Processing part: BIXAFEN_069				oil, solv. extracted	35	< 0.01	< 0.5	< 0.01	—	< 0.02	< 0.66
				oil, crude	35	0.01	0.5	< 0.01	—	0.02	0.66
				crude oil, preclarified	35	< 0.01	< 0.5	< 0.01	—	< 0.02	< 0.66
				crude oil, neutralised	35	< 0.01	< 0.5	< 0.01	—	< 0.02	< 0.66
				oil, refined	35	< 0.01	< 0.5	< 0.01	—	< 0.02	< 0.66
United Kingdom, Bishop Burton	2	0.06 0.06	67 75	seed	44	0.01	—	< 0.01	—	0.02	—
2008 (Castille)				oil, screw-pressed	44	< 0.01	< 1	< 0.01	—	< 0.02	< 1
09-2245-01				pomace	44	0.01	1	< 0.01	—	0.02	1
Field part: BIXAFEN_067				meal	44	0.02	2	< 0.01	—	0.03	1.5
Processing part: BIXAFEN_070				oil, solv. extracted	44	0.02	2	< 0.01	—	0.03	1.5
				oil, crude	44	0.01	1	< 0.01	—	0.02	1
				crude oil, preclarified	44	0.01	1	< 0.01	—	0.02	1
				crude oil, neutralised	44	0.02	2	< 0.01	—	0.03	1.5
				oil, refined	44	0.02	2	< 0.01	—	0.03	1.5

DALT = Days after last treatment

PF = Processing factor

BBCH 64 = 40% of flowers on main raceme open

BBCH 67 = Flowering declining: majority of petals fallen

BBCH 69 = End of flowering

BBCH 71–78 = 10% to 80% of pods have reached final size

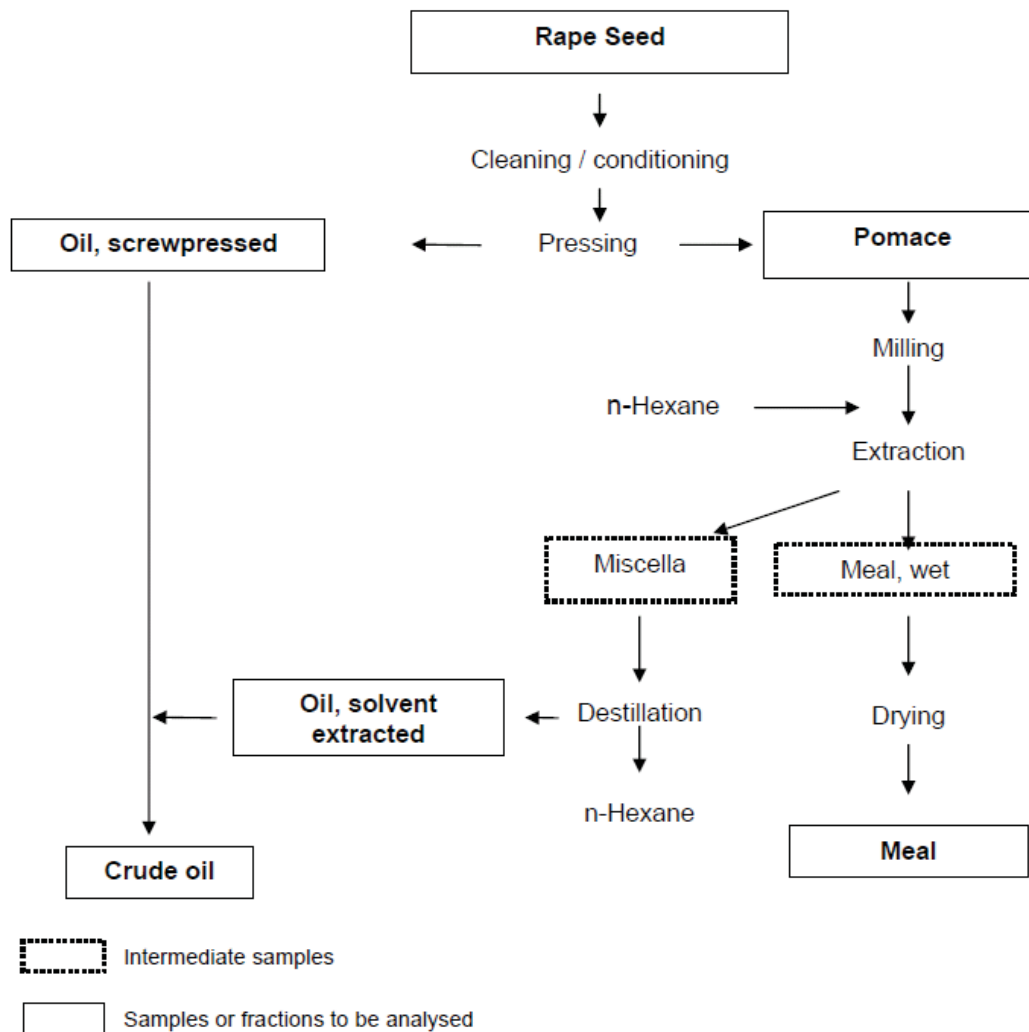


Figure 8 Flow chart of rape seeds processed into pomace, oil, screw-pressed, crude oil, oil, solvent extracted and meal

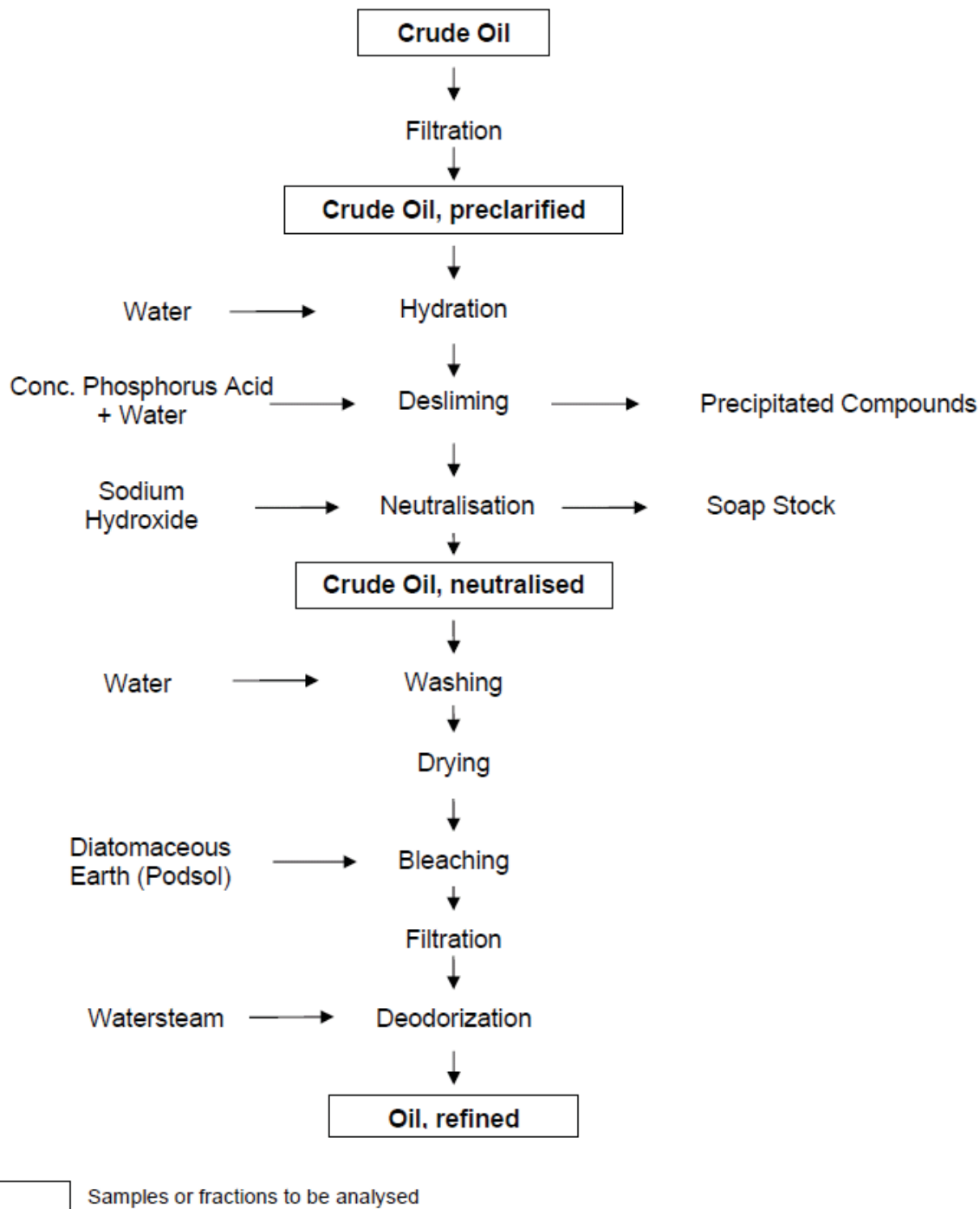


Figure 9 Flow chart for rape seeds processed into crude oil, preclarified, crude oil, neutralised and oil, refined

Barley

In Northern Europe four supervised field trials on barley were conducted involving two treatments at BBCH 37 and 61 with 0.25 kg ai/ha each (Schoening, R and Wolters, A, 2007, BIXAFEN_062). Samples were collected 35 to 46 days after the last treatment.

The production of both beer and pearl barley from grain of these trials was performed on a technical scale simulating commercial procedures (Schoening, R, Billian, P and Wolters, A, 2007, BIXAFEN_063).

In order to prepare pearl barley, the grain was first cleaned to separate husks and other impurities from the barley. Then the seeds were conditioned by adjusting the moisture content to about 14–16%. Depending on the initial moisture content this was done by damping prior to further processing for two of the four samples. Finally, the seeds were decorticated in a mill where they were passed through a vertically rotating cylinder. An abrasion of 30–35% was reached. For analysis, samples of pearl barley and pearl barley rub-off were collected (see Figure).

The beer brewing process starts with sieving and cleaning of the specimen. Before the beginning of the malting, the barley grains undergo a 3-step steeping procedure (combination of wet and dry steeping) at a temperature of 13–14 °C, over 2 days, until a final steeping degree of 44.8–44.9% was reached. Germination took place at a temperature of 14 ± 1 °C for 5 days at a relative air humidity of > 90%. After germination, the malting process is terminated by kiln-drying at maximum 82 °C. At the end of drying, samples of brewing malt and malt culms (malt sprouts) were taken.

In a next step, the malt was ground. Mash was produced by adding water, and heating the mixture at stepwise increasing temperatures with a defined temperature and time regime. The mash was then lautered in a 2-step process (filtering and washing). This process resulted in brewer's grain, of which samples were taken, and wort. The wort was cooked and commercially bought hops were added. After boiling, the flocs (hops draff) were separated in a whirlpool. The deposited hops draff was sampled. After cooling and ventilating of the wort, yeast was added. After a period of 6–7 days, the yeast deposited on the tank bottom and was sampled as brewer's yeast. At the beginning of maturation the young beer was stored at room temperature (warm maturation) for 2 days in casks. Subsequently, the young beer was stored under pressure at 2 °C for about 4 weeks (cold maturation). During this time the remaining extract was fermented and sludge particles and yeast settled at the bottom. The rack beer was then filtered and filled into bottles. Following filtration, beer samples were taken (see Figure & 12).

All samples were analysed for bixafen and M21 (bixafen-desmethyl) according to method 01012. The limit of quantification (LOQ) was 0.01 mg/kg for the individual analytes, and consequently 0.02 mg/kg for the sum of both in all matrices. In the following table the residues found in the processed products are summarised:

Table 80 Residues of bixafen and M21 (bixafen-desmethyl) in processed barley commodities and calculation of processing factors

Location, year, reference (variety)	No.	kg ai/ha	BBCH	Sample	DALT	Bixafen		M21 (bixafen-desmethyl)		Total	
						mg/kg	PF	mg/kg	PF	mg/kg	PF
Sweden, Staffanstorps 2006 (Prestige) R 2006 0444/0 Field part: BIXAFEN_062 Processing part: BIXAFEN_063	2	0.25 0.25	37 61	grain	40	0.23	–	0.03	–	0.26	–
				brewer's malt	40	0.22	0.96	0.06	2	0.27	1
				malt culms	40	0.17	0.74	0.06	2	0.23	0.88
				beer	40	< 0.01	< 0.04	< 0.01	< 0.33	< 0.02	< 0.08
				brewer's	40	0.04	0.17	0.01	0.33	0.05	0.19
				yeast	40	0.23	1	0.04	1.3	0.27	1
				brewer's	40	0.17	0.74	0.03	1	0.20	0.77
				grain	40	0.04	0.17	0.01	0.33	0.05	0.19
				hops draff	40	0.74	3.2	0.09	3	0.84	3.2
				pearl barley							
				pearl barley rub-off							
Germany, Swisttal-Heimerzheim	2	0.25 0.25	37 61	grain	35	0.13	–	0.02	–	0.15	–
				brewer's malt	35	0.12	0.92	0.03	1.5	0.15	1
				malt culms	35	0.14	1.1	0.04	2	0.18	1.2

Location, year, reference (variety)	No.	kg ai/ha	BBCH	Sample	DALT	Bixafen		M21 (bixafen-desmethyl)		Total	
						mg/kg	PF	mg/kg	PF	mg/kg	PF
2006 (Class) R 2006 0445/9 Field part: BIXAFEN_062 Processing part: BIXAFEN_063				beer	35	< 0.01	< 0.08	< 0.01	< 0.5	< 0.02	< 0.13
				brewer's	35	0.01	0.08	< 0.01	< 0.5	0.02	0.13
				yeast	35	0.14	1.1	0.03	1.5	0.16	1.1
				brewer's	35	0.09	0.69	0.02	1	0.10	0.67
				grain	35	0.03	0.23	0.01	0.5	0.04	0.27
				hops draff	35	0.67	5.2	0.07	3.5	0.74	4.9
				pearl barley pearl barley rub-off							
France (North), Fresnoy les Roye 2006 (Scarlet) R 2006 0446/7 Field part: BIXAFEN_062 Processing part: BIXAFEN_063	2	0.25 0.25	37 61	grain	46	0.20	–	0.02	–	0.22	–
				brewer's malt	46	0.16	0.8	0.04	2	0.20	0.91
				malt culms	46	0.14	0.7	0.03	1.5	0.17	0.77
				beer	46	< 0.01	< 0.05	< 0.01	< 0.5	< 0.02	< 0.09
				brewer's	46	0.04	0.2	< 0.01	< 0.5	0.05	0.23
				yeast	46	0.17	0.85	0.03	1.5	0.19	0.86
				brewer's	46	0.13	0.65	0.02	1	0.15	0.68
				grain	46	0.04	0.2	0.01	0.5	0.05	0.23
				hops draff	46	0.91	4.6	0.06	3	0.97	4.4
				pearl barley pearl barley rub-off							
Germany, Burscheid 2006 (Barke) R 2006 0447/5 Field part: BIXAFEN_062 Processing part: BIXAFEN_063	2	0.25 0.25	37 61	grain	43	0.03	–	< 0.01	–	0.04	–
				brewer's malt	43	0.01	0.33	< 0.01	–	0.02	0.5
				malt culms	43	0.01	0.33	< 0.01	–	0.02	0.5
				beer	43	< 0.01	< 0.33	< 0.01	–	< 0.02	< 0.5
				brewer's	43	< 0.01	< 0.33	< 0.01	–	< 0.02	< 0.5
				yeast	43	0.01	0.33	< 0.01	–	0.02	0.5
				brewer's	43	0.01	0.33	< 0.01	–	0.02	0.5
				grain	43	< 0.01	< 0.33	< 0.01	–	< 0.02	< 0.5
				hops draff	43	0.11	3.7	0.01	–	0.12	3
				pearl barley pearl barley rub-off							

DALT = Days after last treatment

PF = Processing factor

BBCH 37 = Flag leaf just visible, still rolled

BBCH 61 = Beginning of flowering: first anthers visible

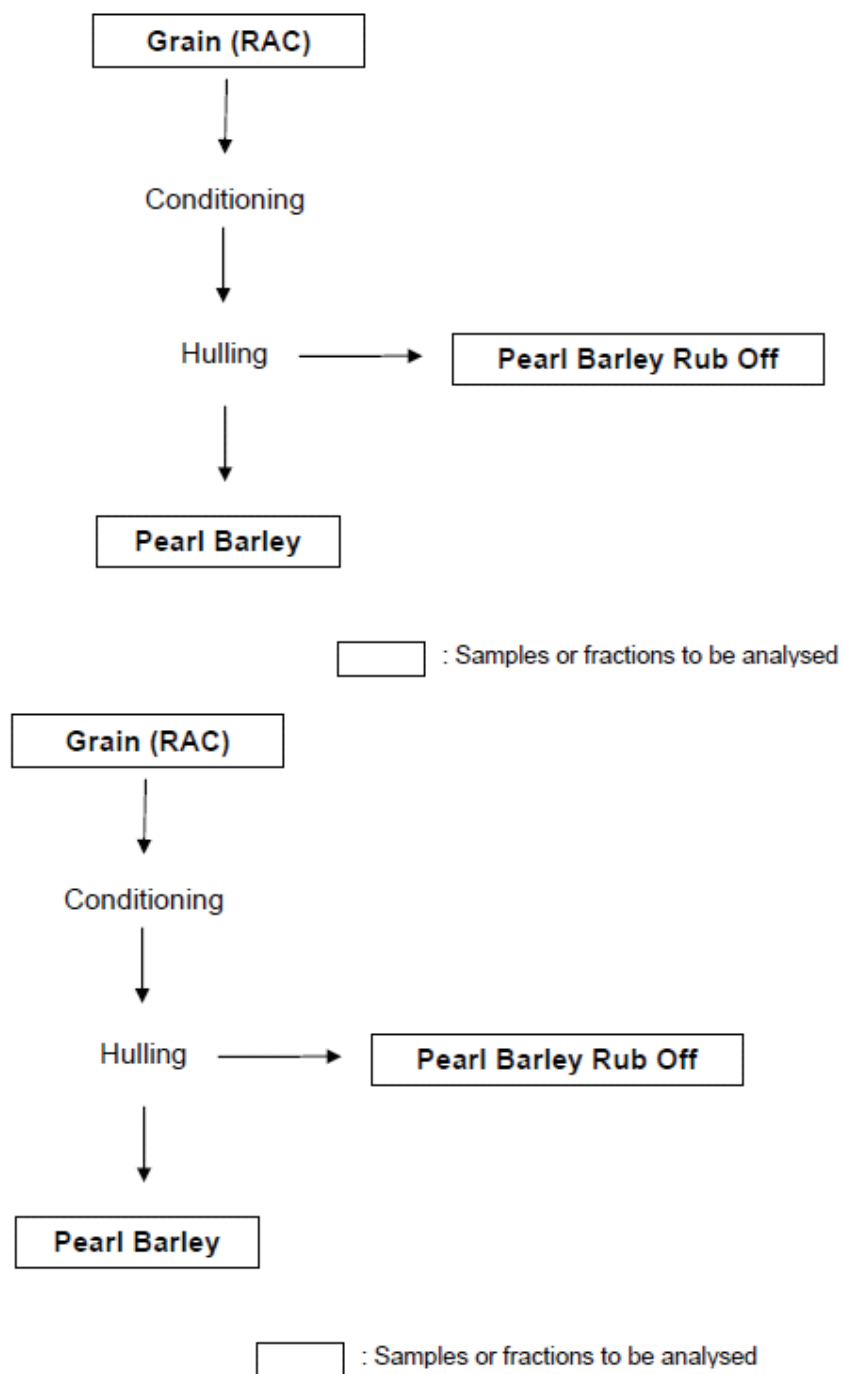


Figure 10 Flow chart of the processing of barley to pearl barley

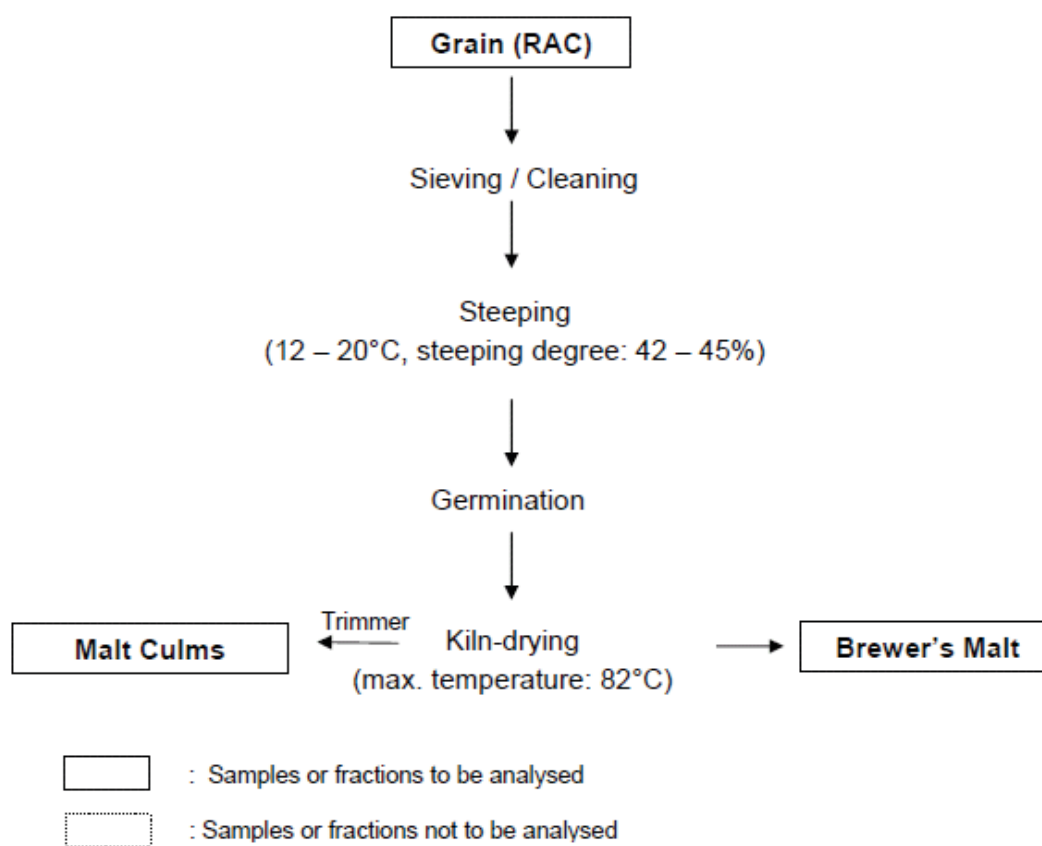


Figure 11 Flow chart of the processing of barley to malt

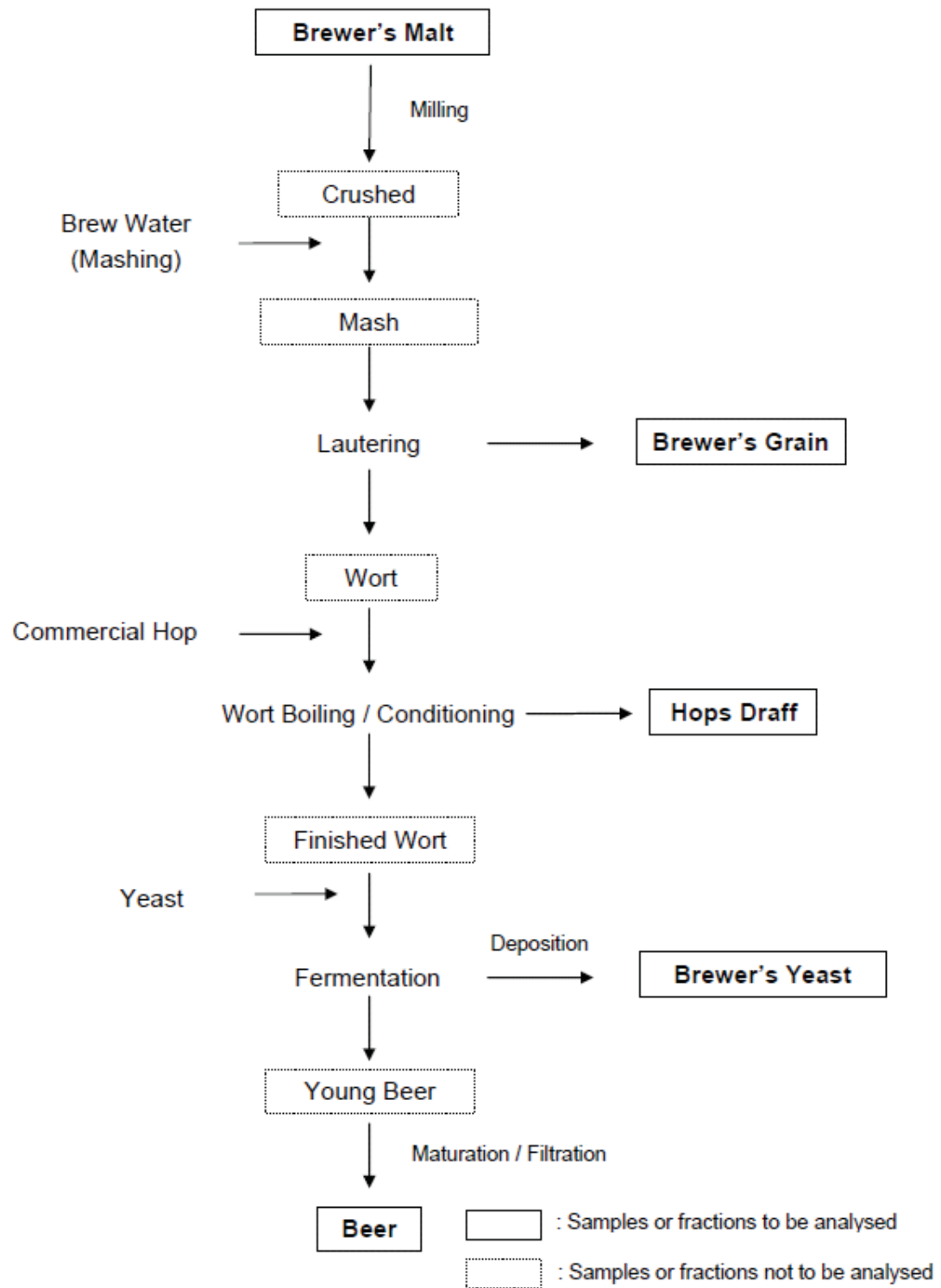


Figure 12 Flow chart of the processing of malt to beer

Wheat

In 2006, four residue studies on winter wheat were conducted in Northern Europe by Schoening, R and Erler, S (2007, BIXAFEN_064). The treatment program consisted of two spray applications at BBCH 47 and BBCH 69 with application rates of 0.232 to 0.250 kg ai/ha each. The sampling dates were 39 to 53 days after the final application.

The processing of wheat grain samples collected from three of the locations into processed fractions (white flour, white flour bran, semolina, semolina bran, white bread, whole-meal, whole-meal bread and wheat germs) was performed in specialised pilot plants to simulate industrial procedures of the milling and bakery industry (Schoening, R and Erler, S, 2007, BIXAFEN_065). The sample originating from the United Kingdom was divided in two portions (A and B). The second portion (B) was processed at a different processing site than portion A.

In order to prepare flour and semolina, the grain was first cleaned and a moisture content of about 17% was adjusted. The cleaned grain was then milled to either white flour and white flour bran, to whole meal flour, or to semolina and semolina bran.

For preparation of white bread the ingredients of the dough were weighed, combined and kneaded. After kneading the dough was placed into the fermentation chamber for fermentation. The bread was baked on one level in the baking oven at a constant heat of 230 °C (oven setting) for 30 min.

For preparation of whole-meal bread the sourdough was prepared one day before the baking process. Whole-meal and water were mixed together with the starter. The mixture was placed into the fermentation chamber. The ingredients of the dough were weighted, combined and kneaded. After kneading the dough was placed into the fermentation chamber for fermentation. The bread was baked on one level in the baking oven at a constant heat of 207 °C (oven setting) for nearly 1 hour.

All samples were analysed for bixafen and M21 (bixafen-desmethyl) according to method 01012. The limit of quantification (LOQ) was 0.01 mg/kg for the individual analytes, and consequently 0.02 mg/kg for the sum of both in all matrices. In the following table the residues found in the processed products are summarised:

Table 81 Residues of bixafen and M21 (bixafen-desmethyl) in processed wheat commodities and calculation of processing factors

Location, year, reference (variety)	No.	kg ai/ha	BBCH	Sample	DALT	Bixafen		M21 (bixafen-desmethyl)		Total	
						mg/kg	PF	mg/kg	PF	mg/kg	PF
United Kingdom, Bury St. Edmunds 2006 (Cordiale) R 2006 0527/7 Field part: BIXAFEN_064 Processing part: BIXAFEN_065 Portion A	2	0.23 0.25	47 69	grain	40	0.05	–	< 0.01	–	0.06	–
				white flour	40	0.01	0.2	< 0.01	–	0.02	0.33
				white flour bran	40	0.13	2.6	0.02	–	0.15	2.5
				semolina	40	< 0.01	< 0.2	< 0.01	–	< 0.02	< 0.33
				semolina	40	< 0.01	< 0.2	< 0.01	–	< 0.02	< 0.33
				bran	40	< 0.01	< 0.2	< 0.01	–	< 0.02	< 0.33
				white bread	40	0.04	0.8	< 0.01	–	0.05	0.83
				whole meal	40	0.02	0.4	< 0.01	–	0.03	0.5
				wholemeal bread	40	0.06	1.2	0.02	–	0.08	1.33
				wheat germ	40						
United Kingdom, Bury St. Edmunds	2	0.23 0.25	47 69	grain	40	0.05	–	< 0.01	–	0.06	–
				white flour	40	0.01	0.2	< 0.01	–	0.02	0.33
				white flour bran	40	0.14	2.4	0.02	–	0.16	2.7
				semolina	40	< 0.01	< 0.2	< 0.01	–	< 0.02	< 0.33

Location, year, reference (variety)	No.	kg ai/ha	BBCH	Sample	DALT	Bixafen		M21 (bixafen-desmethyl)		Total	
						mg/kg	PF	mg/kg	PF	mg/kg	PF
2006 (Cordiale)				semolina	40	0.07	1.4	0.01	–	0.08	1.33
				bran	40	0.01	0.2	< 0.01	–	0.02	0.33
				white bread	40	0.04	0.8	< 0.01	–	0.05	0.83
R 2006 0527/7				whole meal	40	0.03	0.6	< 0.01	–	0.04	0.66
Field part: BIXAFEN_064				wholemeal bread	40	0.03	0.6	0.02	–	0.05	0.83
Processing part: BIXAFEN_065				wheat germ							
Portion B											
France (North), Fresnoy les Roye	2	0.25 0.25	47 69	grain	53	0.02	–	0.01	–	0.03	–
				white flour	53	0.01	0.5	< 0.01	< 1	0.02	0.66
				white flour	53	0.07	3.5	0.05	5	0.12	4
				bran							
2006 (Chango)				semolina	53	< 0.01	< 0.5	< 0.01	< 1	< 0.02	< 0.66
				semolina	53	0.01	0.5	< 0.01	< 1	0.02	0.66
				bran	53	< 0.01	< 0.5	< 0.01	< 1	< 0.02	< 0.66
R 2006 0527/7				white bread	53	0.03	1.5	0.02	2	0.05	1.7
Field part: BIXAFEN_064				whole meal	53	0.01	0.5	0.01	1	0.02	0.66
				wholemeal bread							
Processing part: BIXAFEN_065				wheat germ	53	0.03	1.5	0.05	5	0.08	2.7
France (North), Chambourg sur Indre	2	0.25 0.25	47 69	grain	39	0.04	–	< 0.01	–	0.05	–
				white flour	39	0.01	0.25	< 0.01	–	0.02	0.4
				white flour	39	0.11	2.8	0.01	–	0.12	2.4
				bran							
2006 (Apache)				semolina	39	< 0.01	< 0.25	< 0.01	–	< 0.02	< 0.4
				semolina	39	0.01	0.25	< 0.01	–	0.02	0.4
				bran	39	< 0.01	< 0.25	< 0.01	–	< 0.02	< 0.4
R 2006 0527/7				white bread	39	0.04	1	< 0.01	–	0.05	1
Field part: BIXAFEN_064				whole meal	39	0.02	0.5	< 0.01	–	0.03	0.6
				wholemeal bread							
Processing part: BIXAFEN_065				wheat germ	39	0.03	0.75	0.01	–	0.04	0.8

Portion A/B = Field samples split into two processing samples

DALT = Days after last treatment

PF = Processing factor

BBCH 47 = Flag leaf sheath opening

BBCH 69 = End of flowering: all spikelets have completed flowering but some dehydrated anthers may remain

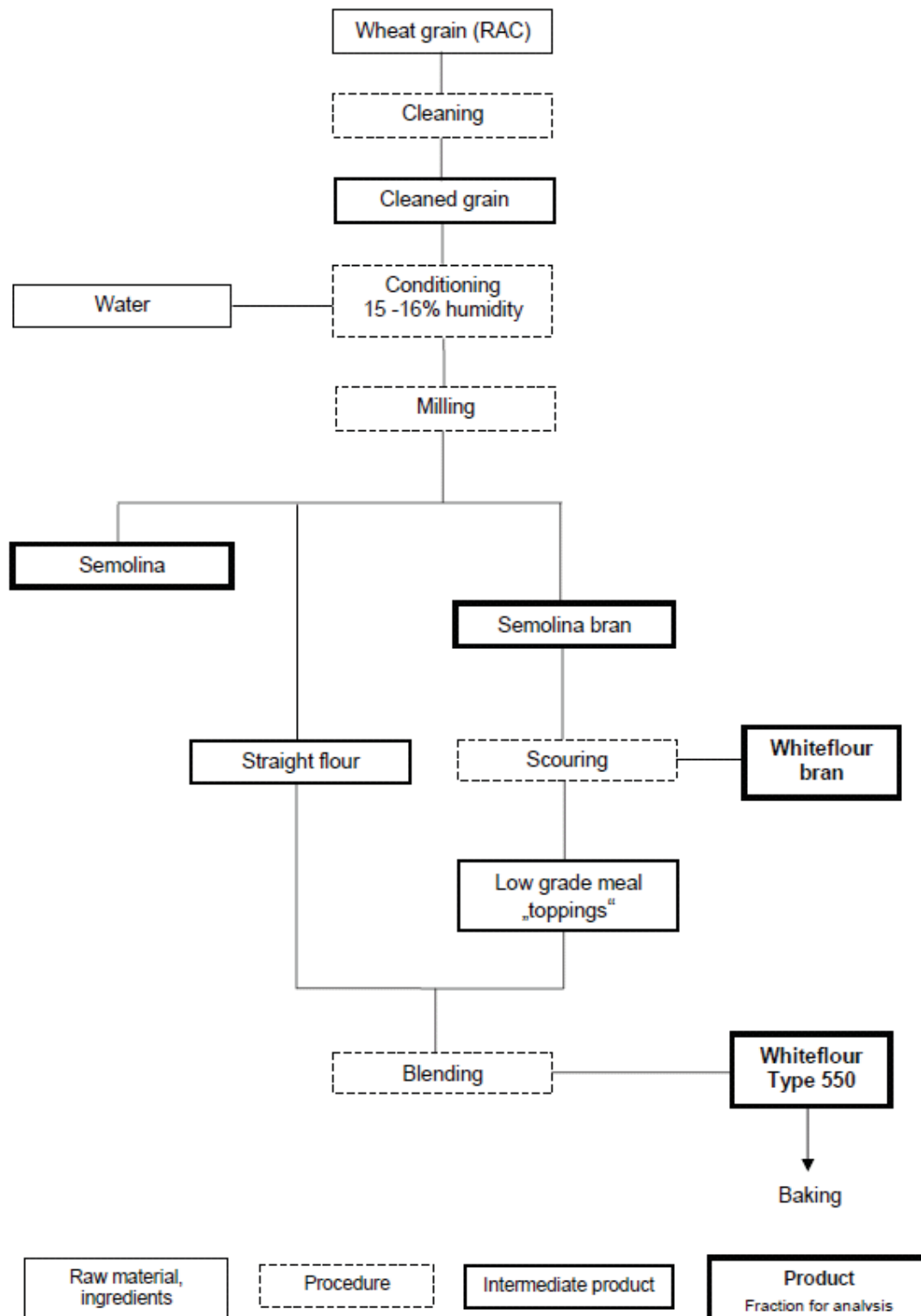


Figure 13 Flow chart for processing wheat grain into white flour, semolina and white flour bran

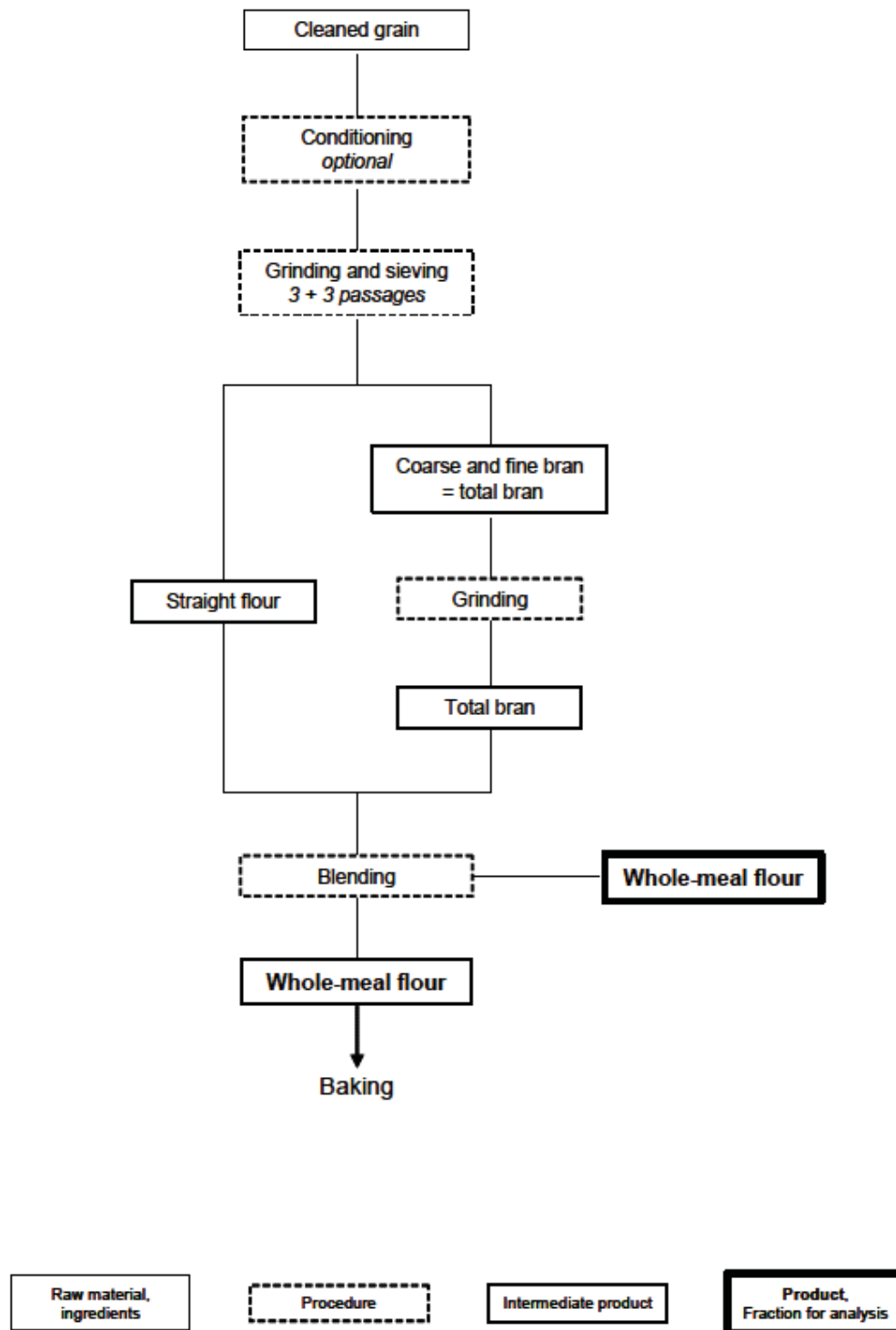


Figure 14 Flow chart for processing wheat grain into wholemeal flour

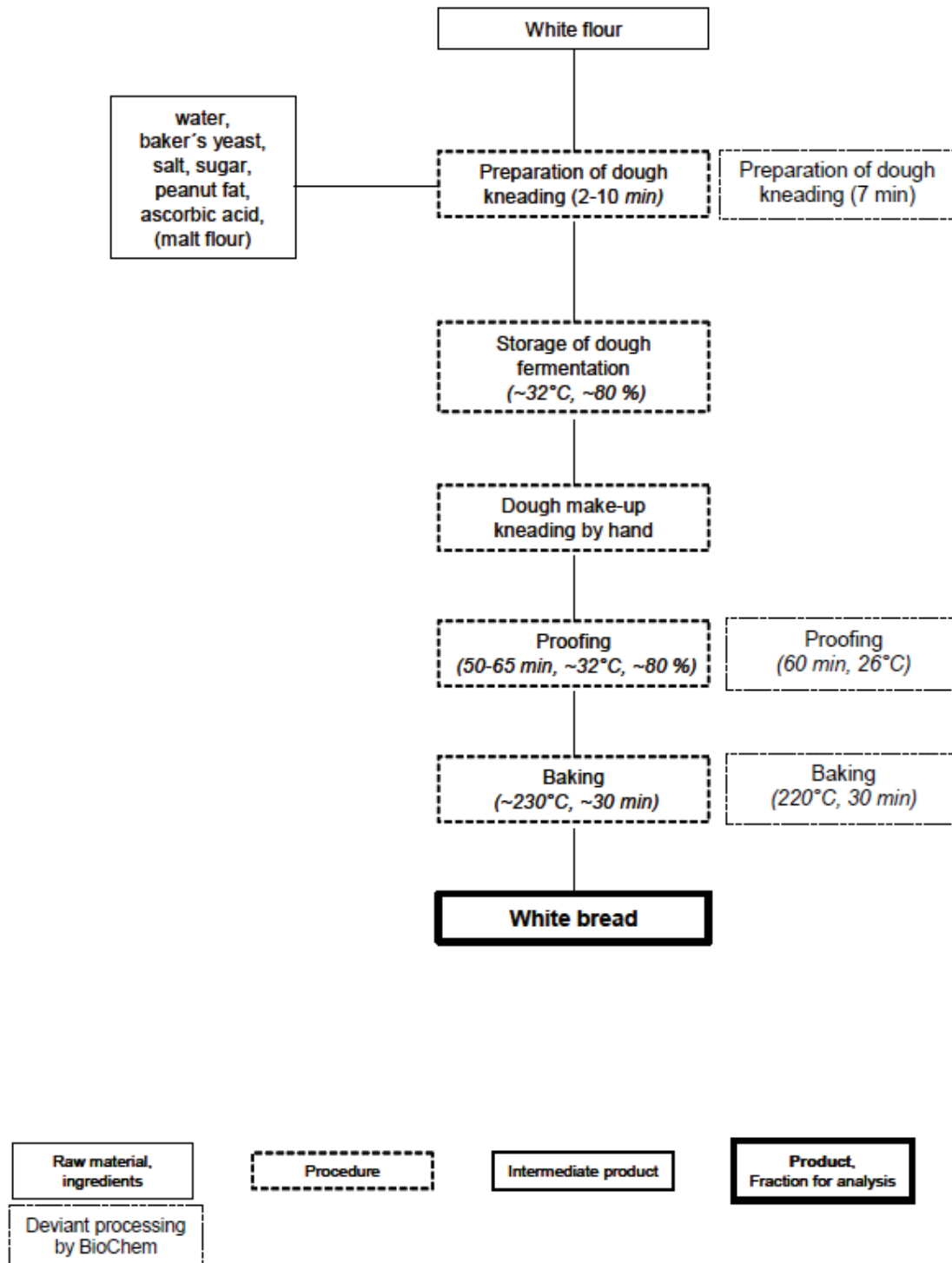


Figure 15 Flow chart for processing wheat grain into white bread

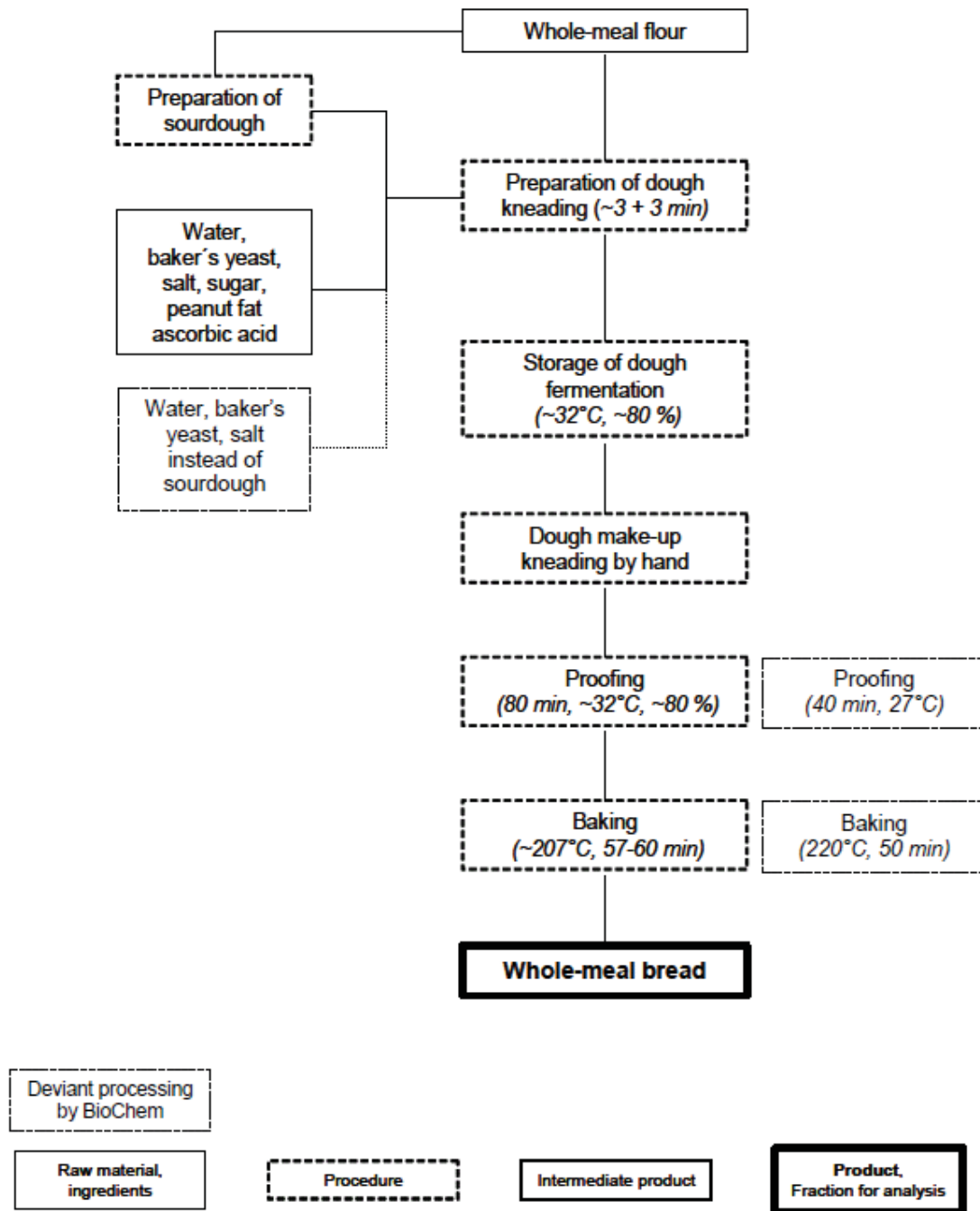


Figure 16 Flow chart for processing wheat grain into wholemeal bread

Table 82 Overview of processing factors for bixafen-derived residues

Raw commodity	Processed commodity	Bixafen		M21 (bixafen-desmethyl)		Total residue	
		Individual processing factors	Mean or best estimate processing factor	Individual processing factors	Mean or best estimate processing factor	Individual processing factors	Median or best estimate processing factor
Rape	oil, screw-pressed	< 0.5, < 1	1 (best estimate)	–	–	< 0.66, < 1	1 (best estimate)
	pomace	0.5, 1	0.75	–	–	0.66, 1	0.83
	meal	< 0.5, 2	2 (best estimate)	–	–	0.66, 1.5	1.5 (best estimate)
	oil, solv. extracted	< 0.5, 2	2 (best estimate)	–	–	< 0.66, 1.5	1.5 (best estimate)
	oil, crude	0.5, 1	0.75	–	–	0.66, 1	0.83
	crude oil, preclarified	< 0.5, 1	1 (best estimate)	–	–	< 0.66, 1	1.5 (best estimate)
	crude oil, neutralised	< 0.5, 2	2 (best estimate)	–	–	< 0.66, 1.5	1.5 (best estimate)
	oil, refined	< 0.5, 2	2 (best estimate)	–	–	< 0.66, 1.5	1.5 (best estimate)
Barley	brewer's malt	0.33, 0.8, 0.92, 0.96	0.86	1.5, 2, 2	2	0.5, 0.91, 1, 1	0.96
	malt culms	0.33, 0.7, 0.74, 1.1	0.72	1.5, 2, 2	2	0.5, 0.77, 0.88, 1.2	0.83
	beer	< 0.04, < 0.05, < 0.08, < 0.33	< 0.065	< 0.33, < 0.5, < 0.5	< 0.5	0.08, < 0.09, < 0.13, < 0.5	< 0.11
	brewer's yeast	0.08, 0.17, 0.2, < 0.33	0.19	0.33, < 0.5, < 0.5	< 0.5	0.13, 0.19, 0.23, < 0.5	0.21
	brewer's grain	0.33, 0.85, 1, 1.1	0.93	1.3, 1.5, 1.5	1.5	0.5, 0.86, 1, 1.1	0.93
	hops draff	0.33, 0.65, 0.69, 0.74	0.67	1, 1, 1	1	0.5, 0.67, 0.68, 0.77	0.68
	pearl barley	0.17, 0.2, 0.23, < 0.33	0.22	0.33, 0.5, 0.5	0.5	0.19, 0.23, 0.27, < 0.5	0.25
	pearl barley rub-off	3.2, 3.3, 4.6, 5.2	4	3, 3, 3.5	3	3, 3.2, 4.4, 4.9	3.8
Wheat	white flour	0.2, 0.2, 0.25, 0.5	0.23	< 1	< 1	0.33, 0.33, 0.4, 0.66	0.37
	White flour bran	2.4, 2.6, 2.8, 3.5	2.7	5	5	2.4, 2.5, 2.7, 4	2.6
	semolina	< 0.2, < 0.2, < 0.25, < 0.5	< 0.23	< 1	< 1	< 0.33, < 0.33, < 0.4, < 0.66	< 0.37
	semolina bran	< 0.2, 0.25, 0.5, 1.4	0.38	< 1	< 1	< 0.33, 0.4, 0.66, 1.33	0.53
	white bread	< 0.2, 0.2, < 0.25, < 0.5	0.2 (best estimate)	< 1	< 1	< 0.33, 0.33, < 0.4, < 0.66	0.33 (best estimate)
	whole meal	0.8, 0.8, 1, 1.5	0.9	2	2	0.83, 0.83, 1, 1.7	0.91
	wholemeal bread	0.4, 0.5, 0.5, 0.6	0.5	1	1	0.5, 0.6, 0.66, 0.66	0.63
	wheat germ	0.6, 0.75, 1.2, 1.5	1	5	5	0.8, 0.83, 1.3, 2.7	1.1

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

For the estimation of residues of bixafen and its metabolite M21 (bixafen-desmethyl) in animal matrices laying hens and lactating cow feeding studies were submitted to the Meeting.

Poultry

The magnitude of the residue of bixafen and its metabolite M21 (bixafen-desmethyl) has been studied in laying hens by Billian, P, Barfknecht, R and Wolters, A (2008, BIXAFEN_071). Adult chickens (12 birds per diet group divided into three subgroups with four animals each, one control group with four birds) were exposed for 28 consecutive days to levels of 1.5 ppm (1× dose group), 4.5 ppm (3× dose group), or 15 ppm feed/day (10× dose group) corresponding to approximately 0.1 , 0.3 and 1.0 mg/kg bw/day. For a depuration study, three groups of hens were fed at the 10× dose rate for 28 consecutive days followed by untreated feed for another 7 days, 14 days or 21 days. Each subgroup comprised five birds.

Eggs were collected during the whole dosing period. On day 29 after the first dose, the hens were sacrificed, and liver, fat and overlaying skin, and muscle from breast and leg were collected for analysis.

Tissues and eggs were pooled and analysed using method 01036 (see analytical method section). The analytical method was validated for bixafen and M21 at a LOQ of 0.01 mg/kg for each analyte. The LOQ of the total bixafen residues (sum of bixafen and bixafen-desmethyl) was calculated to be 0.02 mg/kg. Residue data were obtained by high performance liquid chromatography-electrospray ionization/tandem mass spectrometry (HPLC-MS/MS) using isotopically labelled internal standards.

In the following table the residues found in eggs are summarised. Prior to dosing of bixafen, eggs collected contained no detectable residues of bixafen or M21 (bixafen-desmethyl). The results for these samples are not presented.

Table 83 Residues of bixafen and M21 (bixafen-desmethyl) in eggs after administration of bixafen at 0.1, 0.3 or 1.0 mg/kg bw and day

Days	Residues in mg bixafen-equivalents per kg [mean]		
	1× (1.5 ppm, 0.1 mg/kg bw)	3× (4.5 ppm, 0.3 mg/kg bw)	10× (15 ppm, 1.0 mg/kg bw)
0	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)
1	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)
2	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: < 0.01, < 0.01, 0.01 [0.01] M21: < 0.01(3) Total: < 0.01, < 0.01, 0.01 [0.01]	bixafen: 0.03, 0.03, 0.04 [0.033] M21: 0.01, 0.01, 0.02 [0.013] Total: 0.04, 0.04, 0.06 [0.047]
5	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: 0.01, 0.01, 0.02 [0.013] M21: 0.01, 0.01, 0.02 [0.013] Total: 0.02, 0.02, 0.04 [0.027]	bixafen: 0.05, 0.06, 0.07 [0.06] M21: 0.05, 0.06, 0.07 [0.06] Total: 0.1, 0.12, 0.14 [0.12]
7	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: 0.02, 0.02, 0.04 [0.027] M21: 0.02, 0.03, 0.04 [0.03] Total: 0.04, 0.05, 0.07 [0.053]	bixafen: 0.05, 0.05, 0.07 [0.057] M21: 0.07, 0.07, 0.08 [0.073] Total: 0.12, 0.13, 0.14 [0.13]
9	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: 0.02, 0.02, 0.03 [0.023] M21: 0.02, 0.03, 0.03 [0.027] Total: 0.04, 0.05, 0.06 [0.05]	bixafen: 0.06, 0.07, 0.08 [0.07] M21: 0.08, 0.08, 0.09 [0.083] Total: 0.13, 0.14, 0.16 [0.143]

Days	Residues in mg bixafen-equivalents per kg [mean]		
	1× (1.5 ppm, 0.1 mg/kg bw)	3× (4.5 ppm, 0.3 mg/kg bw)	10× (15 ppm, 1.0 mg/kg bw)
12	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: 0.02, 0.02, 0.03 [0.023] M21: 0.02, 0.02, 0.03 [0.023] Total: 0.04, 0.05, 0.05 [0.047]	bixafen: 0.06, 0.07, 0.11 [0.08] M21: 0.07, 0.08, 0.12 [0.09] Total: 0.13, 0.15, 0.23 [0.17]
14	bixafen: < 0.01(3) M21: < 0.01, < 0.01, 0.01 [0.01] Total: < 0.02(2), 0.02 [0.02]	bixafen: 0.03, 0.03, 0.03 [0.03] M21: 0.03, 0.03, 0.03 [0.03] Total: 0.06, 0.06, 0.06 [0.06]	bixafen: 0.06, 0.06, 0.1 [0.073] M21: 0.07, 0.08, 0.1 [0.083] Total: 0.13, 0.14, 0.2 [0.157]
16	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: 0.03, 0.03, 0.03 [0.03] M21: 0.03, 0.03, 0.03 [0.03] Total: 0.06, 0.06, 0.06 [0.06]	bixafen: 0.05, 0.07, 0.08 [0.067] M21: 0.07, 0.09, 0.09 [0.083] Total: 0.12, 0.16, 0.17 [0.15]
21	bixafen: < 0.01(3) M21: < 0.01, < 0.01, 0.01 [0.01] Total: < 0.02(2), 0.02 [0.02]	bixafen: 0.03, 0.03, 0.03 [0.03] M21: 0.03, 0.03, 0.04 [0.033] Total: 0.06, 0.06, 0.07 [0.063]	bixafen: 0.06, 0.06, 0.08 ^a , 0.09 ^a , 0.09 ^a 0.1 [0.08] M21: 0.07, 0.09, 0.09 ^a , 0.1 ^a , 0.12 ^a , 0.12 [0.098] Total: 0.13, 0.15, 0.18 ^a , 0.18 ^a , 0.21 ^a , 0.22 [0.178]
23	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: 0.02, 0.02, 0.03 [0.023] M21: 0.02, 0.03, 0.03 [0.027] Total: 0.04, 0.05, 0.06 [0.05]	bixafen: 0.06, 0.07, 0.07 ^a , 0.08, 0.08 ^a , 0.09 ^a [0.075] M21: 0.09, 0.09, 0.09 ^a , 0.1 ^a , 0.1 ^a , 0.11 [0.097] Total: 0.15, 0.16, 0.16 ^a , 0.18 ^a , 0.19, 0.19 ^a [0.172]
26	bixafen: < 0.01(3) M21: < 0.01, < 0.01, 0.01 [0.01] Total: < 0.02(2), 0.02 [0.02]	bixafen: 0.02, 0.03, 0.03 [0.027] M21: 0.02, 0.03, 0.04 [0.03] Total: 0.05, 0.06, 0.06 [0.057]	bixafen: 0.07, 0.07, 0.07 ^a , 0.07 ^a , 0.08, 0.09 ^a [0.075] M21: 0.08, 0.08 ^a , 0.09, 0.09 ^a , 0.1, 0.1 ^a [0.09] Total: 0.14, 0.16, 0.17 ^a , 0.17 ^a , 0.17 ^a , 0.18 [0.165]
28	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: 0.02, 0.03, 0.03 [0.027] M21: 0.02, 0.03, 0.03 [0.027] Total: 0.05, 0.05, 0.06 [0.057]	bixafen: 0.05, 0.07, 0.07 ^a , 0.08 ^a , 0.09, 0.09 ^a [0.075] M21: 0.06, 0.08 ^a , 0.09, 0.09, 0.09 ^a , 0.1 ^a [0.085] Total: 0.11, 0.16, 0.17 ^a , 0.17 ^a , 0.17 ^a , 0.18 [0.16]
30	not performed	not performed	bixafen: 0.04 ^a , 0.05 ^a , 0.05 ^a [0.047] M21: 0.06 ^a , 0.08 ^a , 0.08 ^a [0.073] Total: 0.11 ^a , 0.12 ^a , 0.13 ^a [0.12]
33	not performed	not performed	bixafen: 0.02 ^a , 0.02 ^a , 0.02 ^a [0.02] M21: 0.03 ^a , 0.03 ^a , 0.03 ^a [0.03] Total: 0.05 ^a , 0.05 ^a , 0.05 ^a [0.05]
35	not performed	not performed	bixafen: < 0.01 ^a (3) M21: < 0.01 ^a , < 0.01 ^a , 0.01 ^a [0.01] Total: < 0.02 ^a , < 0.02 ^a , 0.02 ^a [0.02]
37, 40, 42	not performed	not performed	bixafen: < 0.01 ^a (2) M21: < 0.01 ^a (2) Total: < 0.02 ^a (2)
44, 48, 49	not performed	not performed	bixafen: < 0.01 ^a M21: < 0.01 ^a Total: < 0.02 ^a

^a Depuration sub-group

The distribution of the residue between egg yolk and egg white was investigated for the 10× group on eggs collected after 22, 25 and 27 days. In the following table the residues of bixafen and M21 (bixafen-desmethyl) are presented:

Table 84 Distribution of bixafen and M21 (bixafen-desmethyl) in egg yolk and egg white after administration of bixafen at 1.0 mg/kg bw and day (10×)

Day	Residues in egg yolk [mg bixafen equiv./kg]			Residues in egg white [mg bixafen equiv./kg]			Residues in whole egg [mg bixafen equiv./kg]		
	bixafen	M21	total	bixafen	M21	total	bixafen	M21	total
22	0.13	0.20	0.33	0.04	0.01	0.05	0.07	0.08	0.15
25	0.14	0.24	0.38	0.05	0.02	0.07	0.08	0.09	0.17
27	0.10	0.20	0.30	0.03	0.01	0.04	0.05	0.07	0.12

For poultry, tissues residues of bixafen and M21 (bixafen-desmethyl) found directly at the end of the dosing period are presented in the following table. In samples collected from animal after depuration, no detectable residue of bixafen or M21 (bixafen-desmethyl) were present.

Table 85 Residues of bixafen and M21 (bixafen-desmethyl) in tissues of laying hens after administration of bixafen at 0.1, 0.3 or 1.0 mg/kg bw and day (1×, 3× or 10×)

Commodity	Residues in mg bixafen-equivalents per kg [mean]		
	1× (1.5 ppm, 0.1 mg/kg bw)	3× (4.5 ppm, 0.3 mg/kg bw)	10× (15 ppm, 1.0 mg/kg bw)
Skin with fat	bixafen: < 0.01, < 0.01, 0.01 [0.01] M21: < 0.01(3) Total: < 0.02, < 0.02, 0.02 [0.02]	bixafen: 0.04, 0.04, 0.05 [0.043] M21: 0.01, 0.01, 0.02 [0.013] Total: 0.05, 0.06, 0.06 [0.057]	bixafen: 0.05, 0.05, 0.07 [0.057] M21: 0.01, 0.01, 0.02 [0.013] Total: 0.06, 0.06, 0.09 [0.07]
Liver	bixafen: < 0.01(3) M21: < 0.01, < 0.01, 0.01 [0.01] Total: < 0.02, < 0.02, 0.02 [0.02]	bixafen: < 0.01, 0.01, 0.01 [0.01] M21: 0.01, 0.02, 0.03 [0.02] Total: 0.02, 0.03, 0.04 [0.03]	bixafen: < 0.01, < 0.01, 0.01 [0.01] M21: 0.02, 0.03, 0.04 [0.03] Total: 0.03, 0.04, 0.05 [0.04]
Muscle	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)

Lactating cows

Residues in lactating cows were investigated by Schoening, R and Wolters, A (2007, BIXAFEN_072). Thirteen lactating Holstein dairy cows (*Bos taurus*; three cows/treatment group, one control cow and a depuration group consisting of three cows) were dosed orally, via capsule, for 29 consecutive days with bixafen with either 0 ppm (control, 0×), 4 ppm (1× dose group), 12 ppm (3× dose group), or 40 ppm (10× dose group), corresponding to 0, 0.15 mg/kg bw, 0.45 mg/kg bw and 1.5 mg/kg bw, respectively.

Milk was collected twice daily. On day 29 after the administration of the first dose, the animals with the exception of the cows of the depuration group were sacrificed and liver, kidney, composite muscle, subcutaneous fat, mesenteric fat and perirenal fat were collected for analysis. For the depuration group (10×), milk for analysis was additionally sampled during the depuration phase. The animals of this group were sacrificed on day 8, 15 or 22 after the last dosing (corresponding to day 36, 43 or 50 after the first dosing), and animal tissues were collected for analysis.

Tissue and milk samples were analysed for bixafen and M21 (bixafen-desmethyl) residue by high performance liquid chromatography-electrospray ionization/tandem mass spectrometry (LC-

MS/MS) using isotopically labelled internal standards (method 01036, see section for analytical methods). The limit of quantitation (LOQ) was 0.01 mg/kg for each analyte, expressed as bixafen equivalents. The LOQ of the total residue of bixafen was calculated to be 0.02 mg/kg.

In milk residues of bixafen and M21 (bixafen-desmethyl) are presented in the following table:

Table 86 Residues of bixafen and M21 (bixafen-desmethyl) in milk after administration of bixafen at 0.15, 0.45 or 1.5 mg/kg bw and day

Days	Residues in mg bixafen-equivalents per kg [mean]		
	1× (4 ppm, 0.15 mg/kg bw)	3× (12 ppm, 0.45 mg/kg bw)	10× (40 ppm, 1.5 mg/kg bw)
0	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: < 0.01(6) M21: < 0.01(6) Total: < 0.02(6)
1	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)	bixafen: < 0.01(3) M21: 0.011, 0.012, 0.017 [0.013] Total: 0.021, 0.022, 0.027 [0.023]	bixafen: 0.017 ^a , 0.023, 0.023 ^a , 0.031, 0.031 ^a , 0.032 [0.026] M21: 0.23 ^a , 0.26 ^a , 0.03, 0.035, 0.41 ^a , 0.043 [0.033] Total: 0.04 ^a , 0.049 ^a , 0.058, 0.062, 0.072 ^a , 0.074 [0.059]
2	bixafen: < 0.01(3) M21: < 0.01, < 0.01, 0.011 [0.01] Total: < 0.02, < 0.02, 0.021 [0.02]	bixafen: < 0.01, 0.014, 0.014 [0.013] M21: 0.023, 0.027, 0.049 [0.033] Total: 0.033, 0.041, 0.063 [0.046]	bixafen: 0.033 ^a , 0.4 ^a , 0.043, 0.053 ^a , 0.064, 0.085 [0.053] M21: 0.072 ^a , 0.073 ^a , 0.086, 0.102 ^a , 0.113, 0.146 [0.099] Total: 0.105 ^a , 0.113 ^a , 0.129, 0.155 ^a , 0.198, 0.210 [0.152]
4	bixafen: < 0.01(3) M21: < 0.01, 0.012, 0.015 [0.012] Total: < 0.02, 0.022, 0.025 [0.022]	bixafen: 0.01, 0.017, 0.025 [0.017] M21: 0.029, 0.042, 0.076 [0.049] Total: 0.039, 0.059, 0.101 [0.066]	bixafen: 0.046 ^a , 0.047 ^a , 0.051 ^a , 0.061, 0.079, 0.143 [0.071] M21: 0.091 ^a , 0.099 ^a , 0.108 ^a , 0.131, 0.18, 0.194 [0.134] Total: 0.138 ^a , 0.15 ^a , 0.154 ^a , 0.192, 0.259, 0.337 [0.205]
8	bixafen: < 0.01(3) M21: < 0.01, 0.013, 0.014 [0.012] Total: < 0.02, 0.023, 0.024 [0.022]	bixafen: 0.014, 0.021, 0.023 [0.0119] M21: 0.032, 0.041, 0.067 [0.047] Total: 0.046, 0.062, 0.09[0.066]	bixafen: 0.054, 0.057 ^a , 0.069, 0.076 ^a , 0.078 ^a , 0.147 [0.08] M21: 0.082, 0.102 ^a , 0.108 ^a , 0.143 ^a , 0.176, 0.214 [0.138] Total: 0.136, 0.165 ^a , 0.18 ^a , 0.219 ^a , 0.245, 0.361 [0.218]
10	bixafen: < 0.01, < 0.01, 0.012 [0.011] M21: 0.013, 0.018, 0.019 [0.017] Total: 0.023, 0.028, 0.031 [0.027]	bixafen: 0.013, 0.022, 0.026 [0.020] M21: 0.028, 0.049, 0.062 [0.046] Total: 0.041, 0.071, 0.088 [0.067]	bixafen: 0.063, 0.063 ^a , 0.067 ^a , 0.072, 0.078 ^a , 0.138 [0.08] M21: 0.087 ^a , 0.107, 0.128 ^a , 0.136 ^a , 0.16, 0.19 [0.135] Total: 0.15 ^a , 0.17, 0.195 ^a , 0.214 ^a , 0.232, 0.328 [0.215]
13	bixafen: < 0.01(3) M21: 0.011, 0.014, 0.021 [0.015] Total: 0.021, 0.024, 0.031 [0.025]	bixafen: 0.014, 0.021, 0.023 [0.019] M21: 0.028, 0.044, 0.059 [0.044] Total: 0.042, 0.065, 0.082 [0.063]	bixafen: 0.05 ^a , 0.058, 0.064, 0.065 ^a , 0.068 ^a , 0.083 [0.065] M21: 0.075 ^a , 0.095, 0.112 ^a , 0.123, 0.128, 0.136 ^a [0.112] Total: 0.125 ^a , 0.159, 0.177 ^a , 0.181, 0.204 ^a , 0.211[0.176]
17	bixafen: < 0.01, 0.011, 0.012 [0.011] M21: 0.022, 0.027, 0.034 [0.028] Total: 0.033, 0.038, 0.046 [0.039]	bixafen: 0.013, 0.018, 0.021[0.017] M21: 0.03, 0.043, 0.054 [0.042] Total: 0.043, 0.054, 0.072 [0.056]	bixafen: 0.053 ^a , 0.061, 0.065, 0.069 ^a , 0.071 ^a , 0.083 [0.067] M21: 0.088 ^a , 0.127, 0.131, 0.135 ^a , 0.142 ^a , 0.149 [0.129] Total: 0.141 ^a , 0.192, 0.206 ^a , 0.21, 0.211 ^a , 0.214 [0.196]

Days	Residues in mg bixafen-equivalents per kg [mean]		
	1× (4 ppm, 0.15 mg/kg bw)	3× (12 ppm, 0.45 mg/kg bw)	10× (40 ppm, 1.5 mg/kg bw)
20	bixafen: < 0.01(3) M21: 0.013, 0.02, 0.02 [0.018] Total: 0.023, 0.03, 0.03 [0.028]	bixafen: 0.012, 0.017, 0.022 [0.017] M21: 0.031, 0.042, 0.072 [0.048] Total: 0.043, 0.059, 0.094 [0.065]	bixafen: 0.029 ^a , 0.052, 0.056 ^a , 0.066 ^a , 0.069, 0.092 [0.061] M21: 0.047 ^a , 0.106, 0.11 ^a , 0.112, 0.123 ^a , 0.132 [0.105] Total: 0.076 ^a , 0.158, 0.166 ^a , 0.189 ^a , 0.201, 0.204 [0.166]
24	bixafen: < 0.01, < 0.01, 0.01 [0.01] M21: 0.01, 0.019, 0.024 [0.018] Total: 0.02, 0.029, 0.034 [0.028]	bixafen: 0.017, 0.021, 0.022 [0.02] M21: 0.038, 0.043, 0.058 [0.046] Total: 0.051, 0.064, 0.080 [0.065]	bixafen: 0.04, 0.051 ^a , 0.063 ^a , 0.084, 0.088 ^a , 0.124 [0.075] M21: 0.102 ^a , 0.128 ^a , 0.134, 0.147, 0.156, 0.172 ^a [0.14] Total: 0.165 ^a , 0.174, 0.179 ^a , 0.24, 0.26 ^a , 0.271 [0.215]
28	bixafen: < 0.01(3) M21: 0.012, 0.015, 0.017 [0.015] Total: 0.022, 0.025, 0.027 [0.025]	bixafen: 0.01, 0.024, 0.026 [0.02] M21: 0.031, 0.052, 0.089 [0.057] Total: 0.041, 0.076, 0.115 [0.077]	bixafen: 0.052 ^a , 0.055 ^a , 0.062, 0.079, 0.083, 0.084 ^a [0.069] M21: 0.104 ^a , 0.105 ^a , 0.135, 0.144, 0.17 ^a , 0.19 [0.141] Total: 0.157 ^a , 0.159 ^a , 0.206, 0.218, 0.254 ^a , 0.269 [0.211]
29	bixafen: < 0.01, < 0.01, 0.012 [0.011] M21: 0.011, 0.021, 0.028 [0.02] Total: 0.021, 0.031, 0.04 [0.031]	bixafen: 0.13, 0.21, 0.22 [0.019] M21: 0.037, 0.046, 0.076 [0.053] Total: 0.05, 0.067, 0.098 [0.072]	bixafen: 0.051, 0.054 ^a , 0.056 ^a , 0.059 ^a , 0.06, 0.091 [0.062] M21: 0.101 ^a , 0.103 ^a , 0.106, 0.118 ^a , 0.143, 0.147 [0.12] Total: 0.157, 0.157 ^a , 0.157 ^a , 0.177 ^a , 0.207, 0.234 [0.182]
31	not performed	not performed	bixafen: < 0.01 ^a , < 0.01 ^a , 0.01 ^a [0.01] M21: 0.035 ^a , 0.039 ^a , 0.049 ^a [0.041] Total: 0.045 ^a , 0.049 ^a , 0.059 ^a [0.051]
34, 36, 41, 43, 48, 50	not performed	not performed	bixafen: < 0.01(3) M21: < 0.01(3) Total: < 0.02(3)

The distribution of the residue between skim milk and cream was investigated for the milk from the 10× group at day 26. In the following table the residues of bixafen and M21 (bixafen-desmethyl) are presented:

Table 87 Distribution of bixafen and M21 (bixafen-desmethyl) in skim milk and cream after administration of bixafen at 1.5 mg/kg bw and day (10×, day 26)

Sample	Residue [mg bixafen equiv./kg]					
	bixafen	ratio	M21	ratio	total	ratio
Whole milk	0.072 ^a	1	0.141 ^a	1	0.213 ^a	1
Skim milk	< 0.01(3)	0.14	0.03, 0.03, 0.03 [0.03]	0.21	0.04, 0.04, 0.04 [0.04]	0.19
Cream	0.562, 0.81, 1.41 [0.927]	13	1.038, 1.163, 1.336 [1.179]	8.4	1.6, 1.973, 2.746 [2.106]	9.9
(milk fat ^b)		(20)		(13)		(15)

^a Residues for whole milk on day 26 not reported. The values represent the mean of the pooled day 24 and day 28 samples

^b Based on average measured milk fat content in cream of 65%

For bovine tissues residues of bixafen and M21 (bixafen-desmethyl) found directly at the end of the dosing period are presented in the following table.

Table 88 Residues of bixafen and M21 (bixafen-desmethyl) in tissues of lactating cows after administration of bixafen at 0.15, 0.45 or 1.5 mg/kg bw and day (1×, 3× or 10×)

Commodity	Residues in mg bixafen-equivalents per kg [mean]		
	1× (4 ppm, 0.15 mg/kg bw)	3× (12 ppm, 0.45 mg/kg bw)	10× (40 ppm, 1.5 mg/kg bw)
Perirenal fat	bixafen: 0.059, 0.09, 0.092 [0.08] M21: 0.08, 0.114, 0.117 [0.104] Total: 0.139, 0.204, 0.209 [0.184]	bixafen: 0.135, 0.213, 0.218 [0.189] M21: 0.191, 0.263, 0.266 [0.24] Total: 0.326, 0.476, 0.484 [0.429]	bixafen: 0.326, 0.667, 1.041 [0.678] M21: 0.474, 0.767, 0.881 [0.707] Total: 0.80, 1.434, 1.922 [1.385]
Mesenteric fat	bixafen: 0.061, 0.076, 0.086 [0.074] M21: 0.075, 0.085, 0.109 [0.09] Total: 0.136, 0.161, 0.195 [0.164]	bixafen: 0.118, 0.204, 0.214 [0.179] M21: 0.178, 0.228, 0.246 [0.217] Total: 0.296, 0.432, 0.46 [0.396]	bixafen: 0.394, 0.615, 0.927 [0.645] M21: 0.503, 0.76, 0.838 [0.7] Total: 0.897, 1.375, 1.765 [1.346]
Subcutaneous fat	bixafen: 0.036, 0.06, 0.062 [0.053] M21: 0.032, 0.051, 0.059 [0.047] Total: 0.068, 0.111, 0.121 [0.1]	bixafen: 0.053, 0.08, 0.117 [0.083] M21: 0.05, 0.064, 0.095 [0.07] Total: 0.103, 0.144, 0.212 [0.153]	bixafen: 0.144, 0.3, 0.849 [0.431] M21: 0.156, 0.278, 0.662 [0.365] Total: 0.3, 0.578, 1.511 [0.796]
Liver	bixafen: 0.033, 0.05, 0.053 [0.045] M21: 0.383, 0.556, 0.632 [0.524] Total: 0.416, 0.606, 0.685 [0.569]	bixafen: 0.083, 0.169, 0.184 [0.145] M21: 1.148, 1.199, 1.523 [1.29] Total: 1.231, 1.368, 1.707 [1.435]	bixafen: 0.377, 0.443, 0.481 [0.434] M21: 4.318, 4.441, 4.889 [4.549] Total: 4.761, 4.818 5.37 [4.983]
Muscle	bixafen: < 0.01, 0.01, 0.011[0.013] M21: 0.029, 0.042, 0.054 [0.042] Total: 0.039, 0.052, 0.065 [0.052]	bixafen: 0.012, 0.029, 0.045 [0.029] M21: 0.069, 0.117, 0.215 [0.134] Total: 0.081, 0.146, 0.26 [0.162]	bixafen: 0.128, 0.135, 0.157 [0.14] M21: 0.505, 0.695, 0.84 [0.68] Total: 0.633, 0.83, 0.997 [0.82]
Kidney	bixafen: 0.012, 0.017, 0.019 [0.016] M21: 0.09, 0.133, 0.133 [0.119] Total: 0.102, 0.15, 0.152 [0.135]	bixafen: 0.03, 0.051, 0.056 [0.046] M21: 0.252, 0.314, 0.318 [0.295] Total: 0.282, 0.365, 0.374 [0.34]	bixafen: 0.134, 0.152, 0.166 [0.151] M21: 0.906, 1.07, 1.14 [1.039] Total: 1.04, 1.222, 1.306 [1.189]

For the 10× group three animals were kept for depuration for an interval of up to 21 additional days. Residues found in tissues sampled after sacrifice are presented in the following table:

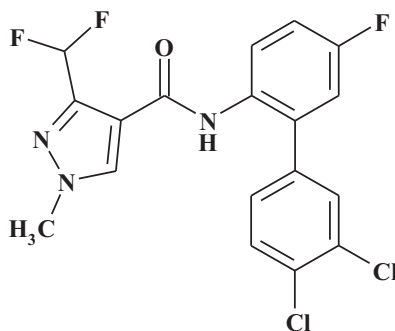
Table 89 Residues of bixafen and M21 (bixafen-desmethyl) in tissues of lactating cows after administration of bixafen at 0.15, 0.45 or 1.5 mg/kg bw and day (1×, 3× or 10×) destined for depuration of up to 21 days

Commodity	Residues in mg bixafen-equivalents per kg [mean]		
	7 day depuration (day 36)	14 day depuration (day 43)	21 day depuration (day 50)
Perirenal fat	bixafen: 0.018 M21: < 0.01 Total: 0.028	bixafen: < 0.01 M21: < 0.01 Total: < 0.02	bixafen: < 0.01 M21: < 0.01 Total: < 0.02

Commodity	Residues in mg bixafen-equivalents per kg [mean]		
	7 day depuration (day 36)	14 day depuration (day 43)	21 day depuration (day 50)
Mesenteric fat	bixafen: 0.02 M21: < 0.01 Total: 0.03	bixafen: < 0.01 M21: < 0.01 Total: < 0.02	bixafen: < 0.01 M21: < 0.01 Total: < 0.02
Subcutaneous fat	bixafen: 0.097 M21: < 0.01 Total: 0.107	bixafen: < 0.01 M21: < 0.01 Total: < 0.02	bixafen: < 0.01 M21: < 0.01 Total: < 0.02
Liver	bixafen: < 0.02 M21: 0.117 Total: 0.137	bixafen: < 0.01 M21: 0.089 Total: 0.099	bixafen: < 0.01 M21: 0.071 Total: 0.081
Muscle	bixafen: < 0.01 M21: < 0.01 Total: < 0.02	bixafen: < 0.01 M21: < 0.01 Total: < 0.02	bixafen: < 0.01 M21: < 0.01 Total: < 0.02
Kidney	bixafen: < 0.01 M21: < 0.01 Total: < 0.02	bixafen: < 0.01 M21: < 0.01 Total: < 0.02	bixafen: < 0.01 M21: < 0.01 Total: < 0.02

APPRAISAL

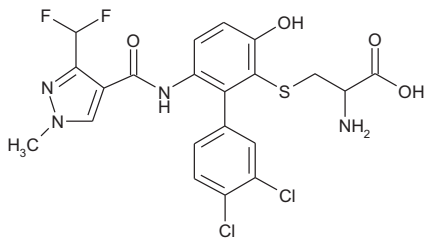
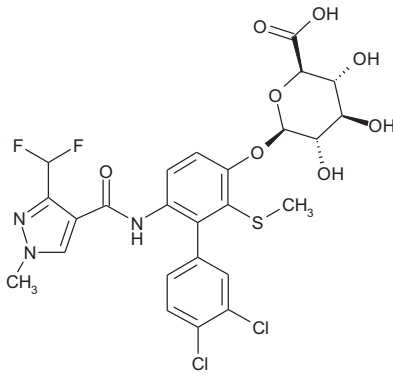
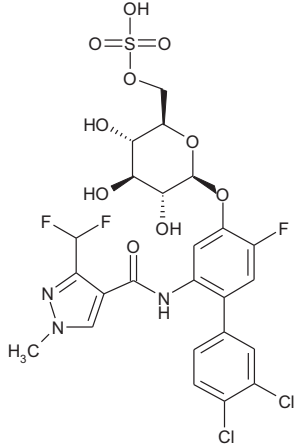
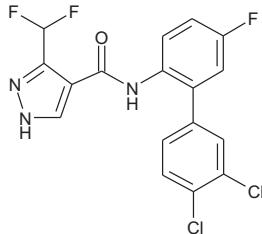
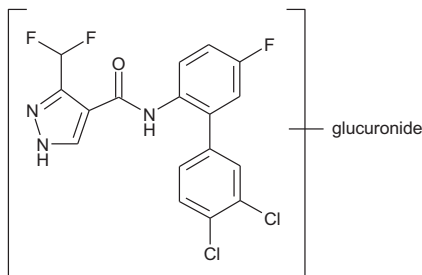
Bixafen (ISO common name) is a pyrazole-carboxamide fungicide used to control diseases on rape plants and cereals. Bixafen inhibits fungal respiration by binding to mitochondrial respiratory complex II. It was considered for the first time by the 2013 JMPR for toxicology and residues.

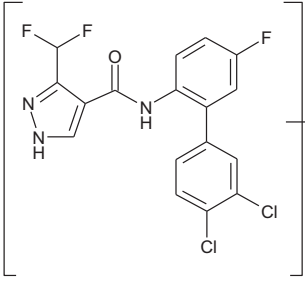
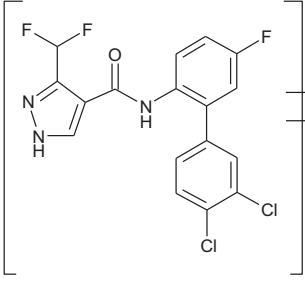
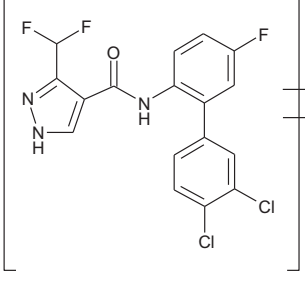
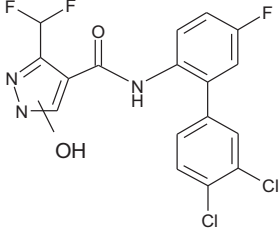
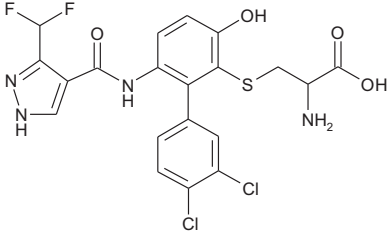
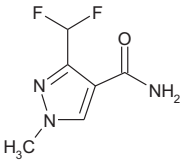


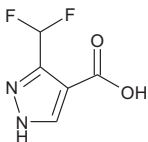
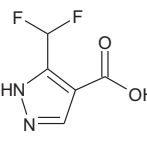
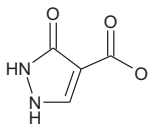
The IUPAC name of bixafen is N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide and the CA name is 1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluoro[1,1'-biphenyl]-2-yl)-3-(difluoromethyl)-1-methyl-.

Bixafen labelled either in the pyrazole- or dichlorophenyl-moiety was used in the metabolism and environmental fate studies.

The following abbreviations are used for the metabolites discussed below:

M14	S-[3',4'-dichloro-6-({[3-(difluoromethyl)-1-methyl-1H-pyrazol-4-yl]carbonyl}amino)-3-hydroxybiphenyl-2-yl]cysteine (IUPAC)	
M18	3',4'-dichloro-6-({[3-(difluoromethyl)-1-methyl-1H-pyrazol-4-yl]carbonyl}amino)-2-(methylthio)biphenyl-3-yl beta-L-glucopyranosiduronic acid (IUPAC)	
M20	not nomenclature possible - position of hydroxy group not specified	 or isomer
M21 (bixafen-desmethyl)	N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1H-pyrazole-4-carboxamide (IUPAC)	
M23	not nomenclature possible - structure not specified	 glucuronide

M24	not nomenclature possible - structure not specified	 glycoside
M25	not nomenclature possible - structure not specified	 OH glycoside
M26	not nomenclature possible - structure not specified	 OH pentoside
M27	not nomenclature possible - structure not specified	
M37	S-[3',4'-dichloro-6-({[3-(difluoromethyl)-1H-pyrazol-4-yl]carbonyl}amino)-3-hydroxybiphenyl-2-yl]cysteine (IUPAC)	
M43	3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (IUPAC)	

M44	3-(difluoromethyl)-1H-pyrazole-4-carboxylic acid (IUPAC)	 proposal for tautomer 1
M45	5-(difluoromethyl)-1H-pyrazole-4-carboxylic acid (IUPAC)	 proposal for tautomer 2
M47	3-hydroxy-1H-pyrazole-4-carboxylic acid (IUPAC)	

Animal metabolism

Information was available on the metabolism of bixafen in laboratory animals, lactating goats and laying hens.

In rats given (dichlorophenyl- U - ^{14}C)-labelled bixafen orally by gavage, absorption was rapid and accounted for at least 83% of the total administered radioactivity after a single low dose (2 mg/kg bw). The maximum plasma concentrations of radioactivity were reached approximately 2–4 and 8 hours after administration of the low and high doses (2 and 50 mg/kg bw), respectively. Radioactivity was widely distributed throughout the body. Elimination of the radioactivity was mainly via faeces ($\geq 91\%$), whereas elimination via urine accounted for 1–3% of the administered dose. In bile duct-cannulated rats, extensive biliary excretion (up to 83%) was demonstrated. Elimination of the radioactivity from the body was rapid, with a half-life in plasma of 8–9 hours and a mean residence time of 13–19 hours (for the low dose). Residues in tissues at 72 hours after a single oral dose as well as after repeated oral dosing accounted for 0.1–3% of the administered radioactivity, with liver and kidneys containing the highest concentrations of residues.

Metabolism of bixafen in rats was extensive, and more than 30 metabolites were identified. The main metabolic routes included demethylation, hydroxylation of the parent and bixafen-desmethyl, and conjugation with glucuronic acid or glutathione. A minor metabolic reaction was the cleavage of the amide bridge of bixafen.

Two studies on metabolism in lactating goats were available. The goats received five daily doses of [pyrazole- ^{14}C]-bixafen or [dichlorophenyl- ^{14}C]-bixafen at rates equivalent to 35 ppm and 46 ppm in the diet, respectively. The animals were sacrificed approximately 24 hours after the last dose. In both studies approximately 1.3% of the total dose was recovered from milk or tissues of the animals. Most of the radioactivity was excreted via faeces (74–82% AR) and urine (1.8–5.4% AR).

The metabolic pattern in both studies was comparable. In milk (TRR: 0.064–0.17 mg eq/kg), muscle (TRR: 0.047–0.057 mg eq/kg) and fat (TRR: 0.47–0.61 mg eq/kg) unchanged bixafen was the major residue, representing 74–77%, 56–66% and 89% of the total radioactivity, respectively. M21 (bixafen-desmethyl) was the only major metabolite being present at 16–18% of the TRR in milk, 34–43% in muscle and 10–11% in fat.

For kidney (TRR: 0.14–0.2 mg eq/kg) and liver (TRR: 0.74–1.2 mg eq/kg) parent bixafen was also a major residue, representing 44–46% of the total radioactivity in kidney and 18–23% in liver. Significant metabolites identified were M21 (bixafen-desmethyl), representing 37–38% of the TRR in

kidney and 19–21% TRR in liver, followed by the two M23 isomers counting for a total of 9.3–15% of the TRR in kidney and 14–19% in liver.

For laying hens groups of hens received daily doses of [pyrazole-¹⁴C]-bixafen or [dichlorophenyl-¹⁴C]-bixafen at rates equivalent to 26 ppm and 32 ppm in the diet for 14 consecutive days. The animals were sacrificed ca. 24 hours after the last dose. Approximately 1.5% of the total dose in both studies was recovered from eggs or tissues of the animals. Most of the radioactivity administered was found in the excreta (88–93% AR). Total radioactive residues were 0.53–0.9 mg eq/kg in eggs, 0.032–0.037 mg eq/kg in muscle, 0.23–0.38 mg eq/kg in fat and 0.64–0.81 mg eq/kg in liver.

Parent bixafen was a major residue in eggs and all tissues except liver, representing 51–69% of the TRR in eggs, 23–41% in muscle and 80% in fat. In hens liver, only minor amounts of bixafen were detected (4.5–6.7% TRR).

M21 (bixafen-desmethyl) was the only major metabolite found in poultry tissues and eggs. It was found at levels of 26–39% of the TRR in eggs, 35–51% in muscle, 19–20% in fat and 24–26% in liver. In liver, M14, M18, M24, M25, M26, M27 and M37 were identified as minor metabolites, representing 1.0–8.8% of the TRR (0.007–0.067 mg eq/kg) each.

In summary bixafen is the major residue in most tissues, milk and eggs. It is moderately metabolized in goats and hens mainly resulting in M21 (bixafen-desmethyl). All major metabolites were also identified in the rat. The metabolites M18, M25 and M26, mainly found in poultry liver, were not directly identified in the rat.

Plant metabolism

The Meeting received plant metabolism studies for bixafen following foliar application of either [pyrazole-¹⁴C]-bixafen or [dichlorophenyl-¹⁴C]-bixafen to soya beans or wheat.

Soya beans were independently treated with both bixafen-labels with three foliar applications of 0.06 kg ai/ha each when the first flowers opened (BBCH 60), at the end of flowering (BBCH 69) and finally when approximately 80% of the pods were ripe (BBCH 88). Samples were collected containing forage (5 days after 2nd application), hay (29 days after 2nd application), straw and seed (26 days after the 3rd application). Total radioactive residues were 4.0–5.3 mg eq/kg for forage, 2.8–4.0 mg eq/kg for hay, 9.5–13 mg eq/kg for straw and 0.005–0.024 mg eq/kg for seeds.

In all plant parts directly affected by the spray solution, unchanged bixafen was the major residue representing 96–98% of the TRR in forage, 92% in hay and 90–92% in straw. The only other metabolite identified was M21 (bixafen-desmethyl), present at 0.5–2.6% of the TRR.

For soya bean seeds, only samples following application of the pyrazole-label contained sufficient total radioactive residues for further investigation. Bixafen was the major residue with 30% of the TRR. Metabolites identified were M44 and M45 (19% TRR, 0.004 mg eq/kg) and M47 (12% TRR, 0.003 mg eq/kg). M21 (bixafen-desmethyl) was not identified in soya bean seeds.

Wheat was independently treated with both bixafen-labels using one foliar application of 0.125 kg ai/ha at the end of tillering / beginning of stem elongation (BBCH 29–31) followed by a second spraying with 0.15 kg ai/ha at the end of flowering (BBCH 69). Forage was harvested 9 days after the 1st application, hay 9 days after the 2nd application and straw and grain at maturity (50 days after the 2nd application). Total radioactive residues were 1.6–1.7 mg eq/kg for forage, 6.6–7.6 mg eq/kg for hay, 23–24 mg eq/kg for straw and 0.16–0.23 mg eq/kg for seeds.

In all samples unchanged bixafen was the major residue, representing > 90% of the TRR. The only other metabolite identified was M21 (bixafen-desmethyl) at 0.8–2.4% of the TRR.

In summary the plant metabolism of bixafen in the plants investigated is very limited. In plant parts directly affected by the spray solution, unchanged bixafen was the only residue significant. M21 (bixafen-desmethyl) was present at low levels up to 2.6% of the TRR.

In soya bean seeds, which were protected by the pod during treatment, bixafen was present at lower concentrations of 0.007 mg eq/kg (30% TRR). Major metabolites in soya bean seeds were M44, M45 and M47, probably taken up from the soil and distributed systemically, however at low levels not exceeding 0.004 mg eq/kg. All three of these metabolites were not identified in the rat.

Environmental fate in soil

The Meeting received information on the fate of bixafen after aerobic degradation in soil and after photolysis on the soil surface. In addition, the Meeting received information on the uptake and metabolism of bixafen soil residues by rotational crops, its dissipation under field conditions and long-term accumulation in soil.

In soil photolysis studies degradation of bixafen was not observed.

In aerobic soil metabolism studies under laboratory conditions bixafen was highly persistent with 80–90% remaining after 120 days. The only metabolite found was M44 (maximum 2.9% of AR), while the rest of the radioactivity remained unextracted or was recovered as $^{14}\text{CO}_2$. DT_{50} values could not be calculated due to the minimal degradation observed within 120 days.

In soil samples from the confined rotational crop metabolism studies mentioned below, bixafen was also slowly degraded. The only metabolite found was identified as M21 (bixafen-desmethyl), slowly increasing from 0.5% (day 30) to 2.3% TRR at the end of the study (day 418). M44 was not detected.

In summary it can be concluded that bixafen is persistent in soil, being degraded to a very minor extent.

Confined rotational crop studies on Swiss chard, turnips and wheat were conducted at rates equivalent to 0.79 kg ai/ha (pyrazole-label) and 0.85 kg ai/ha (dichlorophenyl-label). In plant commodities bixafen (11–78% TRR) and M21 (bixafen-desmethyl, 3–73% TRR) were the major residue components found for both labels. Quantified concentrations for the sum of both analytes were 0.016–0.024 mg eq/kg for Swiss chard, 0.005–0.035 mg eq/kg in turnip roots and tops and 0.011–0.041 mg eq/kg, 0.106–0.18 mg eq/kg and 0.152–0.462 mg eq/kg for wheat forage, hay and straw, respectively. In grain TRR levels were too low for identification ($0.001 < 0.01$ mg eq/kg).

Following application of the pyrazole-labelled active substance, the cleavage products M43 (3–15% TRR), M44 (0.3–37% TRR) and M45 (2–23% TRR) were identified as major metabolites. Concentrations were between 0.001–0.015 mg eq/kg each.

Following treatment with the dichlorophenyl-label, M20 was found in Swiss chard only at levels of 25–38% of the TRR (0.007–0.016 mg eq/kg).

The residue concentrations of bixafen and M21 in plants declined moderately in animal feed commodities while in food commodities only a slow decline of the residue was observed over the three crop rotations investigated. In all commodities investigated, except for wheat grain, detectable residues above the LOQ of 0.01 mg/kg were found for bixafen.

Field rotational crop studies were conducted at four locations in Europe. Bixafen was either applied to bare soil to simulate crop failure (0.28 kg ai/ha) or to barley as a primary crop (0.16 kg ai/ha at BBCH 56 plus 0.125 kg ai/ha at BBCH 69). Turnip/carrots, lettuce and wheat were planted as rotational crops at three rotations. Samples analysed for residues of bixafen and M21 were below the LOQ of 0.01 mg/kg for each analyte, except for one sample of wheat straw (M21: 0.02 mg/kg) and lettuce at a pre-mature growth stage (BBCH 46; bixafen: 0.05 mg/kg).

Field dissipation studies at six locations in Europe (four in the north, two in the south) confirmed the slow degradation of bixafen in soil observed in the aerobic metabolism studies. Within the first 100 days, a significant degradation of the residue concentration in soil was observed, leaving 42–63% of the initial concentrations. However, the decline after this period up to 730 days was minimal, leaving 17–47% of the initial concentration. M21 was not found above the LOQ of the analytical method.

The Meeting observed that the degradation of bixafen in soil follows a bi-phasic kinetics, starting with a fast decline within the first 100 days. After that initial interval, bixafen is highly persistent in soil, accumulating with subsequent treatments over multiple years.

In a long-term soil accumulation study under field conditions residues of bixafen and M21 (bixafen-desmethyl) in soil were investigated involving five and seven years of annual treatment with 0.14 kg ai/ha to the ground. In the first location in France a plateau for the bixafen concentration in soil was reached after five years, resulting in concentrations of up to 0.18 mg per kg soil. In Germany, the study was terminated after 7 years, due to technical reasons, without reaching a plateau, showing a bixafen peak concentration of 0.35 mg per kg soil. Most of the residue (> 95%) was present as unchanged parent substance located in the initial 10 cm soil layer. Based on an average density of 1.5 g/cm³ for soil these concentrations are equivalent to single application rates to the bare soil of 0.27 kg ai/ha in the French trial and 0.53 kg ai/ha in the German trial.

The Meeting concluded that bixafen residues accumulate in soil after annual treatments. Under consideration of the highest annual application rate reported in the authorised GAPs of 0.25 kg ai/ha, soil residue concentrations equivalent to single application rates to bare soil of 0.9 kg ai/ha could be reached.

In summary the Meeting concluded that bixafen is persistent in soil, accumulating after subsequent years of annual treatment. Confined rotational crop studies indicate a potential uptake of residues for bixafen and M21 (bixafen-desmethyl) into plant commodities. The Meeting also recognized that field rotational crop studies involved soil treatment rates not addressing the soil concentrations expected after subsequent annual treatment.

Methods of residue analysis

The Meeting received analytical methods for the analysis of bixafen and M21 (bixafen-desmethyl) in plant and animal matrices. The basic principle employs extraction by homogenisation with acetonitrile/water (4/1, v/v) or n-hexane with acetonitrile partitioning for fatty samples. The extracts were cleaned with filtration and C18 solid-phase extraction. Residues are determined by liquid chromatography (LC) in combination with tandem mass spectroscopy (MS/MS). Mass-transitions are m/z 414→394 (m/z 414→266 for confirmation) for bixafen and m/z 398→378 (m/z 398→358 for confirmation) for M21 (bixafen-desmethyl). The methods submitted are suitable for measuring residues of bixafen and M21 in plant and animal commodities with a LOQ of 0.01 mg/kg for each analyte.

The extraction efficiency with acetonitrile/water (4/1, v/v) was tested for wheat (forage, grain straw) obtained from plant metabolism and confined rotational crop studies. Extraction rates were of > 90% for primary treated commodities and 68–73% (corresponding to 72–99% of the TTR) for commodities from rotational crops.

For the application of multi-residue methods the DFG S-19 was tested, but found to be unsuitable for analysing bixafen or M21 in plant matrices.

Stability of residues in stored analytical samples

The Meeting received information on the storage stability of bixafen and M21 (bixafen-desmethyl) in plant matrices. In wheat grain, wheat straw, wheat green material, lettuce head, potato tuber, rape seed and in soil, no significant degradation of both analytes was observed within 24 months.

For animal matrices no storage stability data were provided. Samples in livestock metabolism or feeding studies were analysed within one month of sampling.

Definition of the residue

Livestock animal metabolism studies were conducted on laying hens (36–32 ppm) and lactating goats (35–46 ppm).

In goats parent bixafen and M21 (bixafen-desmethyl) were the major residue. Bixafen represented 74–77% TRR in milk, 56–66% TRR in muscle, 44–46% TRR in kidney, 18–23% TRR in

liver and 89% TRR in fat. M21 was the major metabolite present at 16–18% TRR in milk, 34–43% TRR in muscle, 37–38% TRR in kidney, 19–21% TRR in liver and 10–11% TRR in fat. In kidney and liver the two isomers of M23 were found at 9–15% of the TRR in kidney (isomer 1: 2.8–4.3%; isomer 2: 6.5–10% TRR) and of 14–19% in liver (isomer 1: 8.6–13% TRR; isomer 2: 5.2–5.8% TRR).

In laying hens again bixafen was the major residue in eggs and all tissues except liver, representing 51–69% TRR in eggs, 23–41% in muscle and 80% in fat. In liver only minor amounts of bixafen were detected (4.5–6.7% of the TRR). M21 (bixafen-desmethyl) was the major metabolite found in poultry tissues and eggs. It accounted for 26–39% of the TRR in eggs, 35–51% in muscle, 19–20% in fat and 24–26% in liver. In liver, M14, M18, M24, M25, M26, M27 and M37 were identified as minor metabolites, representing 1.0–8.8% of the TRR (0.007–0.067 mg eq/kg) each. Of these, M18, M25 and M26 were not identified in the rat, however the exposure of M18 was below the respective acute and chronic TTCs for Cramer class III while M25 and M26 have structural similarity to bixafen-desmethyl and are covered by the ADI for bixafen. As a consequence no consideration of dietary intake is required.

M21 (bixafen-desmethyl) was identified as the major residue in rat studies, suggesting that it is covered by toxicological reference values for parent bixafen. The Meeting concluded that parent bixafen and M21 (bixafen-desmethyl) are suitable marker compounds in animal commodities and should be included into the residue definition for compliance with MRLs and for the estimation of the dietary intake. Analytical methods are capable of measuring both analytes.

In livestock feeding studies the distribution of bixafen and M21 between skim milk/cream and egg white/egg yolk was investigated. The average ratio for cream/skim milk was > 93 for bixafen and 39 for M21. Egg yolk concentrations of bixafen were three times higher than in egg white while M21 showed ratios of 12–20. For the parent substance a log P_{ow} of 3.3 was measured.

The data for milk and eggs suggests that bixafen and M21 partition in the fat portion. In addition, residues in fat tissues were about ten times higher when compared to muscle. The Meeting decided that residues of bixafen are fat-soluble.

The fate of bixafen in plants was investigated following foliar application to soya beans and wheat. In all samples unchanged bixafen was the major residue, normally representing at least 90% of the TRR. M21 was present at very low levels, not exceeding 3% of the TRR. In soya bean seeds, which were not directly exposed to the spray solution due to the pods, only 30% of the TRR (0.007 mg eq/kg) was present as bixafen. Further major metabolites in soya bean seeds were identified as the tautomers M44 and M45 (19% TRR, 0.004 mg eq/kg) and M47 (12% TRR, 0.003 mg eq/kg).

In confined rotational crop studies, plant commodities Swiss chard, wheat and turnips contained concentrations of radioactive residues as high as 0.49 mg eq/kg, in wheat straw. Bixafen (11–78% TRR) and M21 (bixafen-desmethyl, 3–73% TRR) were the major compounds identified. In addition, M43 (3–15% TRR), M44 (0.3–37% TRR) and M45 (2–23% TRR) were identified as major metabolites in all rotational crops. M20 was only found in Swiss chard (25–38% TRR, 0.007–0.016 mg eq/kg). Wheat grain did not contain TRR levels allowing further identification (0.001–< 0.01 mg eq/kg).

The Meeting concluded that parent bixafen is a suitable marker for compliance with MRLs in all plant commodities (primary treated or rotational). For the estimation of the dietary intake M21 was insignificant in wheat and soya beans directly treated, but was identified in high relative amounts in rotational crops. Therefore, the Meeting decided to include M21 (bixafen-desmethyl) into the residue definition for dietary intake with the parent substance. The metabolites M20, M44, M45 and M47, mainly found in rotational crops, were not identified in the rat. However, the estimated exposure levels based on the confined rotational crop study are below the respective acute and chronic TTCs for Cramer class III. As a result, no consideration is required for dietary intake.

Analytical methods are capable of measuring bixafen and M21 (bixafen-desmethyl) in plant matrices.

Definition of the residue for compliance with MRL for plant commodities: *bixafen*

Definition of the residue for compliance with MRL for animal commodities and (for the estimation of dietary intake) for plant and animal commodities: *sum of bixafen and N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1H-pyrazole-4-carboxamide (bixafen-desmethyl), expressed as bixafen*

The residue is fat-soluble.

Results of supervised residue trials on crops

The Meeting received supervised European trial data for applications of bixafen to rape seed, barley and wheat.

Residue values referred to as “total” describe the sum of bixafen and M21 (bixafen-desmethyl), expressed as bixafen.

The Meeting concluded that field rotational crop studies do not address residues in soil expected after subsequent annual application of bixafen. Confined rotational crop studies available are not considered representative of field conditions. In the absence of suitable data, residue concentrations in plant commodities taken up from the soil by annual crops could not be estimated. Therefore, the Meeting decided, that no recommendations on maximum residue levels and median/highest residues could be made for bixafen in non-permanent crops.

Nevertheless, for the benefit of potential future assessments of bixafen uses, the Meeting decided to evaluate GAPs and residue data following direct application.

Rape seed

Bixafen is registered in the UK for use on rape seed at rates of 2×0.075 kg ai/ha with a PHI of 56 days. Supervised field trials conducted in northern Europe, according to this GAP, were submitted.

For MRL compliance purposes residues of parent bixafen in rape seeds were (n=10): < 0.01(6), 0.01(3), 0.017 mg/kg.

For dietary intake purposes the total residues in rape seeds were (n=10): < 0.02(5), 0.02(4), 0.028 mg/kg.

Barley and oats

For barley and oats the maximum GAP in northern Europe was reported from the UK involving two foliar applications of up to 0.125 kg ai/ha each. The last application is conducted at BBCH 61 and the PHI is covered by the growth between treatment and harvest. Supervised field trials conducted in northern Europe according to this GAP were submitted.

For MRL compliance purposes residues of parent bixafen in barley grain in northern Europe were (n=10): 0.02, 0.04(3), 0.05, 0.07, 0.08, 0.09, 0.09, 0.1 mg/kg.

For dietary intake purposes the total residues in barley grain in northern Europe were (n=10): 0.03, 0.05(3), 0.06, 0.08, 0.1, 0.1, 0.11, 0.11 mg/kg.

In Southern Europe a GAP for barley and oats was reported from France with one application of 0.075 kg ai/ha up to BBCH 61 with a 35 day PHI. However, no corresponding residue data were submitted.

The Meeting decided to explore the use of global residue data as outlined in the 2011 JMPR Report (2.4) for the residue data originating from southern Europe against the GAP of the UK.

For MRL compliance purposes residues of parent bixafen in barley grain in southern Europe according to the UK GAP were (n=9): 0.03, 0.04, 0.04, 0.06, 0.06, 0.08, 0.1, 0.25, 0.34 mg/kg.

For dietary intake purposes the total residues in barley grain in southern Europe according to the UK GAP were (n=9): 0.04, 0.05, 0.05, 0.08, 0.08, 0.1, 0.11, 0.29, 0.38 mg/kg.

The Meeting decided to combine that data and evaluate all European supervised field trials against the UK GAP for barley:

For MRL compliance purposes residues of parent bixafen in barley grain in whole Europe (n=19): 0.02, 0.03, 0.04(5), 0.05, 0.06, 0.06, 0.07, 0.08, 0.08, 0.09, 0.09, 0.1, 0.1, 0.25 and 0.34 mg/kg.

For dietary intake purposes the total residues in barley grain in whole Europe were (n=19): 0.03, 0.04, 0.05(5), 0.06, 0.08(3), 0.1(3), 0.11(3), 0.29 and 0.38 mg/kg.

Wheat, rye, triticale and spelt

For wheat, rye and triticale the maximum GAP in Northern Europe was reported from the UK and involved two foliar applications of up to 0.125 kg ai/ha each. The last application is conducted at BBCH 69 and the PHI is covered by the growth between treatment and harvest. Supervised field trials conducted in Northern Europe according to this GAP were submitted.

For MRL compliance purposes residues of parent bixafen in wheat grain in northern Europe were (n=10): < 0.01(6), 0.01, 0.01, 0.03, 0.03 mg/kg.

For dietary intake purposes the total residues in wheat in northern Europe were (n=10): < 0.02(6), 0.02, 0.02, 0.04, 0.04 mg/kg.

In southern Europe a GAP for wheat, rye and triticale was reported from France with one application of 0.094 kg ai/ha up to BBCH 69 with a 35 day PHI. However, no corresponding residue data were submitted.

The Meeting decided to explore the use of global residue data as outlined in the 2011 JMPR Report (2.4) for residue data from southern Europe against UK GAP:

For MRL compliance purposes residues of parent bixafen in wheat grain in Southern Europe according to the UK GAP were (n=10): < 0.01(6), 0.01, 0.02, 0.02, 0.03 mg/kg.

For dietary intake purposes the total residues in wheat grain in southern Europe according to UK GAP were (n=10): < 0.02(6), 0.02, 0.03, 0.03, 0.04 mg/kg.

The Meeting decided to combine that data and evaluate all European supervised field trials against the UK GAP for wheat:

For monitoring purposes residues of parent bixafen in wheat grain in whole Europe (n=20): < 0.01(12), 0.01(3), 0.02, 0.02, 0.03, 0.03 and 0.03 mg/kg.

For dietary intake purposes the total residues in wheat grain in whole Europe were (n=20): < 0.02(12), 0.02(3), 0.03, 0.03, 0.04, 0.04 and 0.04 mg/kg.

Animal feeds

Oilseed rape, forage

The Meeting noted that the only authorisation submitted for bixafen in rape was from UK explicitly relating to oilseed rape. This GAP involves late treatment of the crop 56 days before harvest, which is normally beyond the common timeframe for utilization of oilseed rape as a forage crop, i.e., before winter and up to BBCH 39. This is supported by supervised field trials in northern Europe, where last applications were conducted at growth stages at the end of flowering or at early maturity.

The Meeting concluded that the reported GAP for bixafen is not relevant for the utilization of oilseed rape as an animal forage crop.

Barley, oats, rye, triticale and wheat – forage of cereals

GAPs for barley and oats in the UK are for a maximum of two foliar applications up to flowering (BBCH 61) with 0.125 kg ai/ha each. The PHI is covered by the interval between treatment and harvest (covered by growth stage).

For the calculation of the livestock animal dietary burden the total residues in barley forage (fresh) in northern Europe were (n=10): 2.1, 2.5, 2.6, 2.9, 3.5, 3.9, 4.0, 4.4, 4.5, 7.3 mg/kg.

In southern Europe a GAP for barley and oats was reported from France with one application of 0.075 kg ai/ha up to BBCH 61 with a 35 day PHI. However, no corresponding residue data were submitted.

The Meeting decided to explore the use of global residue data as outlined in the 2011 JMPR Report (2.4) for residue data from southern Europe against the UK GAP:

For the calculation of the livestock animal dietary burden the total residues in barley forage (fresh) in southern Europe were (n=9): 2.7, 3.0, 3.2, 3.4, 3.4, 3.7, 3.8, 4.3, 6.0 mg/kg.

The Meeting decided to combine that data and evaluate all European supervised field trials against the UK GAP for barley and oat forage:

For the calculation of the livestock animal dietary burden the total residues in barley forage (fresh) in whole Europe were (n=19): 2.1, 2.5, 2.6, 2.7, 2.9, 3.0, 3.2, 3.4, 3.4, 3.5, 3.7, 3.8, 3.9, 4.0, 4.3, 4.4, 4.5, 6.0, 7.3 mg/kg.

For wheat, rye and triticale the maximum GAP in northern Europe was reported for the UK involving two foliar applications of up to 0.125 kg ai/ha. The last application is at BBCH 69 with the PHI covered by growth between treatment and harvest. Supervised field trials conducted in northern Europe according to this GAP were submitted.

For the calculation of the livestock animal dietary burden the total residues in wheat forage (fresh) in northern Europe were (n=10): 1.5, 2.4, 2.8, 2.9, 3.1, 3.4, 3.8, 4.7, 4.8, 7.3 mg/kg.

In southern Europe a GAP for wheat, rye and triticale was reported from France with one application of 0.094 kg ai/ha up to BBCH 69 with a 35 day PHI. However, no corresponding residue data were submitted.

The Meeting decided to explore the use of global residue data as outlined in the 2011 JMPR Report (2.4) for residue data from southern Europe against the UK GAP.

For the calculation of the livestock animal dietary burden the total residues in wheat forage (fresh) in southern Europe were (n=10): 2.6, 2.7, 2.9, 3.0, 3.6, 3.9, 4.2, 4.5, 5.2, 5.5 mg/kg.

The Meeting decided to combine that data and evaluate all European supervised field trials against the UK GAP for wheat forage.

For the calculation of the livestock animal dietary burden the total residues in barley and wheat forage (fresh) in Europe were (n=20): 1.5, 2.4, 2.6, 2.7, 2.8, 2.9, 2.9, 3.0, 3.1, 3.4, 3.6, 3.8, 3.9, 4.2, 4.5, 4.7, 4.8, 5.2, 5.5, 7.3 mg/kg.

Barley, oats, rye, triticale and wheat – straw and fodder

GAPs for barley and oats in the UK are for a maximum of two foliar applications up to flowering (BBCH 61) with 0.125 kg ai/ha each. The PHI is covered by the interval between treatment and harvest (covered by growth stage).

For MRL compliance purposes residues of parent bixafen in barley straw (fresh) in northern Europe (n=10): 0.64, 0.7, 0.77, 0.86, 1.1, 1.1, 3.7, 4.8, 5.4, 10 mg/kg.

For the calculation of the livestock animal dietary burden the total residues in barley straw (fresh) in northern Europe were (n=10): 0.72, 0.74, 0.85, 1.0, 1.2, 1.2, 3.9, 5.2, 5.6, 11 mg/kg.

In southern Europe a GAP for barley and oats was reported from France with one application of 0.075 kg ai/ha up to BBCH 61 with a 35 day PHI. However, no corresponding residue data were submitted.

The Meeting decided to explore the use of global residue data as outlined in the 2011 JMPR Report (2.4) for residue data from Southern Europe against the UK GAP.

For MRL compliance purposes residues of parent bixafen in barley straw (fresh) in southern Europe (n=9): 0.46, 0.76, 1.2, 1.5, 1.9, 3.1, 5.2, 5.7, 6.2 mg/kg.

For the calculation of the livestock animal dietary burden the total residues in barley straw (fresh) in southern Europe were (n=9): 0.5, 1.0, 1.3, 1.6, 2.1, 3.3, 5.6, 6.1, 6.7 mg/kg.

Since both datasets are not significantly different (Mann-Whitney-U-testing), the Meeting decided to combine that data and evaluate all European supervised field trials against the UK GAP for barley and oat straw.

For MRL compliance purposes residues of parent bixafen in barley straw (fresh) in whole Europe (n=19): 0.46, 0.64, 0.7, 0.76, 0.77, 0.86, 1.1, 1.1, 1.2, 1.5, 1.9, 3.1, 3.7, 4.8, 5.2, 5.4, 5.7, 6.2 and 10 mg/kg.

For the calculation of the livestock animal dietary burden the total residues in barley straw (fresh) in whole Europe were (n=19): 0.5, 0.72, 0.74, 0.85, 1.0, 1.0, 1.2, 1.2, 1.3, 1.6, 2.1, 3.3, 3.9, 5.2, 5.6, 5.6, 6.1, 6.7, 11 mg/kg.

For wheat, rye and triticale the maximum GAP in Northern Europe was reported from the UK and involved two foliar applications of up to 0.125 kg ai/ha. The last application is at BBCH 69 and the PHI is covered by growth between treatment and harvest. Supervised field trials conducted in northern Europe according to this GAP were submitted.

For MRL compliance purposes residues of parent bixafen in wheat straw (fresh) in northern Europe (n=10): 0.52, 0.93, 0.95, 1.3, 1.8, 1.9, 3.6, 4.1, 8.4 and 10 mg/kg.

For the calculation of the livestock animal dietary burden the total residues in wheat straw (fresh) in northern Europe were (n=10): 0.78, 1.2, 1.3, 1.5, 2.1, 2.5, 3.9, 4.4, 9.6 and 11 mg/kg.

In southern Europe a GAP for wheat, rye and triticale was reported from France with one application of 0.094 kg ai/ha up to BBCH 69 with a 35 day PHI. However, no corresponding residue data were submitted.

The Meeting decided to explore the use of global residue data as outlined in the 2011 JMPR Report (2.4) for residue data from southern Europe against the UK GAP:

For MRL compliance purposes residues of parent bixafen in wheat straw (fresh) in southern Europe (n=10): 0.79, 1.4, 1.7, 1.8, 2.6, 3.2, 3.3, 3.6, 5.4 and 5.7 mg/kg.

For the calculation of the livestock animal dietary burden the total residues in wheat straw (fresh) in southern Europe were (n=10): 1.2, 1.9, 1.9, 2.2, 3.2, 3.7, 3.9, 4.1, 6.0 and 6.2 mg/kg.

The Meeting decided to combine that data and evaluate all European supervised field trials against the UK GAP for wheat, rye and triticale straw:

For MRL compliance purposes residues of parent bixafen in wheat straw (fresh) in whole Europe (n=20): 0.52, 0.79, 0.93, 0.95, 1.3, 1.4, 1.7, 1.8, 1.8, 1.9, 2.6, 3.2, 3.3, 3.6, 3.6, 4.1, 5.4, 5.7, 8.4 and 10 mg/kg.

For the calculation of the livestock animal dietary burden the total residues in wheat straw (fresh) in whole Europe were (n=20): 0.78, 1.2, 1.2, 1.3, 1.5, 1.9, 1.9, 2.1, 2.2, 2.5, 3.2, 3.7, 3.9, 3.9, 4.1, 4.4, 6.0, 6.2, 9.6 and 11 mg/kg.

Residues in rotational crops

Bixafen is highly persistent in soil, showing accumulation over subsequent years of treatment. In field rotational crop studies conducted at rates corresponding to the highest annual application rates registered, no significant residues were found in plant commodities. However, the long-term field accumulation study submitted suggests plateau residues in soil after up to seven years of annual treatment are equivalent to 2–3 times the soil residues expected after a single treatment at the registered maximum annual application rate. In confined rotational crop studies approximating this plateau level observed in soil, residues above the LOQ of 0.01 mg/kg were found for bixafen and M21 (bixafen-desmethyl) in all plant commodities investigated except for wheat grain.

The Meeting concluded that the accumulation of bixafen in soil results in residue concentrations in follow crops which are relevant for MRL compliance, dietary intake assessment and the estimation of livestock dietary burden. However, the Meeting recognized that the available field rotational crop studies were underdosed compared to the soil concentrations following long-term use of bixafen, while confined rotational crop studies are not considered representative for field conditions.

The Meeting decided that further information on bixafen in rotational crops under field conditions are required involving application rates approximating the plateau levels in soil after subsequent years of treatment. The estimation of maximum residue levels and median or highest residues for annual crops is not possible without considering the contribution of residues taken up from soil and will be postponed to a future meeting when new data becomes available to assess the rotational crop situation.

Fate of residues during processing

The Meeting received information on the hydrolysis of radio-labelled bixafen as well as processing studies using unlabelled material on grown residues in oilseed rape, barley and wheat.

In a hydrolysis study using radio-labelled bixafen typical processing conditions were simulated (pH 4,5 and 6 with 90 °C, 100 °C and 120 °C for 20, 60 and 20 minutes). In duplicate samples of sterile buffer solution no degradation was observed.

The Meeting concluded that no recommendations on bixafen residues in plant commodities can be made (see residues in rotational crops section) and therefore no processing factors are required. For an overview of the available information on the fate of bixafen during processing please refer to the 2013 Evaluation.

Residues in animal commodities

Farm animal feeding studies

The Meeting received feeding studies involving bixafen on lactating cows and laying hens.

Three groups of lactating cows were dosed daily at levels of 4, 12 and 40 ppm in the diet (0.15, 0.45 and 1.5 mg/kg bw) for 28 consecutive days. Milk was collected throughout the whole study and tissues were collected on day 29 within 24 hours of the last dose.

In milk highest mean total residues were 0.039 mg/kg for the 4 ppm group, 0.077 mg/kg for the 12 ppm group and 0.218 mg/kg for the 40 ppm group. Investigation of the distribution of the residue in cream gave a 9.9 fold higher concentration than in whole milk (15 between whole milk and milk fat).

Total residues in muscle for the 4, 12 and 40 ppm groups were 0.039–0.065 mg/kg (mean: 0.052 mg/kg), 0.081–0.26 mg/kg (mean: 0.162 mg/kg) and 0.63–1.0 mg/kg (mean: 0.82 mg/kg), respectively. In liver residues were 0.42–0.69 mg/kg (mean: 0.57 mg/kg) for the 4 ppm group, 1.2–1.7 mg/kg (mean: 1.4 mg/kg) for the 12 ppm group and 4.8–5.4 mg/kg (mean: 5.0 mg/kg) for the 40 ppm group. Kidney contained total residues of 0.1–0.15 mg/kg (mean: 0.14 mg/kg), 0.28–0.37 mg/kg (mean: 0.34 mg/kg) and 1.0–1.3 mg/kg (mean: 1.2 mg/kg) for the for the 4, 12 and 40 ppm group.

For fat three different tissues were analysed (perirenal, mesenteric and subcutaneous fat). Highest residues were found in perirenal fat with 0.14–0.21 mg/kg (mean: 0.18 mg/kg) for the 4 ppm group, 0.33–0.48 mg/kg (mean: 0.43 mg/kg) for the 12 ppm group and 0.8–1.9 mg/kg (mean: 1.4 mg/kg) for the 40 ppm group.

For laying hens three groups of animals were dosed with rates of 1.5, 4.5 and 15 ppm in the dry weight feed (0.1, 0.3 and 1.0 mg/kg bw) for 28 consecutive days. Eggs were collected throughout the whole study and tissues were collected on day 29 after the last dose.

In eggs total residues at the plateau phase were < 0.02–0.02 mg/kg (highest daily mean: 0.02 mg/kg) for the 1.5 ppm group and ranged between 0.05 to 0.07 mg/kg (highest daily mean: 0.063 mg/kg) for the 4.5 ppm and between 0.13 to 0.22 mg/kg (highest daily mean: 0.178 mg/kg) for the 15 ppm group.

In tissues no residues above the LOQ were found in muscle. Total residues in fat for the 1.5, 4.5 and 15 ppm groups were < 0.02–0.02 mg/kg (mean: 0.02 mg/kg), 0.05–0.06 mg/kg (mean: 0.057 mg/kg) and 0.06–0.09 mg/kg (mean: 0.07 mg/kg), respectively. In liver residues were < 0.02–0.02 mg/kg (mean: 0.02 mg/kg) for the 1.5 ppm group, 0.02–0.04 mg/kg (mean: 0.03 mg/kg) for the 4.5 ppm group and 0.03–0.05 mg/kg (mean: 0.04 mg/kg) for the 15 ppm group.

Estimated maximum and mean dietary burdens of livestock and animal commodities maximum residue levels

The Meeting noted that the uptake of bixafen and M21 (bixafen-desmethyl) from soil contributes significantly to the overall residues in annual crops. Based on the information available (see residues in rotational crops), no estimation on livestock animal dietary burdens and the corresponding residue levels in animal commodities can be made.

RECOMMENDATIONS

Definition of the residue for compliance with MRL for plant commodities: *bixafen*

Definition of the residue for compliance with MRL for animal commodities and (for the estimation of dietary intake) for plant and animal commodities: *sum of bixafen and N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1H-pyrazole-4-carboxamide (bixafen-desmethyl), expressed as bixafen*

The residue is fat-soluble.

FURTHER WORK OR INFORMATION

The Meeting considered that the currently available information on residues in rotational crops was not sufficient to make recommendations on maximum residue levels in plant and animal commodities. For future recommendations field rotational crop studies approximating plateau concentrations of bixafen in soil are required.

DIETARY RISK ASSESSMENT

The Meeting concluded that the contribution of residues in plant commodities from soil uptake cannot be estimated based on the available data. Thus no estimations on median or highest residues in food commodities of plant and animal origin could be made, precluding both long and short-term dietary risk assessments for bixafen.

Consequently, the dietary risk assessment will be undertaken at a future meeting when the residues derived from both direct application and those taken up from the soil in a rotational crop situation can be evaluated together.

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BIXAFEN_031	Schoening, R and Erler, S	2008	Determination of the residues of BYF 00587 in/on the field rotational crops turnip, lettuce, winter wheat and spring wheat after spraying of BYF 00587 (125 EC) in the field in Germany. Bayer CropScience AG, Monheim, Germany. Bayer CropScience AG, Report No.: RA-2139/06, Edition Number: M-296357-02-1. Unpublished
BIXAFEN_032	Schoening, R and Erler, S	2008	Determination of the residues of BYF 00587 in/on the field rotational crops turnip, lettuce, winter wheat and spring wheat after spraying of BYF 00587 (125 EC) in the field in Northern France. Bayer CropScience AG, Monheim, Germany. Bayer CropScience AG, Report No.: RA-2143/06, Edition Number: M-296525-02-1. Unpublished
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BIXAFEN_040	Schoening, R	2006	Analytical method 01012 for the determination of residues of BYF00587 and its metabolite BYF00587-desmethyl in/on plant matrices by HPLC-MS/MS. Bayer CropScience AG, Monheim, Germany. Bayer CropScience AG, Method No.: 01012, Report No.: MR-06/131, Edition Number: M-277851-02-1. Unpublished
BIXAFEN_041	Sur, R and Kuhnke, G	2007	Extraction efficiency testing of the residue method for the determination of BYF00587 and BYF 00587-desmethyl using aged radioactive residues from a wheat metabolism study. Bayer CropScience AG, Monheim, Germany. Bayer CropScience AG, Report No.: MEF-07/356, Edition Number: M-294920-01-1. Unpublished
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Code	Author	Year	Title, Institute, Report reference
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BIXAFEN_072	Schoening, R and Wolters, A	2007	Bixafen: Feeding Study with dairy cows. Bayer CropScience AG, Monheim, Germany. Bayer CropScience AG, Report No.: MR-07/340, Edition Number: M-296420-01-1. Unpublished
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CHLORANTRANILIPROLE (230)

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BACKGROUND

Chlorantraniliprole is a selective ryanodine receptor agonist insecticide which was evaluated by the JMPR in 2008 (T, R) and 2010 (R). The ADI for chlorantraniliprole is 0–0.03 mg/kg bw and ARfD was considered to be unnecessary. The compound was listed by the Forty-fourth Session of the CCPR (2012) for the evaluation by the 2013 JMPR. This submission presents additional proposed/registered uses of chlorantraniliprole and residue data for strawberries, blueberries, cranberries, legumes, soya bean, radish, carrots, globe artichokes, rice, barley, sorghum, wheat, canola seed, sunflower seed, coffee, avocados, pomegranates, hops and citrus.

USE PATTERNS

Chlorantraniliprole is registered around the world to be used as foliar or seed application, in the field or protected, terrestrial or aerial application. Table 1 shows the uses of chlorantraniliprole in crops and regions that are relevant for this submission.

Table 1 Registered ground uses of chlorantraniliprole on crops included in this evaluation

Crop	Country	Application				Rate per treatment		PHI (days)	Max. per season, kg ai/ha
		F, G	Form	Max. number	Interval (days)	water L/ha ^b	kg ai/ha		
Avocado	New Zealand	F	WG	2	21	Max 3000	0.09	14	
Caneberry	Canada	F	WG	3	14	280-2337	0.07-0.11	3	0.225
	USA	F	WG	3	14	280-2337	0.07-0.11	3	0.225
Carrot	Italy	F	WG	2	10	800-1000	0.03-0.04	21	
Coffee	Brazil	F	WG	2	45	400	0.03	21	
Globe artichoke	Italy	F	ZC	2	14	200–1000	0.03	3	
Globe artichoke	USA	F	SC	4	14	467-2337	0.05 - 0.11	3	0.22
Grape	USA	F	WG	3	7	280-2337	0.07-0.11	14	0.225
Green bean	Italy	G	WG	2	7-14	500-1000	0.05	3	
		F	WG	2	7-14	500-1000	0.04	3	
Hops	USA	F	SC	4	7	467-2337	0.05- 0.07	0	0.22
Legume vegetables	Australia ^a	F	SC	3	7	200-1000	0.020	1	
	USA	F	SC	4	3	93-935	0.05-0.07	1	0.225
Non-grass animal feed	Canada	F	SC	1	-		0.1	0	-
Bushberry (berry and small fruit)	Canada	F	WG	3	7	280-2337	0.07-0.11	1	0.225
	USA	F	WG	3	7	280-2337	0.07-0.11	1	0.225
Oilseeds	USA	F	SC	4	5	47-187	0.05-0.07	21	0.2
	Canada	F	SC	3	5	100	0.025-0.07	1	0.2
Pomegranate	USA	F	WG	3	7	280-1870	0.11	1	0.2
Root and tuber vegetables	USA	F	SC	4	Foliar: 3 drip:10	93-935	0.03-0.07	1	0.225
Rice	Brazil	F	WG	1		100-200	0.030	15	
Rice	USA	F	FS	1		0.06 mg ai/seed ^b	0.09		
Soya bean, dry,	Brazil	F	SC	2	14	150-250	0.01	21	
Strawberry	USA	F	SC	1-4	7	93-2337	0.05-0.07	1	0.225

F= field; G= glasshouse application or indoor application; ^a Do not graze or cut for stock food for 1 day after application.

^b assuming 20000 seeds/lb

RESIDUES RESULTING FROM SUPERVISED TRIALS

Supervised residue trials conducted with chlorantraniliprole on a variety of crops in Europe, Brazil, Canada and USA were submitted to the Meeting. Studies were conducted according to GLP, and specified concurrent determination of residues in untreated crops gave residues < LOQ. Residues of chlorantraniliprole arising from use patterns where rate or PHI or $\pm 25\%$ of GAP are underlined and considered for estimation of maximum residue levels and STMRS. When residues in samples harvested at a later stage were higher than those found at the critical PHI, they were used for the estimations. In the tables, DAT means days after treatment. In Canada and USA trials, two samples were analysed and the mean residues reported.

Berries and other small fruit

Seventeen trials were conducted in blueberry and cranberry in Canada and USA in 2007 (Table 2) and 16 trials were conducted in strawberry in Europe and USA from 2008–2011 (Table 3).

Table 2 Residues of chlorantraniliprole in blueberry and cranberry in North America

Location/year	Crop/variety	Application				Residues ^a		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
Canada/2007 Kentville, NS	Blueberry/ Lowbush wild clones	WG	2	0.11	0.04	1 3 8 14	<u>0.46</u> 0.43 0.38 0.40	IR-4 PR No. 09810, Test NS01
Canada/2007 Rawdon, NS	Blueberry/ Lowbush wild clones	WG	2	0.11	0.04	1	<u>0.75</u>	IR-4 PR No. 09810, Test NS02
Canada/2007 Debert, NS	Blueberry/ Lowbush wild clones	WG	2	0.11	0.04	1	<u>0.84</u>	IR-4 PR No. 09810, Test NS03
Canada/2007 Bothwell, ON	Blueberry/ Bluecrop	WG	2	0.11	0.03	1	<u>0.18</u>	IR-4 PR No. 09810, Test ON22
USA/2007 Jonesboro, ME	Blueberry/ Lowbush	WG	2	0.11	0.03	1	<u>0.18</u>	IR-4 PR No. 09810, Test ME01
USA/2007 Fennville, MI	Blueberry/ Rubel	WG	2	0.11	0.02	1	<u>0.12</u>	IR-4 PR No. 09810, Test MI32
USA/2007 Fennville, MI	Blueberry/ Rubel	WG	2	0.11	0.02	1	<u>0.16</u>	IR-4 PR No. 09810, Test MI33
USA/2007 Castle Hayne, NC	Blueberry/ Pender	WG	2	0.11	0.04	1	<u>0.11</u>	IR-4 PR No. 09810, Test NC13
Castle Hayne, NC USA/2007	Blueberry/ Duke	WG	2	0.11	0.04	1	<u>0.21</u>	IR-4 PR No. 09810, Test NC14
USA/2007 Bridgeton, NJ	Blueberry/ Duke	WG	2	0.11	0.045	1 3 6 13	<u>0.23</u> 0.23 0.22 0.12	IR-4 PR No. 09810, Test NJ10
USA/2007 Aurora, OR	Blueberry/ Bluecrop	WG	2	0.11	0.02	1	<u>0.13</u>	IR-4 PR No. 09810, Test OR06
Canada/2007 Agassiz, BC	Cranberry/ Ben Lear	WG	2	0.11	0.03	1 2 6 11	<u>0.21</u> 0.15 0.13 0.08	AAFC07-050R, Test No. 350
Canada/2007 Manseau, QC	Cranberry/ Stevens	WG	2	0.11	0.02	1	<u>0.29</u>	AAFC07-050R, Test No. 352
USA/2007 Plymouth, MA	Cranberry/ Stevens	WG	2	0.11	0.025	1	<u>0.13</u>	AAFC07-050R, Test No. 346
USA/2007 Langlois, OR	Cranberry/ Stevens	WG	2	0.11	0.03	1	<u>0.12</u>	AAFC07-050R, Test No. 349
USA/2007 Warrens, WI	Cranberry/ Stevens	WG	2	0.11	0.02	1	<u>0.32</u>	AAFC07-050R, Test No. 358

Location/year	Crop/variety	Application				Residues ^a		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
USA/2007 Wareham, MA	Cranberry/ Early Blacks	WG	2	0.11	0.025	1	<u>0.24</u>	AAFC07-050R, Test No. 471

Table 3 Residues of chlorantraniliprole in strawberry in Europe and USA

Location/year	Crop/variety	Application				Residues ^a		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
France/2008 Midi P.	Strawberry/ Gariguette	SC	3	0.05	0.0005	0* 0 1 3 7	0.12 0.14 0.08 0.12 0.06	CEMR-3915- REG, Test 1 (indoor)
France/2009 Midi Pyrénées,	Strawberry/ Gariguette	SC	3	0.05	0.0004	0* 0 1 3 7	0.11 0.08 0.08 0.05 0.05	CEMR-4334- REG, Test 1 (indoor)
Italy/2008 Emilia Romagna,	Strawberry/ Dora	SC	3	0.05	0.0005	0* 0 1 3 7	0.07 0.12 0.07 0.10 0.07	CEMR-3915- REG, Test 2 (indoor)
Spain/2008 Valencia	Strawberry/ Camarrosa	SC	3	0.05	0.0005	0* 0 3 7 14	0.10 0.34 0.15 0.12 0.15	CEMR-3915- REG, Test 3 (indoor)
Spain/2008 Valencia,	Strawberry/ Camarrosa	SC	3	0.05	0.0005	0* 0 1 3 7	0.13 0.08 0.14 0.16 0.19	CEMR-3915- REG, Test 4 (indoor)
Spain/2009 Cádiz	Strawberry/ Camarrosa	SC	3	0.05	0.0005	0* 0 1 3 7	0.33 0.68 0.48 0.35 0.42	CEMR-4334- REG, Test 3 (indoor)
Spain/2009 Andalucia	Strawberry/ Camarrosa	SC	3	0.05	0.0005	0* 0 1 3 7	0.10 0.13 0.13 0.11 0.11	CEMR-4334- REG, Test 4 (indoor)
Spain/2009 Andalucia	Strawberry/ Matisse	SC	3	0.05	0.0005	0* 0 1 3 7	0.14 0.14 0.07 0.10 0.07	CEMR-4334- REG, Test 5 (indoor)
USA/2011 Penn Yan, NY	Strawberry/ Honeoye	SC	2	0.11	0.04	1	<u>0.21</u>	DuPont-30024, Test No. 1
USA/2011 Enigma, GA	Strawberry/ Festival	SC	2	0.11	0.09	1	<u>0.40</u>	DuPont-30024, Test No. 2
USA/2011 Citra, FL 32113	Strawberry/ Festival	SC	2	0.11	0.06	1	<u>0.22</u>	DuPont-30024, Test No. 3
USA/2011 Richland, IA	Strawberry/ Extra Sweet	SC	2	0.11	0.07	1	<u>0.68</u>	DuPont-30024, Test No. 4
USA/2011 Geneva, MN	Strawberry/ Albion	SC	2	0.11	0.06	1	<u>0.24</u>	DuPont-30024, Test No. 5
USA/2011 Porterville, CA	Strawberry/ Albion	SC	2	0.11	0.02	1	<u>0.23</u>	DuPont-30024, Test No. 6
USA/2011 Porterville, CA	Strawberry/ Albion	SC	2	0.11	0.02	1	<u>0.24</u>	DuPont-30024, Test No. 7

Location/year	Crop/variety	Application				Residues ^a		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
USA/2011 Porterville, CA	Strawberry/ Pugen Reliance	SC	2	0.11	0.05	1	<u>0.18</u>	DuPont-30024, Test No. 8

* days before application

Avocado

Eleven trials were conducted in avocado in New Zealand from 2009 to 2012. The results are shown in Table 4.

Table 4 Results of residue trials conducted with chlorantraniliprole in avocado in New Zealand (DuPont-36033 NZ). Residues in fruit with stone removed

Location/year	Crop variety	Application				Residues		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
Katikati/2009–10	Avocado/Hass	WG	3	0.09	0.003	14	0.15	DP 0910
Katikati/2009–10	Avocado/Hass	WG	3	0.19	0.006	14	0.31	DP 0910
Katikati/2009–10	Avocado/Hass	WG	3	0.09	0.003	1 7 14 21 28	0.14 0.16 0.14 0.08 0.06	DP 0914
Katikati/2009–10	Avocado/Hass	WG	3	0.19	0.006	1 7 14 21 28	0.30 ^a 0.25 ^a 0.20 0.21 ^a 0.21 ^a	DP 0914
Katikati/2012	Avocado/Hass	WG	2	0.08	0.003	14	<u>0.03</u>	DP 1183a
Katikati/2012	Avocado/Hass	WG	2	0.08	0.003	14	<u>0.08^a</u>	DP 1183b
Athenree/2012	Avocado/Hass	WG	1	0.085	0.003	15	0.07	Goldwood
Tauranga/2012	Avocado/Hass	WG	1	0.078	0.003	14	0.09	Beetjamen
Pukenui/2012	Avocado/Hass	WG	1	0.019	0.003	14	0.03	Freeman
Glenbrook/2012	Avocado/Hass	WG	1	0.09	0.003	14	0.12	French
Pukenui/2012	Avocado/Hass	WG	1	0.028	0.003	14	0.13	Payton

^a. Average of two or three analyses

Pomegranate

Five trials were conducted in pomegranate in USA from 2010 to 2011. The results are shown in Table 5.

Table 5 Results of residue trials conducted with chlorantraniliprole in pomegranate fruit (IR-4 PR No. 10362)

Location/year	Crop variety	Application				Residues		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
Gridley, CA /2011	Wonderfuls	SC	2	0.11	0.01	1	<u>0.10</u>	CA01
Reedley, CA/2010	Wonderfuls	SC	2	0.11	0.008	1	<u>0.10</u>	CA71
Reedley, CA /2010	Wonderfuls	SC	2	0.11	0.012	1	<u>0.09</u>	CA72
Gridley, CA /2010	Wonderfuls	SC	2	0.11	0.09	1	<u>0.12</u>	CA73
Gridley, CA /2010	Wonderfuls	SC	2	0.11	0.09	1	<u>0.12</u>	CA74

Legume vegetables

A total of 16 trials were conducted in beans in Europe and USA and 24 trials in peas in Australia, Canada and USA in the period of 2008 to 2011. Fresh pods with seeds and seeds only were analyzed. The results are showing in Table 6.

Table 6 Residues of chlorantraniliprole in beans

Location/year	Crop variety	Application				Residues			Study trial no.
		FL	No	kg ai/ha	kg ai/hL	Portion analysed	DAT, days	mg/kg	
Beans									
Queensland Australia/2009	Green beans/ Labrador	SC	3	0.02	0.006	Pods w/seed	0 1 3 7 14	0.09 0.05 0.04 0.04 <u>0.08</u>	HAL0802, S6/T2
Queensland, Australia/2009	Green beans/ Labrador	SC	2	0.1	0.034	Pods w/seed	0 1 7	0.31 0.11 0.09	HAL0802, S6/T3
Tasmania Australia/2010	Beans/ Flavour sweet	SC	3	0.02	0.005-0.007	Pods w/seed	0 1 3 7	0.11 <u>0.08</u> 0.02 0.03	HAL0802, S7/T2
Tasmania Australia/2010	Beans/ Flavour sweet	SC	2	0.11	0.03	Pods w/seed	0 1 7	0.24 0.14 0.04	HAL0802, S7/T3
France, South/2008	Beans/ Booster	SC	2	0.05	0.0005	Whole beans with pods	0* 0 1 3 7	0.72 0.49 0.47 0.24 <u>0.41</u>	T000565-08-REG (CEMS-3913), Test 1
France, South	Field green beans/ Angers	WG	2	0.04	0.004	Mature green beans in pods	1	0.26	DuPont-33033, Test No. 2
Greece	Field green beans/ Magirus	WG	2	0.04	0.004	Mature green beans in pods	1	0.07	DuPont-33033, Test No. 1
Italy /2008	Beans/ Oriente	SC	2	0.05	0.0005	Whole beans with pods	0* 0 1 3 7	0.06 0.18 0.29 <u>0.16</u> 0.13	T000565-08-REG (CEMS-3913), Test 2
Spain/2009	Beans/ Emerite	SC	2	0.05	0.0005	Whole beans with pods	0* 0 1 3 7	0.13 0.41 0.36 <u>0.40</u> 0.38	T000565-08-REG (CEMS-3913), Test 3
Spain/2008	Beans/ Killy	SC	2	0.05	0.0005	Whole beans with pods	0* 0 1 3 7	0.12 0.23 0.32 0.27 <u>0.40</u>	T000565-08-REG (CEMS-3913), Test 4
Spain 25195/2011	Field green beans/ Alquife	WG	2	0.04	0.004	Mature green beans in pods	-0 +0 1 3	0.04 0.16 0.21 <u>0.15</u>	DuPont-33033, Test No. 3
Salisbury, MD USA/2008	Snap bean/ Provider	SC	2	0.11	0.25	Pods w/seed	1	<u>0.14</u>	IR-4 PR No. 10046, Test MD15
Freeville, NY USA/2008	Snap bean/ Hystyle	SC	2	0.11	0.32	Pods w/seed	1	<u>0.12</u>	IR-4 PR No. 10046, Test NY29
Arlington, WI USA/2008	Snap bean/ Hystyle	SC	2	0.11	0.4	Pods w/seed	1	<u>0.10</u>	IR-4 PR No. 10046, Test WI21
Freemont, OH USA/2008	Snap bean/ Eureka	SC	2	0.11	0.37	Pods w/seed	1	<u>≤ 0.01</u>	IR-4 PR No. 10046, Test OH*12
Citra, FL 3 USA/2008	Snap bean/ Dusky	SC	2	0.11	0.38	Pods w/seed	1	<u>0.12</u>	IR-4 PR No. 10046, Test FL29

Location/year	Crop variety	Application				Residues			Study trial no.
		FL	No	kg ai/ha	kg ai/hL	Portion analysed	DAT, days	mg/kg	
Davis, CA USA/2008	Snap bean/ Blue Lake 274	SC	2	0.11	0.28	Pods w/seed	1	<u>0.41</u>	IR-4 PR No. 10046, Test CA01
Prosser, WA USA/2008	Snap bean/ OSU 91G	SC	2	0.11	0.31	Pods w/seed	1	<u>0.14</u>	IR-4 PR No. 10046, Test WA03
Delhi, ON Canada/2008	Snap bean/ Bronco	SC	2	0.11	0.3	Pods w/seed	1	<u>0.16</u>	IR-4 PR No. 10046, Test ON14
Delhi, ON Canada/2008	Snap bean/ Storm	SC	2	0.11	0.3	Pods w/seed	1	<u>0.12</u>	IR-4 PR No. 10046, Test ON15
Peas									
Queensland Australia/2009	Green Peas/ Greenfeast	SC	3	0.02	0.005	Peas	0 1 3 7 12	< 0.01 <u>< 0.01</u> < 0.01 < 0.01 < 0.01	HAL0802, S3/T2
Queensland Australia/2009	Green Peas/ Greenfeast	SC	2	0.11	0.02	Peas	0 1 3 7 12	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	HAL0802, S3/T3
Tasmania Australia/ 2009–10	Processing peas/ Resal	SC	3	0.02	0.007	Peas	0 1 3 7 14	< 0.01 <u>< 0.01</u> < 0.01 < 0.01 < 0.01	HAL0802, S4/T2
Tasmania Australia/ 2009–10	Peas/ Resal	SC	2	0.1	0.04	Peas	0 1 3 7 14	< 0.01 0.01 < 0.01 < 0.01 < 0.01	HAL0802, S4/T3
New South Wales, Australia/2009	Snap peas/ Sugar Bon	SC	3	0.02	0.005	Pods w/seed	0 1 3 6 14	0.02 0.01 0.02 0.03 <u>0.47</u>	HAL0802, S1/T2
New South Wales, Australia/2009	Snap peas/ Sugar Bon	SC	2	0.1	0.027	Pods w/seed	0 1 3 6 14	0.09 0.10 0.14 0.29 1.3	HAL0802, S1/T3
Queensland, Australia/2009	Snow peas/ Dwarf Oregon	SC	3	0.02	0.004-0.006	Pods w/seed	0 1 3 7 14	0.09 0.03 0.03 <u>0.06</u> 0.01	HAL0802, S2/T2
Queensland, Australia/2009	Snow peas/ Dwarf Oregon	SC	2	0.11	0.02	Pods w/seed	0 1 3 7 14	0.24 0.10 0.08 0.08 0.07	HAL0802, S2/T3
Tasmania, Australia/2010	Snow peas/ Sugar Bon	SC	3	0.02	0.005	Pods w/seed	0 1 3 7 14	0.03 0.02 0.01 0.02 <u>0.04</u>	HAL0802, S5/T2
Tasmania, Australia/2010	Snow peas/ Sugar Bon	SC	2	0.11	0.027	Pods w/seed	0 1 3 7 14	0.11 0.07 0.05 < 0.01 0.09	HAL0802, S5/T3

Location/year	Crop variety	Application				Residues			Study trial no.
		FL	No	kg ai/ha	kg ai/hL	Portion analysed	DAT, days	mg/kg	
Simcoe, ON Canada/2008	Pea / Oregon Giant	SC	2	0.11	0.06	Pods w/seed	1	<u>0.61</u>	IR-4 PR No. 10003, Test ON25
Delhi, ON Canada/2008	Garden pea/ Progress	SC	2	0.11	0.04	Seed	1	<u>0.02</u>	IR-4 PR No. 10003, Test ON10
Delhi, ON Canada/2008	Garden pea/ Bolero	SC	2	0.11	0.04	Seed	1	<u>0.03</u>	IR-4 PR No. 10003, Test ON11
Delhi, ON Canada/2008	Garden pea/ Bolero	SC	2	0.11	0.04	Seed	1	<u>0.03</u>	IR-4 PR No. 10003, Test ON12
Kentville, Canada/2008	Garden pea/ Wando	SC	2	0.11	0.04	Seed	1	<u>0.02</u>	IR-4 PR No. 10003, Test NS04
Elm Creek, Canada/2008	Garden pea/ Mr. Big	SC	2	0.11	0.06	Seed	1	<u>0.01</u>	IR-4 PR No. 10003, Test MB01
Freeville, NY USA/2008	Pea/Sugar Snap	SC	2	0.11	0.02	Pods w/seed	1	<u>0.64</u>	IR-4 PR No. 10003, Test NY28
Salinas, CA USA/2008	Pea / Sugar Ann	SC	2	0.11	0.015	Pods w/seed	1	<u>0.48</u>	IR-4 PR No. 10003, Test CA*25
Aurora, OR USA/2008	Pea / Sugar Sprint	SC	2	0.11	0.04	Pods w/seed	1 3 6 13	<u>0.45</u> 0.31 0.23 0.08	IR-4 PR No. 10003, Test OR22
Kimberly, ID USA/2008	Garden pea/ Thomas Laxton	SC	2	0.11	0.05	Seed	1	<u>0.03</u>	IR-4 PR No. 10003, Test ID01

Soya bean, dry

Four residue trials were conducted in soybean in Brasil in 2010. The results are shown in Table 7.

Table 7 Residues of chlorantraniliprole in soya bean seed (Report BPL-JM-036-003-10-RF)

Location/year	Crop variety	Application				Residues		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
Brazil/2010 Sao Paulo	Soya bean/ conquista	SC	2	0.01	0.004	7 14 21 28	0.01 0.01 <u>< 0.01</u> < 0.01	Test No. 1
Brazil/2010 Paraná,	Soya bean/ CD 206	SC	2	0.01	0.005	7 14 21 28	< 0.01 < 0.01 <u>< 0.01</u> <0.0006	Test No. 2
Brazil/2010 Paraná,	Soya bean/ Codetec 206	SC	2	0.01	0.005	21	<u>< 0.01</u>	Test No. 3
Brazil/2010 Mato Grosso do Sul,	Soya bean/ Monsoy 7908 RR	SC	2	0.01	0.005	21	<u>< 0.01</u>	Test No. 4

Carrots

A total of 19 residue trials were conducted in Europe in carrots during 2009/2010. The results are shown in Table 8.

Table 8 Residues of chlorantraniliprole in carrots (Report DuPont-27575)

Location/year	Crop variety	Application				Residues		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
Czech Republic /2009	Carrot/ Kamaran F1	WG	2	0.04	0.004	21	0.014	Test No. 10
Czech Republic/2010	Carrot/ Kamaran F1	WG	2	0.04	0.004	-0 +0 7 14 20 27	<0.004 <0.004 <0.004 <0.004 <0.004 <0.004	Test No. 18
France, North /2009	Carrot/ Mac Kabro	WG	2	0.04	0.008	-0 +0 7 14 21 28	<0.004 <0.004 <0.004 <0.004 <0.004 <0.004	Test No. 3
France, North, /2009	Carrot/ Kingston	WG	2	0.04	0.008	21	<0.004	Test No. 2
France, North/2010	Carrot/ Kiev	WG	2	0.04	0.008	21	0.010	Test No. 12
France, South/2009	Carrot/ Dordogne	WG	2	0.03	0.004	-0 +0 7 14 21 28	<0.004 <0.004 <0.004 0.008 <0.004 <0.004	Test No. 1
France, South/2010	Carrot/ Dordogne	WG	2	0.04	0.008	-0 +0 7 14 21 28	<0.004 <0.004 0.005 <0.004 0.005 <0.004	Test No. 11
Germany/2009	Carrot/ Nantaise 2	WG	2	0.04	0.004	-0 +0 7 14 21 28	0.020 0.010 0.022 0.024 0.021 0.015	Test No. 9
Germany/2010	Carrot/ Nantaise 2	WG	2	0.04	0.004	21	<0.004	Test No. 17
Greece/2009	Carrot/ Tempo F1	WG	2	0.04	0.004	21	0.030	Test No. 7
Greece /2010	Carrot/ Tempo fl	WG	2	0.04	0.004	21	<0.004	Test No. 15
Italy/2009	Carrot/ Dordogne	WG	2	0.04	0.004	21	0.025	Test No. 4
Italy/2009	Carrot/ Maestro	WG	2	0.04	0.004	-0 +0 7 14 20 27	0.004 0.010 0.096 0.006 0.036 0.030	Test No. 5
Italy /2010	Carrot/ Napoli	WG	2	0.04	0.004	19	0.005	Test No. 13
Spain/2009	Carrot/ Nevis	WG	2	0.04	0.004	-0 +0 7 14 21 28	<0.004 <0.004 0.009 0.040 0.004 <0.004	Test No. 6

Location/year	Crop variety	Application				Residues		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
Spain /2010	Carrot/ Namur	WG	2	0.04	0.004	-0 +0 7 14 21 28	<0.004 <0.004 <0.004 <0.004 <u><0.004</u> <0.004	Test No. 14
UK/2009	Carrot/ Romance	WG	2	0.04	0.004	-0 +0 7 14 20 28	0.012 0.008 0.016 0.013 0.009 <u>0.027</u>	Test No. 8
UK /2010	Carrot/ Nairobi	WG	2	0.04	0.004	-0 +0 8 15 22 29	<0.004 <0.004 <0.004 <0.004 <u><0.004</u> <0.004	Test No. 16

Radish

Six trials were conducted in radish in Canada and USA in 2008. Residues in roots and tops at 1 DAT are shown in Table 8

Table 8 Residues of chlorantraniliprole in radish (Report DuPont-25887)

Location/year	Crop variety	Application				Residues			Trial no.
		FL	No	kg ai/ha	kg ai/hL	Portion analysed	DAT, days	mg/kg	
MB Canada/2008	Radish/ Champion	SC	2	0.11	0.05	Roots Tops	1 1	<u>0.03</u> 3.9	No. 5
PA USA/2008	Radish/ French breakfast	SC	2	0.11	0.04	Roots tops	1 1	<u>0.26</u> 11	No. 1
FL USA/2008	Radish/ Crunchy Royale	SC	2	0.11	0.04	Roots tops	1 1	<u>0.04</u> 10	No. 2
FL USA/2008	Radish/ Cherriette	SC	2	0.11	0.04	Roots Tops	1 1	<u>0.05</u> 19	No. 3
IA USA/2008	Radish/ Champion	SC	2	0.11	0.05	Roots Tops	1 1	<u>0.05</u> 7.7	No. 4
CA USA/2008	Radish/ Crunchy royale	SC	2	0.11	0.04	Roots Tops	1 1	<u>0.08</u> 22	No. 6

Globe artichokes

Eight trials were conducted in Europe and USA in globe artichoke from 2008 to 2010. The results are shown in Table 9.

Table 9 Residues of chlorantraniliprole in Globe artichokes

Location/year	Crop variety	Application				Residues			Study trial no.
		FL	No	g ai/ha	g ai/hL	Portion analysed	DAT, days	mg/kg	
France/2008	Globe artichoke/ Macau	ZC	2	0.03	0.0003	Whole fruit	0* 0 3 7 14	nsa 0.14 <u>0.16</u> 0.12 0.06	T000566-08-REG, Test 1

Location/year	Crop variety	Application				Residues			Study trial no.
		FL	No	g ai/ha	g ai/hL	Portion analysed	DAT, days	mg/kg	
Spain/2008	Globe artichoke/ Tudela	ZC	2	0.03	0.0003	Whole fruit	0* 0 3 7 14	0.03 0.20 <u>0.08</u> 0.03 < 0.01	T000566-08- REG, Test 2
Spain/2009	Globe artichoke/ Tudela	ZC	2	0.03	0.0005	Whole fruit	0* 0 3 7 14	0.03 0.09 <u>0.06</u> 0.05 0.06	CEMS- 4441-REG, Test 1
Spain/2009	Globe artichoke/ Tudela	ZC	2	0.03	0.0005	Whole fruit	0* 0 3 7 14	0.02 0.09 <u>0.07</u> 0.03 0.05	CEMS- 4441-REG, Test 2
CA, USA/2010	Artichoke/ Green globe	SC	2	0.11	0.12	Flower buds	3	<u>0.60</u>	IR-4 PR No. 10083, Test No. CA63
CA, USA/2010	Artichoke/ Green globe	SC	2	0.11	0.016	Flower buds	3	<u>0.59</u>	IR-4 PR No. 10083, Test No. CA64
CA, USA/2010	Artichoke/ Green globe	SC	2	0.11	0.016	Flower buds	4	<u>0.72</u>	IR-4 PR No. 10083, Test No. CA65
CA, USA/2010	Artichoke/ Green globe	SC	2	0.11	0.012	Flower buds	3	<u>0.48</u>	IR-4 PR No. 10083, Test No. CA66

Rice

Eight trials were conducted with chlorantraniliprole in rice in Brazil using foliar application and 19 trials were conducted in USA using seed application. The results are shown in Table 9.

Table 9 Residues of chlorantraniliprole in rice grain in Brazil and USA

Location/year	Crop variety	Application				Residues		Report Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
Foliar application								
SP, Brazil/2010	EPAGRI 115	WG	1	0.03	0.015	15 33 45 60	<u>0.13</u> 0.06 < 0.01 < 0.01	BPL-JM-036-008-09 Test No. C1
SP, Brazil/2010	Motti	WG	1	0.03	0.015	13 28 43 58	<u>0.02</u> < 0.01 < 0.01 < 0.01	BPL-JM-036-008-09 Test No. C2
SC, Brazil/2010	EPAGRI 109	WG	1	0.03	0.015	15 30 45 60	<u>0.10</u> 0.03 < 0.01 < 0.01	BPL-JM-036-008-09 Test No. C3
SC, Brazil/2010	EPAGR1 113	WG	1	0.03	0.015	15 30 45 60	<u>0.16</u> < 0.01 < 0.01 < 0.01	BPL-JM-036-008-09 Test No. C4
SC, Brazil/2010	EPAGR1 109	WG	1	0.03	0.015	15 60	<u>< 0.01</u> < 0.01	BPL-JM-036-008-09 Test No. P1
SC, Brazil/2010	SCS 115 – CL	WG	1	0.03	0.015	15 60	<u>0.03</u> < 0.01	BPL-JM-036-008-09 Test No. P2
RS, Brazil/2010	IRGA 117	WG	1	0.03	0.015	15 60	<u>0.13</u> < 0.01	BPL-JM-036-008-09 Test No. P3

Location/year	Crop variety	Application				Residues		Report Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
RS, Brazil/2010	Puitá	WG	1	0.03	0.015	15 60	0.16 < 0.01	BPL-JM-036-008-09 Test No. P4
Seed application		mg ai/seed						
LA, USA/2007	Cocodrie	FS	1	0.1	0.56	127	0.05	DuPont-21999, Test No. 1
LA, USA/2007	Wells	FS	1	0.1	0.56	123	0.03	DuPont-21999, Test No. 2
LA, USA/2007	Wells	FS	1	0.1	0.56	116	0.04	DuPont-21999, Test No. 3
LA, USA/2007	Wells	FS	1	0.1	0.56	122	0.05	DuPont-21999, Test No. 4
LA, USA/2007	Wells	FS	1	0.1	0.56	122	0.05	DuPont-21999, Test No. 5
LA, USA/2007	Cocodrie	FS	1	0.1	0.56	122	0.07	DuPont-21999, Test No. 6
LA, USA/2007	Francis	FS	1	0.1	0.56	122	0.09	DuPont-21999, No. 7
AR, USA/2007	Wells	FS	1	0.1	0.56	134	0.03	DuPont-21999, No. 9
AR, USA/2007	Bengal	FS	1	0.1	0.56	138	0.05	DuPont-21999, No. 10
AR, USA/2007	Wells	FS	1	0.1	0.56	143	0.03	DuPont-21999, No. 11
AR, USA/2007	Bengal	FS	1	0.1	0.56	148	0.03	DuPont-21999, Test No. 12
MO, USA/2007	Francis	FS	1	0.1	0.56	120	0.01	DuPont-21999, No. 13
TX, USA/2007	Cocodrie	FS	1	0.1	0.56	113	0.06	DuPont-21999, No. 14
TX, USA/2007	Cocodrie	FS	1	0.1	0.56	120	0.05	DuPont-21999, No. 15
CA, USA/2007	Calrose	FS	1	0.1	0.56	130	0.05	DuPont-21999, No. 16
CA, USA/2007	Calrose	FS	1	0.1	0.56	117	0.06	DuPont-21999, No. 17
LA, USA/	XL 745	FS	1	0.044	0.09	125	0.02	DuPont-30021, No. 1
LA USA/	XL723	FS	1	0.044	0.09	118	0.01	DuPont-30021, No. 2
MO USA/2011	XL 745	FS	1	0.044	0.09	135	0.01	DuPont-30021, No. 3

Cereals

Eleven trials were conducted with chlorantraniliprole in cereals in USA in 2009/2010. The results are shown in Table 10.

Table 10. Results of residue trials conducted with chlorantraniliprole in cereal grain (IR-4 PR No. 10204)

Location/year	Crop /variety	Application				Residues		Trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
ND, USA/2009	Barley/Tradition	SC	2	0.12	0.1	1	2.0	ND01
SD, USA/2009	Barley/Lacey	SC	2	0.11	0.06	1	1.9	SD07
ID, USA/2009	Barley/Camas Spring	SC	2	0.11	0.06	1	1.9	ID14
ND, USA/2009	Sorghum/LM 5001	SC	2	0.11	0.08	1	1.2	ND02
NM, USA/2009	Sorghum/DK 28E	SC	2	0.11	0.06	1	1.5	NM13
NM, USA/2009	Sorghum/M3838	SC	2	0.11	0.04	1	0.79	NM19
ND, USA/2009	Wheat/Alsen	SC	2	0.12	0.09	1	0.22	ND03
ND, USA/2009	Wheat/Glenn	SC	2	0.11	0.08	1	0.19	ND04
ND, USA/2009	Wheat/Faller	SC	2	0.12	0.10	1	0.18	IND05
SD, USA/2009	Wheat/Briggs Hard Red	SC	2	0.12	0.055	1	0.25	SD08
NM, USA/2010	Wheat/El Dorado	SC	2	0.12	0.05	1	0.41	NM18

^a highest residue values of two individual field samples.

Oil seeds

Twelve trials were conducted with canola and sunflower in Canada and USA in 2010. The results are shown in Table 11.

Table 11 Results of residue trials conducted with chlorantraniliprole in oil seeds (DuPont-26888)

Location/year	Crop/variety	Application				Residues		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
MB, Canada/2010	Canola/Invigor 5440	SC	2	0.11	0.12	1	0.25	4
SK, Canada/2010	Canola/Roundup Ready	SC	2	0.12	0.11	1	0.34	5
AB, Canada/2010	Canola/Liberty 5440	SC	2	0.12	0.11	1	0.23	6
NE, USA/2010	Canola/Patriot RR	SC	2	0.11	0.08	1	1.0	1
NE, USA/2010	Canola/Patriot RR	SC	2	0.11	0.08	1	0.83	2
WA, USA/2010	Canola/72-65RR	SC	2	0.11	0.08	1	0.14	3
SK, Canada/2010	Sunflower/Viper	SC	2	0.12	0.12	1	0.82	11
MB, Canada/2010	Sunflower/Mycogen 8N272	SC	2	0.11	0.12	1	0.16	12
MB, Canada/2010	Sunflower/Dahlgren	SC	2	0.11	0.12	1	0.12	8
IA, USA/2010	Sunflower/Peredovic	SC	2	0.11	0.07	1	0.79	7
NE, USA/2010	Sunflower/3080 DMR, NS	SC	2	0.11	0.08	1	0.21	9
ND, USA/2010	Sunflower/RH9558	SC	2	0.12	0.06	1	0.03	10

Coffee

Eight trials were conducted in coffee in Brazil in 2007 and 2010. The coffee cherries were dried for 24 days in the field and the coffee beans were mechanically separated from the skin. The residues found in the coffee beans are shown in Table 12.

Table 12. Results of residue trials conducted with chlorantraniliprole in coffee beans in Brazil.

Location/year	Crop variety	Application				Residues		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
São Manuel, SP /2010	Coffee/Obata	WG	2	0.03	0.008	7 14 21 28	0.01 0.01 0.01 < 0.01	BPL-JM-036-004-10-RF-Revision 1, Test No. 1
Alvilandia, SP/2010	Coffee/Obata	WG	2	0.03	0.008	7 14 21 28	0.04 0.01 0.01 < 0.01	BPL-JM-036-004-10-RF-Revision 1, Test No. 2
Carlopolis, SP /2010	Coffee/Obata	WG	2	0.03	0.008	21	< 0.01	BPL-JM-036-004-10-RF-Revision 1, Test No. 4
Varginha, MG /2010	Coffee/Catuai	WG	2	0.03	0.008	21	0.01	BPL-JM-036-004-10-RF-Revision 1, Test No. 5
Espirito Santo do Pinhal, SP/2007	Coffee/Acacia	WG	3	0.05	0.013	8 22	0.10 0.02	RE-2007-171, Test No. 1
Machado, MG /2007	Coffee/Topazio	WG	3	0.05	0.013	1 3 7 14 21	0.19 0.16 0.12 0.06 0.02	RE-2007-205, Test No. 1
Arceburgo, MG/2007	Coffee/Ubata	WG	3	0.05	0.013	1 4 7 14 21	0.21 0.14 0.10 0.07 0.02	RE-2007-206, Test No. 1
Indianoplois, MG/2007	Coffee/Ubata	WG	3	0.05	0.013	7 21	0.12 0.03	RE-2007-207, Test No. 1

Hops

Four trials were conducted in hops in USA in the period of 2009-2012. After harvest, the hop cones were dried in ovens/dryer rooms/kilns simulating commercial practices. The hop cones were dried at approximately 60–65 °C for up 2.5 to 24 hours. The results are shown in Table 13.

Table 13 Results of residue trials conducted with chlorantraniliprole hops (IR-4 PR No. A10491). Residues in dried hop cones

Location/year	Crop variety	Application				Residues		Study trial no.
		FL	No	kg ai/ha	kg ai/hL	DAT, days	mg/kg	
ID, USA/2011	Hops/Newport	SC	2	0.1	0.02	0 1 3 8 14	7.8 7.6 <u>8.9</u> 7.0 6.4	ID04
OR, SA/2011	Hops/Nugget	SC	2	0.1	0.02	0	<u>19</u>	OR05
WA, SA/2011	Hops/Nugget	SC	2	0.1	0.01	0 1 3 7 13	7.2 7.5 <u>7.6</u> 5.5 5.9	WA04
WA, SA/2011	Hops/Warrior	SC	2	0.1	0.01	0	<u>13</u>	WA06

Animal feed commodities

In the trials for legume vegetables and cereals reported in the previous tables, commodities for animal consumption were also analysed for chlorantraniliprole residues. The results are shown in Tables 14-16.

Table 14 Residues of chlorantraniliprole in legume animal feed

Location/year	Crop variety	Application				Residues			Study trial no.
		FL	No	kg ai/ha	kg ai/hL	Portion analysed	DAT, days	mg/kg	
Queensland, Australia/2009	Green beans/Labrador	SC	3	0.02	0.006	Foliage	1 7 14	<u>0.31</u> (2.24) 0.15 (0.90) 0.11 (0.50)	HAL0802, S6/T2
Queensland, Australia/2009	Green beans/Labrador	SC	2	0.1	0.03	Foliage	1 7	1.5 (11.66) 0.81 (4.45)	HAL0802, S6/T3
France, South/2008	Beans/Booster	SC	2	0.05	0.0005	Plants wo/pods	0* 0 1 3 7	3.3 6.3 4.7 3.3 <u>6.8</u>	T000565-08-REG (CEMS-3913), Test 1
Italy/2008	Beans/Oriente	SC	2	0.05	0.0005	Plants wo/pods	0* 0 1 3 7	2.0 2.8 4.9 <u>4.3</u> 3.3	T000565-08-REG (CEMS-3913), Test 2
Spain/2009	Beans/Emerite	SC	2	0.05	0.0005	Plants wo/pods	0* 0 1 3 7	2.4 6.0 6.1 3.2 <u>4.5</u>	T000565-08-REG (CEMS-3913), Test 3
Spain/2008	Beans/Killy	SC	2	0.05	0.0005	Plants wo/pods	0* 0 1 3 7	2.9 5.4 6.2 <u>6.6</u> 6.1	T000565-08-REG (CEMS-3913), Test 4
Greece/2011	Beans/Magirus	WG	2	0.04	0.004	Plants wo/pods	1	1.2	DuPont-33033, Test No. 1
South France/2011	Beans/Angers	WG	2	0.04	0.004	Plants wo/pods	1	2.4	DuPont-33033, Test No. 2

Location/year	Crop variety	Application				Residues			Study trial no.
		FL	No	kg ai/ha	kg ai/hL	Portion analysed	DAT, days	mg/kg	
Spain/2011	Beans/ Alquife	WG	2	0.04	0.004	Plants w/ pods	-0 +0 1 3	1.4 2.1 3.0 <u>2.4</u>	DuPont- 33033, Test No. 3
MD USA/2008	Snap bean/ Provider	SC	2	0.11	0.26	Plants w/pods	1	<u>5.2</u>	IR-4 PR 10046, Test MD15
NY USA/2008	Snap bean/ Hystyle	SC	2	0.11	0.32	Plants w/pods	1	<u>6.0</u>	IR-4 PR 10046, Test NY29
WI USA/2008	Snap bean/ Hystyle	SC	2	0.11	0.4	Plants w/pods	1	<u>4.9</u>	IR-4 PR 10046, Test WI21
OH USA/2008	Snap bean/ Eureka	SC	2	0.11	0.37	Plants w/pods	1	<u>0.01</u>	IR-4 PR 10046, Test OH*12
FL USA/2008	Snap bean/ Dusky	SC	2	0.11	0.38	Plants w/pods	1	<u>1.7</u>	IR-4 PR 10046, Test FL29
CA USA/2008	Snap bean/ Blue Lake274	SC	2	0.11	0.28	Plants w/pods	1	<u>6.2</u>	IR-4 PR 10046, Test CA01
WA USA/2008	Snap bean/ OSU 91G	SC	2	0.11	0.3	Plants w/pods	1	<u>4.5</u>	IR-4 PR 10046, Test WA03
ON Canada/2008	Snap bean/ Bronco	SC	2	0.11	0.3	Plants w/pods	1	<u>5.5</u>	IR-4 PR 10046, Test ON14
ON Canada/2008	Snap bean/ Storm	SC	2	0.11	0.3	Plants w/pods	1	<u>3.8</u>	IR-4 PR 10046, Test ON15
NY USA/2008	pea/Sugar Snap	SC	2	0.11	0.02	Plants w/pods	1	<u>3.8</u>	IR-4 PR 10003, Test NY28
CA USA/2008	pea/Sugar Ann	SC	2	0.11	0.015	Plants w/pods	1	<u>4.9</u>	IR-4 PR 10003, Test CA*25
OR USA/2008	pea/Sugar Sprint	SC	2	0.11	0.04	Plants w/pods	1	<u>2.8</u>	IR-4 PR 10003, Test OR22
ON Canada/2008	pea/Oregon Giant	SC	2	0.11	0.06	Plants w/pods	1	<u>4.4</u>	IR-4 PR 10003, Test ON25
ID USA/2008	pea/Thomas Laxton	SC	2	0.11	49 + 49	Plants w/pods	1	<u>6.4</u>	IR-4 PR 10003, Test ID01
ON Canada/2008	pea/ Progress	SC	2	0.11	37 + 37	Plants w/pods	1	<u>4.3</u>	IR-4 PR 10003, Test ON10
ON Canada/2008	pea/Bolero	SC	2	0.11	37 + 37	Plants w/pods	1	<u>5.3</u>	IR-4 PR 10003, Test ON11
ON Canada/2008	pea/Bolero	SC	2	0.11	37 + 37	Plants w/pods	1	<u>4.8</u>	IR-4 PR 10003, Test ON12
NS Canada/2008	Pea/Wando	SC	2	0.11	37 + 38	Plants w/pods	1	<u>3.4</u>	IR-4 PR 10003, Test NS04
MB Canada/2008	Pea/Mr. Big	SC	2	0.11	58 + 58	Plants w/pods	1	<u>3.0</u>	IR-4 PR 10003, Test MB01

Location/year	Crop variety	Application				Residues			Study trial no.
		FL	No	kg ai/ha	kg ai/hL	Portion analysed	DAT, days	mg/kg	
New South Wales, Australia/2009	Peas/ Sugar Bon	SC	3	0.02	0.005	Foliage	1 6 14	0.29 (1.2) ^a 0.60 (3.3) <u>2.2</u> (5.1)	HAL0802, S1/T2
New South Wales, Australia/2009	Peas/ Sugar Bon	SC	2	0.1	0.03	Foliage	1 6	0.16 (1.0) 2.8 (17.2)	HAL0802, S1/T3
Queensland Australia/2009	Peas/Greenf east	SC	3	0.02	0.005	Empty pods	0 1 3 7 12	0.03 0.02 < 0.01 <u>0.05</u> 0.04	HAL0802, S3/T2
Queensland Australia/2009	Peas/ Greenfeast	SC	3	0.1	0.005	Foliage	1 7 12	0.23 (1.5) 0.12 (0.77) 0.86 (5.6)	HAL0802, S3/T2
Queensland Australia/2009	Peas/ Greenfeast	SC	2	0.1	0.005	Empty pods	0 1 3 7 12	0.39 0.15 0.16 0.19 0.30	HAL0802, S3/T3
Queensland Australia/2009	Peas/ Greenfeast	SC	2	0.1	0.005	Foliage	1 7	0.88 (6.2) 0.52 (3.2)	HAL0802, S3/T3
Tasmania Australia/ 2009–10	Peas/ Resal	SC	3	0.02	0.007	Empty pods	0 1 3 7 14	0.07 0.04 0.04 0.10 <u>0.20</u>	HAL0802, S4/T2
Tasmania Australia/ 2009–10	Peas/Resal	SC	3	0.02	0.007	Foliage	1 7 14	0.26 (2.1) 0.13 (0.73) <u>0.78</u> (2.66)	HAL0802, S4/T2
Tasmania Australia/ 2009–10	Peas/ Resal	SC	2	0.1	0.04	Empty pods	0 1 3 7 14	0.28 0.24 0.24 0.26 0.39	HAL0802, S4/T3
Tasmania Australia/2009–10	Peas /Resal	SC	2	0.1	0.04	Foliage	1 7	0.92 (7.2) 0.48 (2.8)	HAL0802, S4/T3

^a Residue values on a dry weight basis are shown parenthetically. Where no quantifiable levels were found, i.e., the result on a fresh weight is <LOQ, the associated result on a dry weight basis is also expressed as <LOQ (0.01 mg/kg).

Table 15 Results of residue trials conducted with chlorantraniliprole cereal animal feed (IR-4 PR No. 10204).

Location/year	Crop variety	Application				Residues			Study trial no.
		FL	No	kg ai/ha	kg ai/hL	Portion analysed	DAT, days	mg/kg	
Fargo, ND, USA/2009	Wheat/ Glenn	SC	2	0.11	0.08	Forage	1	4.3	ND04
						Hay	1	9.5	
						Straw	1	4.7	
Velva, ND 58790, USA/2009	Wheat/ Faller	SC	2	0.11	0.10	Forage	1	4.4	ND05
						Hay	1	8.6	
						Straw	1	15	
Aurora, SD, USA/2009	Wheat/ Briggs Hard Red	SC	2	0.11	0.06	Forage	1	4.3	No. SD08
						Hay	1	11	
						Straw	1	6.4	
Las Cruces, NM 88005, USA/2010	Wheat/ El Dorado	SC	2	0.11	0.06	Forage	1	4.6	No. NM18
						Hay	1	11	
						Straw	1	4.5	
Fargo, ND, USA/2009	Sorghum/ LM 5001	SC	2	0.11	0.08	Forage	1	2.7	ND02
						Stover	1	3.4	

Location/year	Crop variety	Application				Residues			Study trial no.
		FL	No	kg ai/ha	kg ai/hL	Portion analysed	DAT, days	mg/kg	
Las Cruces, NM USA/2009	Sorghum/DK 28E	SC	2	0.11	0.07-0.08	Forage	1	4.0	NM13
						Stover	1	5.9	
Las Cruces, NM USA/2009	Sorghum/M3838	SC	2	0.12	0.05	Forage	1	3.4	NM19
						Stover	1	4.1	
Velva, ND USA/2009	Barley/Tradition	SC	2	0.12	0.1	Hay	1	9.2	ND01
						Straw	1	14	
Aurora, SD, USA/2009	Barley/Lacey	SC	2	0.12	0.05	Hay	1	5.5	SD07
						Straw	1	3.6	
Kimberly, ID USA/2009	Barley/Camas Spring	SC	2	0.11	0.06	Hay	1	11	ID14
						Straw	1	12	

Table 16 Residues of chlorantraniliprole in rice straw from seed treatment in USA in 2007 (Report DuPont-21999)

Location	Crop variety	Application				Residues		Trial.
		FL	No	mg ai/seed	kg ai/ha	DAT, days	mg/kg	
Cheneyville, LA	Rice/Cocodrie	FS	1	0.1	0.56	127	0.12	No. 1
Cheneyville, LA	Rice/Wells	FS	1	0.1	0.56	123	0.12	No. 2
Cheneyville, LA	Rice/Wells	FS	1	0.1	0.56	116	0.24	No. 3
Washington, LA	Rice/Wells	FS	1	0.1	0.56	122	0.13	No. 4
Washington, LA	Rice/Wells	FS	1	0.1	0.56	122	0.09	No. 5
Washington, LA	Rice/Cocodrie	FS	1	0.1	0.56	122	0.14	No. 6
Washington, LA	Rice/Francis	FS	1	0.1	0.56	122	0.22	No. 7
Wynne, AR	Rice/Wells	FS	1	0.1	0.56	134	0.10	No. 9
Augusta, AR	Rice/Bengal	FS	1	0.1	0.56	138	0.12	No. 10
Magness, AR	Rice/Wells	FS	1	0.1	0.56	143	0.05	No. 11
Newport, AR	Rice/Bengal	FS	1	0.1	0.56	148	0.11	No. 12
Dudley, MO	Rice/Francis	FS	1	0.1	0.56	120	0.02	No. 13
East Bernard, TX	Rice/Cocodrie	FS	1	0.1	0.56	113	0.13	No. 14
East Bernard, TX	Rice/Cocodrie	FS	1	0.1	0.56	120	0.16	No. 15
Richvale, CA	Rice/Calrose	FS	1	0.1	0.56	130	0.05	No. 16
Fresno, CA	Rice/Calrose	FS	1	0.1	0.56	117	0.16	No. 17

FATE OF RESIDUES IN PROCESSING

Rice

Two processing studies were conducted with rice in USA in 2007. Rice seed was treated once at 0.2 mg ai/seed and grain harvested after 148 days were processed using two different procedures (DuPont-21999). The results are shown in Table 17.

Table 17 Processing studies in rice

Matrix	Test No. 12		Test 15		Best estimate (median)
		PF		PF	
Grain	0.048		0.044		
Polished rice (mechanical processing)	0.003	0.07	0.003	0.07	0.11
Polished rice (parboil processing)	0.008	0.16	0.007	0.15	
Bran (mechanical processing)	0.061	1.3	0.11	2.5	1.7
Bran (parboil processing)	0.063	1.3	0.093	2.1	
Hulls (mechanical processing)	0.25	5.3	0.15	3.2	3.2
Hulls (parboil processing)	0.15	3.1	0.11	2.4	

Wheat

One processing study was conducted with wheat in USA in 2009 (IR-4 PR No. 10204, Test No. ND03) The plants were treated twice with a SC formulation at 0.1 kg ai/ha and the grain harvested after one day were processed. The results are shown in Table 18

Table 18 Processing study in wheat

Matrix	mg/kg	PF
Grain	0.225	-
AGF	7.56	33.7
Germ	0.260	1.2
Middlings	0.0647	0.3
Flour	0.0883	0.4
Shorts	0.157	0.7
Bran	0.240	1.1

APPRAISAL

The insecticide chlorantraniliprole was evaluated by the JMPR 2008 (T, R) and 2010 (R). The ADI for chlorantraniliprole is 0–2 mg/kg bw and an ARfD was considered unnecessary. The compound was listed by the Forty-fourth Session of the CCPR (2012) for the evaluation by the 2013 JMPR of residue data for avocados, pomegranates, strawberries and other berries, soya bean, radish, carrots, globe artichokes, wheat, rape seed, sunflower seed, coffee and hops.

The residue definition for compliance with MRL and for dietary intake for plant and animal commodities is chlorantraniliprole. The residue is considered fat-soluble.

Results from supervised residue trials on crops*Berries and other small fruits*

Currently, there is a Codex MRL of 1 mg/kg for chlorantraniliprole in Berries and other small fruits, which replaced the previous MRL of 1 mg/kg in grapes.

In the USA, GAP for chlorantraniliprole in strawberry is for up to 4×0.05 – 0.07 kg ai/ha (7 days interval; total 0.225 kg ai/ha/season). Eight trials conducted in the USA in 2011 at 2×0.11 kg ai/ha (7 days interval) gave residues at 1 day PHI of 0.18, 0.21, 0.22, 0.23, 0.24 (2), 0.40 and 0.68 mg/kg. Eight indoor trials were conducted in southern Europe, where there is no approved use.

Residues of chlorantraniliprole in grapes from 17 trials in Canada and the USA evaluated by the 2008 JMPR complying with GAP of the USA (3×0.07 – 0.11 kg ai/ha and 14 days PHI) were 0.02, 0.04 (3), 0.08, 0.09 (2), 0.11, 0.12, 0.18, 0.20, 0.26, 0.32, 0.34, 0.46, 0.48 and 0.52 mg/kg.

In the USA and Canada, GAP in bushberries (include cranberry and blueberry) is 3×0.07 – 0.11 kg ai/ha and 1 day PHI, total 0.

225 kg ai/ha/season). Seventeen trials were conducted in Canada and USA in cranberry and blueberry using 2 applications of the maximum GAP rate, with residues at 1 day PHI of 0.11, 0.12 (2), 0.13 (2), 0.16, 0.18 (2), 0.21 (2), 0.23, 0.24, 0.29, 0.32, 0.46, 0.75 and 0.84 mg/kg.

Data evaluated by the 2010 JMPR on residues of chlorantraniliprole in caneberries (raspberries and blackberries) from eight trials in Canada and the USA complying with GAP of the USA were: 0.05, 0.09 (2), 0.24, 0.44, 0.48 (2) and 0.51 mg/kg

The Meeting confirms its previous recommendation of a maximum residue level of 1 mg/kg for chlorantraniliprole in berries and other small fruits.

Avocado

The GAP of chlorantraniliprole in avocado in New Zealand is 2×0.09 kg ai/ha (21 days interval) and a 14 day PHI. Two trials conducted in the country according to GAP gave residues in fruit of 0.03 and 0.08 mg/kg. Six other trials conducted at higher or lower GAP gave residues ranging from 0.07 to 0.31 mg/kg at 14 days DAT.

As only two trials were conducted according to GAP, the Meeting could not recommend a maximum residue level for chlorantraniliprole in avocado.

Pomegranate

The GAP of chlorantraniliprole in pomegranate in USA is 3×0.07 – 0.11 kg ai/ha (7 days interval; max. 0.2 kg ai/ha/season) and a 1 day PHI. Five trials conducted in the country according to GAP gave residues of 0.09, 0.10 (2) and 0.12 (2) mg/kg.

The Meeting recommended a maximum residue level of 0.4 mg/kg and a STMR of 0.10 mg/kg for chlorantraniliprole in pomegranate.

Radish tops

Currently, there is a Codex MRL of 20 mg/kg for chlorantraniliprole in leafy vegetables.

In the USA, chlorantraniliprole is registered in root and tuber vegetables at a maximum rate of 4×0.07 kg ai/ha (3 day interval; max of 0.22 kg ai/ha/season) and a 1 day PHI. In six trials conducted in radish at 2×0.11 kg ai/ha gave residues in radish tops at a 1 day PHI of 3.9, 7.7, 10, 11, 19 and 22 mg/kg.

The Meeting recommended a maximum residue level of 40 mg/kg and a STMR of 10.5 mg/kg for chlorantraniliprole in radish leaves (including radish tops).

The Meeting agreed to withdraw its previous recommendation of 20 mg/kg for leafy vegetables for 20 mg/kg in leafy vegetables, except radish leaves.

Legume vegetables

In Italy, chlorantraniliprole is registered in beans at up to 2×0.04 kg ai/ha with a 3 day PHI. In five trials conducted in France, Italy and Spain in 2008/2009, according to this GAP, residues in fresh bean pods with seeds were 0.15, 0.16, 0.40 (2) and 0.41 mg/kg. Five residue trials conducted in southern Europe according to the Italian GAP and submitted to the 2010 JMPR gave residues in fresh pods with seeds of 0.08, 0.09, 0.12, 0.16 and 0.25 mg/kg.

Trials conducted in southern Europe according to GAP (n=9) gave residues in bean pods with seeds of 0.08 (2), 0.12, 0.15, 0.16 (2), 0.40 (2) and 0.41 mg/kg.

In USA, the rate for legume vegetables is up to 4×0.07 kg ai/ha (max. of 0.225 kg ai/ha/season) and a 1 day PHI. In nine trials conducted in the USA and Canada (2008) at 2×0.11 kg ai/ha, residues in bean pods with seeds were: < 0.01, 0.10, 0.12 (3), 0.14 (2), 0.16 and 0.41 mg/kg.

In Australia, GAP for legume vegetable is 3×0.02 kg ai/ha and a 1 day PHI. In two trials conducted according to GAP, residues in bean pods with seeds were 0.08 (2) mg/kg.

Based on the European trials, the Meeting recommended a maximum residue level of 0.8 mg/kg and a STMR of 0.16 mg/kg for chlorantraniliprole in beans, except broad bean and soya bean (green pods and immature seeds).

In four trials conducted in peas in the USA and Canada according to GAP, residues in pea pods with seeds were 0.45, 0.48, 0.61 and 0.64 mg/kg.

In three trials conducted in Australia according to the Australian GAP for legume vegetables (3×0.02 kg ai/ha, 1 day PHI), residues in pea pods with seeds were 0.04, 0.06 and 0.47 mg/kg.

Based on the US and Canadian trials, and with the support of the Australian trials, the Meeting recommended a maximum residue level of 2 mg/kg and a STMR of 0.545 mg/kg for chlorantraniliprole in Peas (pods and succulent = immature seeds).

In six trials conducted in the USA and Canada, according to GAP, residues in pea seed were 0.01, 0.02 (2) and 0.03 (3) mg/kg. In two trials conducted in Australia according to GAP, residues in pea seed were < 0.01 (2) mg/kg.

Based on trials conducted in Canada and the USA, and with the support of the Australian trials, the Meeting recommends a maximum residue level of 0.05 mg/kg and a STMR of 0.025 mg/kg for chlorantraniliprole in peas, shelled.

Soya bean, dry

The GAP chlorantraniliprole in soya bean in Brazil is 2×0.01 kg ai/ha, and a PHI of 21 days. Four trials conducted in 2010 according to GAP gave residues of < 0.01 mg/kg (4).

Four trials submitted to the 2010 JMPR used a furrow application (0.1 kg ai/ha) followed by two applications at the GAP rate gave residues at 21 days PHI of 0.10, 0.11 (2) and 0.12 mg/kg.

As only four trials according to GAP were submitted, the Meeting could not recommend a maximum residue level for chlorantraniliprole in soya beans.

Root and tuber vegetables

The current Codex MRL for chlorantraniliprole in Root and tuber vegetables is 0.02 mg/kg, following the recommendation made by the 2008 JMPR based on rotation crop data (0.01 mg/kg on radish root) and foliar trials on potatoes (< 0.01 mg/kg, n=27).

In the USA, chlorantraniliprole is registered in Root and tuber vegetables at a maximum rate of 4×0.07 kg ai/ha (3 days interval; max of 0.22 kg ai/ha/season) and a 1 day PHI. Six trials conducted in radish at 2×0.11 kg ai/ha gave residues at a 1 day PHI of 0.03, 0.04, 0.05, 0.06, 0.08 and 0.26 mg/kg in the radish root. The Meeting agreed that the contribution from previous use on the rotation regime would not significantly impact the final residues.

The Meeting estimates a maximum residue level of 0.5 mg/kg and a STMR of 0.055 mg/kg for chlorantraniliprole in radish.

Chlorantraniliprole is registered to be used in Italy in carrots at up to 2×0.04 kg ai/ha (7–10 days interval) and 21 days PHI. Nine trials conducted in southern Europe in 2009/2010 according to this GAP gave residues of < 0.004 (3), 0.004, 0.005 (2), 0.025, 0.03, and 0.036 mg/kg. Eight trials conducted in northern Europe at the same rate gave residues of < 0.004 (5) 0.01, 0.021, and 0.027 mg/kg. Residues in Europe can be combined as < 0.004 (8), 0.004, 0.005 (2) 0.01, 0.021, 0.025, 0.027, 0.03 and 0.036 mg/kg.

Considering the contribution from rotation crops (0.01 mg/kg), the Meeting estimated a maximum residue level of 0.08 mg/kg and a STMR of 0.02 mg/kg for chlorantraniliprole in carrots.

The Meeting agreed to replace its previous recommendation of 0.02 mg/kg for chlorantraniliprole in Root and tuber vegetables for 0.02 mg/kg in Root and tuber vegetables, except carrot and radish.

Globe artichoke

Chlorantraniliprole is registered for use in Italy in globe artichoke at 2×0.03 kg ai/ha (14 days interval) and a 3 day PHI. Four trials conducted in southern Europe at this GAP gave residues of 0.06, 0.07, 0.08 and 0.16 mg/kg.

The product is registered in the USA at 4×0.05 –0.11 kg ai/ha (4 days interval; max of 0.22 kg ai/ha/season) and a 3 day PHI. Four trials conducted with 2 applications of the GAP rate gave residues of 0.47, 0.53, 0.59 and 0.69 mg/kg.

Based on the US trials, the Meeting recommended a maximum residue level of 2 mg/kg and a STMR of 0.56 for chlorantraniliprole in globe artichoke.

Rice

Chlorantraniliprole is registered to be used in Brazil in rice as a foliar treatment at 1×0.03 kg ai/ha and a 15 day PHI. In eight trials conducted in the country according to GAP, residues were < 0.01, 0.02, 0.03, 0.10, 0.13 (2) and 0.16 (2) mg/kg.

In the USA, the product is registered as seed treatment at 0.06 mg ai/seed (0.09 kg ai/ha). Sixteen trials conducted at 0.10 mg ai/seed (0.56 kg ai/ha) gave residues ranging from 0.01 to 0.09 mg/kg. Three trials conducted within GAP gave residues in the grain of 0.01 (2) and 0.02 mg/kg.

Based on the Brazilian foliar trials conducted according to GAP, the Meeting estimated a maximum residue level of 0.4 mg/kg and a STMR of 0.115 mg/kg for chlorantraniliprole in rice grain.

Two processing studies were submitted to the Meeting. In each, two different procedures were used to produce polished rice, with processing factors of 0.07 (2), 0.15 and 0.16, median of 0.11. This PF was applied to the residue data on rice grain to derive data on polish rice.

The Meeting estimates a maximum residue level of 0.04 mg/kg and a STMR of 0.013 mg/kg for chlorantraniliprole in polished rice.

Cereals, except rice

Currently, the Codex MRL for chlorantraniliprole in cereals is 0.02 mg/kg, following the recommendation made by the 2008 JMPR based on rotation crop data.

In the USA, three trials were conducted in barley, three in sorghum and five trials were conducted in wheat using 2×0.11 kg ai/ha. Residues in samples harvested at 1 DAT ranged from 0.19 to 2.2 mg/kg. As the compound is not registered for use in these crops in the USA, no estimations were made.

The Meeting replaced its previous recommendation of 0.02 mg/kg for cereals for 0.02 mg/kg in cereals, except rice.

Rape and sunflower seeds

Chlorantraniliprole is registered in Canada for oilseeds, except cotton, at 3×0.025 –0.07 kg ai/ha (max of 0.2 kg ai/ha/season) and a 1 day PHI. Twelve trials were conducted in the USA and Canada in rape seed (canola) and sunflower according to this GAP.

Six trials conducted in rape seed (canola) gave residues at of 0.14, 0.23, 0.25, 0.34, 0.83 and 1.0 mg/kg.

Six trials conducted in sunflower gave residues at of 0.03, 0.12, 0.16, 0.21, 0.79 and 0.82 mg/kg.

The Meeting estimates a maximum residue level of 2 mg/kg for chlorantraniliprole in rape seed and sunflower seed.

The Meeting estimates a STMR of 0.295 mg/kg for chlorantraniliprole in rape seed and of 0.185 mg/kg for sunflower seed.

Coffee

Chlorantraniliprole is registered in Brazil for use on coffee at 2×0.03 kg ai/ha with a 21 day PHI. Eight trials were conducted in Brazil matching this GAP, giving residues of < 0.01, 0.01 (3), 0.02 (3) and 0.03 mg/kg.

The Meeting recommended a maximum residue level of 0.05 mg/kg and a STMR of 0.015 mg/kg for chlorantraniliprole in coffee.

Hops

Chlorantraniliprole is registered in the USA for use in hops at 4×0.072 kg ai/ha (max. of 0.22 kg ai/ha/season) with a 0 day PHI. Four trials conducted at GAP (2×0.1 kg ai/ha) gave residues in dried cones of 7.6, 8.9, 13 and 19 mg/kg.

The Meeting estimated a maximum residue level of 40 mg/kg and a STMR of 10.9 mg/kg for chlorantraniliprole in hops, dry.

Animal feeds

Three Australian trials conducted according to GAP gave residues at a 1 day PHI in bean and pea foliage of 0.31, 0.78 and 2.2 mg/kg. In two pea trials, residues in empty pods were 0.05 and 0.20 mg/kg.

Five trials conducted in southern Europe in beans according to Italian GAP gave residues at a 3 day PHI in bean plants without pods of 2.4, 4.3, 4.5, 6.6 and 6.8, mg/kg.

The US label has no additional information covering the grazing of legume vegetables. Nineteen trials conducted in Canada and USA according to US GAP (4×0.07 kg ai/ha; max. of 0.225 kg ai/ha/season) gave residues at a 1 day PHI in bean or pea plants with pods of 0.01, 1.7, 2.8, 3.0, 3.4, 3.8, 3.8, 4.3, 4.4, 4.5, 4.8, 4.9, 4.9, 5.2, 5.3, 5.5, 6.0, 6.2 and 6.4 mg/kg.

Based on Canadian and US data, the Meeting estimated a median residue of 4.4 mg/kg and a highest residue of 6.4 mg/kg for chlorantraniliprole in bean forage (green) and pea vines (green).

In ten trials conducted in wheat, sorghum and barley in the USA, residues were determined in forage, hay and straw. However, as these are not registered uses for chlorantraniliprole in USA, the data was not considered further.

Sixteen trials conducted in rice after seed treatment at a higher than GAP rate in USA, residues in straw ranged from 0.05 to 0.24 mg/kg.

Fate of residues during processing

At the present Meeting, a STMR of 0.115 mg/kg was estimated for rice grain. Two studies were conducted in rice.

The best Pf estimated for rice bran (n=4) was 1.7, leading to an estimated STMR-P of 0.196 mg/kg.

The best Pf estimated for rice hull (n=4) was 3.3. For animal dietary burden purposes, a median of 0.368 mg/kg was calculated for rice hull.

*Residues in animal commodities**Farm animal dietary burden*

The Meeting estimated the dietary burden of chlorantraniliprole in farm animals on the basis of the OECD Animal Feed data published in the 2009 FAO Manual, the STMR, STMR-Ps or highest residue levels estimated at the present and previous JMPR Meetings (2008 and 2010). Dietary burden calculations are provided in Annex 6 of the 2013 Report.

Livestock dietary burden for chlorantraniliprole, ppm of dry matter diet

Commodity	US-Canada		EU		Australia		Japan	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	7.6	3.4	19.9	10.7	31.7 ^a	15.7 ^c	3.5	1.5
Dairy cattle	13.4	6.0	22.4 ^b	10.1	26.8	13.1 ^d	15.8	6.7
Poultry - broiler	0.06	0.06	0.06	0.032	0.11	0.11	1.06	0.55
Poultry - layer	0.06	0.06	4.42 ^c	2.51 ^f	0.11	0.11	0.05	0.05

^a Highest maximum beef or dairy cattle dietary burden suitable for maximum residue level estimated for mammalian tissues

^b Highest maximum dairy cattle dietary burden suitable for maximum residue level estimated for mammalian milk

^c Highest mean beef or dairy cattle dietary burden suitable for STMR estimated for mammalian tissues.

^d Highest mean dairy cattle dietary burden suitable for STMR estimated for milk.

^e Highest maximum poultry dietary burden suitable for maximum residue level estimated for poultry tissues and eggs.

^f Highest mean poultry dietary burden suitable for STMR estimated for poultry tissues and eggs.

Animal commodity maximum residue level

The dietary burden estimated by the present Meeting for cattle is similar to that estimated by the 2010 JMPR and would not impact the previous recommendations for chlorantraniliprole in edible offal (mammalian), meat (from mammals other than marine mammals) and milk fats.

The calculated maximum poultry dietary burden suitable for maximum residue level estimated for poultry tissues and eggs was 4.4 ppm, about 2.4 times higher than the previous estimation. The calculated dietary burden for STMR estimation is 0.007 ppm.

In a metabolism study evaluated by the 2008 JMPR, poultry laying hens were dosed with [¹⁴C]chlorantraniliprole for 14 days at 10 ppm in the diet. Residues found in eggs, muscle, liver and skin/fat and the residues expected in poultry commodities based on the calculated animal burden are shown in the table below. The levels which the estimations were based are in bold.

	Feed level, ppm, for	Residue, mg/kg			
	Tissues and eggs residues	Eggs	Muscle	Liver	Fat
Highest residue level, hens					
Feeding study	10	0.308	0.0008	0.0196	0.009
Calculated burden	4.42	0.135	0.0004	0.008	0.004
STMR, hens					
Feeding study	10	0.282	0.0008	0.0196	0.009
Calculated burden	2.5	0.07	0.0002	0.005	0.002

The Meeting confirms its previous maximum residue level recommendation of 0.01* mg/kg for chlorantraniliprole in poultry meat (fat) and poultry edible offal, and estimated a STMR of 0 for poultry meat (fat) and 0.005 for poultry edible offal.

The Meeting estimated a maximum residue level of 0.2 mg/kg and a STMR of 0.07 for chlorantraniliprole in eggs.

The meeting withdraws its previous recommendation of 0.1 mg/kg for chlorantraniliprole in eggs.

RECOMMENDATIONS

Definition of the residue for compliance with for compliance with maximum residue levels and estimation of dietary intake in plant and animal commodities: *chlorantraniliprole*.

CCN	Commodity name	Maximum residue level (mg/kg)		STMR, STMR (P) mg/kg
		New	Previous	
VS 0620	Artichoke, globe	2		0.56
VP 0061	Beans, except broad bean and soya bean (green pods and immature seeds)	0.8		0.16
VR 0577	Carrot	0.08		0.02
GC 0080	Cereal grains	W	0.02	

CCN	Commodity name	Maximum residue level (mg/kg)		STMR, STMR (P) mg/kg
		New	Previous	
GC 0080	Cereal grains, except rice	0.02		0.01
SB 0716	Coffee beans	0.05		0.015
PE 0112	Eggs	0.2	0.1	0.07
DH 1100	Hops, dry	40		10.9
VL 0053	Leafy vegetables	W	20	
VL 0053	Leafy vegetables, except radish leaves	20		
VP 0063	Peas (pods and succulent = immature seeds)	2		0.545
VP 0064	Peas, shelled (succulent seeds)	0.05		0.025
FL 0355	Pomegranate	0.4		0.11
PM 0110	Poultry meat	0.01*	0.01*	0
PO 0111	Poultry , edible offal of	0.01*	0.01*	0.005
VR 0494	Radish	0.5		0.055
VL 0494	Radish leaves (includes radish tops)	40		10.5
SO 0495	Rape seed	2		0.295
GC 0649	Rice	0.4		0.115
	Rice, polished	0.04		0.013
	Rice, bran			0.196
VR 0075	Root and tuber vegetables	W	0.02	
VR 0075	Root and tuber vegetables, except carrot and radish	0.02		0.01
SO 0702	Sunflower seed	2		0.185

DIETARY RISK ASSESSMENT

Long-term intake

The ADI for chlorantraniliprole is 0–2 mg/kg bw. The International Estimated Daily Intakes (IEDI) for chlorantraniliprole was estimated for the 13 GEMS/Food cluster diets using the STMR or STMR-P values estimated by the current and previous JMPR. The results are shown in Annex 3 of the 2013 Report. The IEDI was 0% of the maximum ADI. The Meeting concluded that the long-term intake of residues of chlorantraniliprole from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The 2008 JMPR decided that an ARfD for chlorantraniliprole was unnecessary. The Meeting therefore concluded that the short-term intake of chlorantraniliprole is unlikely to present a public health concern.

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CHLORPYRIFOS-METHYL (090)

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APPRAISAL

Chlorpyrifos-methyl was evaluated for residues by the 2009 JMPR under the periodic review program, when a recommendation of 3 mg/kg for wheat, barley and maize was made based on post-harvest use. The long-term dietary risk assessment for the compound indicated an exceedance of up to 140% of the ADI of 0.01 mg/kg bw, with maize accounting for about 73% of the IEDI. This recommendation was made using an alternative Spanish GAP (2.2 g ai/ton).

The 2012 JMPR received a new Spanish label indicating that the post-harvest use of chlorpyrifos-methyl was no longer allowed on maize. The 2012 Meeting withdrew its previous recommendation of 3 mg/kg (Po) on maize, and the new long-term dietary risk assessment indicated that the highest IEDI was 60% of the ADI.

The 2013 JMPR received a request from CCPR to reconsider the current recommendation of chlorpyrifos-methyl in wheat and barley of 3 mg/kg (Po). The Meeting received a new label from Australia for post-harvest use of chlorpyrifos-methyl on cereals, except maize at up to 5 g ai/ton (for 3 to 6 months protection). Residues coming from post-harvest trials evaluated by the 2009 JMPR conducted in wheat and barley according to Australian GAP ranged from 1.6, 1.9 (2), 2.2, 2.3, 2.4, 2.6, 2.9 (2), 3.0 (2), 3.1 (2), 3.2 (3), 3.3, 3.5 and 4.7 mg/kg (n=19).

Processing studies on wheat evaluated by the 2009 JMPR gave processing factors (PF) of 0.25 for flour, 1 for whole meal, 1.9 for germ, 2.45 for bran, 0.05 for white bread, and 0.48 for whole bread. Based on a STMR of 3 mg/kg, the Meeting estimated a STMR-P of 0.75 mg/kg for wheat flour, 3 mg/kg for whole meal wheat, 5.7 mg/kg for wheat germ, 7.35 mg/kg for wheat bran, 0.15 mg/kg for white bread and 1.44 in whole meal bread. The Meeting also estimated a HR-P of 11.5 mg/kg for wheat bran, unprocessed, of 10.8 mg/kg in wheat germ, and 4.7 in wheat whole meal. These estimations were extended to triticale processed products. A processing study on barley lead to a PF of < 0.01 for beer and a STMR-P of 0.03 was estimated for beer.

As no processing studies were submitted on rice, the Meeting considered the published study conducted by Cogburn *et al.* (1990). Harvested rice grain were treated with 6 or 12 mg/kg chlorpyrifos-methyl and stored for 1, 6 and 12 weeks. After storage, treated grain was processed to brown rice (husked) or milled to produce polished rice and bran. The mean processing factors (n=6) were 0.22 for husked rice, 0.033 for polished rice, 1.7 for rice bran and 0.012 for cooked polish rice. The data are shown in Table 1.

Table 1 Residues of chlorpyrifos-methyl in rice grain and processed commodities (Cogburn *et al.* (1990))

Rice grain	Husked rice		Polished rice		Rice bran		Cooked polish rice	
Residues, mg/kg	Residues, mg/kg	PF	Residues, mg/kg	PF	Residues, mg/kg	PF	Residues, mg/kg	PF
4.45	0.87	0.20	0.14	0.03	6.7	1.5	0.07	0.016
3.23	0.75	0.23	0.07	0.02	4.7	1.4		
2.3	0.58	0.25	0.15	0.06	5.7	2.5	0.06	0.026
9.9	1.85	0.19	0.25	0.02	15.3	1.5	0.08	0.008
8.3	1.99	0.24	0.18	0.02	10.3	1.2	0.04	0.004
7.43	1.61	0.22	0.28	0.04	13.3	1.8	0.04	0.005
Mean of PF		0.22		0.034		1.67		0.012

The Meeting agreed to estimate a maximum residue level of 5 mg/kg, a STMR of 3 mg/kg and a HR of 4.7 mg/kg for chlorpyrifos-methyl in cereals, except maize and rice

Rice grain is not a trade commodity. Hence the Meeting agrees to use the residue data for wheat and barley according to Australian GAP and the processing factors estimated for husked rice and polished rice to estimate maximum residue levels, STMR-Ps and HR-Ps for these commodities.

The Meeting estimated a maximum residue level of 1.5 mg/kg for rice, husked and of 0.2 mg/kg for rice, polished.

The Meeting estimated a STMR-P of 0.661 mg/kg for husked rice, of 0.101 mg/kg for polished rice, of 5.0 mg/kg for rice bran and of 0.036 mg/kg for cooked polished rice

The Meeting estimated a HR of 1.04 mg/kg for rice, husked of 0.15 mg/kg for rice, polished, of 7.8 mg/kg for rice bran and of 0.056 mg/kg for cooked polished rice.

The Meeting withdrew its previous recommendation of 3 mg/kg for chlorpyrifos-methyl in barley and wheat.

RECOMMENDATION

Residues: For plant and animal commodities is chlorpyrifos-methyl for compliance with the MRL and for the estimation of the dietary intakes.

CCN	Commodity name	Recommended maximum residue level (mg/kg)		STMR (P) mg/kg	HR (P) mg/kg
		New	Previous		
GC 0640	Barley	W	3		
GC 0080	Cereals, except maize and rice	5 Po		3	4.7
CM 0649	Rice, husked	1.5 Po		0.66	1.04
CM 1205	Rice, polished	0.2 Po		0.101	0.15
GC 0654	Wheat	W	3		
	Barley beer			0.03	
CM0654	Rice bran, unprocessed				7.8
	Rice, polished, cooked			0.036	0.056
CF 1211	Wheat flour			0.5	
CF 1210	Wheat germ			5.7	10.8
CF 1212	Wheat wholemeal			3	4.7
CM 0654	Wheat bran, unprocessed			7.35	11.5
CP 1211	White bread			0.15	
CP 1212	Wholemeal			1.44	

DIETARY RISK ASSESSMENT

Long-term intake

The IEDI of chlorpyrifos-methyl based on the STMRs estimated by this and previous Meetings for the 13 GEMS/Food regional diets were 0-110% of the maximum ADI of 0–0.01 mg/kg bw (see Annex 3 of the Report).

The highest % of the ADI (110%) was found in the Cluster diet J, for which 95% of the IEDI was from the consumption of millet and sorghum (include raw grain, flour and beer for both commodities). Processing studies on other cereal grains treated with chlorpyrifos-methyl have shown that residues decrease during processing, including cooking grain in water. It is expected that the fate of residues during processing will be similar for millet and sorghum. The Meeting concluded that the long-term dietary intake of residues of chlorpyrifos-methyl are unlikely to present a public health concern.

Short-term intake

An ARfD for chlorpyrifos-methyl is 0.1 mg/kg bw. The International Estimated Short-Term Intake (IESTI) for chlorpyrifos-methyl was calculated for the plant commodities for which STMRS, HRs and maximum residue levels were estimated by the current Meeting and for which consumption data were available. The results are shown in Annex 4. The IESTI represented a maximum of 10% of the ARfD for husked rice. The Meeting concluded that the short-term intake of chlorpyrifos-methyl residues from uses considered by the current Meeting was unlikely to present a public health concern.

REFERENCES

Cogburn, Robert R.; Simonaitis, R. A.; Webb, B. D.
Fate of Malathion and Chlorpyrifos Methyl in Rough Rice and Milling Fractions Before and After Parboiling and Cooking.
Journal of Economic Entomology, 1 August 1990, vol. 83, no. 4, pp. 1636-1639(4)

CYANTRANILIPROLE (263)

The first draft was prepared by Mr. David Lunn New Zealand Food Safety Authority, Wellington, New Zealand

EXPLANATION

Cyantraniliprole is a diamide insecticide with a mode of action (ryanodine receptor activation) similar to chlorantraniliprole and flubendiamide. It has root systemic activity with some translaminar movement and is effective against the larval stages of lepidopteran insects; and also on thrips, aphids, and some other chewing and sucking insects.

Authorisations exist for the use of cyantraniliprole in Canada, Columbia, Malaysia, New Zealand, Vietnam and the CLISS countries in West Africa. Authorisations are also being progressed in Australia, Europe and USA under an OECD Joint Review exercise.

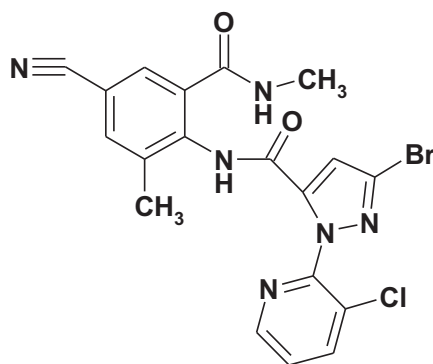
Cyantraniliprole was scheduled by the Forty-fourth Session of the CCPR as a new compound for consideration by the 2013 JMPR. Residue and analytical aspects of cyantraniliprole were considered for the first time by the present meeting. The manufacturer submitted studies on metabolism, analytical methods, supervised field trials, processing, freezer storage stability, environmental fate in soil and rotational crop residues.

In this evaluation, the values presented in the tables are as reported in the various studies, but in the accompanying text, they have generally been rounded to two significant digits. Abbreviations have also been used for the various cyantraniliprole metabolites mentioned in the study reports. These include:

IN-F6L99	3-Bromo-N-methyl-1 <i>H</i> -pyrazole-5-carboxamide
IN-HGW87	N-[2-(Aminocarbonyl)-4-cyano-6-methylphenyl]-3-bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazole-5-carboxamide
IN-J9Z38	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-3,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarbonitrile
IN-JCZ38	4-[[[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]carbonyl]amino]-N',5-dimethyl-1,3-benzenedicarboxamide
IN-K7H19	4-[[[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]carbonyl]amino]-5-methyl-1,3-benzenedicarboxamide
IN-MLA84	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-1,4-dihydro-8-methyl-4-oxo-6-quinazolinecarbonitrile
IN-MYX98	3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-[(hydroxymethyl)amino]carbonyl]-6-methylphenyl]-1 <i>H</i> -pyrazole-5-carboxamide
IN-N5M09	6-Chloro-4-methyl-1 <i>H</i> -pyrido[2,1- <i>b</i>]quinazoline-2-carbonitrile
IN-N7B69	3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-(hydroxymethyl)-6-[(methylamino)carbonyl]phenyl]-1 <i>H</i> -pyrazole-5-carboxamide

IDENTITY

ISO common name:	Cyantraniliprole
Code number	DPX-HGW86, SYN545377
IUPAC name:	3-bromo-1-(3-chloro-2-pyridyl)-4'-cyano-2'-methyl-6'-(methylcarbamoyl)pyrazole-5-carboxanilide
Chemical Abstracts name:	3-bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-methyl-6-[(methylamino)carbonyl]phenyl]-1H-pyrazole-5-carboxamide
CAS number	736994-63-1
CIPAC number	not allocated
Molecular mass:	473.72 g/mol
Molecular formula	C ₁₉ H ₁₄ BrClN ₆ O ₂
Structural formula:	

**PHYSICAL AND CHEMICAL PROPERTIES***Pure active ingredient*

Property	Findings			Reference
Test Item	DPX-HGW86-209 (98.4% purity)	DPX-HGW86-412 (97% purity)	DPX-HGW86-141 (93.3% purity)	
Melting point	217-219 °C			DP-27440
Boiling point	232 °C			DP-27440
Relative density (20°C)	1.497	1.384	1.496	DP-18863 DP-27440
Vapour pressure (extrapolated)	5.133 × 10 ⁻¹⁵ Pa (20 °C) 1.787 × 10 ⁻¹⁴ Pa (25 °C) < 6.15 × 10 ⁻⁸ Pa (80 °C)			DP-17052
Henry's law constant (calculated)	1.7 × 10 ⁻¹³ Pa m ³ mol ⁻¹ (20 °C)			DP-18861
Appearance	white powder, no noticeable odour			DP-18863 DP-27440
pH (1% dispersion)	5.61			DP-19177

Property	Findings						Reference
Test Item	DPX-HGW86-209 (98.4% purity)		DPX-HGW86-412 (97% purity)		DPX-HGW86-141 (93.3% purity)		
Solubility in water (20 °C)	pH 4	17.43 mg/L					DP-17050
	pH 7	12.33 mg/L					
	pH 9	5.94 mg/L)					
	In pure (Milli-RO) water:						
	pH 7.2	14.23 mg/L					
Solubility in organic solvents (20°C)	acetone	6.54 g/L					DP-27447
			ethyl acetate	1.96 g/L			
			dichloromethane	5.05 g/L			
			n-octanol	0.79 g/L			
			methanol	4.73 g/L			
			n-hexane	0.00007 g/L			
			o-xylene	0.29 g/L			
			acetonitrile	2.45 g/L			
n-Octanol/water partition coefficient	log P _{ow} 1.94 at 22 °C (shake flask method) Not pH-dependant (pH 4–9)						DP-17054
Hydrolysis (sterile buffer solutions, [cyano- ¹⁴ C] and [pyrazole carbonyl- ¹⁴ C] radiolabels	Hydrolysis of cyantraniliprole (99% purity) is pH and temperature dependant:						DP-17058
		DT ₅₀ (days)			DT ₉₀ (days)		
		15 °C	25 °C	35 °C	15 °C	25 °C	35 °C
	pH 4	362	212	55.2	1204	705	183
	pH 7	126	30.3	7.51	417	101	25
	pH 9	3.1	0.85	0.58	10.3	2.82	1.91
	IN-J9Z38 is the major hydrolysis product accounting for up to 28% AR (pH 4), 89% AR (pH 7) and 98% AR (pH 9). Estimated degradation rates:						
		DT ₅₀ (days) @ 35 °C			DT ₉₀ (days) @ 35 °C		
	pH 7	227			755		
	pH 9	376			1248		
Photolysis [CN- ¹⁴ C] and [PC- ¹⁴ C] radiolabels purity > 98%	Cyantraniliprole is rapidly degraded by photolysis. Degradation rates in natural water and pH 4 sterile buffer at 25 °C, exposed to continuous artificial sunlight for 15 days are:						DP-17060
		DT ₅₀ (days)			DT ₉₀ (days)		
	pH 4 buffer	0.17			0.57		
	natural water	0.22			0.72		
	Degradation products include four major (> 5% AR) degradation products (IN-NXX69, IN-QKV54, IN-NXX70, IN-QKV55).						
	Quantum yield: (φ)=1.195 × 10 ⁻⁴ molecules degraded/photon						
Dissociation constant	pKa=8.8 at 20 °C (pH range of 2–11, wavelength of 316 nm)						DP-19176

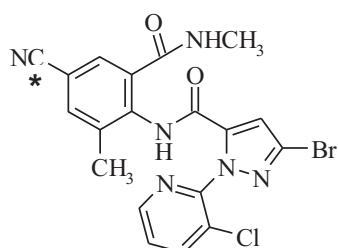
Formulations

Formulations of cyantraniliprole are available for use as foliar applications and soil or seed treatments.

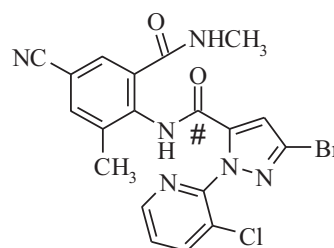
Formulation type	Active substance/s and content	Application type
OD (Oil Dispersion)	Cyantraniliprole 100 g/L	Foliar applications
SC (Soluble Concentrate)	Cyantraniliprole 200 g/L	Soil and seed treatments
FS (Flowable suspension)	Cyantraniliprole 625 g/L	Seed treatment

METABOLISM AND ENVIRONMENTAL FATE

The Meeting received cyantraniliprole metabolism studies on animals (rats, lactating goats and laying hens), plants, soil and rotational crops. Cyantraniliprole radiolabelled on the 4-cyano or the pyrazole carbonyl groups were used in these studies. The label positions are given below:



[CN-¹⁴C]-cyantraniliprole (CN-label)
*=location of the radiolabel

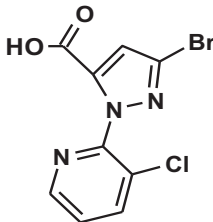
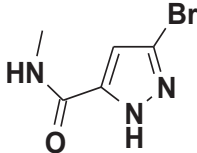
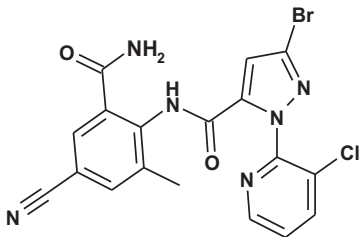
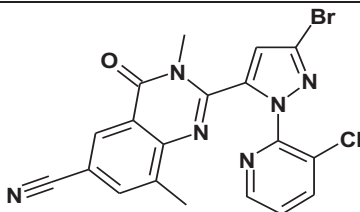
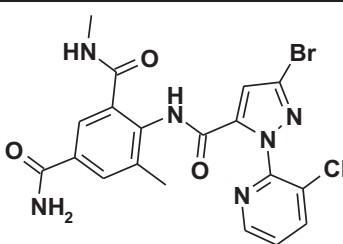
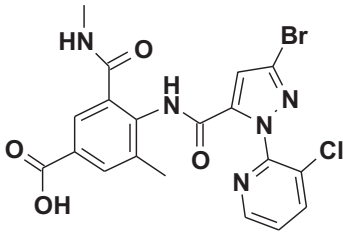


[PC-¹⁴C]-cyantraniliprole (PC-label)
#=location of the radiolabel

Major metabolites identified in these studies and discussed in this evaluation are listed below.

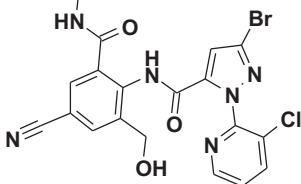
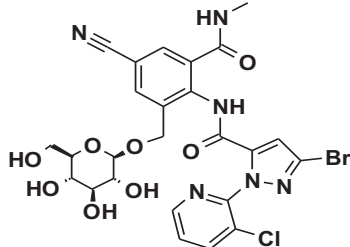
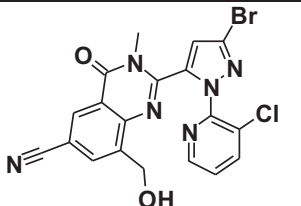
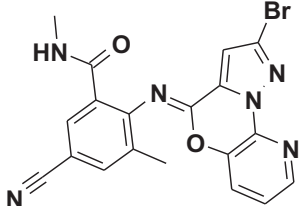
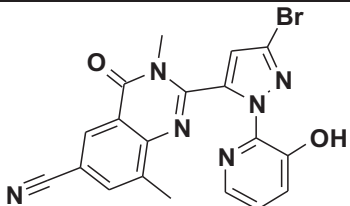
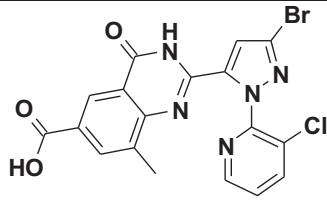
Table 1 Major cyantraniliprole metabolites identified in plant, animal and soil matrices

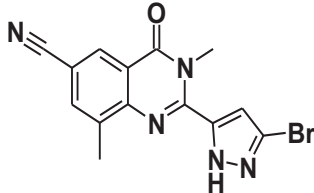
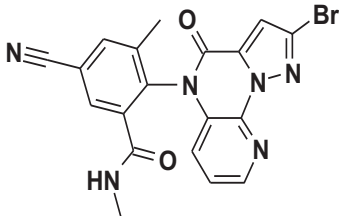
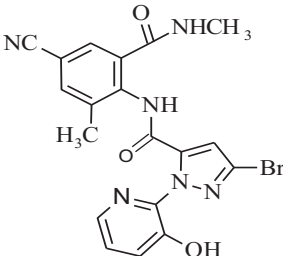
Codes	Names	Molecular formula	Occurrence
DPX-HGW86	3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-methyl-6-[(methylamino)carbonyl]phenyl]-1H-pyrazole-5-carboxamide		sediment soil hydrolysis photolysis plants rat livestock water
Bis hydroxy DPX-HGW86	3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-(hydroxymethyl)-6-[[[(hydroxymethyl)amino]carbonyl]phenyl]-1H-pyrazole-5-carboxamide		rat poultry

Codes	Names	Molecular formula	Occurrence
IN-DBC80	3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazole-5-carboxylic acid		Soil rat urine livestock
IN-F6L99	3-Bromo-N-methyl-1 <i>H</i> -pyrazole-5-carboxamide		soil high temperature hydrolysis
IN-HGW87	N-[2-(Aminocarbonyl)-4-cyano-6-methylphenyl]-3-bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazole-5-carboxamide		Plants rat livestock
IN-J9Z38	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-3,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarbonitrile		Sediment degradation soil hydrolysis photolysis plants livestock rat
IN-JCZ38	4-[[[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]carbonyl]amino]-N'3',5-dimethyl-1,3-benzenedicarboxamide		Sediment degradation soil plants livestock
IN-JSE76	4-[[[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]carbonyl]amino]-3-methyl-5-[(methylamino)carbonyl]benzoic acid		Sediment degradation soil plants livestock

Codes	Names	Molecular formula	Occurrence
IN-K5A77	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-3,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarboxamide		Sediment degradation soil plants livestock
IN-K5A78	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-3,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarboxylic acid		Sediment degradation soil plants livestock
IN-K5A79	3-(Aminocarbonyl)-4-[[[3-bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]carbonyl]amino]-5-methylbenzoic acid		Sediment degradation soil plants livestock
IN-K7H19	4-[[[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]carbonyl]amino]-5-methyl-1,3-benzenedicarboxamide		Soil plants livestock
IN-M2G98	3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazole-5-carboxylic acid, amide		Soil degradation
IN-MLA84	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-1,4-dihydro-8-methyl-4-oxo-6-quinazolinecarbonitrile		Plants livestock rat

Codes	Names	Molecular formula	Occurrence
IN-MLA84 carboxylic acid	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-6-cyano-1,4-dihydro-4-oxo-8-quinazolinecarboxylic acid		Plants rat poultry
Hydroxy-IN- MLA84	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-3,4-dihydro-8-(hydroxymethyl)-4-oxo-6-quinazolinecarbonitrile		Poultry
Hydroxy-IN- MLA84 glucoside	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-8-[(β-D-glucopyranosyloxy)methyl]-1,4-dihydro-4-oxo-6-quinazolinecarbonitrile		Plants
Hydroxy-IN- MLA84 glucuronide	[2-[3-bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-6-cyano-1,4-dihydro-4-oxo-8-quinazolinyl]methyl β-D-glucopyranosiduronate		Rats
IN-MYX98	3-Bromo-1-(3-chloro-2-pyridinyl)- <i>N</i> -[4-cyano-2-[(hydroxymethyl)amino]carbonyl]-6-methylphenyl]-1 <i>H</i> -pyrazole-5-carboxamide		Plants livestock rat
IN-N5M09	6-Chloro-4-methyl-1 <i>H</i> -1-oxo-1 <i>H</i> -pyrido[2,1- <i>b</i>]quinazoline-2-carbonitrile		High temperature hydrolysis

Codes	Names	Molecular formula	Occurrence
IN-N7B69	3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-(hydroxymethyl)-6-[(methylamino)carbonyl]phenyl]-1 <i>H</i> -pyrazole-5-carboxamide		rat plants livestock
IN-N7B69 glucoside	3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-[(β-D-glucopyranosyloxy)methyl]-6-[(methylamino)carbonyl]phenyl]-1 <i>H</i> -pyrazole-5-carboxamide		plants
IN-NBC94	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-3,4-dihydro-8-(hydroxymethyl)-3-methyl-4-oxo-6-quinazolinecarbonitrile		plants rat poultry
IN-NXX69	2-[[[(4 <i>Z</i>)-2-bromo-4 <i>H</i> -pyrazolo[1,5- <i>d</i>]pyrido[3,2- <i>b</i>][1,4]oxazin-4-ylidene]amino]-5-cyano-N,3-dimethylbenzamide		aqueous photolysis soil photolysis
IN-NXX70	2-[3-Bromo-1-(3-hydroxy-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-3,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarbonitrile		plants aqueous photolysis soil photolysis
IN-PLT97	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-1,4-dihydro-8-methyl-4-oxo-6-quinazolinecarboxylic acid		soil sediment

Codes	Names	Molecular formula	Occurrence
IN-QKV54	2-(3-Bromo-1 <i>H</i> -pyrazol-5-yl)-1,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarbonitrile		rat plants aqueous photolysis, soil photolysis
IN-RNU71	2-(2-Bromo-4-oxopyrazolo[1,5- <i>a</i>]pyrido[3,2- <i>e</i>]pyrazin-5(4 <i>H</i>)-yl)-5-cyano- <i>N</i> ,3-dimethylbenzamide		soil photolysis
IN-QKV55	3-bromo- <i>N</i> -[4-cyano-2-methyl-6-(methylcarbamoyl)phenyl]-1-(3-hydroxypyridin-2-yl)-1 <i>H</i> -pyrazole-5-carboxamide		aqueous photolysis

Animal metabolism

The Meeting received animal metabolism studies on rats, lactating goats and laying hens, following oral dosing with [3-¹⁴C-thienyl] dimethenamid (the racemic mixture).

Rats

The metabolism of cyantraniliprole in rats was evaluated by the WHO Core Assessment Group of the 2013 JMPR, where it was concluded that majority of the dose was excreted within 24 to 48 hours, with about 1-5.5% TRR being recovered in tissues. Tissue elimination half-lives ranged from 2.6 days (fat) to 5.1 days (kidney).

The metabolic pathway was primarily through hydroxylation (to form IN-N7B69 and IN-MYX98), with IN-N7B69 being further metabolized to a glucuronide. Cyantraniliprole undergoes ring closure to generate IN-J9Z38 which is then in turn hydroxylated to form IN-NBC94, its carboxylic acid, and its glucuronide conjugate. IN-MYX98 is also metabolized to the closed-ring metabolite IN-MLA84, which, like IN-NBC94, is further oxidized to a hydroxylated metabolite, a carboxylic acid, and the glucuronide of the hydroxyl metabolite. Further, the hydroxylated metabolite IN-MYX98 can be N-dealkylated to form IN-HGW87 as well as being hydroxylated a second time to form bis-hydroxy-HGW86. Cyantraniliprole can also be hydroxylated on the pyridine ring, followed by a ring closure analogous to the conversion of cyantraniliprole to IN-J9Z38. Cyantraniliprole can also be N-dealkylated and cleaved at the carbonyl bridge to form IN-DBC80glutathione conjugation, with other pathways involving reductive dechlorination, oxidation, hydroxylation, *O*-demethylation and cyclization as well as conjugation with glucuronic acid.

Lactating goats

One lactating goat was orally administered [CN-¹⁴C]-cyantraniliprole in a gelatine capsule at a dose rate equivalent to 13.7 ppm in the diet for seven consecutive days and a second goat was similarly

dosed with the dietary equivalent of 12.5 ppm [PC-¹⁴C]-cyantraniliprole. The results of this study have been reported by McLellan, Vance and Lowry, 2008 [Ref: DP-16987].

Urine and faeces were collected before the first dose and daily thereafter. Milk samples were collected twice daily, in the morning before each dosing and in the afternoon, about 7 hours after dosing, with the afternoon milk being combined with the milk collected the next morning. The animals were sacrificed 23 hours after last of the seven daily doses.

Samples were double or triple-extracted with acetonitrile/water mixtures, centrifuged and radioactivity was measured by LSC with the liver samples being further processed by enzyme (protease) digestion. Milk samples were extracted with acetonitrile and partitioned with hexane. Extracts were analysed using reversed phase HPLC (UV detection at 254 nm) to detect reference standards, with quantification either by on-line radiodetection with peak integration or by fraction collection and LSC. LC-MS/MS (electrospray positive ion mode) was used to confirm the presence of cyantraniliprole and major metabolites. All samples were stored at -20 °C and were extracted within 25 days and analysed within 33 days of sampling.

Overall ¹⁴C recoveries were 96–97% of the administered dose, primarily in faeces (84–88%), urine (7%), milk (1–2%), liver (0.3%) and 0.01% or less in kidney, muscle and fat.

Table 2 Total radioactive residues in dissected tissues, excreta and milk of the lactating goat following 7 daily oral administrations of [¹⁴C]-cyantraniliprole

Matrix	[CN- ¹⁴ C]-cyantraniliprole		[PC- ¹⁴ C]-cyantraniliprole	
	% administered dose	TRR (mg/kg)	% administered dose	TRR (mg/kg)
Urine	6.7	NA	6.9	NA
Faeces	87.5	NA	84.3	NA
Total excreted ^a	95.5		93.5	
Liver	0.3	0.46	0.3	0.495
Kidney	0.01	0.117	0.01	0.177
Total body muscle	NA	0.02	NA	0.043
Total body fat	NA	0.137	NA	0.336
Milk (day 1)	0.123	0.074	0.154	0.099
Milk (day 2)	0.16	0.089	0.239	0.148
Milk (day 3)	0.132	0.082	0.289	0.181
Milk (day 4)	0.151	0.078	0.27	0.156
Milk (day 5)	0.15	0.092	0.259	0.171
Milk (day 6)	0.135	0.093	0.314	0.18
Milk (day 7)	0.186	0.109	0.287	0.164
Milk composite (day 1-7)	1.04	0.08	1.81	0.147
Total	96.8			95.6

^a Total excreted includes bile and cage wash

Solvent extraction was able to retrieve 99% TRR from milk, 90–98% TRR from fat, 61–81% TRR from muscle, 63–79% TRR from kidney and while the solvent extractable TRR in the liver were lower (54–60% TRR), an additional 21–27% TRR were recovered following digestion of the post extracted solids (PES) with protease.

Characterization and identification of residues used HPLC and/or LC/MS/MS with 88–90% TRR in milk, 69–70% TRR in liver and 75–80% TRR in fat being characterised and/or identified. In kidney and muscle, 42–43% of the CN-¹⁴C label and 71% of the PC-¹⁴C label was able to be characterised and/or identified.

In milk from the goat dosed with [CN-¹⁴C]-cyantraniliprole, TRR on Day 1 were 0.07 mg/kg, reaching a plateau about Day 2 (0.09 mg/kg) and up to 0.11 mg/kg on Day 7. The major

radiochemical residue was cyantraniliprole, accounting for 40% TRR (0.03 mg/kg) with IN-MYX98 (15% TRR–0.01 mg/kg) being the significant metabolite found.

IN-N7B69 (12% TRR), IN-JCZ38 (7.2% TRR), IN-K7H19 (2.6% TRR), IN-HGW87 (1% TRR) and IN-J9Z38 (0.48% TRR) were identified as minor metabolites in milk, all present at less than 0.01 mg/kg.

In the goat dosed with [PC-¹⁴C]-cyantraniliprole, results were similar, with TRR in milk on Day 1 being 0.1 mg/kg, reaching a plateau about Day 3 (0.18 mg/kg). Cyantraniliprole was the major residue, representing 50% TRR (0.07 mg/kg). The major metabolite was IN-MYX98, comprising 18% of TRR (0.03 mg/kg).

Other metabolites were identified as IN-K7H19, IN-JCZ38, IN-N7B69, IN-HGW87, IN-K5A78, IN-MLA84 and IN-J9Z38, each representing ≤ 0.01 mg/kg and $< 4\%$ TRR.

Table 3 Distribution of radioactive residues in goat milk following administration of [CN-¹⁴C]-cyantraniliprole

Component	Milk ^a		Milk ^a	
	[CN- ¹⁴ C]-cyantraniliprole		[PC- ¹⁴ C]-cyantraniliprole	
	% TRR	mg/kg	% TRR	mg/kg
TRR	100.0	0.076	100.0	0.14
Extracted	99.3	0.075	99	0.139
Cyantraniliprole	39.5	0.03	49.6	0.07
IN-K7H19	2.6	0.00133	0.57	0.001
IN-JCZ38	7.2	0.005	1.32	0.002
IN-N7B69	11.8	0.008	2.01	0.003
IN-MYX98	15.1	0.011	18.3	0.026
IN-HGW87	1.1	< 0.001	0.69	0.001
IN-K5A78	ND		1.26	0.002
IN-MLA84	ND		2.24	0.003
IN-J9Z38	0.48	< 0.001	3.72	0.005
Unknowns	12.7	0.006	8.81	0.012
Total Char./Ident.	90.5	0.061	88.4	0.125
Total Unextracted	0.7	0.001	0.83	0.001

^a Day 1–7 composite sample

Liver from the goat dosed with [CN-¹⁴C]-cyantraniliprole contained 0.43 mg/kg TRR with cyantraniliprole being the major residue, accounting for 17% TRR (0.07 mg/kg). IN-K5A77 and IN-MLA84 were also found at up to 0.02 mg/kg (5% TRR).

Other minor components (0.6–2.6% TRR) were IN-K7H19, IN-JCZ38, IN-N7B69, IN-K5A79, IN-MYX98, IN-HGW87 and IN-K5A78, each at ≤ 0.01 mg/kg. About 32% TRR was made up of a large number of unknown components, none of which were found at levels greater than 0.006 mg/kg (1.5% TRR).

In the goat dosed with [PC-¹⁴C]-cyantraniliprole, liver contained 0.5 mg/kg TRR, the major component being cyantraniliprole at 27% TRR (0.14 mg/kg). IN-K5A77 and IN-MLA84 were each present at 0.02–0.03 mg/kg (5–6% TRR) with IN-K5A78 and IN-MYX98 also found at about 3.5% TRR (< 0.02 mg/kg).

Other minor components were IN-K7H19, IN-HGW87, IN-J9Z38, IN-K5A79, IN-JCZ38 and IN-N7B69, each at ≤ 0.01 mg/kg and not more than 1% TRR. About 18% TRR was made up of a number of unknown components, none of which were found at levels above 0.009 mg/kg (1.8% TRR).

In kidney from the goat dosed with [CN-¹⁴C]-cyantraniliprole, TRR were 0.14 mg/kg with the major residue being cyantraniliprole, accounting for 13% TRR (0.02 mg/kg).

Minor metabolites, present at up to 7% TRR (0.01 mg/kg or less) were IN-MYX98, IN-MLA84, IN-K7H19, IN-J9Z38 and IN-HGW87. Unknown peaks (13% TRR) individually accounted for ≤ 0.01 mg/kg.

In the goat dosed with [PC- ^{14} C]-cyantraniliprole, kidney contained TRR of 0.21 mg/kg, 19% of which was cyantraniliprole (0.04 mg/kg). The IN-MYX98 metabolite (7.1% TRR–0.014 mg/kg) and one unknown component, more polar than parent, (present at 11% TRR–0.02 mg/kg) were the only residues found at levels above 0.01 mg/kg.

IN-K7H19, IN-JCZ38, IN-N7B69, IN-HGW87, IN-K5A77 and IN-MLA84 were identified as minor metabolites ($< 2.5\%$ TRR) each representing ≤ 0.01 mg/kg parent equivalents.

In muscle from the [CN- ^{14} C]-cyantraniliprole dosed goat, TRR were 0.03 mg/kg with the only significant residue being cyantraniliprole, this making up 30% TRR (0.01 mg/kg).

IN-K7H19 was also identified as a minor metabolite (< 0.01 mg/kg). Minor unknowns totalled 7.6% TRR for three peaks each < 0.01 mg/kg parent equivalents.

In the goat dosed with [PC- ^{14} C]-cyantraniliprole, muscle contained 0.04 mg/kg TRR the principal ^{14} C-residue was IN-MYX98, accounting for 33% TRR (0.01 mg/kg parent equivalents) with cyantraniliprole making up 15% TRR (0.01 mg/kg).

IN-K5A77 and IN-J9Z38 each represented ≤ 0.01 mg/kg and unidentified components accounted for a total of 17% TRR (0.01 mg/kg).

For fat, omental, subcutaneous and renal fat were sampled and analyzed separately. TRR levels were similar in the three types of fat, with the respective PC-label residues of 0.117, 0.119 and 0.115 mg/kg and 0.047, 0.046 and 0.049 mg/kg for the CN-label. Results are reported as the mean values of the three types of fat in this evaluation.

For the goat dosed with [CN- ^{14} C]-cyantraniliprole, the calculated mean TRR in fat was 0.05 mg/kg with cyantraniliprole (31% TRR–0.02 mg/kg) being the major residue. In the three types of fat, cyantraniliprole residues were 23% TRR (omental), 42% TRR (subcutaneous) and 34% TRR (renal). The metabolite IN-J9Z38 accounted for an average of 27% TRR (0.01 mg/kg), present at 24% TRR in omental fat, 22% TRR in subcutaneous fat and 37% TRR (0.02 mg/kg) in renal fat.

All other individual metabolites accounted for ≤ 0.01 mg/kg each (IN-K7H19, IN-N7B69, IN-K5A79, IN-MYX98, IN-NBC94, IN-K5A78, and IN-MLA84. Unknown metabolite peaks individually accounted for ≤ 0.01 mg/kg.

For the goat dosed with [PC- ^{14} C]-cyantraniliprole, the calculated mean TRR in fat was 0.12 mg/kg. Cyantraniliprole was the major residue, representing 45% TRR (0.05 mg/kg) on average, with 58% TRR (0.07 mg/kg) in omental fat, 43% TRR in subcutaneous fat and 36% TRR in renal fat. The IN-J9Z38 metabolite was present at 24% TRR (0.03 mg/kg) on average with 0.5% TRR in omental fat, 17% TRR in subcutaneous fat and 56% TRR (0.06 mg/kg) in renal fat.

IN-K7H19, IN-DBC80, IN-N7B69, IN-K5A79, IN-MYX98, IN-K5A77, IN-NBC94, IN-K5A78, and IN-MLA84 were all identified as minor metabolites, each accounted for < 0.01 mg/kg. Individual unknowns accounted for < 0.01 mg/kg parent equivalents.

Table 4 Distribution of radioactive residues in goat tissues following administration of [CN- ^{14} C]-cyantraniliprole

Component	Liver				Kidney		Muscle		Fat ^a	
	Solvent Extract		Protease Digest							
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
TRR	100.0	0.43	100.0	0.43	100.0	0.136	100.	0.027	100.	0.052
Extracted	54.3	0.233	26.8	0.115	62.7	0.085	61.0	0.016	90.4	0.047
Cyantraniliprole	17.1	0.073	0.3	0.002	12.7	0.017	30.3	0.009	30.8	0.016
IN-K7H19	1.0	0.004	0.9	0.005	3.0	0.004	4.6	0.001	1.9	< 0.001
IN-JCZ38	0.83	0.004	0.4	0.003	ND		ND		ND	
IN-N7B69	0.64	0.002	1.8	0.008	ND		ND		1.9	< 0.001

Component	Liver				Kidney		Muscle		Fat ^a	
	Solvent Extract		Protease Digest		% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
	% TRR	mg/kg	% TRR	mg/kg						
IN-K5A79	0.61	0.003	ND		ND		ND		1.9	< 0.001
IN-MYX98	2.5	0.011	0.1	< 0.001	7.1	0.01	ND		1.9	< 0.001
IN-HGW87	1.1	0.004	0.1	0.001	0.61	0.001	ND		ND	
IN-K5A77	5.4	0.023	ND		ND		ND		ND	
IN-NBC94	ND		ND		ND		ND		1.9	< 0.001
IN-K5A78	0.83	0.003	0.2	0.001	ND		ND		1.9	< 0.001
IN-MLA84	3.7	0.017	0.2	0.001	4.1	0.005	ND		1.9	0.001
IN-J9Z38	ND		ND		1.1	0.001	ND		26.9	0.014
Unknowns	13.2 ^b	0.053 ^b	18.6 ^c	0.080 ^c	13.2	0.018	7.6	0.003	11.5	0.006
Total Char./Ident.	46.9	0.202	22.6	0.101	41.8	0.056	42.5	0.013	75.0	0.039
Total Unextracted	45.7	0.197	18.9 ^d	0.082 ^d	37.4	0.051	39.2	0.011	9.6	0.005

^a Concentrations are a mean of omental, renal, and subcutaneous fat samples analysed

^b 13 components, none greater than 0.006 mg/kg (1.4% TRR)

^c 32 components, none greater than 0.006 mg/kg (1.5% TRR)

^d Terminal unextracted residues following protease digestion

Table 5 Distribution of radioactive residues in goat tissues following administration of [PC-¹⁴C]-cyantraniliprole

Component	Liver				Kidney		Muscle		Fat ^a	
	Solvent Extract		Protease Digest		% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
	% TRR	mg/kg	% TRR	mg/kg						
TRR	100.0	0.5	100.0	0.5	100.0	0.206	100.0	0.040	100.0	0.119
Extracted	59.5	0.296	20.7	0.103	78.6	0.162	80.9	0.032	98.3	0.117
Cyantraniliprole	27.3	0.136	ND		18.9	0.04	15.3	0.006	45.4	0.054
IN-K7H19	0.95	0.005	0.5	0.003	2.3	0.004	ND		< 0.8	< 0.001
IN-JCZ38	0.42	0.002	ND		0.64	0.001	ND		ND	
IN-DBC80	ND		ND		ND		ND		< 0.8	< 0.001
IN-N7B69	0.32	0.002	ND		1.7	0.003	ND		< 0.8	< 0.001
IN-K5A79	0.61	0.003	ND		ND		ND		2.5	< 0.003
IN-MYX98	3.6	0.017	ND		7.1	0.014	32.8	0.014	< 0.8	< 0.001
IN-HGW87	1.0	0.005	ND		1.1	0.002	ND		ND	
IN-K5A77	5.7	0.028	ND		0.70	0.001	4.4	0.001	< 0.8	< 0.001
IN-NBC94	ND		ND		ND		ND		1.7	0.002
IN-K5A78	3.4	0.017	0.3	0.002	ND		ND		< 0.8	< 0.001
IN-MLA84	5.3	0.026	0.4	0.002	1.8	0.004	ND		1.7	0.002
IN-J9Z38	0.9	0.004	ND		ND		1.1	< 0.001	24.4	0.029
Unknowns	6.2 ^b	0.031 ^b	11.6 ^c	0.059 ^c	36.9 ^d	0.076 ^d	17.1	0.006	5.0	0.006
Total Char./Ident.	55.7	0.279	12.8	0.066	71.0	0.145	70.9	0.027	79.8	0.095
Total Unextracted	40.5	0.204	19.9 ^e	0.101	21.5	0.044	19.2	0.008	1.7	0.002

^a Concentrations are a mean of omental, renal and subcutaneous fat samples analysed

^b 7 components, none greater than 0.008 mg/kg (1.6% TRR)

^c 19 components, none greater than 0.009 mg/kg (1.8% TRR)

^d 10 components, none greater than 0.023 mg/kg (11.4% TRR)

^e Terminal unextracted residues following protease digestion

Cyantraniliprole was rapidly eliminated by the lactating goat, primarily in the excreta (94–96% of the applied dose). There was no significant transfer of residues of cyantraniliprole and its metabolites to fat, meat or edible offal as these tissues contained only ca. 1–2% of the total administered dose. Approximately 1–2% of the total administered dose was eliminated via the milk.

Significant metabolites found at more than 10% TRR or 0.01 mg/kg were IN-MYX98 in milk and muscle and IN-J9Z38 in fat.

The biotransformation of cyantraniliprole in the goat is consistent with pathways proposed for poultry (laying hens) and the rat and is outlined below.

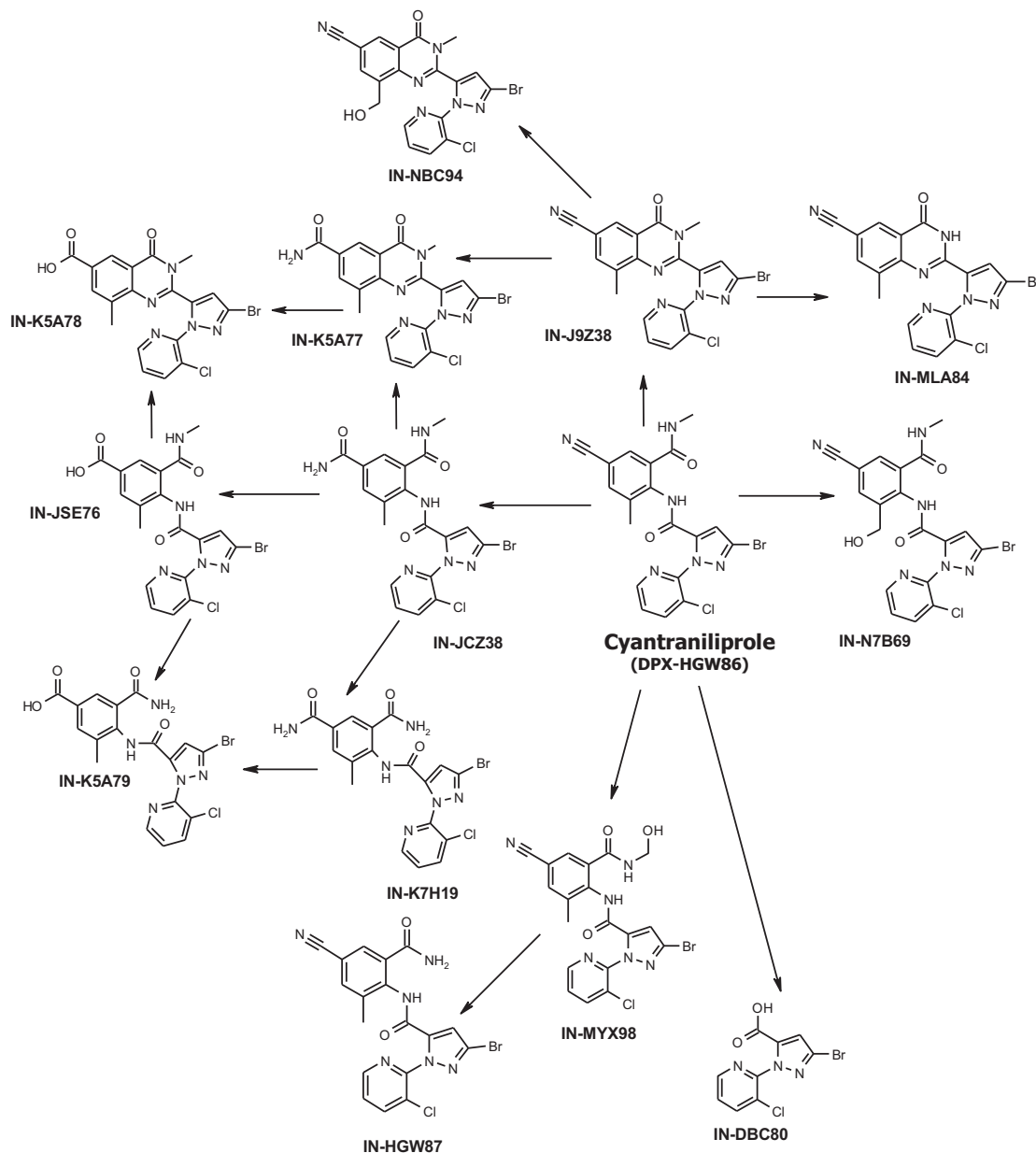


Figure 1 Proposed metabolic pathway of cyantraniliprole in lactating goats

Laying hens

In a study reported by McLellan Lowry, 2008 [Ref: DP-16988], one group of five hens was orally administered [CN-¹⁴C]-cyantraniliprole in gelatine capsules at a dose rate equivalent to 11.6 ppm in the diet for 14 consecutive days and a second group of five hens was similarly dosed with the dietary equivalent of 11.2 ppm [PC-¹⁴C]-cyantraniliprole.

For each group, eggs were collected twice daily, excreta were collected daily, and tissues were collected after sacrifice, approximately 23 hours after the last dose.

Samples were triple-extracted with acetonitrile:water (9:1) centrifuged and the radioactive content was determined by LSC analysis of duplicate aliquots. Liver samples were further processed by enzyme digestion using protease. Extracts were analysed using reversed phase HPLC (UV detection at 254 nm) eluted with a gradient of acetonitrile and water containing 0.1% formic acid and quantification of radioactive residues was accomplished either by on-line radio detection with peak integration or by fraction collection and LSC. Identification of radioactive residues was based on comparison of HPLC retention times with those of authentic reference standards. LC-MS/MS in electrospray positive ion mode was conducted to confirm the presence of parent and selected metabolites. All samples were stored frozen (-20 °C) for no more than 55 days before extraction and analyzed within 62 days after sampling.

The overall ^{14}C recoveries of the administered dose for both radiolabels were consistent with 97–100% of the total administered dose found in the excreta. Based on composite Day 1–14 samples, egg whites accounted for 0.4–0.5% (0.20–0.26 mg/kg) while egg yolks contained 0.07% (0.09 mg/kg) of the total administered dose. The highest concentrations of total radioactivity in tissues were observed in liver (0.2 mg/kg PC- ^{14}C label, 0.14 mg/kg CN- ^{14}C label). Abdominal fat, skin with fat and muscle each contained $\leq 0.1\%$ of the total administered dose for either label, each equivalent ≤ 0.01 mg/kg.

The concentration of radioactivity in egg whites was variable, increasing to 0.26 mg/kg (PC- ^{14}C label) and 0.56 mg/kg (CN- ^{14}C label) in eggs sampled 2 days after the first dose, decreasing to a steady state of about 0.2–0.24 mg/kg after 7 days but with concentrations of the PC- ^{14}C label dropping to 0.12 mg/kg on day 13 and increasing to 0.38 mg/kg on day 14. Radioactivity in egg yolks increased steadily reaching a plateau concentration of about 0.1 mg/kg after 5 days (CN- ^{14}C label) and 7 days (PC- ^{14}C label).

Table 6. Total radioactive residues in dissected tissues, excreta and eggs of laying hens following 14 daily oral administrations of [^{14}C]-cyantraniliprole

Matrix	[CN- ^{14}C]-cyantraniliprole				[PC- ^{14}C]-cyantraniliprole			
	% administered dose		TRR (mg/kg)		% administered dose		TRR (mg/kg)	
Excreta	96.95		NA		99.72		NA	
Cage wash	3.83		NA		2.52		NA	
Total excreted	100.8							
Fat	0.004		0.004		0.01		0.005	
Liver	0.026		0.141		0.04		0.205	
Muscle	0.006		0.003		0.01		0.005	
Skin with fat	0.01		0.005		0.01		0.007	
Eggs	white	yolk	white	yolk	white	yolk	white	yolk
Day 1	0.01	0.0	0.081	0.004	0.017	0.0	0.127	0.008
Day 2	0.066	0.002	0.56	0.051	0.035	0.001	0.259	0.027
Day 3	0.064	0.005	0.356	0.066	0.034	0.002	0.244	0.038
Day 4	0.057	0.005	0.388	0.084	0.034	0.003	0.256	0.062
Day 5	0.05	0.006	0.329	0.106	0.016	0.004	0.117	0.065
Day 6	0.037	0.006	0.241	0.101	0.026	0.005	0.185	0.084
Day 7	0.031	0.007	0.207	0.114	0.02	0.005	0.186	0.098
Day 8	0.035	0.006	0.242	0.111	0.03	0.006	0.218	0.109
Day 9	0.036	0.006	0.237	0.11	0.024	0.006	0.168	0.106
Day 10	0.027	0.006	0.174	0.1	0.034	0.009	0.195	0.112
Day 11	0.022	0.005	0.191	0.1	0.022	0.006	0.159	0.099
Day 12	0.023	0.005	0.155	0.087	0.03	0.006	0.221	0.103
Day 13	0.03	0.006	0.198	0.092	0.01	0.004	0.12	0.1
Day 14	0.05	0.008	0.233	0.099	0.065	0.009	0.377	0.126
Eggs—composite (Days 1–14)	0.54	0.07	0.259	0.092	0.4	0.07	0.203	0.087
Total	101.4				102.7		95.6	

Solvent extraction was able to retrieve more than 99% TRR from egg white, 79–83% TRR in egg yolk and 17–23% TRR in liver. An additional 38% TRR were recovered following digestion of the post extracted solids (PES) with protease. Low levels of radioactivity (< 0.001 mg/kg) were

detected in muscle, abdominal fat and skin + fat, with solvent extraction recovering 100% TRR in muscle, 63% TRR (PC-¹⁴C label) and 120% TRR (CN-¹⁴C label) in abdominal fat and 53% TRR (PC-¹⁴C label) and 72% TRR (CN-¹⁴C label) in skin + fat.

Characterization and identification of residues by HPLC (with LC-MS confirmation) was conducted on composite egg white and egg yolk samples (day 1–14) and liver. No analysis was carried out with muscle, abdominal fat or skin + fat samples because of the low residues (< 0.004 mg/kg) present. About 95% TRR in egg white, 71% TRR in egg yolk and 35–42% TRR in liver was able to be characterised and/or identified.

In egg white, TRRs were 0.26 mg/kg (CN-¹⁴C label) and 0.2 mg/kg (PC-¹⁴C label). Cyantraniliprole was the major ¹⁴C-residue representing 32–42% TRR (0.09 mg/kg). IN-MLA84 (18–19% TRR) and IN-J9Z38 (17–29% TRR) were principal egg white metabolites, found at 0.04–0.05 mg/kg and 0.03–0.08 mg/kg respectively.

IN-HGW87, IN-K7H19, IN-MYX98, and IN-NBC94 were also identified in each composite sample, present at ≤ 8.1% TRR (≤ 0.017 mg/kg).

In egg yolk, TRRs were 0.09 mg/kg, with cyantraniliprole making up about 9–10% TRR (0.01 mg/kg). Significant metabolites were IN-MLA84, IN-HGW87 and IN-J9Z38, each present at 12–17% TRR (up to 0.015 mg/kg).

IN-JSE76, IN-K5A77, IN-K5A79, IN-MYX98, and IN-NBC94 were also found in egg yolks as minor metabolites each representing 1–6% TRR (≤ 0.006 mg/kg).

In liver, TRRs were 0.14 mg/kg (CN-¹⁴C label) and 0.17 mg/kg (PC-¹⁴C label). Cyantraniliprole was not found any samples. IN-JCZ38, IN-K5A78, IN-K5A79, IN-K7H19, IN-MLA84, IN-MYX98 and IN-N7B69 were found as minor metabolites, each representing < 4% TRR (< 0.01 mg/kg).

Table 7 Distribution of radioactive residues in hen eggs and liver following administration of [CN-¹⁴C]-cyantraniliprole

Component	Egg white (Day 1–14)		Egg yolk (Day 1–14)		Liver			
	% TRR	mg/kg	% TRR	mg/kg	Aqueous ACN		Protease digest	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
Total	100.0	0.259	100.0	0.092	100.0	0.137	100.0	0.137
Total extracted	99.01	0.256	79.3	0.073	17.07	0.023	38.09	0.052
Cyantraniliprole	32.48	0.084	10.28	0.009	ND		ND	
IN-HGW87	0.61	0.002	11.98	0.011	ND		ND	
IN-J9Z38	29.21	0.075	7.42	0.006	2.08	0.003	ND	
IN-MLA84	18.66	0.049	11.56	0.011	0.89	0.001	ND	
IN-MYX98	6.4	0.017	5.42	0.006	0.42	0.001	1.1	0.002
IN-NBC94	0.96	0.002	0.86	0.001	ND		0.4	0.001
Total characterized unknowns ^a	7.75	0.021	23.62	0.025	7.58	0.010	22.33	0.042
Total characterized/identified ^b	96.07	0.25	71.14	0.068	10.97	0.015	23.82	0.045
Total uncharacterized/unidentified ^c	2.94	0.008	8.16	0.005	6.1	0.008	16.94	0.023
Total unextracted	0.99	0.003	20.7	0.019	82.93	0.114	44.97 ^d	0.062 ^e

^a Up to 32 components, each <5% TRR and < 0.005 mg/kg (except one liver component at 0.008 mg/kg)

^b Total characterized/identified=Sum of identified metabolites + Total characterized unknowns

^c Total uncharacterized/unidentified=Total extracted–Total characterized/identified

^d Does not include 16.9% TRR unaccounted for during sample processing

^e Does not include 0.023 mg/kg unaccounted for during sample processing

ND=Not Detected

Table 8 Distribution of radioactive residues in hen eggs and liver following administration of [PC-¹⁴C]-cyantraniliprole

Residue	Egg white (Day 1–14)		Egg yolk (Day 1–14)		Liver			
	% TRR	mg/kg	% TRR	mg/kg	Aqueous ACN		Protease digest	
					% TRR	mg/kg	% TRR	mg/kg
Total	100.0	0.203	100.0	0.087	100.0	0.174	100.0	0.174
Total extracted	99.7	0.202	83.1	0.072	23.0	0.04	37.6	0.065
Cyantraniliprole	41.7	0.085	9.33	0.008	ND		ND	
IN-HGW87	0.74	0.001	ND		ND		ND	
IN-J9Z38	17.1	0.034	13.1	0.011	ND		ND	
IN-JSE76	ND		1.9	0.002	ND		ND	
IN-JCZ38	ND		ND		ND		0.23	< 0.001
IN-K5A77	ND		6.19	0.005	ND		ND	
IN-K5A78	ND		ND		0.23	< 0.001	ND	
IN-K5A79	3.9	0.007	1.52	0.001	0.27	< 0.001	0.45	0.001
IN-K7H19	ND		ND		ND		0.46	< 0.001
IN-MLA84	18.2	0.037	16.8	0.015	3.98	0.007	ND	
IN-MYX98	8.13	0.016	2.09	0.002	0.27	< 0.001	ND	
IN-N7B69	ND		ND		ND		0.55	0.001
IN-NBC94	2.86	0.005	1.24	0.001	ND		ND	
Total characterized unknowns ^a	0.98	0.002	17.4	0.015	10.5	0.02	25.0	0.045
Total characterized/identified ^b	93.6	0.187	69.6	0.06	15.2	0.027	26.7	0.047
Total uncharacterized/unidentified ^c	6.09	0.014	13.5	0.012	7.8	0.013	10.9	0.018
Total unextracted	0.33	0.001	16.9	0.015	77.0	0.134	39.5 ^d	0.053 ^e

^a Up to 24 components, each < 5% TRR and < 0.005 mg/kg (except one liver component at 7% TRR–0.007 mg/kg)

^b Total characterized/Identified=Sum of identified metabolites + Total characterized unknowns

^c Total uncharacterized/unidentified=Total extracted–Total characterized/identified

^d Does not include 23.0% TRR unaccounted for during sample processing

^e Does not include 0.056 mg/kg unaccounted for during sample processing

ND=Not Detected

Cyantraniliprole was rapidly eliminated in laying hens with more than 97% being excreted, mostly as unchanged parent compound (68–74%). About 0.5–0.6% of the total administered dose was observed in eggs, fat, liver, and muscle, with unchanged cyantraniliprole being the principal (0.08 mg/kg) residue found in egg whites and found at lower levels in yolks (0.01 mg/kg). Cyantraniliprole was not detected in any of the liver samples.

A number of metabolites were identified in egg whites and egg yolks. IN-J9Z38 and IN-MLA84 were the principal metabolites (0.03–0.08 mg/kg) in egg whites but accounted for ≤ 0.02 mg/kg in yolks. In liver, about 35–40% TRR was characterized/identified with most of the TRR remaining bound following solvent and protease extractions.

The proposed metabolic pathway in laying hens was consistent with that proposed for rats and lactating goats, and is outlined below:

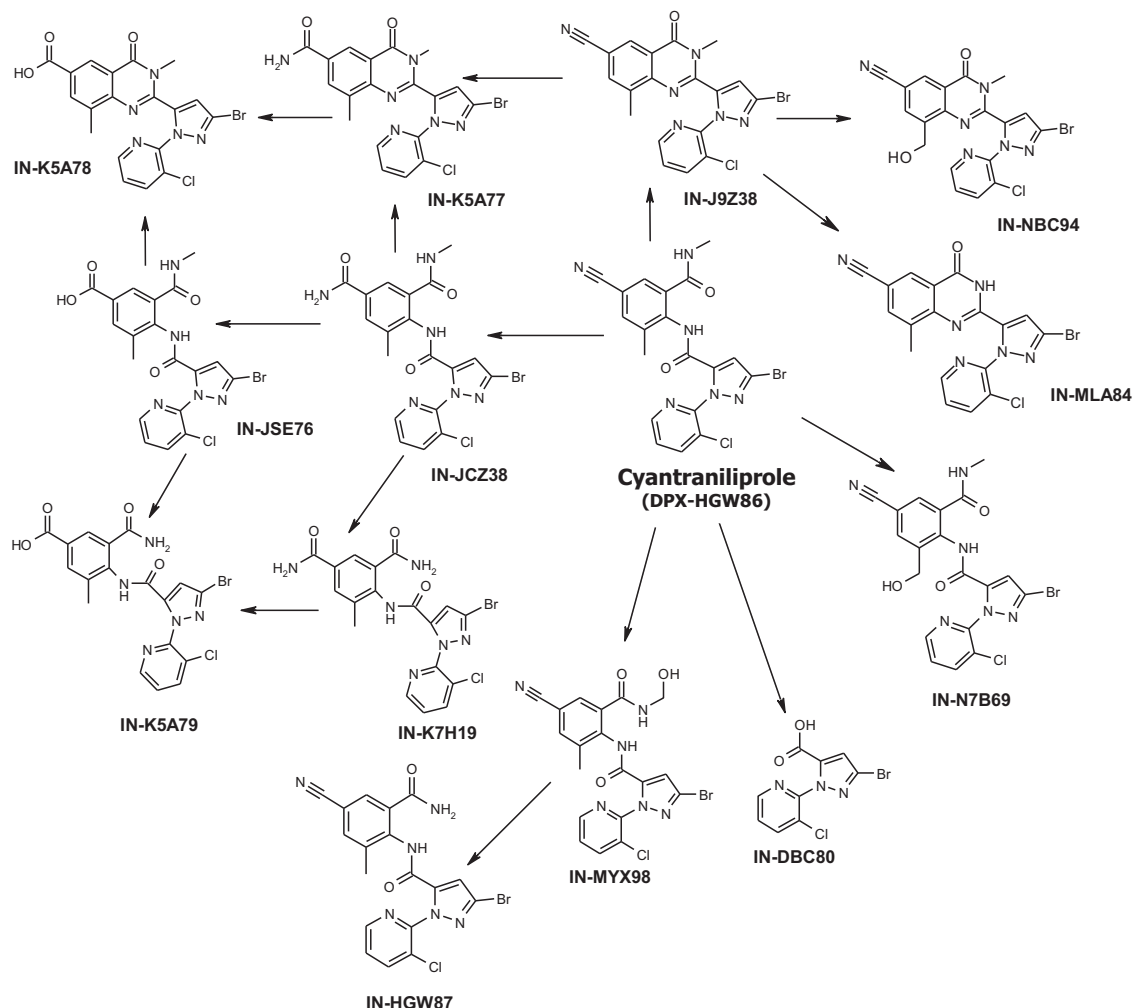


Figure 2 Proposed metabolic pathway of cyantraniliprole in laying hens

Plant metabolism

The Meeting received plant metabolism studies on cotton, lettuce, tomato and rice seedlings following foliar and soil treatments with [^{14}C]-cyantraniliprole. A 1:1 ($\mu\text{Ci}/\mu\text{Ci}$ ratio) mixture of [$\text{CN-}^{14}\text{C}$]-cyantraniliprole and [$\text{PC-}^{14}\text{C}$]-cyantraniliprole was used in the foliar treatments and separate treatments of the two radiolabels were applied as soil treatments.

The Meeting noted that the IN-DBC80 metabolite was the only cleavage product containing just the PC- ^{14}C label and as this was found only at low concentrations in some metabolism studies, it was agreed that the use of the mixed radiolabels in the foliar treatment studies did not significantly impact on the results of these studies.

Cotton

In a study reported by MacDonald, MacKinnon & Chapleo (2008) [Ref: DP-16984], three applications of [^{14}C]-cyantraniliprole equivalent to 150 g ai/ha/treatment, were made to cotton plants grown in 30 cm pots containing an acidic (pH 6.4) commercial growing medium (since abiotic degradation of cyantraniliprole occurs at alkaline pH). Foliar applications (SC formulation) were made to plants 3 weeks post-emergence and at 7 and 14 days after the initial application. Soil drench

applications (SC formulation), pipetted onto wetted soil were made 7 weeks post-emergence and at 7 and 14 days after the first application.

Leaves were collected from immature plants after the first application (foliar treatment only), immediately prior to and following the second and third applications, and at ca. 7 and 14 days after the third application. Cotton bolls (seed plus lint) and the remaining aerial portions (cotton-gin by-products, gin trash) were sampled at crop maturity (ca. 125 days after the third application). The bolls were separated into undelinted (fuzzy) seed and lint.

Selected samples from the foliar-treatment regime were surface washed with acetonitrile:water (7:3, v/v) immediately after sampling. Plant samples from both regimes were pulverized and total tissue residues determined by oxidative combustion analysis. Where characterization of radioactivity was warranted, samples were extracted three times using acetone:1N formic acid (9:1). The unextracted radioactivity in the post-extracted solids (PES) was determined by combustion analysis. Extracts containing significant radioactivity (≥ 0.01 mg/kg) were analysed by high performance liquid chromatography (HPLC) and identification of ^{14}C -residues was accomplished by HPLC and liquid chromatography mass spectrometry (LC-MS), with reference to authenticated reference standards. Samples were stored at ca -20°C for up to 28 days before analysis.

To assess if storage at -20°C resulted in degradation of radioactive residues, a subsample of stored tissue (7 days post-application 3, foliar treatment) was extracted with acetone:formic acid following a storage period of 392 days. The TRR and extractability values after prolonged storage (0.449 mg/kg, 74.4% TRR) were similar to those obtained originally (0.505 mg/kg, 81.5% TRR). The residue composition also remained unchanged with cyantraniliprole being the principle component (30.8% TRR, 0.138 mg/kg) and minor components individually making up $\leq 4.6\%$ TRR (≤ 0.021 mg/kg).

A comparison of the extraction efficiency of acetone:formic acid and acetonitrile:water showed similar results, with the extracted radioactivity from unwashed leaves from the foliar-treated plants being 76% TRR in the acetonitrile extract and 74% TRR in the acetone extract. HPLC analysis of the two extracts also reported comparable results, with cyantraniliprole making up 27% of the TRR in the acetone extract and 21% of the TRR in the acetonitrile extract.

In plants from the soil drench treatments, TRRs in leaves from immature plants, lint and undelinted seed were all ≤ 0.005 mg/kg with TRR values in cotton gin by-products being 0.1 mg/kg (CN-label) and 0.02 mg/kg (PC-label).

The majority of the radioactivity in cotton gin by-products (79.6–99.9% TRR) was extracted into acetone:formic acid. Additional amounts of radioactivity were extracted from the CN-label sample using enzymes (7.4% TRR), 1 M HCl at 60°C (3.9% TRR), 6 M HCl at 90°C (2.2% TRR) and 6 M NaOH at 90°C (1.8% TRR), each releasing < 0.01 mg/kg.

Cyantraniliprole was the major radioactive residue in gin by-products at concentrations of 25.6% TRR (0.02 mg/kg) for the CN-label and 46.8% TRR (0.01 mg/kg) for the PC-label.

Gin by-products from [CN- ^{14}C]-treated cotton also contained IN-J9Z38, IN-JCZ38, IN-JSE76, IN-HGW87, IN-QKV54 and unresolved IN-MLA84/IN-NXX70, each at ≤ 0.01 mg/kg and less than 8% TRR. The only identified metabolite in gin by-products from [PC- ^{14}C]-treated cotton was IN-J9Z38 (< 0.01 mg/kg).

Table 9 Total radioactive residues (mg/kg) in cotton samples following soil drench treatments with [^{14}C]-cyantraniliprole

Treatment	Leaves				Lint	Seed	Gin by-products
Sample point	7 DAT1	7 DAT2	7–8 DAT3	13–14 DAT3	124–125 DAT3		
[CN- ^{14}C]-cyantraniliprole	< 0.001	0.005	< 0.001	0.002	< 0.001	< 0.001	0.095
[PC- ^{14}C]-cyantraniliprole	0.002	0.002	< 0.001	0.002	< 0.001	< 0.001	0.023

Table 10 Distribution of radioactive residues in cotton gin by-products 124 days after the last of three soil drench treatments with [^{14}C]-cyantraniliprole

^{14}C -Residue	[CN- ^{14}C]-cyantraniliprole		[PC- ^{14}C]-cyantraniliprole	
	%TRR	mg/kg	%TRR	mg/kg
TRR, mg/kg		0.095		0.023
Extracted	95.7	0.09	99.9	0.023
Cyantraniliprole	25.6	0.025	46.8	0.011
IN-HGW87	2.6	0.003		ND
IN-J9Z38	7.5	0.006	4.7	0.001
IN-JCZ38	1.2	< 0.001		ND
IN-JSE76	1.7	< 0.001		ND
IN-MLA84/ IN-NXX70	5.7	0.004		ND
IN-QKV54	6.4	0.005		ND
Unidentified	16.4 ^a	0.007	11.6 ^b	0.003

^a 48 components; none greater than 0.002 mg/kg (2.6%TRR)^b One component

TRRs in cotton leaves following foliar treatment with the 1:1 mixture of [CN- ^{14}C]-cyantraniliprole + [PC- ^{14}C]-cyantraniliprole were 2.7 mg/kg immediately after the first application, 14.5 mg/kg immediately after the second application and 7.9 mg/kg just after the last application. Residues decreased to 0.43 mg/kg at 13 days after the last application. At harvest, TRRs in cotton gin by-products, lint and undelinted seed were 0.13, 0.01, and < 0.01 mg/kg, respectively.

The majority of the radioactivity (74–87%TRR) in immature leaves was removed by surface washing (56–70% TRR) and extraction into acidified aqueous acetone (27–33% TRR). Low concentrations of radioactivity were subsequently extracted using enzymes (4.1–7.7% TRR), 1 M HCl at 60 °C (2.9–4.7% TRR), 6 M HCl at 90 °C (0.6–4.5% TRR) and 6 M NaOH at 90 °C (1.1–8.0% TRR).

Cyantraniliprole was the major residue in leaves, decreasing from 69.7% TRR immediately after the first application to 19.7% TRR seven days later and accounted for 37.3 and 27.1% TRR, respectively, 7 and 13 days after the final application.

The photodegradate, IN-NXX70, found predominately in the surface wash, accounted for 21.7% TRR seven days after the first application, declining to 1.1% TRR 7 days after the third application.

The metabolite IN-QKV54 accounted for 10.3% TRR in leaf extracts 7 days after the first application. Other metabolites identified in leaf samples (IN-DBC80, IN-J9Z38, IN-JCZ38, IN-JSE76, IN-K5A77, IN-K7H19, IN-MYX98 and IN-N7B69) each did not exceed 5% TRR. Numerous other metabolites detected but not identified were each present at less than 10% TRR (0.04 mg/kg). Unextracted leaf residues accounted for ≤ 13.2% TRR (≤ 0.38 mg/kg).

Surface washing of cotton gin by-products removed about 19% TRR (0.025 mg/kg) with a further 40% TRR being extracted using acidified aqueous acetone. Additional radioactivity was extracted using enzymes (7.4% TRR), 1 M HCl at 60 °C (5.4% TRR), 6 M HCl at 90 °C (7.5% TRR) and 6 M NaOH at 90 °C (4.2% TRR), giving a total extraction efficiency of 83.8% TRR (0.11 mg/kg).

Cyantraniliprole was the main component, accounting for 34.4% TRR (0.04 mg/kg). Other metabolites including IN-J9Z38 (5.7% TRR), IN-JCZ38 (6.1% TRR) and IN-N7B69 (1.2% TRR) were present at ≤ 0.01 mg/kg. Other metabolites detected but not identified did not individually exceed 0.9% TRR or 0.001 mg/kg. Unextracted residues accounted for 16.2% TRR (0.02 mg/kg).

Table 11 Distribution of radioactive residues in leaves and cotton gin by-products from plants treated with foliar applications of a 1:1 mixture of [CN- ^{14}C]-cyantraniliprole and [PC- ^{14}C]-cyantraniliprole

Sampling point	0 DAT1 Leaves	7 DAT1 Leaves	7 DAT2 Leaves	7 DAT3 Leaves	13 DAT3 Leaves	124 DAT3 Gin by-products

TRR, mg/kg	2.709		5.414		2.654		0.505		0.425		0.131	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
Surface wash	55.9	1.514	66.6	3.606	69.9	1.855					19.1	0.025
Tissue extracts ^a	30.9	0.837	33.4	1.808	26.8	0.711					64.7	0.086
Total Extracted	86.8	2.35	100	5.414	96.7	2.566	97.8	0.494	97.9	0.416	83.8	0.111
Unextracted	13.2	0.358	< 0.1	< 0.001	3.5	0.093	2.2	0.011	2	0.009	16.2	0.021
Cyantraniliprole	69.7	1.89	19.7	1.066	70.7	1.873	37.3	0.187	27.1	0.115	34.4	0.043
IN-DBC80	ND		1.2		ND		ND		ND		ND	
IN-J9Z38	1.0	0.028	3.5	0.19	2.9	0.078	2.3	0.011	1.5	0.006	5.7	0.008
IN-JCZ38	ND		1.3	0.069	ND		ND		ND		6.1	0.007
IN-JSE76	ND		0.7	0.039	0.1	0.003	ND		ND		ND	
IN-K5A77	ND		0.9	0.05	ND		ND		ND		ND	
IN-K7H19	ND		1.7	0.089	0.7	0.018	4.1	0.019	4.9	0.021	ND	
IN-MLA84	3.3	0.091	0.8	0.049	0.5	0.013	3.5	0.017	3.3	0.014	ND	
IN-MYX98	ND		2.0	0.106	ND		ND		ND		ND	
IN-N7B69	ND		0.3	0.017	ND		ND		1.1	0.005	1.2	0.001
IN-NXX70	--		21.7	1.172	--		1.1	0.006	--		--	
IN-QKV54	ND		10.3	0.577	1.5	0.039	5.0	0.025	3.8	0.016	ND	
Unidentified	4.4 ^b	0.12	13.9 ^c	0.749	6.9 ^d	0.167	25.2 ^e	0.122	41.3 ^f	0.176	7.3 ^g	0.002

Note: TRR in leaves at 0 DAT2 were 14.5 mg/kg and were 7.9 mg/kg at 0 DAT3

^a Sequential extraction with acetone:1 N formic acid (3×); a mixture of cellulase, beta-glucosidase and driselase (2× for 24 hours at 37 °C); 1 M HCl (6 hours at 60 °C); 6 M HCl (6 hours at 90 °C) and 6 M NaOH (6 hours at 60 °C)

^b 8 components; none greater than 0.035 mg/kg (1.3%TRR)

^c 47 components; none greater than 0.163 mg/kg (3.0%TRR)

^d 28 components; none greater than 0.047 mg/kg (1.8%TRR)

^e 32 components; none greater than 0.031 mg/kg (6.2%TRR)

^f 31 components; none greater than 0.042 mg/kg (9.9%TRR)

^g 20 components; none greater than 0.001 mg/kg (0.9%TRR)

The proposed pathway is outlined below.

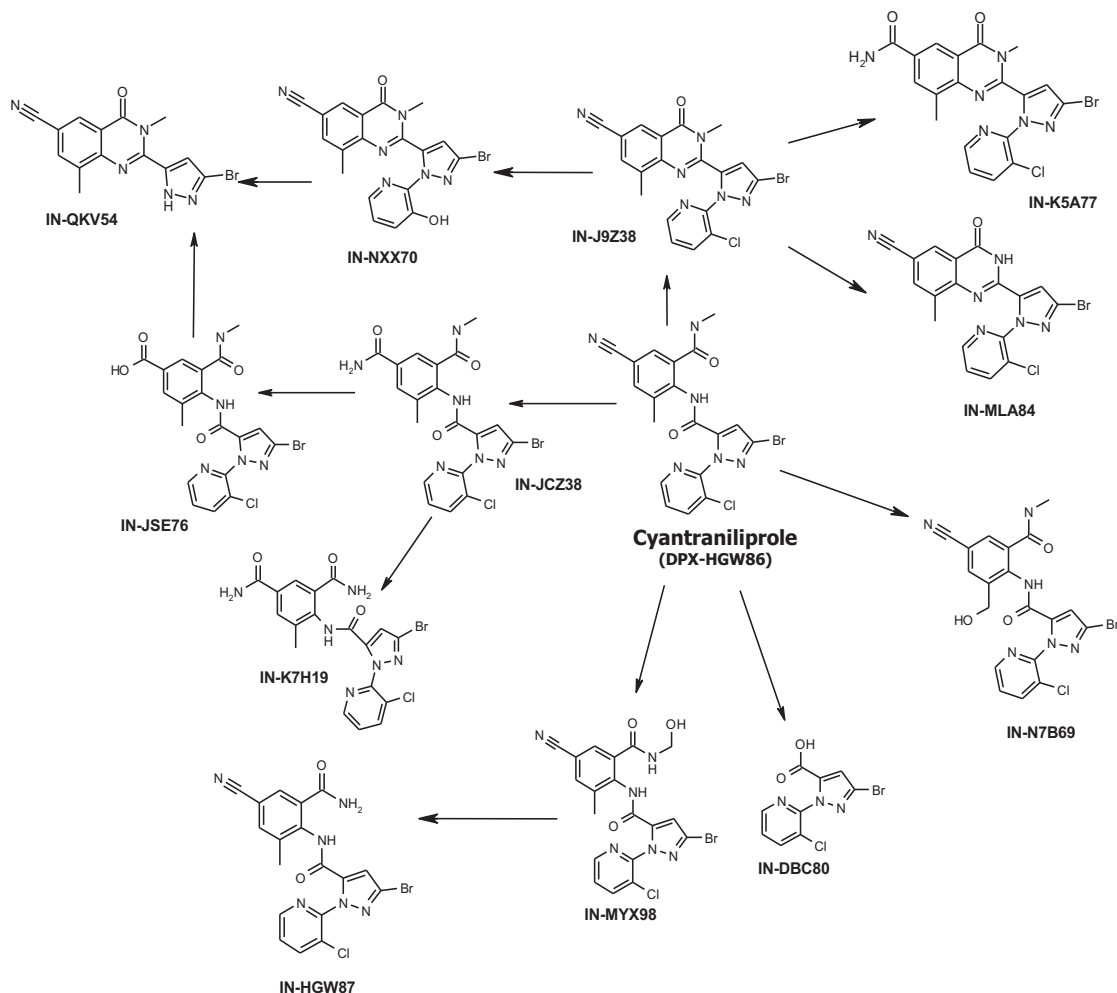


Figure 3 Proposed metabolic pathway for $[^{14}\text{C}]$ -cyantraniliprole in cotton plants

Lettuce

In a study reported by MacKinnon (2008) [Ref: DP-16986], three applications of $[^{14}\text{C}]$ -cyantraniliprole equivalent to 150 g ai/ha/treatment, were made to lettuce plants grown in 1 square metre outdoor sandy loam plots (pH 6.5) commercial growing medium (since abiotic degradation of cyantraniliprole occurs at alkaline pH). Foliar applications (SC formulation) were made to plants 3 weeks post-emergence and at 7 and 14 days after the initial application. Soil drench applications were made 7 weeks post-emergence and at 7 and 14 days after the first application.

Leaves were collected from immature plants after the first application (foliar treatment only), immediately before and after the second and third applications, and 7 and 14 days after the third application and mature plants were collected 32 days after the last application.

Selected samples from the foliar-treatment regime were surface washed with acetonitrile: water (7:3, v/v) immediately after sampling. Plant samples from both regimes were pulverized and total tissue residues determined by oxidative combustion analysis. Where characterization of radioactivity was warranted, samples were extracted three times using acetone:1 N formic acid (9:1). The unextracted radioactivity in the post-extracted solids (PES) was determined by combustion analysis. Extracts containing significant radioactivity (≥ 0.01 mg/kg) were analysed by high performance liquid chromatography (HPLC) and identification of ^{14}C -residues was accomplished by HPLC and liquid chromatography mass spectrometry (LC-MS), with reference to authenticated

reference standards. Samples were stored at ca -20 °C for up to 72 days before analysis (up to 28 days before extraction).

To assess if storage at -20 °C resulted in degradation of radioactive residues, a subsample of stored tissue (7 days after the third foliar treatment) was extracted with acetone:formic acid following a storage period of 405 days. Frozen storage did not influence the extractability (%) of TRR (97.3% TRR in stored samples and 98.4% TRR in the original samples). The residue composition also remained unchanged with cyantraniliprole making up 77.2% TRR (1.55 mg/kg) compared to 78.5% TRR (1.56 mg/kg) in the original samples. Minor components in the stored samples individually accounted for < 10% TRR (0.01–0.05 mg/kg).

A comparison of the extraction efficiency of acetone:formic acid and acetonitrile:water showed similar results, with the extracted radioactivity from unwashed leaves from the foliar-treated plants being 97.8% TRR in the acetonitrile extract and 98.4% TRR in the acetone extract. HPLC analysis of the two extracts also reported comparable results, with cyantraniliprole making up 72.1% of the TRR in the acetone extract and 71.6% of the TRR in the acetonitrile extract.

In plants from the soil drench treatments, TRR in leaves from the [CN-¹⁴C]-cyantraniliprole plots declined from 0.14 mg/kg (7 days after the first application) to 0.01 mg/kg at final harvest. TRRs following PC-label soil treatment were ≤ 0.06 mg/kg in immature leaves and at crop maturity. Higher residues were observed following foliar application.

The majority (76.7–98.4% TRR) of the radioactivity in lettuce leaves was extracted into acetone:formic acid.

Cyantraniliprole was the major radioactive component in leaves from the [CN-¹⁴C]-cyantraniliprole treated plants, accounting for up to 76.7% TRR in young leaves and 37.1% TRR in mature leaves. Minor components (IN-K5A79 and unresolved IN-MLA84/IN-NXX70) were detected at ≤ 0.01 mg/kg in samples taken prior to the second application. Cyantraniliprole was the only component detected (< 0.01 mg/kg) at maturity.

Following the PC-label soil drench treatment, cyantraniliprole was the only detectable component in immature lettuce samples accounting for 75.3% to 84.1.0% TRR and was the major residue (69% TRR–0.039 mg/kg) in mature leaves. Low level metabolites (< 10% TRR) detected in mature leaves were unresolved IN-MLA84/IN-NXX70 and IN-J9Z38, both present at < 0.01 mg/kg.

Table 12 Total radioactive residues (mg/kg) in lettuce leaves following soil drench treatments with [¹⁴C]-cyantraniliprole

Treatment	Leaves				
Sample point	7 DAT1	7 DAT2	7 DAT3	14 DAT3	32 DAT3
[CN- ¹⁴ C]-cyantraniliprole	0.144	0.049	0.046	0.035	0.012
[PC- ¹⁴ C]-cyantraniliprole	0.017	0.035	0.009	0.007	0.057

Table 13 Distribution of radioactive residues in lettuce leaves following soil drench treatments with [¹⁴C]-cyantraniliprole

Sample point	7 DAT1		7 DAT2		7 DAT3		14 DAT3		32 DAT3	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
¹⁴ C-Residue	[CN- ¹⁴ C]-cyantraniliprole									
TRR, mg/kg		0.144		0.049		0.045		0.035		0.012
Extracted	98.4	0.142	96.7	0.047	92.9	0.042	89.2	0.031	76.7	0.009
Cyantraniliprole	67.9	0.099	76.8	0.037	72.1	0.033	51	0.018	37.1	0.004
IN-K5A79	7.1	0.011		ND		ND		ND		ND
IN-MLA84/ IN-NXX70	3	0.004		ND		ND		ND		ND
Unidentified	11.4 ^a	0.017	1.9	< 0.001	5.1	0.004	6.9	< 0.001	7.8	< 0.001
¹⁴ C-Residue	[PC- ¹⁴ C]-cyantraniliprole									
TRR, mg/kg		0.017		0.035						0.057
Extracted	96.4	0.016	96	0.034					85.9	0.049
Cyantraniliprole	75.3	0.014	84.1	0.03					69	0.039

Sample point	7 DAT1		7 DAT2		7 DAT3		14 DAT3		32 DAT3	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
IN-J9Z38		ND		ND					10	0.005
IN-MLA84/ IN-NXX70		ND		ND					3.4	0.002
Unidentified	6.6 ^b	< 0.001		ND						ND

^a 13 components; none greater than 0.003 mg/kg (2.7% TRR)

^b 4 components; none greater than 0.001 mg/kg (2% TRR)

In plants from the foliar treatments of a 1:1 mixture of [CN-¹⁴C]-cyantraniliprole + [PC-¹⁴C]-cyantraniliprole, TRRs in leaves declined from 10.8 mg/kg (immediately after the first foliar application) to 0.03 mg/kg at maturity (32 days after the final application).

The majority of the radioactivity (more than 92% TRR) was removed from leaves by surface washing and/or extraction into acidified aqueous acetone.

Cyantraniliprole was the major residue in leaves, decreasing from about 98% TRR immediately after the first application to 50% TRR in mature leaves, 32 days after the last application.

The only metabolite accounting for more than 5% TRR was IN-J9Z38, present in mature leaves at about 23% TRR (0.011 mg/kg). Other metabolites identified in immature leaf samples (IN-MLA84/IN-NXX70, IN-DBC80, IN-QKV54, IN-K5A77, IN-K5A79, IN-N7B69, IN-HGW87 and IN-JSE76) each did not exceed 5% TRR or 0.06 mg/kg. Numerous other metabolites detected but not identified were each present at less than 1% TRR (0.01 mg/kg). Unextracted leaf residues accounted for ≤ 1.5% TRR (≤ 0.03 mg/kg).

The main HPLC method did not resolve the two components IN-MLA84 and the photodegradate IN-NXX70. Subsequent analysis indicated that the photodegradate, IN-NXX70, accounted for 1.9% TRR (0.03 mg/kg) seven days after the first application and was found predominantly in the surface wash. At 7 days after the first application, IN-MLA84 was present in tissue extracts at much lower levels (0.4% TRR, 0.01 mg/kg).

Table 14 Distribution of radioactive residues in lettuce leaves from plants treated with foliar applications of a 1:1 mixture of [CN-¹⁴C]-cyantraniliprole and [PC-¹⁴C]-cyantraniliprole

Sampling point	0 DAT1		7 DAT1		0 DAT2		7 DAT2		0 DAT3		7 DAT3		14 DAT3		32 DAT3	
	TRR, mg/kg		TRR, mg/kg		TRR, mg/kg		TRR, mg/kg		TRR, mg/kg		TRR, mg/kg		TRR, mg/kg		TRR, mg/kg	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
Surface wash	90.7	9.84	82.9	1.38			57.3	1.61					65.6	0.645	12.5	0.004
Tissue extracts ^a	9.2	0.1	16.1	0.27			41.3	1.16			98.4	1.96	32.1	0.315	79.3	0.026
Total Extracted	99.9	10.83	99	1.65			98.6	2.76			98.4	1.96	97.7	0.96	91.7	0.029
Unextracted	< 0.1	< 0.001	1.1	0.018			1.3	0.036			1.5	0.03	2.3	0.023	8.3	0.003
Cyantraniliprole	97.9	10.6	79.1	1.32			87.3	2.45			78.5	1.56	72.6	0.716	50.3	0.016
IN-DBC80	ND		1.2				3.8				3.8		ND		ND	
IN-N7B69	ND		1	0.017			0.4	0.012					ND		ND	
IN-K5A79	ND		1.2	0.018			ND				ND		ND		ND	
IN-JSE76	ND		0.7	0.012			ND				0.7	0.014	ND		ND	
IN-HGW87	ND		0.6	0.01			ND				0.9	0.018	ND		ND	
IN-K5A77	ND		ND				1.2	0.036			ND		ND		ND	
IN-QKV54	ND		ND				1.4	0.042			0.9	0.017	ND		ND	
IN-MLA84/ IN-NXX70	0.3	0.034	3	0.05			2	0.058			1.4	0.027	2.6	0.027	4.9	0.001
IN-J9Z38	0.4	0.042	ND				1	0.028			0.8	0.021	2.3	0.023	23.3	0.011
Unidentified	0.3 ^b	0.035	6.6 ^c	0.103			4.1 ^d	0.117			3.8 ^e	0.078	6.4 ^f	0.067	0.7	0.001

^a Triple extraction with acetone:1 N formic acid

^b 7 components; none greater than 0.006 mg/kg (0.1% TRR)

^c 46 components; none greater than 0.009 mg/kg (0.6% TRR)

^d 29 components; none greater than 0.011 mg/kg (0.4% TRR)

^e 27 components; none greater than 0.009 mg/kg (0.4% TRR)

^f 13 components; none greater than 0.007 mg/kg (0.7% TRR)

The metabolic fate of cyantraniliprole in lettuce grown outdoors was complex, with the formation of many low level metabolites. The proposed metabolic pathway is outlined below.

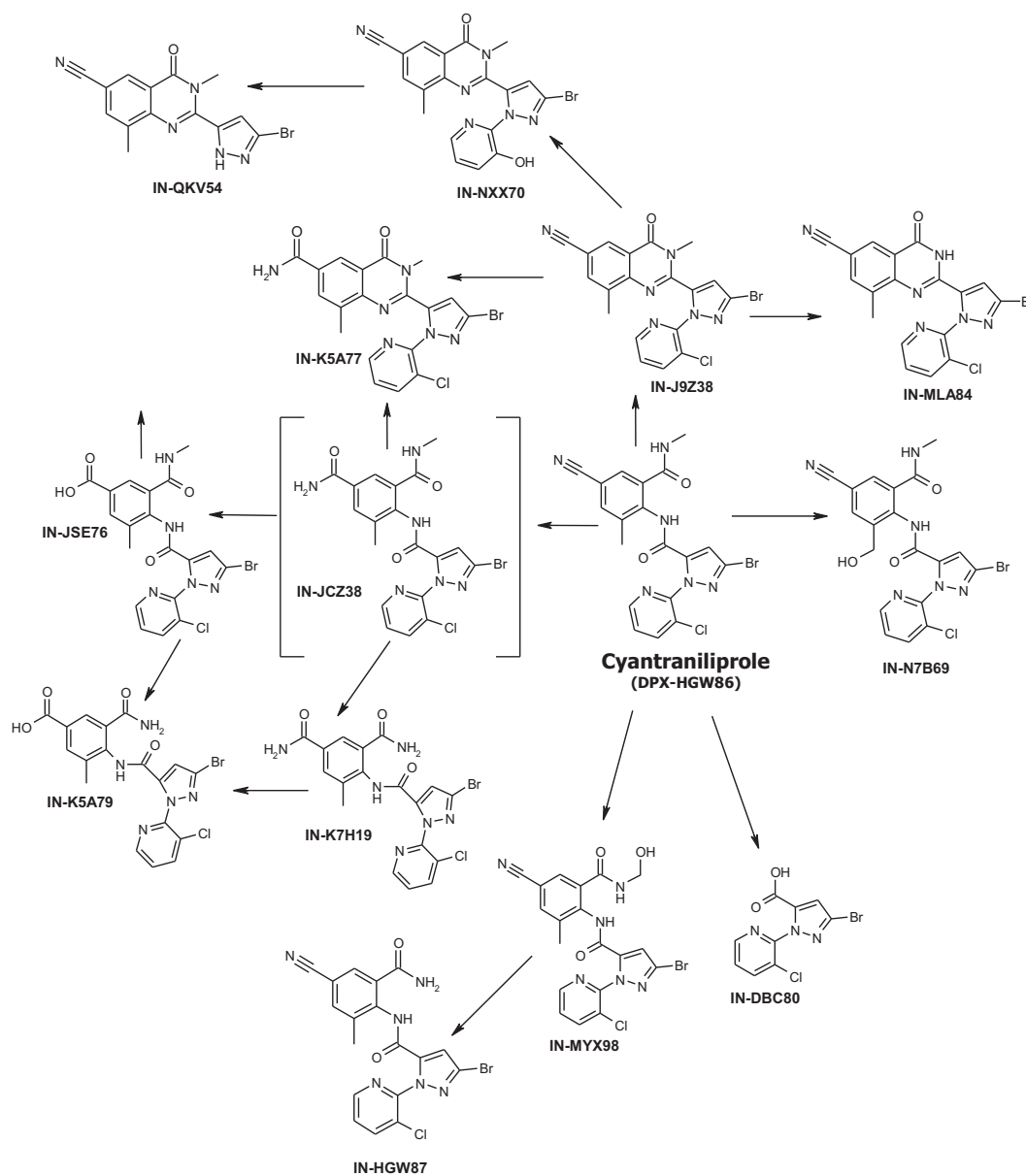


Figure 4 Proposed metabolic pathway for cyantraniliprole in lettuce

Tomatoes

In a study reported by MacKinnon (2008) [Ref: DP-16985], three applications of [^{14}C]-cyantraniliprole equivalent to 150 g ai/ha/treatment, were made to tomato plants grown in 24 cm pots containing an acidic (pH 6.4) commercial growing medium.). Foliar applications (SC formulation) were made to plants 3 weeks post-emergence and at 7 and 14 days after the initial application. Soil drench applications were made 7 weeks post-emergence and at 7 and 14 days after the first application.

Leaves were collected from immature plants after the first application (foliar treatment only), immediately prior to and following the second and third applications, and at ca. 7 and 14 days after the third application. Leaves and fruit were also sampled at crop maturity (ca. 125 days after the third application).

Selected samples from the foliar-treatment regime were surface washed with acetonitrile: water (7:3, v/v) immediately after sampling. Plant samples from both regimes were pulverized and total tissue residues determined by oxidative combustion analysis. Where characterization of radioactivity was warranted, samples were extracted three times using acetone:1 N formic acid (9:1). Insoluble residues from immature leaves were subjected to further sequential extraction using enzyme digestion (2 $\times$ 24 hours with cellulose, glucosidase, driselase), 1 M HCl (6 hours, 60 °C), 6 M HCl (6 hours, 90 °C) and 6 M NaOH (6 hours, 90 °C) hydrolysis. The unextracted radioactivity in the post-extracted solids (PES) was determined by combustion analysis.

Extracts containing significant radioactivity (≥ 0.01 mg/kg) were analysed by high performance liquid chromatography (HPLC) and identification of ^{14}C -residues was accomplished by HPLC and liquid chromatography mass spectrometry (LC-MS), with reference to authenticated reference standards. Samples were stored at ca -20 °C for up to 69 days before analysis.

To assess if storage at -20 °C resulted in degradation of radioactive residues, a subsample of stored leaf tissue (7 days post-application 3, foliar treatment) was extracted with acetone:formic acid following a storage period of 392 days. The TRR and extractability values after prolonged storage (1.86 mg/kg, 84.4% TRR) were similar to those obtained originally (2.21 mg/kg, 87.1% TRR). The residue composition also remained unchanged with cyantraniliprole being the principle component (55.3% TRR, 1.03 mg/kg) and minor components individually making up $\leq 5.4\%$ TRR (< 0.01 mg/kg).

A comparison of the extraction efficiency of acetone:formic acid and acetonitrile:water showed similar results, with the extracted radioactivity from unwashed leaves from the foliar-treated plants being 84% TRR in the acetonitrile extract and 82.8% TRR in the acetone extract. HPLC analysis of the two extracts also reported comparable results, with cyantraniliprole making up 43.4% of the TRR in the acetone extract and 36.6% of the TRR in the acetonitrile extract.

In plants from the soil drench treatments, TRRs in leaves from immature plants reached a maximum of 0.03 mg/kg seven days after the last CN-label application and 0.01 mg/kg 14 days after the last PC-label application. In mature leaves (125 days after the last application), TRRs were < 0.01 mg/kg in leaves and 0.001 mg/kg in fruit.

Only extractable residues from immature leaves taken 7 and 14 days after the last CN-label application were sufficiently high to permit HPLC analysis. Cyantraniliprole was the major radioactive component ranging from 22.2% to 26.1% TRR (0.01 mg/kg). Minor components (unresolved IN-MLA84/IN-NXX70 and IN-J9Z38) each at < 0.01 mg/kg, were also detected in leaves taken 7 days after the last application.

Table 15 Total radioactive residues (mg/kg) in tomato samples following soil drench treatments with [^{14}C]-cyantraniliprole

Treatment	Leaves				Leaves	Fruit
Sample point	7 DAT1	7 DAT2	7 DAT3	14 DAT3	125 DAT3	
[CN- ^{14}C]-cyantraniliprole	0.005	0.023	0.03	0.026	0.008	0.001
[PC- ^{14}C]-cyantraniliprole	0.002	0.012	0.014	0.014	0.009	0.001

Table 16 Distribution of radioactive residues in tomato leaves, 7 and 14 days after the last of three soil drench treatments with [CN-¹⁴C]-cyantraniliprole

Sample point	7 DAT3		14 DAT3	
	%TRR	mg/kg	%TRR	mg/kg
TRR, mg/kg		0.03		0.026
Extracted	86	0.026	78.4	0.02
Cyantraniliprole	22.2	0.006	26.1	0.008
IN-MLA84/ IN-NXX70	6.4	0.002	5.8	0.002
IN-J9Z38	5.4	0.002		ND
Unidentified	11.8	0.006	13.7	0.002

TRRs in tomato leaves immediately following foliar treatments with the 1:1 mixture of [CN-¹⁴C]-cyantraniliprole + [PC-¹⁴C]-cyantraniliprole ranged between 2.55 and 4.81 mg/kg and decreased to 1.3 mg/kg at 14 days after the last application. At harvest, 125 days after the last application, TRRs in leaves and fruit were < 0.01 mg/kg.

In immature leaves, 74–87% TRR was removed by surface washing and/or extraction into acidified aqueous acetone. Low concentrations of radioactivity were subsequently extracted using enzymes (1.2–5.6% TRR), 1 M HCl at 60 °C (1–3.4% TRR), 6 M HCl at 90 °C (0.2–3.7% TRR) and 6 M NaOH at 90 °C (0.7–2.9% TRR).

Cyantraniliprole was the major residue in leaves, decreasing from 95% TRR immediately after the first application to 61% TRR seven days later and accounted for 62 and 43% TRR, respectively, 7 and 14 days after the final application.

Concentrations of the unresolved radioactivity corresponding to both IN-MLA84 and IN-NXX70 were highest 7 days after the first application (11.5% TRR), decreasing to 5.8% TRR thereafter. Further analysis indicated that the photodegrade IN-NXX70 accounted for 12% TRR (0.23 mg/kg) 7 days after the first application, mostly (10% TRR) in the surface wash and declined to 3.8% TRR, 0.08 mg/kg, 7 days after final application. Seven days after the first application, IN-MLA84 was present in tissue extracts at lower levels ($\leq 2.3\%$ TRR, ≤ 0.02 mg/kg).

Other minor metabolites were identified as IN-J9Z38, IN-K7H19, IN-JCZ38, IN-DBC80, IN-N7B69, IN-MYX98, IN-JSE76, IN-K5A77 and IN-QKV54, with no single metabolite exceeding 5% TRR. Numerous other metabolites were detected which did not correspond to known reference standards, none exceeding 5.6% TRR (0.07 mg/kg). The unextracted residue accounted for $\leq 2.3\%$ TRR (≤ 0.03 mg/kg).

In leaves taken at maturity, low levels of radioactivity were present in the surface wash (< 0.01 mg/kg) and the acidified aqueous acetone extract (0.01 mg/kg). The unextracted residues also accounted for < 0.01 mg/kg.

Table 17 Distribution of radioactive residues in leaves from tomato plants treated with foliar applications of a 1:1 mixture of [CN-¹⁴C]-cyantraniliprole and [PC-¹⁴C]-cyantraniliprole

Sampling point	0 DAT1		7 DAT1		7 DAT2		7 DAT3		14 DAT3	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
TRR, mg/kg	2.546		1.849		4.806		2.216		1.298	
Surface wash	65.5	1.668	72.3	1.337	85	4.085				
Tissue extracts	33.6	0.854	27.6 ^a	0.509	15 ^a	0.723	99.2 ^a	2.197	97.7 ^a	1.269
Total Extracted	99	2.52	99.8	1.845	100	4.807	99.2	2.197	97.7	1.269
Unextracted	1.0	0.025	0.1	0.002	0.1	0.005	0.8	0.018	2.3	0.03
Cyantraniliprole	95.3	2.429	61.1	1.132	86.5	4.154	62.2	1.377	43.4	0.562
IN-MLA84/ IN-NXX70	0.9	0.023	11.5	0.213	3.1	0.149	6.6	0.147	5.8	0.074
IN-J9Z38	0.9	0.022	1.6	0.029	1.2	0.051	5.1	0.114	4.4	0.055

Sampling point	0 DAT1		7 DAT1		7 DAT2		7 DAT3		14 DAT3	
TRR, mg/kg	2.546		1.849		4.806		2.216		1.298	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
IN-QKV54	ND		ND		0.8	0.04	2.8	0.062	4.3	0.054
IN-N7B69	ND		ND		0.3	0.016	0.8	0.019	2.9	0.037
IN-JCZ38	ND		1.0	0.019	0.2	0.01	1.0	0.022	2.8	0.036
IN-K7H19	ND		ND		ND		1.2	0.025	1.4	0.019
IN-DBC80	ND		3.8		1.0		3.0		ND	
IN-MYX98	ND		ND		ND		1.0	0.023	1.5	0.018
IN-JSE76	ND		ND		ND		ND		1.0	0.012
IN-HGW87	ND		ND		0.6	0.028	ND		ND	
Unidentified	5.0 ^b	0.102	10.7 ^c	0.197	2.6 ^d	0.137	15.9 ^e	0.352	22.2 ^f	0.265

^a Sequential extraction with acetone:1 N formic acid (3×); a mixture of cellulase, beta-glucosidase and driselase (2× for 24 hours at 37 °C); 1 M HCl (6 hours at 60 °C); 6 M HCl (6 hours at 90 °C) and 6 M NaOH (6 hours at 60 °C)

^b 32 components; none greater than 0.008 mg/kg (0.4%TRR)

^c 23 components; none greater than 0.025 mg/kg (1.3%TRR)

^d 28 components; none greater than 0.02 mg/kg (0.4%TRR)

^e 51 components; none greater than 0.07 mg/kg (3.1%TRR)

^f 45 components; none greater than 0.07 mg/kg (5.6%TRR)

The proposed pathway is outlined below.

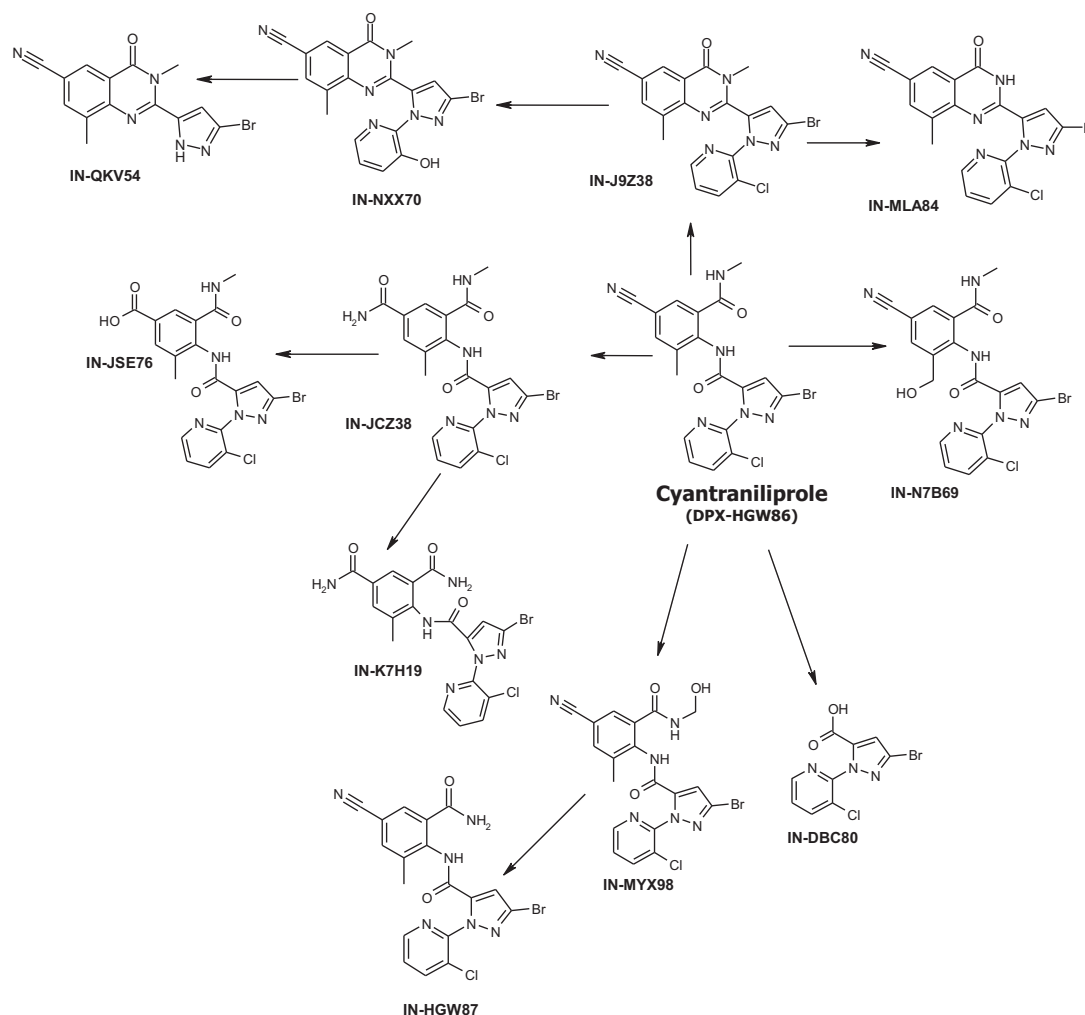


Figure 5 Proposed metabolic pathway for $[^{14}\text{C}]$ -cyantraniliprole in tomatoes

Rice

In a study reported by Chapleo, Hobbs & Grant-MacDonald (2010) [Ref: DP-18780], single soil applications of $[^{14}\text{C}]$ -cyantraniliprole (granular formulations), equivalent to 300 g ai/ha, was applied at the 3–4 leaf stage to rice plants grown in a glasshouse in a sandy-loam soil (pH 6.2) and three foliar applications (SC formulation) of 0.15 kg ai/ha were made to other plants at the 3–4 leaf stage and 7 and 14 days later. In both cases the plants were grown under flooded conditions (pots immersed in about 3 cm water) from 2 days after the initial treatment until 2–3 days before harvest.

Leaves and shoots from foliar-treated plants were sampled 0 and 7 days after the first treatment, 7 days after the second treatment and 7, 14 days after the last treatment with roots being collected 7 days after each treatment. At maturity, 140 days after the last treatment, whole plants were separated into straw, roots, and panicles.

Leaves and shoots from plants grown in treated soil were sampled 3, 7, 14 and 56 days after treatment and roots were collected 7 and 56 days after treatment. At maturity (175 days after treatment), whole plants were separated into straw, roots, and panicles.

Selected samples from the foliar-treatment regime were surface washed with acetonitrile: water (9:1) immediately after sampling. Plant samples from both regimes were homogenised and residues extracted in acetonitrile:water (9:1 then 7:3). Where required, samples were subjected to

further sequential extraction using enzyme digestion (2×24 hours with cellulose, glucosidase, drisease), 1 M HCl (6 hours, 60 °C), 6 M HCl (6 hours, 90 °C) and 6 M NaOH (6 hours, 90 °C). The unextracted radioactivity in the post-extracted solids (PES) was determined by combustion analysis.

Extracts containing significant radioactivity (≥ 0.01 mg/kg) were analysed by reversed phase HPLC and identification of ^{14}C -residues was accomplished by HPLC and liquid chromatography mass spectrometry (LC-MS), with reference to authenticated reference standards. Samples were stored at ca -20 °C for up to 37 days before analysis.

In plants grown in treated soil, TRRs in immature leaves ranged from 0.4–0.42 mg/kg 56 days after treatment and were 0.28–0.37 mg/kg in roots. At maturity (175 days after treatment), TRRS were 0.28–0.3 mg/kg in straw and 0.01–0.03 mg/kg in grain.

Table 18 Total radioactive residues (mg/kg) in rice samples following granular soil treatments with [^{14}C]-cyantraniliprole

	Foliage				Roots		Roots	Straw	Grain
Sample point	3 DAT	7 DAT	14 DAT	56 DAT	7 DAT	56 DAT	175 DAT		
[CN- ^{14}C]-cyantraniliprole	ND	0.076	0.15	0.404	< 0.017	0.253	0.282	0.278	0.012
[PC- ^{14}C]-cyantraniliprole	0.153	0.068	0.145	0.42	< 0.04	0.297	0.367	0.297	0.029

The majority of the radioactivity was extracted into aqueous acetonitrile with 85–87% TRR extracted from immature foliage, 79–80% TRR from straw and 61–67% TRR from grain.

Cyantraniliprole was the major radioactive residue in immature 56 DAT foliage extracts, found at up to 49% TRR and 0.2 mg/kg (PC-label), 57% TRR and 0.23 mg/kg (CN-label). The IN-J9Z78 metabolite was found in these samples at 22% TRR (PC-label) and 16% TRR (CN-label). Other metabolites (including IN-JCZ78, IN-N7B69, IN-K5A77, IN-MLA84 and IN-DBC80) did not exceed 0.011 mg/kg or 3% TRR. The unextracted residue accounted for 4.1–9.8% TRR (< 0.02 mg/kg).

The major residue in straw was also cyantraniliprole (42–45% TRR, 0.125 mg/kg), with IN-J9Z38 (14–18% TRR) being the only significant metabolite, found at 14–18% TRR. Other minor metabolites, each present at less than 4% TRR or 0.01 mg/kg were IN-JCZ38, IN-K5A78, IN-K5A77, IN-MLA84 and IN-DBC80. The unextracted residue accounted for 8.9 % TRR (0.03 mg/kg).

In grain, cyantraniliprole accounted for 46–63% TRR, 0.007–0.014 mg/kg), with IN-J9Z38 (5.9–10.2 % TRR) being the only significant metabolite

Table 19 Distribution of radioactive residues in rice samples following granular soil treatments with [^{14}C]-cyantraniliprole

	Foliage								Straw		Grain	
Sample point	3 DAT		7 DAT		14 DAT		56 DAT		175 DAT		175 DAT	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
CN-label												
Extracted	ND		96.1	0.073	90.9	0.136	86.8	0.351	79.7	0.222	61.1	0.007
Unextracted	ND		3.9	0.003	9.1	0.014	13.2 ^a	0.053	20.3 ^b	0.056	38.9	0.005
Cyantraniliprole			102	0.077	67.1	0.101	57.4	0.232	44.9	0.125	62.7	0.007
IN-J9Z38	ND		ND		16.9	0.025	16.2	0.066	18.4	0.051	10.2	0.001
IN-JCZ38			ND		ND		1.5	0.006	3.6	0.01	ND	
IN-K5A77			ND		ND		ND		3.0	0.008	ND	
IN-K5A78			ND		ND		ND		0.3	0.001	ND	
IN-MLA84			ND		ND		ND		1.4	0.004	ND	
IN-N7B69			ND		ND		1.7	0.007	ND		ND	
Unidentified			ND		ND		ND		8.0	0.023	6.9	< 0.001
PC-label												
Extracted	100	0.153	94.7	0.064	90.2	0.131	85.5	0.359	78.5	0.233	67	0.002
Unextracted	ND		5.3	0.004	9.8	0.014	14.5 ^c	0.061	21.5 ^d	0.064	32.9	0.01
Cyantraniliprole	107.8	0.165	86.2	0.059	58.6	0.085	48.7	0.205	42.1	0.125	46.2	0.014
IN-J9Z38	ND		12.3	0.008	27.9	0.041	22.1	0.093	14.3	0.042	5.9	0.002

	Foliage								Straw		Grain	
Sample point	3 DAT		7 DAT		14 DAT		56 DAT		175 DAT		175 DAT	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
IN-JCZ38	ND		ND		ND		2.3	0.01	2.8	0.008	ND	
IN-K5A77	ND		ND		ND		0.8	0.003	3.7	0.011	ND	
IN-DBC80	ND		ND		ND		0.7	0.003	2.8	0.008	1.1	< 0.001
IN-K5A78	ND		ND		ND		ND		0.6	0.002	ND	
IN-MLA84	ND		ND		ND		0.8	0.003	1.2	0.004	ND	
Unidentified	7.7	0.012	ND		ND		ND		3.0	0.01	3.4	< 0.001

^a Further extraction released a total of 9.6% TRR (0.038 mg/kg)

^b Further extraction released a total of 11.7% TRR (0.034 mg/kg)

^c Further extraction released a total of 10.4% TRR (0.043 mg/kg)

^d Further extraction released a total of 10.7% TRR (0.032 mg/kg)

TRRs in foliage following foliar treatments with the 1:1 mixture of [CN-¹⁴C]-cyantraniliprole + [PC-¹⁴C]-cyantraniliprole were 2.13 mg/kg immediately after the first application, decreasing to 0.38 mg/kg after 7 days. TRRS 7 and 14 days after the last application were 1.56 mg/kg and 1.21 mg/kg respectively. At harvest, 140 days after the last application, TRRs in straw were 0.45 mg/kg and 0.02 mg/kg in grain. In roots, TRRs increased from 0.24 mg/kg seven days after the first application to 0.68 mg/kg seven days after the last application and were 0.45 mg/kg at harvest (140 DAT3).

In immature leaves, 92–99% TRR was removed by surface washing and/or extraction into aqueous acetonitrile (75% TRR in the 7 DAT3 surface wash and 47% TRR in the 14 DAT3 wash). In straw, aqueous acetonitrile extraction removed 87% TRR and further 10.9% TRR was recovered in enzyme, acid and alkali digests. In grain, 49% TRR (0.012 mg/kg) was extracted in aqueous acetonitrile.

Cyantraniliprole was the major residue in immature foliage, making up more than 75% TRR and 0.35–2.13 mg/kg). IN-J9Z38 was the predominant metabolite found at 0.6% TRR immediately after the first application and increasing to 10.9% TRR 14 days after the last application. IN-JCZ38, IN-JSE76, IN-K5A77, IN-K5A78 IN-MLA84, and IN-N7B69 were also detected, none exceeding 2% TRR. Multiple unknown metabolites were detected, none exceeding 2.3% TRR. Unextracted residues accounted for 0.1–7.8% TRR.

In straw, cyantraniliprole was the major extractable component, accounting for 24.4% TRR (0.11 mg/kg). Significant metabolites included IN-JCZ38 (9.4% TRR) and IN-JSE76 (9.0% TRR). Other metabolites were identified as IN-K5A77 (5.3% TRR), IN-DBC80 (3.2% TRR), IN-J9Z38 (4.0% TRR), and IN-K7H19 (2.4% TRR) and seven unidentified metabolites were present (including 2 highly polar metabolites) at 6.6–8.1% TRR. 5.5% TRR (0.02 mg/kg) were not extracted.

Cyantraniliprole was the main extractable component in grain, accounting for 21% TRR (0.01 mg/kg). Metabolites included IN-J9Z38, IN-N7B69 and IN-K5A78 made up 1.5–2.6% TRR and 17 unidentified metabolites were also detected, each at less than 8.0% TRR.). Unextracted residues accounted for 51.3% TRR (0.01 mg/kg).

Table 20 Distribution of radioactive residues in rice samples following three foliar applications of a 1:1 mixture of [CN-¹⁴C]-cyantraniliprole and [PC-¹⁴C]-cyantraniliprole

	Foliage										Straw		Grain	
Sample point	0 DAT1		7 DAT1		7 DAT2		7 DAT3		14 DAT3		140 DAT3		140 DAT3	
TRR (mg/kg)	2.126		0.383		1.0		1.56		1.207		0.446		0.024	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
Surface wash							74.5	1.162	46.8	0.565				
Tissue extracts	99.9	2.124	92.1	0.353	99	0.99	20.0	0.311	51.5	0.623	83.7	0.374	48.7	0.012
Total extracted	99.9	2.124	92.1	0.353	99	0.99	96.6	1.506	95.3	1.151	83.7	0.374	48.7	0.012
Unextracted	0.1	0.002	7.8	0.03	1.0	0.01	3.4	0.053	4.7	0.057	16.3 ^(a)	0.073	51.3	0.012

	Foliage										Straw		Grain	
Sample point	0 DAT1		7 DAT1		7 DAT2		7 DAT3		14 DAT3		140 DAT3		140 DAT3	
TRR (mg/kg)	2.126		0.383		1.0		1.56		1.207		0.446		0.024	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
Cyantraniliprole	100	2.127	90.7	0.347	95.5	0.956	75.6	1.179	81.1	0.98	24.4	0.109	20.9	0.005
IN-J9Z38	0.6	0.014	2.5	0.01	6.3	0.063	7.2	0.112	10.9	0.131	4.0	0.018	1.5	< 0.001
IN-JCZ38	ND		ND		ND		0.6	0.009	0.8	0.009	9.4	0.042	ND	
IN-JSE76	ND		ND		ND		ND		0.2	0.002	9.0	0.04	ND	
IN-K5A77	0.6	0.012	ND		ND		ND		0.8	0.01	5.3	0.024	ND	
IN-K5A78	ND		ND		ND		ND		0.2	0.005	ND		2.6	0.001
IN-DBC80	ND		ND		ND		ND		ND		3.2	0.014	ND	
IN-K7H19	ND		ND		ND		ND		ND		2.4	0.011	ND	
IN-MLA84	ND		ND		0.6	0.006	1.5	0.024	1.9	0.023	ND		ND	
IN-N7B69	ND		ND		ND		1.7	0.027	ND		ND		2.2	0.001
Unidentified	ND		ND		0.5	0.005	5.3 ^(b)	0.084	0.9	0.011	29.4 ^(c)	0.131	15.7	0.003

^a Further extraction released a total of 10.9% TRR (0.048 mg/kg)

^b 8 components; none greater than 0.035 mg/kg (2.3%TRR)

^c 7 components; none greater than 0.036 mg/kg (8.1%TRR)

The metabolic fate of cyantraniliprole in rice growing under flooded conditions was complex with the formation of many low level metabolites. Metabolism following foliar and soil applications appear to be similar. The proposed metabolic pathway is outlined below.

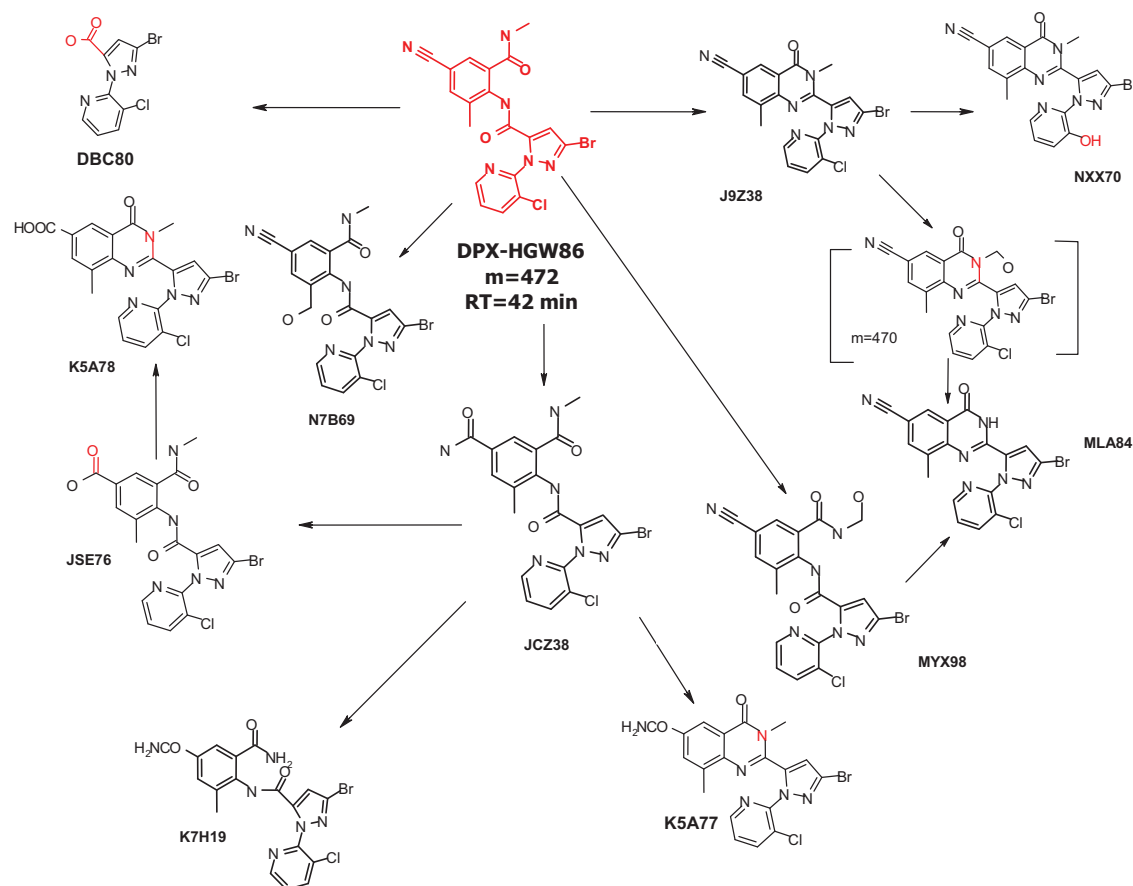


Figure 6 Proposed metabolic pathway for $[^{14}\text{C}]$ -cyantraniliprole in rice

Environmental fate

The Meeting received information on the environmental fate and behaviour of cyantraniliprole, including hydrolytic stability, aerobic metabolism, photolysis and degradation in soil, water/sediment degradation and rotational crop metabolism and field studies.

Hydrolysis

The hydrolytic stability of cyantraniliprole in sterile buffer solutions was reported by Lowrie (2005) [Ref: DP-17058]. Sterile buffered solutions of $1\ \mu\text{g/ml}$ radiolabelled cyantraniliprole at pH 4, 7, and 9 were incubated in the dark at 15, 25 and $35\ ^\circ\text{C}$ for up to 30 days and sampled for analysis by LSC and HPLC at selected time intervals.

Hydrolysis of cyantraniliprole was pH and temperature dependant. At lower pH and temperature, the rate of hydrolysis was significantly less than at high pH and temperature. At all pHs, the only hydrolysis product detected at more than 5% of applied radioactivity (AR) was the cyclisation product IN-J9Z38, which accounted for a maximum of 28% AR (pH 4), 89% AR (pH 7) and 98% AR in the pH 9 samples. Calculated DT_{50} and DT_{90} values for cyantraniliprole and the IN-J9Z38 metabolite are summarised below.

Table 21 Calculated DT₅₀ and DT₉₀ values for cyantraniliprole and the IN-J9Z38 metabolite

pH	Temperature (°C)	Cyantraniliprole			IN-J9Z38		
		Rate constant, K (days)	DT ₅₀ (days)	DT ₉₀ (days)	Rate constant, κ (days)	DT ₅₀ (days)	DT ₉₀ (days)
4	15	0.0019	362	1204			
4	25	0.0033	212	705			
4	35	0.0126	55.2	183			
7	15	0.0055	126	417			
7	25	0.0229	30.3	101			
7	35	0.0923	7.51	25	0.0031	227	755
9	15	0.2234	3.1	10.3			
9	25	0.8152	0.85	2.82			
9	35	1.203	0.576	1.91	0.0018	376	1248

Aerobic soil metabolism

In a study reported by Malekani & Mattson (2006) [Ref: DP-15775], a loam soil (pH 7.9, 2% organic matter) and a silty clay loam soil (pH 6.2, 2.7 % organic matter) were treated with the equivalent of 0.4 kg ai/ha [CN-¹⁴C]-cyantraniliprole or [PC-¹⁴C]-cyantraniliprole and incubated at 22 ± 3 °C in the dark for 358 days. The moisture content of the soils was maintained at 40–60% maximum water holding capacity (MWHC).

Samples were taken immediately following application and at selected intervals up to 358 days after application, extracted with CaCl₂ (to assess aged sorption of cyantraniliprole in conjunction with degradation) and then triple-extracted with acetone:formic acid (9:1) for analysis by LSC and HPLC.

The extractability of cyantraniliprole from both soils was quantitative at Day 0, but extractability decreased while the non-extractable residues (NER) increased as the study progressed, reaching a peak of approximately 16 to 22% in both soils.

Volatile organics were not produced in significant amounts in either soil. The amount of ¹⁴CO₂ evolved was significant, up to 11.8% AR for systems involving with [CN-¹⁴C]-cyantraniliprole and 4.1% AR for [PC-¹⁴C]-cyantraniliprole systems.

Cyantraniliprole levels declined to less than 5% AR in the loam soil and to 30–40% of AR in the silty clay loam by Day 121. Degradation continued past Day 121, with the silty clay loam containing 11–12% AR as cyantraniliprole on Day 358 and was not detected in the loam soil.

Seven major transformation products were observed in the study, with IN-JSE76 being the major component (43% AR) at the end of the study period, with IN-K5A78 and IN-PLT97 also present at 23–29% AR at day 358.

Table 22 Maximum percent of each metabolite in route of degradation study

Component	Maximum% AR [CN- ¹⁴ C]-cyantraniliprole		Maximum% AR [PC- ¹⁴ C]-cyantraniliprole	
	Loam (Namsheim)	Silty clay loam (Tama)	Loam (Namsheim)	Silty clay loam (Tama)
Cyantraniliprole	100.0 (Day 0)	104.9 (Day 0)	101.7 (Day 0)	109.1 (Day 0)
IN-J9Z38	16.0 (Day 16)	11.6 (Day 300)	12.9 (Day 100)	10.8 (Day 300)
IN-JCZ38	16.6 (Day 7)	13.1 (Day 22)	16.1 (Day 22)	12.5 (Day 16)
IN-JSE76	40.4 (Day 41)	42.6 (Day 358)	42.3 (Day 41)	42.9 (Day 358)
IN-K5A77	8.6 (Day 100)	3.8 (Day 358)	8.9 (Day 100)	3.3 (Day 300)
IN-K5A78	28.8 (Day 358)	5.4 (Day 358)	27.2 (Day 358)	4.0 (Day 358)
IN-K5A79 ^a	8.4 (Day 63)	ND	9.3 (Day 41)	ND
IN-PLT97 ^a	22.7 (Day 358)	ND	26.3 (Day 358)	ND

^a IN-K5A79 and IN-PLT97, observed as significant metabolites in Namsheim soil, were not detected (ND) in Tama soil

In a similar study reported by Malekani (2008) [Ref: DP-17055], three additional soils (a silt loam—pH 7, 2.1% organic matter; a sandy loam soil—pH 4.6, 1.6 % organic matter and a silty clay loam—pH 8.05, 4.5% organic matter) were treated with the equivalent of 0.4 kg ai/ha [CN-¹⁴C]-cyantraniliprole or [PC-¹⁴C]-cyantraniliprole, the moisture content was adjusted to 45% MWHC and the soils were incubated at 20 ± 2 °C in the dark for 120 days. One soil was also incubated at 10 ± 2 °C for 120 days.

Observed degradation in all soils was similar to that described in the above study, with the major metabolites present at the end of the 120-day study period being IN-JSE76 and IN-JCZ38 (26-33% AR).

Table 23 Maximum percent of each metabolite in the route of degradation study

Component	Maximum% AR [CN- ¹⁴ C]-cyantraniliprole				Maximum% AR [PC- ¹⁴ C]-cyantraniliprole			
	Silt loam (Gross- Umstadt)	Sandy loam (Sassafras)	Silty clay loam (Lleida)	Silt loam (Gross- Umstadt)	Silt loam (Gross- Umstadt)	Sandy loam (Sassafras)	Silty clay loam (Lleida)	Silt loam (Gross- Umstadt)
Cyantraniliprole	98.5 (Day 0)	97.6 (Day 0)	101.3 (Day 0)	104.6 (Day 0)	101.1 (Day 0)	98 (Day 0)	97 (Day 0)	102 (Day 0)
IN-J9Z38	16.7 (Day 45)	11.9 (Day 45)	16.4 (Day 45)	19.4 (Day 120)	17.9 (Day 60)	6.2 (Day 91)	18.3 (Day 60)	13.3 (Day 90)
IN-JCZ38	18.2 (Day 45)	11.9 (Day 45)	16.4 (Day 45)	19.4 (Day 120)	14.3 (Day 120)	32.8 (Day 120)	11.5 (Day 115)	13.7 (Day 60)
IN-JSE76	25.6 (Day 120)	6.2 (Day 120)	33.3 (day 120)	9.7 (Day 120)	28.5 (Day 120)	4.5 (Day 120)	32.5 (Day 120)	13.7 (Day 120)
IN-K5A77	6.2 (Day 30)	1.6 (Day 120)	5.7 (Day 60)	1.9 (Day 30)	6.1 (Day 120)	4.0 (Day 91)	5.1 (Day 120)	1.4 (Day 30)
IN-K5A78	2.4 (Day 120)	ND	9.7 (Day 90)	ND	3.1 (Day 120)	0.15 (Day 30)	10.5 (Day 120)	ND
IN-K5A79	ND	ND	2.4 (Day 120)	ND	ND	ND	3.0 (Day 120)	2.4 (Day 120)
IN-K7H19	1.3 (Day 120)	ND	ND	ND	1.6 (Day 120)	ND	ND	ND

The residue decline data for the various soils were analyzed using a number of kinetics models. The FOMC model provided the best visual and statistical fit for the observed data across the entire data range.

Table 24 Summary of cyantraniliprole DT₅₀ and DT₉₀ values in soils

Soil	Site	DT ₅₀ -P (days)	DT ₉₀ -P (days)	pH(water)	% OC	CEC	%Clay
Silt loam	Gross-Umstadt	43.7	235	7.04	1.2	8.7	6
Silty clay loam	Lleida	20.9	156	8.05	2.6	17.4	32
Loam	Nambsheim	8.7	66.2	7.9	1.2	6.7	10
Sandy loam	Sassafras	91.9	376	4.62	0.9	6.1	9
Silty clay loam	Tama	39.2	580	6.2	1.6	21.4	34

Degradation rates for all significant metabolites (found at more than 10% of total residue or exceeded 5% at multiple sampling intervals) were investigated in a series of studies. DT₅₀ and DT₉₀ values from these studies are summarised below.

Table 25 Summary of cyantraniliprole metabolite DT₅₀ and DT₉₀ values in soils

Compound	Site	DT ₅₀ -P	DT ₉₀ -P	pH(water)	% OC	CEC	%Clay
IN-JCZ38	Gross-Umstadt	12.1	63.4	6.98	1.0	11.1	12
IN-JCZ38	Lleida	5.0	29.9	7.93	2.0	17.5	38
IN-JCZ38	Nambsheim	3.6	19.4	8.12	1.2	7.0	15
IN-JCZ38	Sassafras	11.2	77.5	5.95	0.6	9.8	13

Compound	Site	DT ₅₀ -P	DT ₉₀ -P	pH(water)	% OC	CEC	%Clay
IN-JCZ38	Tama	9.1	237	6.38	2.2	23.4	34
IN-JSE76	Gross-Umstadt	219	726	6.98	1.0	11.1	12
IN-JSE76	Lleida	157	522	7.93	2.0	17.5	38
IN-JSE76	Nambsheim	86.3	1089	8.12	1.2	7.0	15
IN-JSE76	Sassafras	343	1319	5.95	0.6	9.8	13
IN-JSE76	Tama	1249	5929	6.38	2.2	23.4	34
IN-K5A79	Gross-Umstadt	42.8	142	7.6	1.2	10.2	20
IN-K5A79	Lleida	16.4	54.6	7.64	2	17.6	45
IN-K5A79	Nambsheim	25.4	84.3	7.55	1.6	7.7	13
IN-K5A79	Sassafras	105	350	6.8	1.7	7.1	11
IN-K5A79	Tama	130	432	7.67	1.9	17.1	41
IN-J9Z38	Gross-Umstadt	119	1117	6.99	1.1	8.67	6.8
IN-J9Z38	Lleida	104	346	7.89	1.63	15.74	32.8
IN-J9Z38	Nambsheim	76.8	255	7.95	1.57	7.57	9.6
IN-J9Z38	Sassafras	220	1168	5.37	1.4	7.39	7.6
IN-J9Z38	Tama	177	588	6.17	1.86	19.42	29.6
IN-K5A77	Gross-Umstadt	202	1216	6.99	1.1	8.67	6.8
IN-K5A77	Lleida	27.4	154	7.89	1.63	15.74	32.8
IN-K5A77	Nambsheim	24.0	109	7.95	1.57	7.57	9.6
IN-K5A77	Sassafras	328	1680	5.37	1.4	7.39	7.6
IN-K5A77	Tama	79	1460	6.17	1.86	19.42	29.6
IN-K5A78	Gross-Umstadt	305	1013	6.99	1.1	8.67	6.8
IN-K5A78	Lleida	500	1662	7.89	1.63	15.74	32.8
IN-K5A78	Nambsheim	977	3244	7.95	1.57	7.57	9.6
IN-K5A78	Sassafras	97.8	929	5.37	1.4	7.39	7.6
IN-K5A78	Tama	237	788	6.17	1.86	19.42	29.6
IN-PLT97	Gross-Umstadt	1744	5792	7.6	1.16	10.2	20
IN-PLT97	Lleida	439	1458	7.64	2	17.6	45
IN-PLT97	Nambsheim	711	2363	7.99	1.5	6.7	12
IN-PLT97	Sassafras	1837	6103	6.25	0.93	5.8	17
IN-PLT97	Tama	429	1426	6.71	2.5	22.5	35
IN-QKV54	Gross-Umstadt	215	714	6.9	1.4	9.8	13
IN-QKV54	Lleida	74	247	7.8	1.7	15.0	45
IN-QKV54	Nambsheim	138	457	7.3	2.0	11.7	11
IN-QKV54	Sassafras	179	595	5.3	0.8	5.4	3
IN-QKV54	Tama	161	536	6.7	3.3	17.3	31
IN-RNU71	Gross-Umstadt	107	356	6.9	1.4	9.8	13
IN-RNU71	Lleida	43	142	7.8	1.7	15.0	45
IN-RNU71	Nambsheim	42	139	7.3	2.0	11.7	11
IN-RNU71	Sassafras	175	580	5.3	0.8	5.4	3
IN-RNU71	Tama	46	152	6.7	3.3	17.3	31

Results for IN-JCZ38 reported by Wardrope (2007) [Ref: DP-17597]

Results for IN-JSE76 reported by McCorquodale & Wardrope (2007) [Ref: DP-17598]

Results for IN-K5A79 reported by Pedersen (2008) [Ref: DP-18868]

Results for IN-J9Z38 reported by McCorquodale (2006) [Ref: DP-17596]

Results for IN-K5A77 reported by Morriss (2006) [Ref: DP-17602]

Results for IN-K5A78 reported by McCorquodale & Wardrope (2007) [Ref: DP-17599]

Results for IN-PLT97 reported by Malekani (2008) [Ref: DP-19077]

Results for IN-QKV54 reported by Wardrope (2010) [Ref: DP-29555]

Results for IN-RNU71 reported by McCorquodale (2010) [Ref: DP-29801]

The aerobic degradation of cyantraniliprole in soil is outlined below.

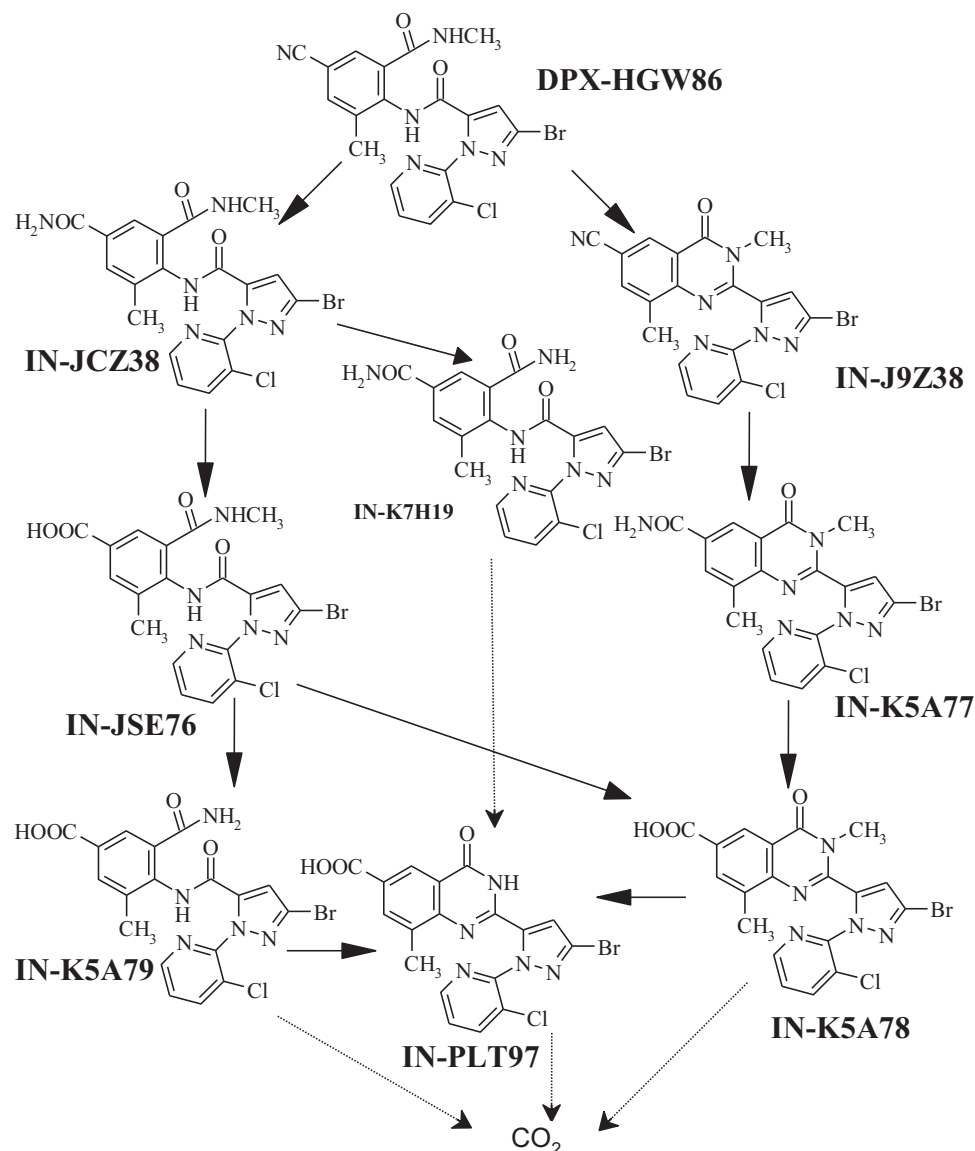


Figure 7 Proposed degradation pathway for cyantraniliprole in aerobic soil

Soil photolysis

The meeting received two studies investigating the soil photolysis of cyantraniliprole on a sandy loam soil (Nambshiem, pH 7.51, 1.22% organic carbon) under continuous irradiation for up to 15 days at 20 ± 2 °C in the study on air-dried soil reported by Morriss (2005) [Ref DP-17056] and up to 30 days at 20 ± 2 °C in the study on moist soil reported by Wardrope (2010) [Ref: DP-28730].

In the 2005 study [Ref DP-17056] the moisture content of the air dried soil was about 14% and the radiolabels were applied to achieve a nominal concentration of 0.4 µg ai/g soil (equivalent to 0.4 kg ai/ha soil) while in the 2010 study [Ref: DP-28730] a higher treatment rate equivalent to 1 kg ai/ha and the moisture level was maintained at about 75% field capacity throughout the study.

The experimental design of both studies were similar, with [CN-¹⁴C]-cyantraniliprole and [PC-¹⁴C]-cyantraniliprole being applied by pipette to thinly-layered soil and irradiated continuously in artificial irradiation (filtered to eliminate wavelengths of < 290 nm). Both studies included an NaOH trap for the collection of ¹⁴CO₂ and soil samples were extracted twice with acetone:formic acid (9:1)

followed by an extraction with acetone. The extracts were combined, concentrated to a small volume and analysed by reverse-phase HPLC. Identification of the degradation products was performed by HPLC and LC/MS/MS or TLC analysis.

No significant photolysis of cyantraniliprole was observed in the air-dried soil (2005) study, as the results from the irradiated and non-irradiated systems were very similar. One major degradation product, IN-J9Z38, was formed in both irradiated and non-irradiated systems, accounting for < 10% AR and three minor transformation products were observed, each of which were only observed at one sampling occasion and accounted for < 5% AR.

Using a first-order kinetic model, the DT₅₀ and DT₉₀ values for cyantraniliprole in non-irradiated samples were 115 days and 381 days, respectively. In irradiated samples the DT₅₀ and DT₉₀ values were 84 days and 278 days, respectively. Levels of IN-J9Z38 were rising at the end of the study.

To isolate the rate of degradation of cyantraniliprole due to photolysis only, the first order rate of degradation constant (k) in the non-irradiated samples was subtracted from the first order rate of degradation constant in the irradiated samples. The resulting corrected DT₅₀ and DT₉₀ values, extrapolated from this 15-day study, were 308 days and 1024 days, respectively.

In the 2010 moist soil study [Ref: DP-28730], cyantraniliprole residues decreased from a mean value of 102% AR at Day 0, to a mean of 1.2% AR after 30 days in the irradiated soil and to a mean of 33% AR in non-irradiated soil. Three significant degradation products were detected over the course of the study. One of these degradation products was identified as IN-J9Z38, reaching a maximum of 49% AR at Day 10 then declining to 34% AR in the irradiated soil and 49% AR in the non-irradiated soil by the end of the study. IN-J9Z38 was likely a result of non-photolytic reactions and has been seen earlier in all soil degradation studies in dark. Two additional degradation products were attributed to photo-degradations, and were identified as IN-RNU71 and IN-QKV54. IN-RNU71 reached a maximum mean value of 13% AR by the end of the study, while IN-QKV54 reached a maximum mean value of 14% AR at Day 10. A further six minor degradation products were also found at < 5% AR and with the exception of IN-NXX70 (3.8% AR), are likely due to non-photolytic reactions.

Using a simple first-order (SFO) model, the calculated DT₅₀ and DT₉₀ values for cyantraniliprole in irradiated soil were 6.9 days and 23 days, respectively and 16 days and 53.3 days, respectively in non-irradiated (dark control) samples.

To calculate the rate of degradation due to photolysis only, the first-order rate of degradation constant in the non-irradiated samples was subtracted from the first-order rate of degradation constant in the irradiated samples. The dark corrected DT₅₀ and DT₉₀ values were 12.2 days and 40.5 days respectively.

Table 26 Photodegradation, DT₅₀ and DT₉₀ for [¹⁴C]-cyantraniliprole in moist soil

System	Kinetic model	Optimized parameters ± standard error	χ ² error	r ²	DT ₅₀ (days)	DT ₉₀ (days)
Parent only irradiated soil system	SFO	M0=97.01 ± 4.4 k _{SFO} =0.1001 ± 0.001	12	0.943	6.9	23.0
	SFO ^a	k _{photolysis} =0.0567 ^b	—	—	12.2	40.6
Dark control system	SFO–SFO	M0 (AR)=95.44 ± 5.27 k _{cyantraniliprole} (d ⁻¹)=0.0434 ± 0.0056 k _{J9Z38} =0.0234 ± 0.0117	8	0.829	10.8	36
Parent plus four metabolites irradiated system	All SFO	M0= 96.2 ± 2.6 Fr _{cyantraniliprole} to J9Z38=0.66 ± 0.058 k _{cyantraniliprole} =0.0976 ± 0.0059	12	0.94	7.1	23.6
		k _{IN-J9Z38} =0.0269 ± 0.0072	25	0.716	25.8	85.6
		k _{IN-RNU71} =0.065 ± 0.044	18	0.918	10.7	35.4
		k _{IN-NXX70} =0.442 ± 0.217	36	0.360	1.6	5.0
		k _{IN-QKV54} =0.091 ± 0.034	16	0.834	7.7	25.4

^a Corrected first-order rate of degradation (k) calculated by subtracting the dark control sample

^b Obtained by subtraction (0.1001–0.0434)

Kinetic modelling suggested that nearly 34% of the parent compound degraded via the photolysis pathway while ca 64% degraded via the soil degradation pathway, indicating that photolysis on the surface of moist soil may be a significant dissipation pathway for cyantraniliprole in the environment.

Significant degradation of cyantraniliprole in irradiated moist soil samples occurred primarily via the non-photolytic soil degradation transformations observed in the absence of light. IN-J9Z38 observed as a major metabolite along with IN-JCZ38, IN-JSE76, IN-K5A77, IN-K5A79, and IN-K7H19 were all identified in the aerobic soil metabolism study. Photodegradation products observed, IN-NXX70 and IN-QKV54, were derived sequentially from photolysis of cyantraniliprole; while IN-RNU71 is proposed to be generated from photolysis of IN-J9Z38. Similar light induced transformations have been observed in the aqueous photolysis and the outdoor water sediment study.

Degradation in soil

Ten field studies were conducted to investigate the degradation and mobility of cyantraniliprole under field conditions. In all of the trials a single application of 0.3 kg ai/ha or 0.45 kg ai/ha was made to bare soil in late spring or early summer.

Soil samples were collected, down to a maximum depth of 90 cm, immediately prior to application and at pre-determined intervals over an 18 month period. Samples were extracted in aqueous acetone, cleaned up via SPE columns and analysed using reverse phase HPLC separation coupled to tandem mass spectrometry (LC-MS/MS). The Limit of Quantification (LOQ) for all analytes was 0.001 mg/kg and mean recovery rates ranged from 74–96%. Analytes included the major soil metabolites (IN-J9Z38, IN-JCZ38, IN-JSE76, IN-K5A77, IN-K5A78, IN-K5A79, and IN-PLT97) in addition to the parent compound. In order to determine the extent of formation of photodegradation products, analysis of IN-NXX70, IN-QKV54, and IN-RNU71 was also carried out in a number of the studies and reported by Vogl & Sharma (2010) [Refs: DP-29556 and DP-29557].

The field studies demonstrated rapid degradation of the cyantraniliprole in field soils (17–51 day half lives). While laboratory studies suggested that pH had some effect on degradation rates, degradation rate under field conditions does not appear to be pH-dependent. Approximately 75% or more of the applied mass dissipated in most of the field studies during the study duration. Downward mobility of the parent compound as well as its metabolites was limited, with residues rarely found below 15 cm. Uptake of the test compound or its metabolites by the crop was generally very low, despite the systemic nature of cyantraniliprole. Soil metabolites, especially those from the IN-JCZ38 side of the degradation pathway (IN-JCZ38, IN-JSE76, and IN-K5A79) were not observed in the field studies to the extent that was expected based on the lab studies. Photochemical degradation was only a minor degradation mechanism (<< 5%) in the field.

Table 27 Maximum formation [%] of all metabolites in soil dissipation studies with cyantraniliprole

Study Ref Location	kg ai/ha ^a	IN-J9Z38	IN-JCZ38	IN-JSE76	IN-K5A77	IN-K5A78	IN-K5A79	IN-PLT97
DP-17061 Spain	0.4	35.8	5.2	4.0	7.7	3.7	0.0	1.5
DP-17062 France	0.45	41.7	11.1	11.6	11.0	13.4	8.2	7.7
DP-17063 Germany	0.35	16.0	2.7	0.4	1.7	0.4	1.4	0.0
DP-17458 Italy	0.22	28.4	13.2	11.7	9.2	7.2	6.1	2.4
DP-17065 USA (WA)	0.43	33.3	9.8	5.6	10.2	7.9	3.5	4.4

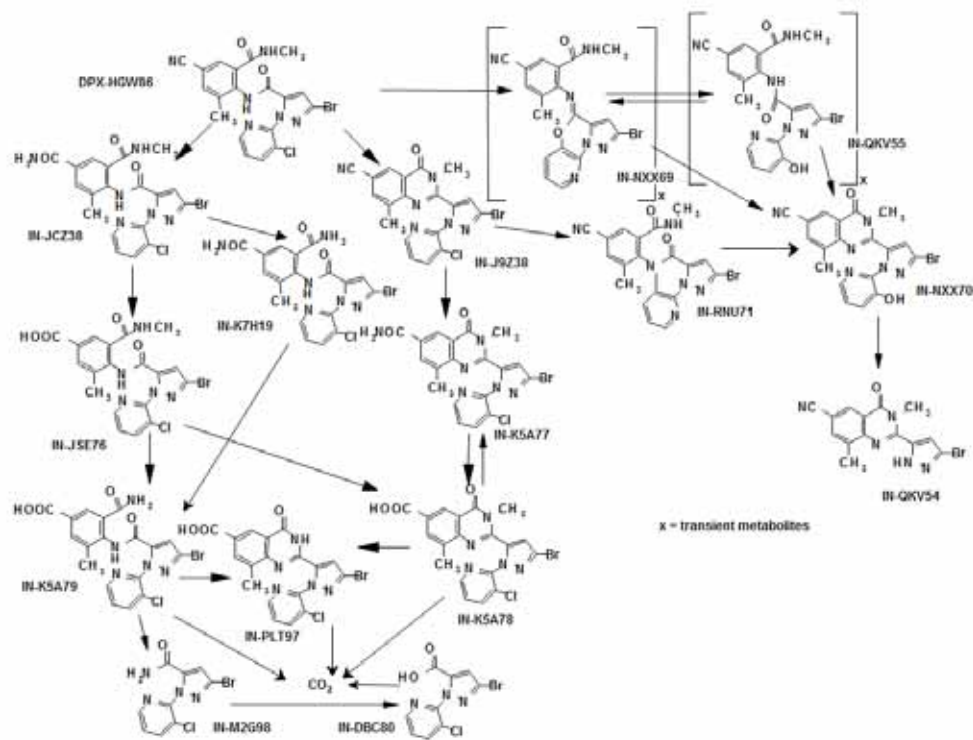


Figure 8 Overall degradation pathway for cyantraniliprole in soil

Degradation in water/sediment systems

A study on the fate of [^{14}C]-cyantraniliprole in the absence of light under anaerobic conditions in two aquatic sediment test systems was reported by McCorquodale & Wardrope, 2006 [Ref: DP-17059]. The sand sediment system, at a pH of 5.6 contained 2% organic carbon with overlying water at pH 6.1 and 56.4 mg/L organic carbon and the silt loam sediment system, at a pH of 7.7 contained 4.9% organic carbon with overlying water at pH 7.6 and 21.2 mg/L organic carbon. [$\text{CN-}^{14}\text{C}$]-cyantraniliprole and [$\text{PC-}^{14}\text{C}$]-cyantraniliprole were separately applied to the two sediment systems at a rate of 0.4 $\mu\text{g ai/g}$ and incubated for up to 100 days in the dark at $20 \pm 2^\circ\text{C}$.

Under anaerobic conditions, cyantraniliprole degraded in the water phase and also partitioned to the sediment where it was further degraded to other metabolites that eventually were incorporated into the sediment organic fraction.

The major metabolite in both systems was IN-J9Z38 which increased to about 23% AR (0.09 ppm) at Day 28 before declining to 7.3% AR (0.03 ppm) in the sand system at the end of the study period (Day 100) and increased to about 40% AR (0.16 ppm) at Day 7 before declining to 5.1% AR (0.02 ppm) by day 100 in the silt loam system.

The IN-K5A77 metabolite accounted for greater than 5% AR at two non-subsequent sampling occasions in the silt loam sediment, but was a minor metabolite in the sand system and silt loam surface water. Additional minor metabolites IN-K5A78 and IN-JSE76 were also observed at $\leq 1.6\%$ and 0.8% AR, respectively. The remaining, combined, unidentified metabolites did not exceed *ca* 1.3% of the applied radioactivity.

The first-order DT_{50} and DT_{90} values for dissipation from the water phase and degradation in the water phase, sediment and total system are summarised below.

Table 29 Cyantraniliprole and metabolite DT₅₀ and DT₉₀ in anaerobic water sediment systems (in the absence of light)

Compound	System	Endpoint type	DT ₅₀ (days)	DT ₉₀ (days)
Loamy sand sediment				
Cyantraniliprole	Water	Dissipation	15.9	53.0
	Total system	Degradation	25.1	83.4
	Water	Degradation	37.7	125
	Sediment	Dissipation	76.6	254
IN-J9Z38	Water	Dissipation	39.0	130
	Total system	Degradation	155	515
	Water	Degradation	324	1077
	Sediment	Degradation	122	405
Silt loam sediment				
Cyantraniliprole	Water	Dissipation	2.74	9.09
	Total system	Degradation	3.87	12.8
	Water	Degradation	3.34	11.1
	Sediment	Dissipation	35.91	1191
IN-J9Z38	Water	Dissipation	17.8	59.1
	Total system	Degradation	272	905
	Water	Degradation	544	1807
	Sediment	Degradation	312	1036
IN-K5A77	Total system	Degradation	19.7	65.4

The aerobic degradation of [¹⁴C]-cyantraniliprole in two irradiated water/sediment systems was studied by Wardrope & Sharma, 2010 [Ref: DP-24798]. A sand sediment system (pH 5.6 containing 2% organic carbon with overlying water at pH 6.1 and 56.4 mg/L organic carbon) and a silt loam sediment system (pH 7.7 containing 4.9% organic carbon with overlying water at pH 7.6 and 21.2 mg/L organic carbon) were treated with [PC-¹⁴C]-cyantraniliprole at a rate of 0.5 µg ai/g and incubated outdoors for 14 days under natural sunlight at 23 ± 2 °C.

At zero time the majority of the radioactivity was detected in the surface water (92–94% AR) decreasing to about 16% AR (silt loam system) and 33% AR (sand system) by Day 14. Solvent extractable radioactivity in the sediment increased from 1% AR at Day 0, to a maximum value of 64% AR (silt loam system) and 55% AR (sand system) by Day 14. Non-extractable residues increased to a maximum value of 5–10% AR by the end of the study period. No radioactivity associated with ¹⁴CO₂ was detected throughout the study period.

HPLC analysis of irradiated water sediment systems demonstrated that [¹⁴C]-cyantraniliprole degraded rapidly in the water phase, from 90% AR at Day 0 to 1–2% AR at Day 14, through a combination of degradation and transfer into the sediment. One significant metabolite was identified as IN-J9Z38, found in the surface water at a maximum of about 15% AR at Day 3 (silt loam system) and 27% AR at Day 5 (sand system) then declining to 4.5% AR and 12% AR respectively on Day 14. Metabolite IN-RNU71 was present at about 4–10% AR and but not observed in dark controls, implying that it was a photolysis product of IN-J9Z38. Minor degradation products (14) accounted for a combined maximum of 6–11% AR and individually less than 3% AR.

The amount of [¹⁴C]-cyantraniliprole in the sediment of the irradiated silt loam system increased initially due to transfer from the water phase, from about 1% AR at Day 0 to a maximum of 22% AR at Day 2 (silt loam system) and 15% AR at Day 3 (sand system) before declining to 9% and 6% AR respectively at 14 days. Six to seven metabolites were detected in the sediment extracts including IN-J9Z38 which increased from about 2% AR at Day 1 to about 42% AR at Day 14. The IN-RNU71 metabolite was present at up to 5% AR and the remaining components each accounted for less than 3% AR.

Table 30 Aerobic degradation of cyantraniliprole in an irradiated silt-loam sediment/water system

Compound	System	% Applied Radioactivity							
		Sampling Intervals (days)							
		0	1	2	3	5	7	10	14
Cyantraniliprole	Water	90.33	68.12	56.14	23.65	10.39	3.77	2.49	2.00
	Sediment	1.10	16.52	22.10	21.94	19.46	15.82	17.26	9.03
	Total	91.43	84.64	78.24	45.59	29.85	19.59	19.75	11.03
	Water (dark)						17.55		9.67
	Sediment (dark)						37.80		30.85
	Total (dark)						55.35		40.52
IN-J9Z38	Water	1.67	4.50	3.11	14.75	14.53	13.42	8.65	4.50
	Sediment	ND	1.57	3.16	22.48	32.57	35.28	41.65	43.29
	Total	1.67	6.07	6.27	37.23	47.10	48.70	50.30	47.79
	Water (dark)						4.06		2.78
	Sediment (dark)						21.04		39.01
	Total (dark)						25.10		41.79
IN-RNU71	Water	ND	ND	ND	1.53	4.27	3.71	3.78	2.52
	Sediment	ND	ND	ND	ND	1.81	2.16	4.52	3.73
	Total	ND	ND	ND	1.53	6.08	5.87	8.30	6.25
Unidentified Radioactivity	Water	ND	1.96	2.76	1.89	3.04	4.00	6.20	6.11
	Sediment	ND	1.09	ND	2.02	2.94	1.69	ND	8.11
	Total	ND	3.05	2.76	3.91	5.98	5.69	6.20	14.22
	Water (dark)						1.65		2.61
	Sediment (dark)						1.93		2.46
	Total (dark)						3.58		5.07
Total extracted residues	Water	92.00	74.56	62.00	41.82	32.24	24.91	21.12	15.70
	Sediment	1.10	19.19	25.26	46.44	56.78	54.96	63.44	64.15
	Water (dark)						23.26		15.05
	Sediment (dark)						60.77		72.31

Table 31 Aerobic degradation of cyantraniliprole in an irradiated sand sediment/water system

Compound	System	% Applied Radioactivity							
		Sampling Intervals (days)							
		0	1	2	3	5	7	10	14
Cyantraniliprole	Water	91.45	78.32	60.40	61.02	25.34	31.61	6.27	1.22
	Sediment	0.88	7.61	9.80	14.78	8.00	14.31	9.72	6.30
	Total	92.33	85.93	70.20	75.80	33.34	45.92	15.99	7.52
	Water (dark)						50.68		7.53
	Sediment (dark)						18.92		22.84
	Total (dark)						69.90		30.37
IN-J9Z38	Water	2.80	4.47	13.78	8.28	26.78	13.42	20.26	11.86
	Sediment	ND	2.06	7.31	7.16	20.88	15.05	34.86	41.71
	Total	2.80	6.53	21.09	15.44	47.66	28.47	55.12	53.57
	Water (dark)						9.91		8.03

Compound	System	% Applied Radioactivity							
		Sampling Intervals (days)							
		0	1	2	3	5	7	10	14
	Sediment (dark)						13.78		48.27
	Total (dark)						23.69		56.30
IN-RNU71	Water	ND	ND	0.36	1.11	4.55	3.28	9.71	9.92
	Sediment	ND	ND	ND	ND	ND	ND	2.50	5.14
	Total	ND	ND	0.36	1.11	4.55	3.28	12.21	15.06
Unidentified Radioactivity	Water	ND	1.92	2.49	2.89	4.85	11.37	6.56	10.16
	Sediment	ND	1.86	0.73	ND	2.91	2.64	1.54	1.59
	Total	ND	3.78	3.22	2.89	7.76	14.01	8.10	11.75
	Water (dark)						ND		1.75
	Sediment (dark)						0.60		2.85
	Total (dark)						0.60		4.60
Total extracted residues	Water	94.25	84.71	77.03	73.31	61.53	59.66	43.19	33.17
	Sediment	0.88	11.53	17.84	21.94	31.79	32.01	48.63	54.75
	Water (dark)						60.59		17.32
	Sediment (dark)						33.30		73.96

The % AR for the silt loam and sandy irradiated sediment/water systems, the dark control systems and the pH 7 buffer system, were analyzed using ModelMaker to derive various degradation rates. The calculated DT₅₀ and DT₉₀ values for cyantraniliprole, IN-J9Z38 and IN-RNU71 are summarized below.

Table 32 Cyantraniliprole and metabolite DT₅₀ and DT₉₀'s in irradiated aerobic water sediment systems

Sediment/water system	Model (All SFO)	Component	DT ₅₀ (days)	DT ₉₀ (days)
Silt loam outdoor	Parent only, total system	cyantraniliprole	3.5	11.6
	Parent + 2 metabolites, total system	cyantraniliprole	3.6	11.9
		IN-J9Z38	40.1	133
		IN-RNU71	13.5	45.0
	Parent + 2 metabolites, two phase system	cyantraniliprole_sediment	2.6	8.3
		cyantraniliprole_water	6.7	
Sandy, outdoor	Parent only, total system	cyantraniliprole	4.4	14.8
	Parent + 2 metabolites, total system	cyantraniliprole	4.5	14.9
		IN-J9Z38	40.8	135
	Parent + 2 metabolites, two phase system	cyantraniliprole_sediment	2.3	7.6
		cyantraniliprole_water	10.1	33.4
		IN-J9Z38_sediment	49.4	
		IN-J9Z38_water	11.3	
		IN-RNU71_water	42.9	
Silt loam and sandy ^a dark control	Parent + 1 metabolite	cyantraniliprole	7.7	25.6
Buffer control outdoor	Parent + 3 metabolites	cyantraniliprole	14.1	47
		IN-J9Z38	2.5	8.4
		IN-RNU71	12.1	40.3

^a Both sediments modelled as replicates

In summary, cyantraniliprole degrades rapidly in outdoor water sediment systems, with total system DT_{50} values of 3.5 and 4.4 days in the silt loam and sand systems, respectively. The corresponding parent only total system DT_{90} values were 11.6 and 14.8 days in the silt loam and sand systems, respectively. The degradation rate was significantly faster than corresponding systems shielded from sunlight. The degradation rate was also faster than degradation observed in sterilized buffer exposed to sunlight.

Significant metabolites formed in the water/sediment system exposed to sunlight were IN-J9Z38 and IN-RNU71. While IN-J9Z38 was also identified in the silt loam and sand system dark controls, degradation was faster in the presence of light, suggesting that photodegradation is an important pathway. The formation of IN-RNU71, a photodegrade of IN-J9Z38 supports this conclusion.

Cyantraniliprole degradation in water/sediment systems involved a number of pathways and is outlined below.

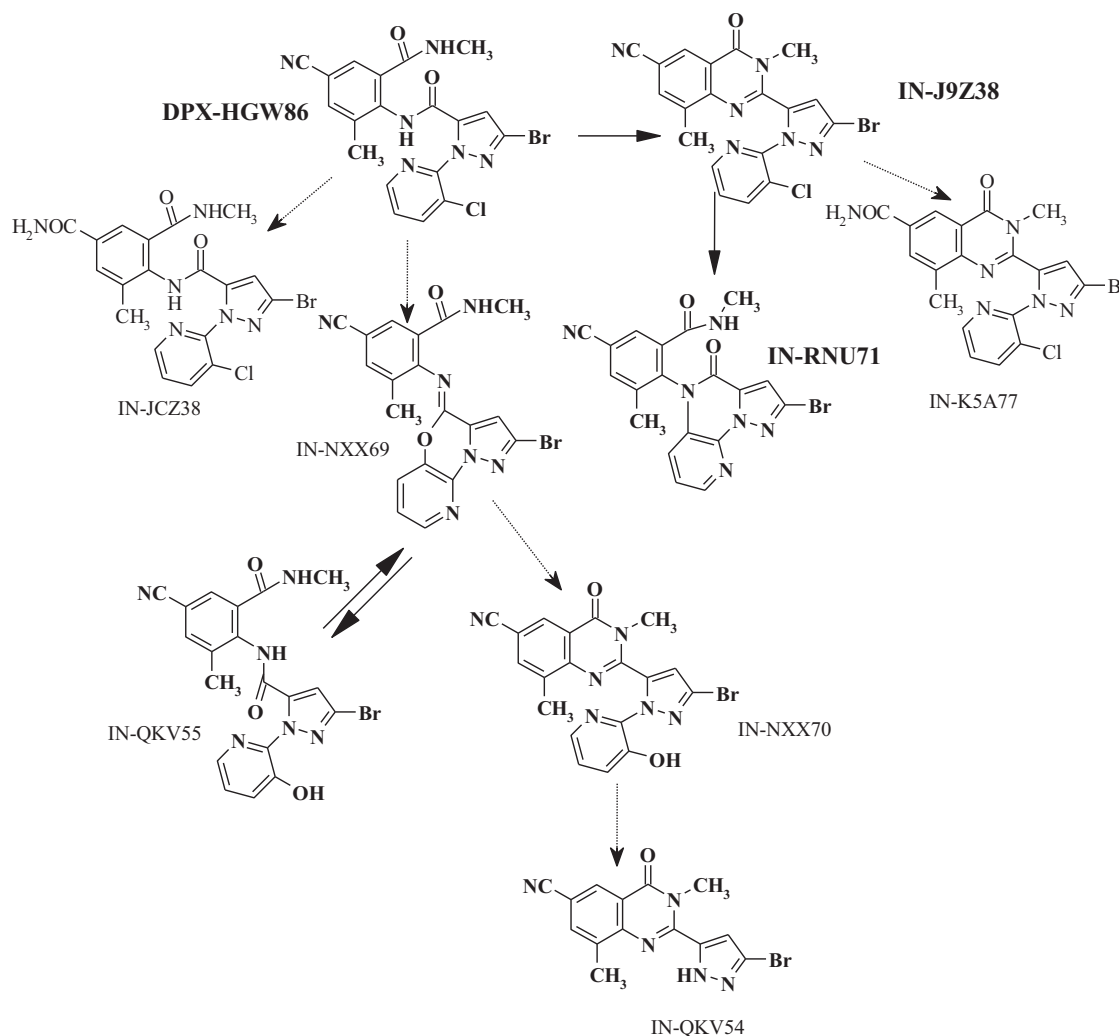


Figure 9 Degradation of cyantraniliprole in outdoor water-sediment

Residues in rotational crops

Rotational crops metabolism

The Meeting received information on the fate of residues in lettuce, red beet, wheat, soya bean and wheat grown as rotational crops in cyantraniliprole-treated soil.

In a preliminary glasshouse study reported by Scott, Swain & Young (2006) [Ref: DP-15513], a sandy loam soil was treated with the equivalent of 0.3 kg ai/ha of [PC-¹⁴C]-cyantraniliprole (SC formulation) and wheat, soya bean, and red beet seeds were sown 25 and 120 days after treatment.

Crop samples from each soil-aging interval were taken, pulverised in dry ice and total radioactive residues (TRR) determined by combustion analysis and LSC. Samples were extracted using acetonitrile:water (9:1) followed by acetonitrile:water (7:3 or 1:1), cleaned up by SPE and analysed by HPLC, with confirmation by LC-MS and LC-MS/MS.

TRRs in wheat straw were 1.15 mg/kg and 0.75 mg/kg (cyantraniliprole equivalents) from the 25 and 120 day soil aging intervals, respectively. Lower TRRs were observed in the corresponding wheat chaff (0.37 and 0.21 mg/kg) and grain (0.02 mg/kg). Cyantraniliprole was the predominant residue in wheat straw (0.52 mg/kg) and chaff (0.23 mg/kg) after the 25-day soil aging period and 0.36 and 0.1 mg/kg respectively after the 120-day aging period. Components in straw from the 25-day aging period included IN-N7B69 (0.01 mg/kg), IN-N7B69 glucoside (0.07 mg/kg), IN-JCZ38 (0.08 mg/kg), IN-K5A77 (0.03 mg/kg), IN-JSE76 (0.1 mg/kg), IN-J9Z38 (0.05 mg/kg), IN-MLA84 (0.01 mg/kg), IN-K5A78 (0.01 mg/kg), IN-K5A79 (0.01 mg/kg) and polars (0.03 mg/kg). In general all the components (with the exception of IN-K5A78) were observed in the straw from the 120-day soil aging period but at lower concentrations. In grain, residues included cyantraniliprole, IN-N7B69, IN-N7B69 glucoside, IN-JSE76 and polars, each at ≤ 0.01 mg/kg.

Table 33 Distribution of residues in wheat planted as a rotational crop 25 days and 120 days after soil treatment with [PC-¹⁴C]-cyantraniliprole (0.3 kg ai/ha)

Aging period	25 day						120 days					
	Grain		Chaff		Straw		Grain		Chaff		Straw	
Residue	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
TRR		0.021		0.374		1.149		0.019		0.201		0.749
Extracted	90.5	0.019	87.7	0.328	94.6	0.966	97.6	0.019	106	0.213	92.4	0.692
Cyantraniliprole	9.7	0.002	61.6	0.23	45.3	0.521	14.6	0.003	47.4	0.101	47.9	0.359
Polars ^a	37.9	0.008	3.1	0.012	3.0	0.034	39.8	0.008	7.0	0.015	23.8	0.028
IN-K5A77	ND		ND		0.91	0.011	ND		ND		1.7	0.013
IN-K5A78	ND		ND		0.87	0.010	ND		5.9	0.013	ND	
IN-K5A79	ND		ND		2.5	0.029	ND		ND		ND	
IN-J9Z38	ND		4.1	0.015	4.6	0.053	ND		ND		5.7	0.043
IN-JCZ38	ND		5.0	0.019	6.5	0.075	ND		6.9	0.015	7.4	0.056
IN-JSE76	ND		3.3	0.012	9.2	0.105	3.5	0.001	8.3	0.018	9.4	0.07
IN-MLA84	ND		4.2	0.016	3.7	0.014	ND		ND		5.7	0.043
IN-N7B69	13.2	0.003	ND		1.1	0.013	25.1	0.005	ND		3.1	0.023
IN-N7B69gluc ^b	22.0	0.005	ND		6.7	0.07	ND		ND		1.9	0.014

^a Polars are one or more components individually present at ≤ 0.02 mg/kg

^b IN-N7B69 glucoside

TRRs in soya bean foliage, pods, and seed grown in soil aged 25 days were 0.18, 0.09, and 0.04 mg/kg, respectively. TRRs in the corresponding soya bean fractions from the 120-day interval were 0.13, 0.07, and 0.02 mg/kg, respectively. Cyantraniliprole accounted for 0.07 and 0.02 mg/kg in soya bean foliage from the 25-day and 120-day soil aging periods, respectively. Other foliage components included IN-JCZ38 (0.01 mg/kg), IN-JSE76, IN-MLA84 (≤ 0.03 mg/kg) and IN-J9Z38 (0.02 mg/kg). Soya bean (seed) components included IN-JCZ38, IN-K5A78, IN-N7B69, and polar components, each at ≤ 0.01 mg/kg. No cyantraniliprole was detected in the soya bean seed.

Table 34 Distribution of residues in soya beans planted as a rotational crop 25 days and 120 days after soil treatment with [PC-¹⁴C]-cyantraniliprole (0.3 kg ai/ha)

Aging period	25 day						120 days					
	Seed		Foliage		Pod		Seed		Foliage		Pod	
Residue	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
TRR		0.038		0.185		0.094		0.018		0.127		0.073
Extracted	98.1	0.037	94.1	0.174	86.4	0.081	101	0.018	72.5	0.092	88.6	0.065
Cyantraniliprole	ND		36.3	0.067	14.0	0.013	ND		14.8	0.019	14.2	0.01
Polars ^a	ND		ND		ND		33.6	0.006	ND		11.2	0.008
IN-K5A77	ND		ND		ND		ND		ND		ND	
IN-K5A78	ND		ND		ND		11.1	0.002	ND		ND	
IN-K5A79	ND		ND		ND		ND		ND		ND	
IN-J9Z38	ND		ND		ND		ND		15.6	0.02	ND	
IN-JCZ38	23.6	0.009	7.4	0.014	24.1	0.023	10.9	0.002	ND		9.4	0.007
IN-JSE76	ND		14.4	0.027	ND		ND		9.5	0.012	ND	
IN-MLA84			15.0	0.028	ND		ND		15.6	0.02	ND	
IN-N7B69	23.3	0.009	ND		ND		ND		ND		ND	
IN-N7B69gluc ^b	ND		ND		ND		ND		ND		ND	

^a Polars are one or more components individually present at ≤ 0.02 mg/kg^b IN-N7B69 glucoside

TRRs in red beet were 0.11 and 0.04 mg/kg for foliage samples; 0.02 mg/kg and 0.01 mg/kg in root samples taken from red beets grown in soil aged 25 and 120 days, respectively. No cyantraniliprole was found in beet foliage from either aging period. Foliage components included IN-N7B69 glucoside (≤ 0.05 mg/kg) and polars (0.01 mg/kg). Low levels (≤ 0.01 mg/kg) of cyantraniliprole, IN-N7B69 glucoside, IN-N7B69, IN-J9Z38, and IN-JCZ38 were found in beet roots.

Table 35 Distribution of residues in red beet planted as a rotational crop 25 days and 120 days after soil treatment with [PC-¹⁴C]-cyantraniliprole (0.3 kg ai/ha)

Aging period	25 day				120 days			
	Roots		Foliage		Roots		Foliage	
Residue	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
TRR		0.021		0.107		0.008		0.039
Extracted	99	0.021	92	0.098	99	0.008	94	0.037
Cyantraniliprole	26.8	0.006	ND		16.9	0.001	ND	
Polars ^a	ND		ND		ND		12.9	0.005
IN-K5A77	ND		ND		ND		ND	
IN-K5A78	ND		ND		ND		ND	
IN-K5A79	ND		ND		ND		ND	
IN-J9Z38	11.5	0.002	ND		13.9	0.001	ND	
IN-JCZ38	ND		ND		9.6	0.001	ND	
IN-JSE76	ND		ND		ND		ND	
IN-MLA84	ND		ND		ND		ND	
IN-N7B69	24.8	0.005	ND		14.7	0.001	ND	
IN-N7B69gluc ^b	16.3	0.003	49.5	0.053	ND		40.0	0.015

^a Polars are one or more components individually present at ≤ 0.02 mg/kg^b IN-N7B69 glucoside

In a glasshouse study reported by Chapleo & Green (2012) [Ref: DP-15778], a sandy loam soil (pH 6.2, 1.4% organic matter) was treated with the equivalent of 0.45 kg ai/ha of either [CN-¹⁴C]-cyantraniliprole or [PC-¹⁴C]-cyantraniliprole (SC formulation) and wheat, lettuce, and red beet seeds were sown 30 and 120 days after treatment. After 365 days aging, a further sowing of spring wheat was made into the soil which had received the 30 day sowing.

Crop samples from each soil-aging interval were taken, pulverised in dry ice and total radioactive residues (TRR) determined by combustion analysis and LSC. Samples were extracted using either acetone:1N formic acid (9:1) or acetonitrile:water (9:1) followed by acetonitrile:water

	Sowing	Maturity	Sowing	Maturity	Sowing	Maturity
Days after soil treatment	30	146	120	263	365	493
Extracted	0.195 (93.5%)	0.158 (81.3%)	0.167 (83.1)	0.150 (74.2%)	0.109 (66.7%)	0.141 (63.3%)
Unextracted	0.014 (6.5)	0.036 (18.7)	0.034 (16.9)	0.052 (25.8)	0.054 (33.3)	0.081 (36.7)
Total	0.209	0.194	0.201	0.202	0.163	0.222

The predominant residue was cyantraniliprole, contributing 14–36% TRR (≤ 0.02 mg/kg) in wheat grain, 21–24% TRR (< 0.01 mg/kg) in red beet roots, and 40–69% TRR (0.01 to 0.08 mg/kg) in lettuce. Cyantraniliprole was also the principal radioactive component (0.01 to 0.85 mg/kg, 6 to 73% TRR) in wheat forage (71–73% TRR, 0.2–0.23 mg/kg), hay (52–53% TRR, 0.78–0.85 mg/kg) and straw 941–45% TRR, 0.4–0.44 mg/kg). Unchanged cyantraniliprole in the beet foliage accounted for no more than 0.005 mg/kg (4.1% TRR).

The IN-MYX98 metabolite was found in lettuce at up to 16% TRR (0.007 mg/kg in the 120 day rotation. Minor components individually present at ≤ 0.01 mg/kg ($< 10\%$ TRR) included IN-J9Z38, IN-JCZ38, IN-K5A79, IN-K7H19, IN-MLA84, and IN-N7B69 in grain; IN-DBC80, IN-J9Z38, IN-K5A77, IN-MYX98, and IN-N7B69 in red beet roots; and IN-J9Z38, IN-JCZ38, IN-MLA84 in lettuce. Uncharacterised fractions accounted for ≤ 0.01 mg/kg.

The main metabolites detected in wheat forage, hay and straw were IN-J9Z38 (≤ 0.18 mg/kg, 12% TRR), IN-K7H19 (≤ 0.06 mg/kg, 11% TRR), and IN-MLA84 (≤ 0.11 mg/kg, 6.6% TRR) and IN-JCZ38 (≤ 0.05 mg/kg); concentrations of minor metabolites (IN-DBC80, IN-HGW87 IN-JSE76, IN-K5A77, IN-K5A78, IN-K5A79, IN-MYX98, IN-N7B69, and IN-NBC94) were individually ≤ 0.02 mg/kg. Unextracted residues in the wheat feed samples accounted for no more than 10% TRR.

Red beet foliage contained low level (≤ 0.01 mg/kg) metabolites, IN-DBC80, IN-HGW87, IN-J9Z38, IN-JCZ38, IN-JSE76, IN-K5A77, IN-K5A78, IN-K5A79, IN-K7H19, IN-MLA84, IN-MYX98, IN-N7B69, and IN-NBC94. Unidentified components accounted for up to 0.03 mg/kg. Following enzyme treatment, these unidentified components decreased and levels of cyantraniliprole and IN-N7B69 increased, indicating that both IN-N7B69 and cyantraniliprole were present in conjugated form or associated with soluble natural products. Unextracted residues accounting for no more 9.1% TRR and did not exceed 0.01 mg/kg.

Table 38 Nature of residue in wheat grain from plants sown in soil treated with 0.45 kg ai/ha [^{14}C]-cyantraniliprole

Planting interval:	[CN- ^{14}C]-cyantraniliprole				[PC- ^{14}C]-cyantraniliprole			
	30 DAT		365 DAT		30 DAT		365 DAT	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
TRR (mg/kg) ^a	0.056		0.014		0.054		0.018	
Solvent extractable	43.3	0.024	56.5	0.008	54.5	0.03	71.2	0.013
Cyantraniliprole	20.0	0.011	33.0	0.005	36.3	0.02	13.6	0.003
IN-J9Z38	2.9	0.002	2.8	< 0.001	5.1	0.003	ND	
IN-JCZ38	5.7	0.003	ND		0.8	< 0.001	ND	
IN-K5A79	ND		ND		ND		3.4	0.001
IN-K7H19	ND		ND		ND		7.2	0.002
IN-MLA84	1.9	0.001	ND		1.2	0.001	ND	
IN-N7B69	ND		ND		ND		5.2	0.001
Total unidentified metabolites	1.3	< 0.001	ND		2.3	0.001	23.8	0.005
Total solubilized fractions ^b	48.2	0.026			35.1	0.019		
Total extractable ^c	91.5	0.050	56.5	0.008	89.6	0.049	71.2	0.013
Terminal unextracted ^d	14.1	0.008	43.6	0.006	8.1	0.004	28.8	0.005

^a Solvent extractable + solubilised fractions + unextracted

^b Sum of residues released in enzyme, acid and alkaline digests; no digest contained > 0.01 mg/kg

^c Values include losses or gains incurred during processing of samples.

^d Residues remaining in the PES after exhaustive extraction

Table 39 Nature of residue in red beet roots from plants sown in soil 30 days after treatment with 0.45 kg ai/ha [¹⁴C]-cyantraniliprole

	[CN- ¹⁴ C]-cyantraniliprole		[PC- ¹⁴ C]-cyantraniliprole	
	% TRR	mg/kg	% TRR	mg/kg
TRR (mg/kg) ^a	0.021		0.031	
Solvent extractable ^b	83.3	0.017	87.2	0.027
Cyantraniliprole	21.0	0.005	23.8	0.007
IN-DBC80			4.1	< 0.001
IN-J9Z38	3.2	< 0.001	5.5	0.002
IN-K5A77	1.2	< 0.001	2.2	< 0.001
IN-MYX98	ND	ND	2.4	0.001
IN-N7B69	6.3	< 0.001	2.9	< 0.001
Total unidentified metabolites	10.3	< 0.001	8.6	0.001
Unextracted	16.4	0.003	15.4	0.005

^a Solvent extractable + unextracted^b Values include losses or gains incurred during processing of samples.Table 40 Nature of residue in lettuce foliage from plants sown in soil treated with 0.45 kg ai/ha [¹⁴C]-cyantraniliprole

Planting interval:	[CN- ¹⁴ C]-cyantraniliprole				[PC- ¹⁴ C]-cyantraniliprole			
	30 DAT		120 DAT		30 DAT		120 DAT	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
TRR (mg/kg) ^a	0.114		0.036		0.078		0.023	
Solvent extractable ^b	89.4	0.103	97.9	0.035	90.2	0.070	102.4	0.024
Cyantraniliprole	68.1	0.079	69.1	0.025	60.0	0.047	39.6	0.009
IN-J9Z38	4.5	0.005	1.4	0.001	1.2	0.001	ND	ND
IN-JCZ38	3.7	0.005	1.6	0.001	ND	ND	ND	ND
IN-MLA84	4.3	0.005	2.3	0.001	3.5	0.003	2.1	< 0.001
IN-MYX98	0.7	0.001	16.4	0.007	ND	ND	9.1	0.003
Total unidentified metabolites	0.6	0.001	1.5	0.001	6.7	0.002	15.8	0.004
Unextracted	6.5	0.007	4.7	0.002	8.2	0.006	4.1	0.001

^a Solvent extractable + unextracted^b Values include losses or gains incurred during processing of samples.Table 41 Nature of residue in wheat forage from plants sown in soil treated with 0.45 kg ai/ha [¹⁴C]-cyantraniliprole

Planting interval:	30 DAT		120 DAT		365 DAT	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
[CN- ¹⁴ C]-cyantraniliprole						
TRR (mg/kg) ^a	0.313		0.129		0.128	
Solvent extractable	84.4	0.263	95.3	0.122	81.8	0.105
Cyantraniliprole	72.7	0.226	70.5	0.090	25.2	0.032
IN-J9Z38	4.0	0.013	11.0	0.015	3.9	0.005
IN-JCZ38	1.8	0.006	1.1	0.001	6.2	0.008
IN-MLA84	3.9	0.012	4.8	0.006	6.8	0.008
Total unidentified metabolites	ND		ND		5.1	0.006
Total solubilized fractions ^b					4.7	0.006
Total extractable ^c	84.4	0.263	95.3	0.122	86.5	0.111
Terminal unextracted ^d	7.6	0.024	9.8	0.013	8.5	0.011
[PC- ¹⁴ C]-cyantraniliprole						
TRR (mg/kg) ^a	0.287		0.103		0.089	
Solvent extractable	93.0	0.267	88.7	0.092	86.7	0.077
Cyantraniliprole	71.0	0.205	34.6	0.036	6.4	0.006
IN-J9Z38	3.8	0.011	11.5	0.011	ND	
IN-JCZ38	1.6	0.004	0.5	0.001	ND	

Planting interval:	30 DAT		120 DAT		365 DAT	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
IN-JSE76	0.2	0.001	6.2	0.007	1.2	0.001
IN-HGW87	0.5	0.002	ND		3.4	0.003
IN-K7H19	1.4	0.005	ND		1.2	0.001
IN-K5A79	ND		ND		2.1	0.002
IN-MYX98	ND		ND		1.5	0.001
IN-MLA84	5.0	0.015	1.5	0.002	ND	
IN-N7B69	ND		3.3	0.004	4.4	0.004
Total unidentified metabolites	2.9	0.008	12.3	0.012	27.0	0.023
Total solubilized fractions ^b			4.2	0.004	4.7	0.004
Total extractable ^c	93.0	0.267	92.9	0.096	91.4	0.081
Terminal unextracted ^d	9.0	0.026	7.1	0.007	8.7	0.008

^a Solvent extractable + solubilised fractions + unextracted

^b Total solubilized fractions= residues released by enzymes

^c Values include losses or gains incurred during processing of samples.

^d Residues remaining in the PES after enzyme extraction

Table 42 Nature of residue in wheat hay from plants sown in soil treated with 0.45 kg ai/ha [¹⁴C]-cyantraniliprole

Planting interval:	[CN- ¹⁴ C]-cyantraniliprole						[PC- ¹⁴ C]-cyantraniliprole					
	30 DAT		120 DAT		365 DAT		30 DAT		120 DAT		365 DAT	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
TRR (mg/kg) ^a	1.463		0.312		0.561		1.625		0.449		0.555	
Solvent extracted	60.0	0.88	77.4	0.241	79.4	0.447	83.8	1.361	81.5	0.366	77.2	0.429
Cyantraniliprole	53.4	0.78	50.0	0.155	40.8	0.23	52.2	0.848	35.8	0.161	29.5	0.163
IN-DBC80							1.5	0.025	ND		1.5	0.008
IN-HGW87	ND		ND		0.6	0.004	0.3	0.005	ND		ND	
IN-J9Z38	12.3	0.18	7.2	0.022	12.9	0.073	10.9	0.178	6.6	0.03	7.1	0.039
IN-JCZ38	2.3	0.03	ND		3.7	0.021	2.7	0.044	5.1	0.022	4.0	0.022
IN-JSE76	ND		1.7	0.005	1.0	0.006	0.6	0.01	ND		2.6	0.015
IN-K5A77	ND		ND		0.8	0.004	ND		ND		0.2	0.001
IN-K5A78	0.1	0.001	ND		0.2	0.001	ND		ND		0.3	0.001
IN-K5A79	ND		ND		0.7	0.004	ND		0.8	0.004	0.2	0.001
IN-K7H19	ND		ND		1.3	0.007	0.9	0.014	ND		10.9	0.060
IN-MLA84	6.1	0.09	3.8	0.012	5.5	0.031	6.6	0.108	2.7	0.012	2.9	0.016
IN-MYX98	0.8	0.01	1.2	0.004	3.3	0.018	ND		5.1	0.024	ND	
IN-N7B69	1.3	0.02	ND		1.6	0.01	0.3	0.005	ND		0.7	0.004
IN-NBC94	ND		ND		0.3	0.002	ND		ND		ND	
Total unidentified	1.4	0.02	4.9	0.015	3.3	0.017	3.5	0.057	6.2	0.027	9.7	0.054
Total solubilized ^b	35.4	0.52	11.5	0.036	12.6	0.08	9.8	0.152	10.9	0.049	7.0	0.038
Total extractable ^(c)	95.4	1.4	88.9	0.277	92.0	0.517	93.6	1.521	92.4	0.415	84.2	0.467
Unextracted ^(d)	2.1	0.03	7.6	0.024	7.0	0.039	4.3	0.07	5.6	0.025	7.9	0.044

^a Solvent extractable + solubilised fractions + unextracted

^b Sum of residues released by enzyme, acid and/or alkali digestion

^c Values include losses or gains incurred during processing of samples.

^d Residues remaining in the PES after exhaustive extraction

Table 43 Nature of residue in wheat straw from plants sown in soil treated with 0.45 kg ai/ha [¹⁴C]-cyantraniliprole

Planting interval	[CN- ¹⁴ C]-cyantraniliprole						[PC- ¹⁴ C]-cyantraniliprole					
	30 DAT		120 DAT		365 DAT		30 DAT		120 DAT		365 DAT	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
TRR (mg/kg) ^a	0.973		0.347		0.429		0.966		0.272		0.482	
Solvent extracted	81.9	0.797	80.2	0.278	66.9	0.288	79.8	0.771	72.2	0.196	93.2	0.448
Cyantraniliprole	44.8	0.437	38.4	0.133	33.0	0.141	41.3	0.399	22.9	0.062	35.1	0.153
IN-DBC80							ND		ND		1.8	0.008
IN-HGW87	ND		ND		ND	0.6	0.006	8.1	0.021	ND		
IN-J9Z38	10.9	0.108	4.5	0.016	8.9	0.038	9.5	0.091	2.2	0.006	8.1	0.035
IN-JCZ38	4.3	0.040	4.7	0.017	1.8	0.007	5.5	0.053	0.6	0.001	5.5	0.024
IN-JSE76	1.5	0.013	ND	ND	4.8	0.021	0.8	0.008	0.2	< 0.001	3.9	0.017
IN-K5A77	0.3	0.002	0.6	0.002	1.2	0.005	0.3	0.003	ND		1.3	0.007
IN-K5A78	0.2	0.002	ND		ND		ND		ND		0.4	0.002
IN-K5A79	1.6	0.015	6.4	0.024	1.5	0.007	ND		1.1	0.003	ND	
IN-K7H19	0.3	0.003	ND	ND	0.8	0.003	ND		0.1	< 0.001	10.1	0.043
IN-MLA84	5.8	0.056	3.6	0.012	5.1	0.022	5.5	0.053	0.6	0.002	4.5	0.019
IN-MYX98	1.2	0.012	5.8	0.02	ND		1.5	0.014	0.1	< 0.001	1.6	0.007
IN-N7B69	ND	ND	0.5	0.002	4.2	0.018	ND		2.2	0.006	ND	
IN-NBC94	ND		ND		ND		0.5	0.004	ND		0.1	0.001
Total unidentified	1.5	0.013	4.4	0.018	1.7	0.007	5.9	0.054	12.4	0.029	12.7	0.057
Total solubilised ^b	10.7	0.103	10.7	0.037	13.3	0.057	9.9	0.095	4.2	0.011	6.4	0.031
Total extractable ^c	92.6	0.9	90.9	0.315	80.2	0.345	89.7	0.866	75.6	0.205	99.6	0.436
Unextracted ^d	6.9	0.067	8.2	0.028	8.0	0.034	5.8	0.056	8.1	0.022	9.7	0.047

^a Solvent extractable + solubilised fractions + unextracted^b Sum of residues released by enzyme, acid and/or alkali digestion^c Values include losses or gains incurred during processing of samples.^d Terminal unextracted=Residues remaining in the PES after exhaustive extractionTable 44 Nature of residue in red beet foliage from plants sown in soil treated with 0.45 kg ai/ha [¹⁴C]-cyantraniliprole

Planting interval:	[CN- ¹⁴ C]-cyantraniliprole				[PC- ¹⁴ C]- cyantraniliprole			
	30 DAT		120 DAT		30 DAT		120 DAT	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
TRR (mg/kg) ^a	0.063		0.013		0.145		0.045	
Solvent extractable ^b	94.1	0.059	95.3	0.012	94.0	0.136	85.5	0.038
Cyantraniliprole	3.0	0.003	2.1	< 0.001	4.1	0.005	0.8	< 0.001
IN-DBC80	ND		ND		1.7	0.002	ND	
IN-HGW87	ND		ND		0.2	< 0.001	ND	
IN-J9Z38	ND		ND		ND		0.7	< 0.001
IN-JCZ38	1.5	0.001	2.0	< 0.001	1.8	0.003	ND	
IN-JSE76	ND		ND		1.0	0.001	3.8	0.002
IN-K5A77	ND		ND		0.2	< 0.001	ND	
IN-K5A78	ND		ND		0.6	< 0.001	ND	
IN-K5A79	1.1	0.001	ND		5.0	0.007	ND	
IN-K7H19	0.7	< 0.001	ND		3.2	0.006	ND	
IN-MLA84	ND		ND		1.7	0.002	ND	
IN-MYX98	ND		ND		0.5	< 0.001	ND	
IN-N7B69	0.7	< 0.001	ND		1.4	0.002	ND	
IN-NBC94	ND		ND		ND		0.7	< 0.001
Total unidentified metabolites	79.9 ^(c)	0.048	52.3	0.006	66.2 ^(d)	0.095	37.2	0.012
Unextracted	7.7	0.005	9.1	0.001	6.8	0.010	5.6	0.003

^a Solvent extractable + unextracted^b Values include losses or gains incurred during processing of samples for HPLC.

^c Comprised of 12 components, none > 0.01 mg/kg

^d Comprised of 12 components, individually ≤ 0.03 mg/kg

The metabolic fate of cyantraniliprole in the confined rotational crop study was complex with the formation of over 20 metabolites. A proposed pathway for the metabolism of cyantraniliprole in confined rotational crops is presented below:

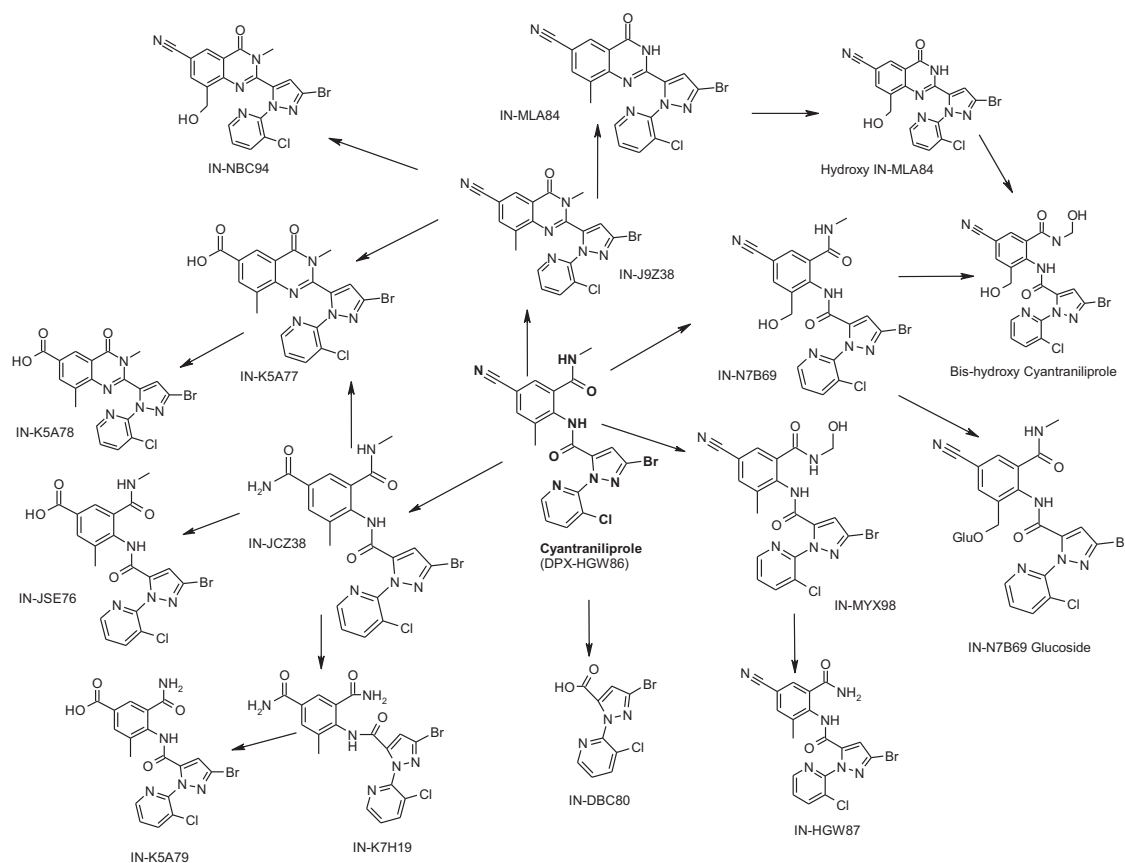


Figure 10 Proposed metabolic pathway for cyantraniliprole in confined rotational crops

Rotational crop field studies

In one European (Scotland) study reported by Haigh & Woodmansey, 2010 [Ref: DP-21447], bare soil plots were treated with two applications of 0.1 kg ai/ha cyantraniliprole (OD formulation) about 7 days apart to achieve a total application rate of 0.2 kg ai/ha and spinach, spring barley and radish were planted as rotational crops, 14, 30, 120, and 270 days after the last application.

In a further European study (Spain), reported by Old & Woodmansey, 2010 [Ref: DP-19678], bare soil plots were treated with three applications of 0.15 kg ai/ha cyantraniliprole (OD formulation) about 7 days apart to achieve a total application rate of 0.45 kg ai/ha and lettuce, spring oats, soya bean and radish were planted as rotational crops, 14, 30, 120, and 365 days after the last application.

All crop samples were harvested at normal maturity, with immature samples also being taken for some leafy crops. Samples were stored for up to 39 months before extraction and analysis (within 72 days after extraction) for cyantraniliprole and six metabolites using analytical method DP15736, with reported LOQs of 0.01 mg/kg. Mean recovery rates ranged from 76–102% (cyantraniliprole) and 71–109% (metabolites) in samples spiked with 0.01 to 0.5 mg/kg.

With the exception of soya bean (seeds and forage) and radish tops, residues of cyantraniliprole and metabolites were not found in succeeding crops following bare ground applications of 0.2–0.45 kg ai/ha.

Table 45 Cyantraniliprole residues in rotational crops (30-day plantback interval) following bare ground applications of cyantraniliprole in Europe

Commodity		Total application rate (kg ai/ha)	Plant back interval (days)	cyantraniliprole	IN-N7B69
Root/tubers	Radish roots	0.2–0.45	14	ND	ND
			30	ND	ND
			120	ND	ND
			275-365	ND	ND
Root/tubers	Radish tops	0.2–0.45	14	0.005	ND
			30	0.007	ND
			120	0.006	ND
			275-365	ND	ND
Legume	Soya bean seeds	0.45	14	ND	0.006
			30	ND	0.008
			120	ND	ND
			365	ND	ND
Legume	Soya bean forage	0.45	14	0.027	ND
			30	0.024	ND
			120	0.018	ND
			365	ND	ND
Cereal	Oat, barley ears	0.45	14	ND	ND
			30	ND	ND
			120	ND	ND
			365	ND	ND
Cereal	Oat, barley grain	0.2–0.45	14	ND	ND
			30	ND	ND
			120	ND	ND
			275-365	ND	ND
Cereal	Oat, barley forage	0.2–0.45	14	ND	ND
			30	ND	ND
			120	ND	ND
			275-365	ND	ND
Cereal	Oat, barley hay	0.2	14	ND	ND
			30	ND	ND
			120	ND	ND
			275	ND	ND
Cereal	Oat, barley straw	0.2–0.45	14	ND	ND
			30	ND	ND
			120	ND	ND
			275-365	ND	ND
Leafy vegetables	Immature leaves (spinach, lettuce)	0.2–0.45	14	ND	ND
			30	ND	ND
			120	ND	ND
			275-365	ND	ND
Leafy vegetables	Mature leaves (spinach, lettuce)	0.2–0.45	14	ND	ND
			30	ND	ND
			120	ND	ND
			275-365	ND	ND

Note: Residues of other metabolites (IN-J9Z38, IN-JCZ38, IN-K7H19, IN-MLA84 and IN-MYX98) not detected in any samples

Five field rotational crop studies were conducted in North America and two studies were conducted in Europe, all involving bare soil treatments with cyantraniliprole prior to planting a wide range of representative rotational crops.

In three North American studies, bare soil plots were treated with 2–3 applications of cyantraniliprole (OD formulation) about 5 days apart to achieve a total application rate of 0.45 kg ai/ha and four rotational crops (lettuce/spinach, oat, radishes and soya bean) were planted 14, 30, 120, and 365 days after the last application. These studies were reported by Thiel, 2009 and 2010 [Ref: DP-19640][Ref: DP-19639][Ref: DP-21446].

Table 46 Cyantraniliprole residues in rotational crops following bare ground applications of 0.45 kg ai/ha cyantraniliprole in North America. [Ref DP-19640, DP-19639, DP-21446]

Commodity	PBI (days)	Residues (mg/kg)			
		Cyantraniliprole	IN-J9Z38	IN-JCZ38	IN-MLA84
Study DP-19640 (Loamy sand, 1.0% OM, pH 7.4, CEC 12.4)					
Lettuce, mature leaves	14	0.033	ND	0.007	0.004
	30	0.011	ND	0.008	ND
	120	ND	ND	ND	ND
	365	ND	ND	ND	ND
Lettuce, immature leaves	14	0.039	ND	0.006	0.005
	30	0.029	ND	0.006	ND
	120	ND	ND	ND	ND
	365	ND	ND	ND	ND
Oat forage	14	0.036	0.007	0.014	ND
	30	0.032	0.008	0.019	ND
	120	0.048	0.003	0.015	ND
	365	ND	ND	ND	ND
Oat grain	14	0.007	ND	ND	ND
	30	0.005	ND	ND	ND
	120	ND	ND	ND	ND
	365	ND	ND	ND	ND
Oat hay	14	0.13	0.035	0.04	ND
	30	0.063	0.019	0.056	ND
	120	0.021	0.008	0.029	ND
	365	ND	ND	ND	ND
Oat straw	14	0.045	0.029	0.018	ND
	30	0.022	0.01	0.019	ND
	120	0.015	0.015	0.029	ND
	365	ND	ND	ND	ND
Radish root	14	0.003	ND	ND	ND
	30	ND	ND	ND	ND
	120	ND	ND	ND	ND
	365	ND	ND	ND	ND
Radish top	14	0.046	0.006	0.005	ND
	30	0.041	0.005	0.006	ND
	120	ND	ND	ND	ND
	365	ND	ND	ND	ND
Soya bean forage	14	0.18	0.008	0.022	0.023
	30	0.14	0.009	0.024	0.02
	120	0.048	ND	0.025	0.005
	365	ND	ND	ND	ND
Soya bean hay	14	0.023	ND	0.023	0.012
	30	0.012	ND	0.037	0.007
	120	0.018	ND	0.013	0.008
	365	ND	ND	0.007	ND
Soya bean seed	14	ND	ND	ND	ND
	30	ND	ND	ND	ND
	120	ND	ND	ND	ND
	365	ND	ND	ND	ND
DP-19639 (Loamy sand, 0.6% OM, pH 7.5)					
Spinach, mature leaves	14	ND	ND	ND	ND
	30	ND	ND	ND	ND
	119	ND	ND	ND	ND
	367	ND	ND	ND	ND
Spinach, immature leaves	14	ND	0.003	ND	ND

Commodity	PBI (days)	Residues (mg/kg)			
		Cyantraniliprole	IN-J9Z38	IN-JCZ38	IN-MLA84
	30	0.003	0.005	ND	ND
	119	ND	0.004	ND	ND
	367	ND	ND	ND	ND
Oat grain	14	0.008	ND	ND	ND
	30	0.01	ND	ND	ND
	119	ND	ND	ND	ND
	365	ND	ND	ND	ND
Oat hay	14	0.066	0.014	0.039	ND
	30	0.096	0.021	0.048	ND
	119	0.006	0.008	0.004	ND
	365	ND	ND	ND	ND
Oat spring forage	14	0.018	ND	0.005	ND
	30	0.015	ND	0.007	ND
	119	ND	ND	ND	ND
	365	ND	ND	ND	ND
Oat straw	14	0.052	0.02	0.023	ND
	30	0.073	0.033	0.029	ND
	119	0.008	0.017	0.007	ND
	365	ND	ND	ND	ND
Oat winter forage	14	0.014	ND	0.006	ND
	30	0.022	0.003	0.01	ND
	119	ND	ND	ND	ND
	365	ND	ND	ND	ND
Radish root	14	ND	0.003	ND	ND
	31	ND	0.003	ND	ND
	119	ND	0.004	ND	ND
	367	ND	ND	ND	ND
Radish top	14	0.019	0.008	0.007	ND
	31	0.008	0.008	0.005	ND
	119	ND	0.005	ND	ND
	367	ND	ND	ND	ND
Soya bean forage	14	0.043	0.005	0.014	0.015
	31	0.024	ND	0.015	0.01
	119	ND	ND	ND	ND
	365	ND	ND	ND	ND
Soya bean hay	14	0.1	0.023	0.054	0.062
	31	0.058	0.01	0.049	0.028
	119	ND	ND	ND	ND
	365	ND	ND	ND	ND
Soya bean seed	14	ND	ND	ND	ND
	31	ND	ND	ND	ND
	119	ND	ND	ND	ND
	365	ND	ND	ND	ND
DP-21446 (Loam, 1.8% OM, pH 6.9, CEC 12.8)					
Lettuce, immature leaves	16	0.026	0.006	0.005	ND
	29	0.018	0.003	0.003	ND
	366	ND	ND	ND	ND
Lettuce, mature leaves	16	0.011	0.003	ND	ND
	29	0.018	0.007	0.004	ND
	366	ND	ND	ND	ND
Radish top	16	0.039	0.005	0.007	ND
	29	0.011	0.007	0.005	ND
	121	0.01	0.007	0.003	ND
	366	ND	ND	ND	ND
Radish root	16	0.005	ND	ND	ND
	29	0.015	0.01	0.003	ND
	121	0.009	0.01	0.003	ND
	366	ND	ND	ND	ND
Oat forage	14	0.011	ND	0.004	ND
	31	0.006	ND	ND	ND

Commodity	PBI (days)	Residues (mg/kg)			
		Cyantraniliprole	IN-J9Z38	IN-JCZ38	IN-MLA84
	188	0.004	ND	ND	ND
	365	ND	ND	ND	ND
Oat hay	14	0.034	0.011	0.012	ND
	31	0.02	0.006	0.01	ND
	188	0.012	0.009	0.006	ND
	365	0.003	0.003	ND	ND
Oat grain	14	0.021	0.016	0.009	ND
	31	0.011	0.014	0.005	ND
	188	0.007	0.01	0.004	ND
			0.004	ND	ND
Oat straw	14	0.003	ND	ND	ND
	31	ND	ND	ND	ND
	188	ND	ND	ND	ND
	365	ND	ND	ND	ND
Soya bean forage	15	0.023	ND	0.003	ND
	29	0.007	ND	ND	ND
	195	ND	ND	ND	ND
	366	ND	ND	ND	ND
Soya bean hay	15	0.061	0.004	0.01	0.01
	29	0.017	ND	0.005	ND
	195	0.011	ND	0.003	ND
	366	0.004	ND	ND	ND
Soya bean seed	15	ND	ND	ND	ND
	29	ND	ND	ND	ND
	195	ND	ND	ND	ND
	366	ND	ND	ND	ND

Note: Residues of other metabolites (IN-K7H19, IN-MYX98 and IN-N7B69) not detected in any samples

In the fourth North American study reported by Thiel, 2010 [Ref: DP-27972], bare soil plots were treated with three applications of cyantraniliprole (SE formulation), 5 days apart to achieve a total application rate of 0.45 kg ai/ha and seventeen rotational crops (turnip, sugar beet, garden beet, carrot, bean, pea, soya bean, field corn, sweet corn, sorghum, rice, wheat, Bermuda grass, alfalfa, brome-grass, clover, and bluegrass) were planted 30 days after the last application.

Table 47 Cyantraniliprole residues in rotational crops (30-day plantback interval) following bare ground applications of 0.45 kg ai/ha cyantraniliprole in North America. [Ref DP-27972]

Commodity	Residues (mg/kg)				
	Cyantraniliprole	IN-J9Z38	IN-JCZ38	IN-MLA84	IN-N7B96
Alfalfa forage	0.054	0.006	0.006	0.02	ND
Alfalfa hay	0.14	0.02	0.011	0.051	ND
Bean dry seed	ND	ND	ND	ND	ND
Bean forage	0.029	ND	ND	0.003	ND
Bean hay	0.14	0.014	0.008	0.017	0.007
Bean seed	0.003	ND	ND	ND	ND
Bean succulent seed	ND	ND	ND	ND	ND
Bermuda grass forage	0.011	0.005	0.006	ND	ND
Bermuda grass hay	0.025	0.008	0.01	ND	ND
Bluegrass forage	0.092	0.008	ND	0.004	ND
Bluegrass hay	0.23	0.028	0.007	0.006	ND
Brome grass forage	0.011	ND	0.006	ND	ND
Brome grass hay	0.024	0.005	0.008	ND	ND
Carrot root	0.011	ND	ND	ND	ND
Clover forage	0.009	0.011	0.003	0.005	ND
Clover hay	0.034	0.028	0.019	0.012	0.01
Field corn forage	0.006	0.003	ND	ND	ND
Field corn stover	0.012	0.012	ND	ND	ND
Garden beet root	0.003	ND	ND	ND	ND
Garden beet top	0.008	ND	ND	ND	ND

Commodity	Residues (mg/kg)				
	Cyantraniliprole	IN-J9Z38	IN-JCZ38	IN-MLA84	IN-N7B96
Pea dry seed	ND	ND	ND	ND	ND
Pea forage	0.035	0.003	0.004	ND	ND
Pea hay	0.13	0.01	0.016	ND	ND
Pea seed	ND	ND	ND	ND	ND
Pea succulent seed	ND	ND	ND	ND	ND
Rice straw	0.005	0.009	0.003	ND	ND
Sorghum forage	0.01	0.005	0.004	0.004	ND
Sorghum stover	0.008	0.009	ND	0.006	ND
Soya bean forage	0.091	ND	0.009	0.014	ND
Soya bean hay	0.63	0.012	0.029	0.069	ND
Soya bean seed	ND	ND	ND	ND	ND
Sugar beet root	ND	ND	ND	ND	ND
Sugar beet top	ND	ND	ND	ND	ND
Sweet corn forage	0.009	ND	ND	ND	ND
Sweet corn stover	0.01	0.013	ND	ND	ND
Turnip root	ND	0.005	ND	ND	ND
Turnip top	ND	ND	ND	ND	ND
Wheat forage	0.11	0.007	0.006	0.004	ND
Wheat hay	0.21	0.017	0.014	0.012	ND
Wheat straw	0.081	0.012	0.015	0.012	ND

Note: Residues of other metabolites (IN-K7H19, IN-MYX98, and IN-N7B69) not detected in any samples

In the fifth North American study, reported by Thiel, 2011 [Ref: DP-29456], bare soil plots were treated with three applications of cyantraniliprole (SE formulation), 5 days apart to achieve a total application rate of 0.45 kg ai/ha and ten rotational crops (turnip, sugar beet, radish, carrot, pea, soya bean, alfalfa, clover, peanut, and strawberries) were planted 30 days after the last application.

Table 48 Cyantraniliprole residues in rotational crops (30-day plantback interval) following bare ground applications of 0.45 kg ai/ha cyantraniliprole in North America. [Ref DP-29456]

Commodity	Residues (mg/kg)					
	Cyantraniliprole	IN-J9Z38	IN-JCZ38	IN-K7H19	IN-MLA84	IN-N7B96
Alfalfa forage	0.008	ND	ND	ND	ND	ND
Alfalfa hay	0.021	0.004	0.008	0.006	ND	ND
Carrot root	0.005	0.01	ND	ND	ND	ND
Clover forage	0.023	ND	0.013	ND	ND	0.007
Clover hay	0.046	0.013	0.034	0.011	0.008	ND
Pea forage	ND	0.005	ND	ND	ND	ND
Pea hay	0.008	0.017	ND	ND	ND	ND
Pea seed	ND	ND	ND	ND	ND	ND
Peanut hay	0.009	0.015	0.004	0.005	ND	ND
Peanut nutmeat	ND	ND	ND	ND	ND	ND
Radish root	0.004	ND	ND	ND	ND	ND
Soya bean forage	0.039	ND	0.005	0.005	ND	ND
Soya bean hay	0.19	0.021	0.026	0.025	ND	ND
Soya bean pod	ND	ND	ND	ND	ND	ND
Soya bean seed	ND	ND	ND	ND	ND	ND
Strawberry fruit	0.005	ND	ND	ND	ND	ND
Sugar beet root	ND	ND	ND	ND	ND	ND
Sugar beet top	ND	ND	ND	ND	ND	ND
Turnip top	0.02	0.008	0.004	ND	ND	ND

Residues of IN-MYX98 were not detected in any samples

In the North American studies, residues of cyantraniliprole and metabolites in the first rotation crops (30 day plant-back interval) were below 0.05 mg/kg in commodities for human consumption (cereal grains, root crops, legumes and pulses, leafy vegetables). Higher residues were

reported in animal feed commodities, up to 0.2 mg/kg in forage crops and 0.3 mg/kg in most hays and straws. Highest residues were found in soya bean hay, up to 0.63 mg/kg.

Table 49 Summary of highest residues of cyantraniliprole and metabolites in rotational crops (30-day plantback interval) following bare ground applications of 0.45 kg ai/ha cyantraniliprole (North America)

Commodity group	Sample	Cyantraniliprole	Total (parent plus metabolites)
Root/tubers (roots)	carrot roots	0.01	0.02
	beet roots	< 0.01	< 0.01
	radish roots	0.02	0.03
	sugar beet roots	ND	ND
	turnip roots	ND	ND
Root/tubers (tops)	beet tops	< 0.01	< 0.01
	radish tops	0.04	0.05
	sugar beet tops	ND	ND
	turnip tops	0.02	0.03
Legume seeds	bean seed (dry)	ND	ND
	pea seed (dry)	ND	ND
	bean seed (succulent)	< 0.01	< 0.01
	pea seed (succulent)	ND	ND
	soya bean seed	ND	ND
Legume forage	alfalfa forage	0.05	0.09
	bean forage	0.03	0.03
	clover forage	0.02	0.04
	pea forage	0.04	0.04
	soya bean forage	0.14	0.19
Legume hay	alfalfa hay	0.14	0.22
	bean hay	0.14	0.19
	clover hay	0.05	0.11
	pea hay	0.13	0.16
	peanut hay	< 0.01	0.03
	soya bean hay	0.63	0.74
Leafy vegetables	Lettuce (immature leaves)	0.03	0.04
	Spinach (immature leaves)	< 0.01	< 0.01
	Lettuce (mature leaves)	0.02	0.03
	spinach (mature leaves)	ND	ND
Cereal grains	oat grain	0.01	0.03
Cereal forage	corn forage	< 0.01	< 0.01
	oat forage	0.03	0.06
	sorghum forage	0.01	0.02
	wheat forage	0.11	0.13
Cereal hay	oat hay	0.1	0.17
	wheat hay	0.21	0.25
Cereal stover	corn stover	0.01	0.02
	sorghum stover	< 0.01	0.02
Cereal straw	oat straw	0.07	0.14
	rice straw	< 0.01	0.02
	wheat straw	0.08	0.12
Grass forage	Bermuda grass forage	0.01	0.02
	Bluegrass forage	0.09	0.1
	Brome grass forage	0.01	0.02
Grass hay	Bermuda grass hay	0.03	0.04
	Bluegrass hay	0.23	0.27
	Brome grass hay	0.02	0.04
Peanut	nutmeat	ND	ND
Strawberry	fruit	< 0.01	< 0.01

Total residues are the sum of cyantraniliprole and metabolites IN-J9Z38, IN-JCZ38, IN-MLA84 and IN-N7B96.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The meeting received analytical method descriptions and validation data for cyantraniliprole and major metabolites in crop and animal commodities and in soil and water. A summary of the analytical methods for plant and animal commodities is provided below.

Table 50 Summary of cyantraniliprole analytical methods developed for plant and animal matrices

Matrix	Analyte	Method	Principle	LOQ	Reference
tomato wheat grain orange almond	cyantraniliprole	21328	DFG S19 extraction (aqueous acetone) LC-MS/MS analysis	0.01 mg/kg	DP-21328
cucumber tomato lime almond wheat straw grape apple peach almond (nutmeat) lettuce wheat grain potato lemon oilseed rape onion tomato (paste) tomato (dried)	cyantraniliprole IN-J9Z38 IN-JCZ38 IN-K5A79 IN-K7H19 IN-MLA84 IN-MYX98 IN-N7B69 IN-F6L99	15736 [1187]	Aqueous acetonitrile extraction LC-MS/MS analysis	0.05 mg/kg (wheat straw) 0.01 mg/kg (other matrices)	DP-15736 DP-18846 DP-2600 DP-15736-S1
meat liver milk eggs	cyantraniliprole	25544	DFG S19 extraction (aqueous acetone) SPE clean-up LC-MS/MS	0.01 mg/kg	DP-25544 DP17942
milk	cyantraniliprole IN-HGW87 IN-J9Z38 IN-JCZ38 IN-K5A79 IN-K7H19 IN-MLA84 IN-MYX98 IN-N7B69	25544	DFG S19 extraction (aqueous acetone) SPE clean-up LC-MS/MS	0.01 mg/kg	DP-25544
muscle fat liver kidney milk skim milk heavy cream eggs	cyantraniliprole IN-J9Z38 IN-JCZ38 IN-K5A79 IN-K7H19 IN-MLA84 IN-MYX98 IN-N7B69	18844 [1552]	aqueous acetonitrile extraction SPE clean-up LC-MS/MS analysis		DP-18844 DP-25543 DP-26458

Data collection methods

Method 21328 (plant matrices)

The analytical method 21328, based on the German method DFG S19, was described and reported by Bacher, 2009 [Ref: DP-21328] as suitable for as a data-collection method to measure residues of cyantraniliprole in plant commodities, with an LOQ of 0.01 mg/kg.

Cyantraniliprole was extracted from the plant tissue according to extraction module E 1 (tomato), E 2 (wheat grain), E 3 (orange), and E 7 for (almond) of the DFG Method S 19 method. Extracts of tomato, orange, wheat grain, and almond were analyzed by liquid chromatography with electrospray ionization and tandem mass spectrometry detection. The report noted that degradation of cyantraniliprole was observed under GC/MS conditions.

The E1 extraction module involved the addition of water and acetone prior to homogenization for 2 minutes and then the addition of 1:1 ethyl acetate:cyclohexane and NaCl. The sample was homogenized a second time for 1 minute, allowed to separate and the organic phase was removed and filtered through a cellulose folded filter, which was coated with Na₂SO₄. The extract was evaporated until only aqueous remained and a mixture of ethyl acetate and 1:1 Na₂SO₄:NaCl was added. An additional aliquot of cyclohexane was added to adjust the volume of the organic layer.

The E2 extraction module involved the addition of water and a 30-minute soaking period before the addition of acetone and homogenization. After the addition of 1:1 ethyl acetate:cyclohexane and 35 g NaCl, the sample was homogenized a second time for 1 minute and the phases were allowed to separate. The organic phase was removed and filtered through a cellulose folded filter coated with Na₂SO₄. The extract was evaporated until only aqueous remained and a mixture of ethyl acetate and 1:1 Na₂SO₄:NaCl was added. An additional aliquot of cyclohexane was added to adjust the volume of the organic layer.

The E3 extraction module involved mixing with NaHCO₃, the addition of water and after allowing the sample to stand for about 30 minutes, the addition of acetone prior to homogenization. This was followed by an addition of 1:1 ethyl acetate:cyclohexane and 35 g NaCl and a second homogenization. After the phases were allowed to separate, the organic phase was removed and filtered through a cellulose folded filter coated with Na₂SO₄. The extract was evaporated until only aqueous remained and a mixture of ethyl acetate and 1:1 Na₂SO₄:NaCl was added. An additional aliquot of cyclohexane was added to adjust the volume of the organic layer.

The E7 extraction module involved the addition of acetone, acetonitrile, Calflo E and Celite before homogenization and vacuum filtration through a Buchner porcelain funnel. The filtrate was then passed through a dry fluted cellulose filter paper coated with Calflo E and rotary evaporated into an oil residue and bathed at 40 °C. The samples were then mixed with ethyl acetate, sonicated until completely dissolved and after the addition of a 1:1 mixture of Na₂SO₄:NaCl, cyclohexane was added to adjust the volume of the organic layer.²

The extracts were purified using gel permeation chromatography using 1:1 ethyl acetate:cyclohexane as the eluant. The eluate was evaporated to dryness using a rotary evaporator, re-constituted in ethyl acetate, evaporated to dryness in a gentle stream of nitrogen and re-constituted in methanol/water.

The final extracts were analysed by liquid chromatography with tandem mass spectrometric detection (LC-MS/MS) using a C18 column gradient elution using 0.1% formic acid in water to 0.1% formic acid in acetonitrile as the mobile phase. MS/MS detection in the positive ionization mode was used to monitor ion transitions 475→286 and 475→112 for cyantraniliprole.

Average (n=2) recovery rates in tomato, orange, wheat grain and almond (nutmeat) ranged from 92–104% (RSD ≤ 8%) in samples spiked with 0.01 mg/kg cyantraniliprole and from 93–115% (RSD ≤ 7%) in samples spiked with 0.1 mg/kg. The LOQ was 0.01 mg/kg.

Method 21328 was independently validated in a study by Weber, 2010 [Ref: DP-21326] with similar average (n=5) recovery rates (94–107%, ≤ 11% RSD) in tomatoes, oranges, wheat grain and almond nutmeat spiked with 0.01 mg/kg or 0.1 mg/kg cyantraniliprole, demonstrating the reproducibility of this method.

While the DFG S 19 extraction procedures used in Method 21328 include a pre-soak in water followed by an acetone extraction, the cyantraniliprole metabolism study [Ref: DP-16986] demonstrated that incurred residues could be completely extracted using an acetonitrile:water, 9:1 extraction. Based on the physicochemical properties of cyantraniliprole, including the higher

solubility in acetone (6.45 g/L) than in acetonitrile (2.45 g/L), acetone is considered a suitable solvent for the extraction of incurred cyantraniliprole residues.

Method 15736 (plant matrices)

The analytical method 15736, described and reported by McClory, Stevens-Shreve & Hense, 2011, [Ref DP-15736] was developed to measure residues of cyantraniliprole and seven metabolites (IN-J9Z38, IN-JCZ38, IN-K5A79, IN-K7H19, IN-MLA84, IN-MYX98 and IN-N7B69) in representative commodities with a high water content (cucumber and tomato), a high acid content (lime), a high oil content (almond nutmeat) and a low water content (wheat straw). This method is also known as DuPont method 1187.

A supplement to this study, reported by McClory, Stevens-Shreve & Hense, 2011, [Ref DP-15736-S1] also validated this method for tomato paste and sun-dried tomato for the above analytes and for the IN-N5M09 and IN-F6L99 metabolites as potential breakdown products formed during processing.

Samples were extracted twice with 9:1 acetonitrile:water by high-speed shaking (2 minutes at 700 cycles/minute in the presence of ball bearings) and centrifugation. The supernatants from the two extracts were combined, diluted with acetonitrile:water and mixed vigorously. Aliquots of these extracts were filtered (0.2 µm PTFE) and after the addition of methanol and de-ionized water, were analyzed using LC/MS/MS.

The final extracts were analysed by liquid chromatography with tandem mass spectrometric detection (LC-MS/MS) using a C18 column gradient elution using formic acid/ammonium formate in water to formic acid/ammonium formate in methanol as the mobile phase. MS/MS detection in the positive ionization mode was used to monitor the following ion transitions:

Cyantraniliprole	475→286	and	475→443.9
IN-J9Z38	457→188	and	457→290
IN-JCZ38	493→286	and	493→462
IN-K5A79	480→286	and	480→463
IN-K7H19	479→286	and	479→462
IN-MLA84	443→298	and	443→407.4
IN-MYX98	491→444	and	491→473
IN-N7B69	491→285.7	and	491→473
IN-F6L99	204→173	and	204→66

Average (n=2) recovery rates in samples spiked with 0.01 mg/kg ranged from 74–121% (RSD ≤ 15) and in samples spiked with 0.1 mg/kg were 67–96% (RSD ≤ 13). The method LOQ was 0.01 mg/kg.

This method was validated under GLP by two additional laboratories. One of the additional validations reported by Kinney, 2008 [Ref: DP-18846] investigated the performance of Method 15736 for grapes, apples, peaches, tomatoes, almonds (nutmeat), lettuce, wheat grain, wheat straw, potatoes, lemons, and rape seed and the second validation, reported by Seal, 2010 [Ref: DP-26000] evaluated the performance of the method for almonds, onions, tomato paste, and sun-dried tomatoes.

Average (n=5) recovery rates in all matrices and for all analytes in samples spiked with 0.01 mg/kg, 0.05 mg/kg (wheat straw), 0.1 mg/kg or 0.5 mg/kg (wheat straw) were within the range 70–111% (RSD ≤ 13).

Extraction efficiency of this method was demonstrated in a study reported by Lowrie and MacKinnon, 2009 [Ref: DP-24754] where samples of lettuce leaf, beet foliage, wheat grain, and wheat hay from the confined rotational crop metabolism study [Ref: DP-15778] containing weathered residues of radiolabelled parent and metabolites were extracted using the Method 15736 extraction procedure. The levels of the parent and metabolites obtained using the residue method were within 89–100% of those found in the metabolism study, which indicates that the residue method provides acceptable extraction efficiency.

Method 15736 was shown to be suitable for the purposes of residue data collection and enforcement of MRLs, with an LOQ of 0.05 mg/kg for wheat straw and 0.01 mg/kg for all other matrices.

Method 25544 (animal matrices)

The analytical Method 25544, based on the German multi-residue method DFG S19 (module E1 extraction and module GPC clean-up) with LC-MS/MS detection, was described and reported by Bacher, 2010 [Ref: DP-25544] as suitable for use as a data-collection method to measure residues of cyantraniliprole in animal commodities, with an LOQ of 0.01 mg/kg and was also suitable to measure residues of the metabolites IN-J9Z38, IN-JCZ38, IN-HGW87, IN-K7H19, IN-MLA84, IN-MYX98, and IN-N7B69 in milk (but not other animal commodities).

Samples of meat, milk, egg and liver were mixed with water and after the addition of acetone, were homogenized for 2 minutes before the addition of 1:1 ethyl acetate:cyclohexane and NaCl and further homogenization for 1 minute. The phases were allowed to separate and the organic phase was filtered through cellulose folded filter coated with Na₂SO₄. After repeat rinsing with ethyl acetate:cyclohexane the filtrate was evaporated to an aqueous remainder (not to dryness), re-dissolved in ethyl acetate, mixed with 1:1 Na₂SO₄:NaCl and the volume adjusted with cyclohexane.

Extracts were cleaned up by gel permeation chromatography using a 1:1 mixture of ethyl acetate:cyclohexane as eluant (5.0 mL/min) and an automated gel permeation chromatograph. The collected eluate was evaporated to dryness, reconstituted in ethyl acetate, evaporated to dryness in a gentle stream of nitrogen and re-constituted in 1:1 methanol:water.

The final extracts were analysed by liquid chromatography with electrospray ionisation and tandem mass spectrometric detection (LC-MS/MS) using a C18 column gradient elution using formic acid in water to formic acid in methanol as the mobile phase. MS/MS detection in the positive ionization mode was used to monitor the following ion transitions:

Cyantraniliprole	475→444	and	475→286
IN-J9Z38	457→188	and	457→112
IN-JCZ38	493→462	and	493→286
IN-K7H19	479→462	and	479→286
IN-MLA84	443→298	and	443→407
IN-MYX98	491→444	and	491→442
IN-N7B69	491→286	and	491→473
IN-HGW87	459→284	and	459→112

Average (n=5) recovery rates in samples spiked with 0.01 mg/kg ranged from 74–107% (RSD ≤ 14%) and in samples spiked with 0.1 mg/kg were 70–103% (RSD ≤ 14%). The method LOQ was 0.01 mg/kg.

This method was independently validated for the detection, quantitative analysis, and confirmation of cyantraniliprole in milk, eggs, meat, and liver in a study reported by Weber, 2010

[Ref: DP-17942]. Average (n=5) recovery rates in all matrices spiked with 0.01 mg/kg ranged from 98–106% (RSD < 6%) and were 95–108% (RSD < 7%) in the 0.1 mg/kg spiked samples.

While the DFG S 19 extraction procedures used in Method 25544 include a pre-soak in water followed by an acetone extraction, the cyantraniliprole metabolism study [Ref: DP-16987] demonstrated that incurred residues could be completely extracted using an acetonitrile:water, 9:1 extraction. Based on the physicochemical properties of cyantraniliprole, including the higher solubility in acetone (6.45 g/L) than in acetonitrile (2.45 g/L), acetone is considered a suitable solvent for the extraction of incurred cyantraniliprole residues in animal commodities.

The residue Method 25544, is suitable for the determination of cyantraniliprole in milk, eggs, meat, and liver, with an LOQ of 0.01 mg/kg for animal commodities.

Method 18844 (animal matrices)

The analytical method 18844, also reported as DuPont method 1552, was described and reported by Henze and McClory, 2010 [Ref: DP-18844] as suitable for use as a data-collection method to measure residues of cyantraniliprole and the metabolites IN-J9Z38, IN-JCZ38, IN-HGW87, IN-K5A79, IN-K7H19, IN-MLA84, IN-MYX98, and IN-N7B69 in muscle, fat, kidney, liver, egg, whole milk, skim milk and heavy cream, with an LOQ of 0.01 mg/kg.

In this method, samples were extracted twice with acetonitrile, cleaned up by shaking with hexane and centrifugation, with the hexane fractions then being discarded. The extracts were then evaporated to near-dryness in a gentle stream of nitrogen and after the addition of methanol, made up to volume with water, vortexed, sonicated and filtered.

Residues of cyantraniliprole, IN-HGW87, IN-J9Z38, IN-JCZ38, IN-K5A79, IN-K7H19, IN-N7B69, IN-MLA84, and IN-MYX98 were separated from co-extracts by reversed phase liquid chromatography (C18 column gradient elution using formic acid/ammonium formate in water to formic acid/ammonium formate in methanol as the mobile phase) and detected by mass spectrometry/mass spectrometry (MS/MS) using positive ion atmospheric pressure chemical ionization to monitor the following ion transitions:

Cyantraniliprole	475→443	and	475→286
IN-J9Z38	457→298	and	457→188
IN-JCZ38	493→462		
IN-K7H19	479→462	and	479→286
IN-K5A79	480→463	and	480→286
IN-MLA84	443→298	and	443→407
IN-MYX98	491→444		
IN-N7B69	491→286		
IN-HGW87	459→284	and	459→112

Average (n=5) recovery rates in samples spiked with 0.01 mg/kg ranged from 80–116% (RSD ≤ 20% except 34% RSD for IN-JCZ38 in eggs) and in samples spiked with 0.1 mg/kg were 74–116% (RSD < 13%). The method LOQ was 0.01 mg/kg.

This method was validated in a study reported by Ward, 2010 [Ref: DP-25543] on the detection and measurement of cyantraniliprole and metabolites (except IN-K5A79) in bovine muscle, fat, kidney, liver, milk and in eggs. An independent validation study was also conducted by Schwartz, 2010 [Ref: DP-26458] for cyantraniliprole, IN-J9Z38, IN-MLA84 and IN-N7B69 in whole milk, kidney and muscle.

In these studies, average (n=5) recovery rates in all matrices spiked with 0.01 mg/kg ranged from 72–131% (RSD < 13%) and were 71–112% (RSD < 12%) in the 0.1 mg/kg spiked samples.

Extraction efficiency of this method was demonstrated in a study reported by Kinney and Melville, 2010 [Ref: DP-27356] where samples of muscle, milk, liver, egg yolks, and egg whites from the cattle metabolism study [Ref: DP-16987] containing weathered residues of radiolabelled parent and metabolites were extracted using the Method 18844 procedure. The levels of extracted radioactivity obtained using the residue method were equivalent to those found in the metabolism extraction; 75.5% (liver), 92.7% (muscle), 103.7% (milk), 99.5% (egg white), and 125.1% (egg yolk), indicating that the method 18844 provides acceptable extraction efficiency.

The residue method 18844 for the determination of cyantraniliprole, IN-N7B69, IN-K7H19, IN-K5A79, IN-JCZ38, IN-MYX98, IN-HGW87, IN-J9Z38, and IN-MLA84 in muscle, fat, kidney, liver, heavy cream, skim milk, whole milk, and eggs involves simple extraction, clean-up, and analytical determination by HPLC/MS/MS detection. A limit of quantification of 0.01 mg/kg can be achieved consistently for all tissues.

Method 25544 (soil)

The analytical Method 15440, involving acetone extraction, SPE clean-up and LC-MS/MS analysis was reported by Henze, Devine and McClory, 2006 [Ref: DP-15440] as suitable for use as a data-collection method to measure residues of cyantraniliprole and metabolites IN-J9Z38, IN-JCZ38, IN-JSE76, IN-K5A77, IN-K5A78, IN-K5A79, IN-K7H19, and IN-PLT97 in soil.

Soil samples were extracted twice with 9:1 acetone:formic acid by shaking at high speed on a platform shaker. After dilution with water, extracts were passed through an NH₂ and an ENV SPE column. The NH₂ removed co-extracts with cyantraniliprole and or its photoproducts being retained on the ENV SPE column. Cyantraniliprole and its photoproducts were eluted from the ENV column with ammonium hydroxide in acetonitrile. The extracts were evaporated to dryness, reconstituted in methanol:formic acid, filtered and analyzed by LC/MS/MS.

Average (n=5) recovery rates in samples spiked with 0.001 mg/kg ranged from 75–102% (RSD < 17% and in samples spiked with 0.01 mg/kg were 72–96% (RSD < 9%). The method LOQ was 0.001 mg/kg.

The method 15440 was independently validated in a study reported by Schwartz, 2010 [Ref: DP-18847] with average (n=5) recovery rates in sandy loam soil samples spiked with 0.001 mg/kg ranging from 81–99% (RSD < 10%) and were 78–118% (RSD < 15%) in samples spiked with 0.01 mg/kg. The method LOQ was 0.001 mg/kg.

Method 29747 (soil)

Method 29747, an extension of the above method 15440 to include the measurement of the cyantraniliprole photoproducts IN-NXX70, IN-QKV54, and IN-RNU71, was described in a report by Vogl, 2010 [Ref: DP-29747], with average (n=5) recovery rates of 93–116% (RSD ≤ 12%) in a sandy clay loam soil spiked with 0.001 mg/kg or 0.01 mg/kg.

Enforcement methods

Multi-residue method DFG S19

Method 21328, the German method DFG S19 with LC-MS/MS analysis is suitable for enforcement of the MRL for cyantraniliprole in plant commodities, based on the method validation for tomato (representing high water content), orange (high acid content), wheat grain (high starch content) and almond (high oil content).

Method 26459, a GC/ECD procedure for crops was developed and validated in DuPont-26459. This method is intended for monitoring purposes in regions where LC/MS/MS is not readily available.

FDA PAM Multi-residue method

Rockwell, 2010 [Ref: DP-21329] evaluated the suitability of the FDA PAM Multi-residue methods for measuring residues of cyantraniliprole and six metabolites. The test substances were naturally fluorescent (with the exception of IN-MLA84-000, which was not soluble in methanol) but were not capable of being evaluated further without modifying the methods outlined in Protocol A. IN-JCZ38-004 and IN-K7H19-001 were found to chromatograph according to one Module DG 18, Level II, in Protocol C. However the two analytes were insoluble in the solvents required for the methods outlined in Protocols D, E, and F and further testing was suspended. Based on these results, none of the FDA multi-residue method test procedures are suitable for the regulatory analysis of DPX-HGW86-307 and its metabolites.

Analytical (concurrent) recoveries in supervised crop trials

Analytical recovery rates were measured in all the supervised crop field trials, with control samples being fortified with cyantraniliprole and metabolites at 0.01 mg/kg and at higher levels that generally reflected the range of expected residues. In most trials analysis was with Method 15736.

For each study, average recoveries per fortification level generally fell within the 70–120% range, with a relative standard deviation of 20% or less). Information on the concurrent recovery rates for individual commodities are summarised in the relevant supervised crop field trial sections.

Stability of residues in stored analytical samples

Plant matrices

The Meeting received information on the stability of residues of cyantraniliprole and metabolites in various substrates with a high water content (apple), a high starch content (potato), a high protein content (dry bean seed), a high oil content (peanut) and a high acid content (grape) stored at freezer temperatures for 24 months.

In a study by Rodgers, 2010, [Ref: DP-16990], samples of the test commodities were fortified at 0.2 mg/kg of each analyte. Spiked and the control samples were sealed and stored in the dark at -20 ± 10 °C. Samples were taken for extraction and analysis after 0, 1, 3, 6, 12, 18 and 24 months (and also peanuts after 63 days), with the stored control samples being freshly fortified with each analyte and analysed concurrently to determine the procedural recovery efficiency. Analysis was by LC-MS/MS (Method 15736), with mean procedural recovery rates of 83–94% for all analytes and matrices (fortified at 0.2 mg/kg and also at 0.01 mg/kg in peanuts).

After 24 months storage the measured residues of cyantraniliprole and major metabolites in stored samples of representative plant matrices with high water, acid, starch and protein content were greater than 80% of the spiked levels.

For peanut (high oil content), 24-month stability was demonstrated for cyantraniliprole, IN-F6L99, IN-J9Z38, IN-MLA84, IN-MYX98 and IN-N5M09, with measured residues also greater than 80% of the spiked levels. However, for the IN-JCZ38, IN-K7H19, and IN-N7B69 metabolites, the results showed reduced recoveries, attributed to extractability issues associated with the higher lipid content of this matrix.

Table 51 Stability of cyantraniliprole residues in plant matrices spiked at 0.2 mg/kg and stored at -20 ± 10 °C

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Apples	0			100.5
	1	0.18, 0.18	89.5	96.5
	3	0.17, 0.18	87	89
	6	0.16, 0.16	81.5	86.5
	12	0.17, 0.18	86	81.5
	18	0.18, 0.18	88.5	94
	24	0.19, 0.2	96	98.5

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Peanuts	0			93.5
	1	0.16, 0.15	78.5	93.5
	2	0.17, 0.17	84.5	87
	3	0.16, 0.16	80.5	100
	6	0.16, 0.15	77.5	82.5
	12	0.14, 0.14	71.5	75
	18	0.14, 0.16	75	88.5
	24	0.13, 0.13	66	79.5
Dried beans	0			94
	1	0.19, 0.17	88	89
	3	0.19, 0.18	91	92.5
	6	0.16, 0.14	75.5	88.5
	12	0.15, 0.15	75	78.5
	18	0.19, 0.19	94.5	103.5
	24	0.13, 0.13	65.5	71
Potatoes	0			98.5
	1	0.16, 0.17	83.5	87.5
	3	0.19, 0.19	96.5	97.5
	6	0.16, 0.17	83.5	87
	12	0.17, 0.17	85.5	87.5
	18	0.19, 0.18	92	93
	24	0.18, 0.19	91.5	94.5
Grapes	0			107
	1	0.17, 0.17	85	83
	3	0.18, 0.19	93.5	93.5
	6	0.17, 0.18	86	86
	12	0.18, 0.17	87	80
	18	0.19, 0.18	92.5	95
	24	0.2, 0.19	98	105.5

Table 52 Stability of cyantraniliprole metabolite IN-F6L99 residues in plant matrices spiked at 0.2 mg/kg and stored at -20 ± 10 °C.

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Apples	0			106.5
	1	0.16, 0.16	79.5	85
	3	0.15, 0.16	77	80
	6	0.16, 0.17	83	83.5
	12	0.16, 0.17	82.5	78.5
	18	0.19, 0.19	94	94.5
	24	0.17, 0.17	83	84.5
Peanuts	0			89
	1	0.19, 0.18	92	107.5
	2	0.19, 0.19	93	96.5
	3	0.18, 0.17	86.5	103
	6	0.18, 0.17	87.5	90.5
	12	0.17, 0.17	83.5	84.5
	18	0.15, 0.15	75	85
	24	0.15, 0.13	73	82.5
Dried beans	0			94
	1	0.2, 0.18	93.5	96.5
	3	0.18, 0.17	89.5	92
	6	0.19, 0.17	91	95
	12	0.17, 0.16	83	87.5
	18	0.17, 0.17	86	86
	24	0.14, 0.14	70	90.5

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Potatoes	0			103
	1	0.19, 0.21	100	96.5
	3	0.18, 0.18	91	89.5
	6	0.18, 0.18	90.5	90
	12	0.17, 0.17	85.5	87
	18	0.21, 0.21	104	103.5
	24	0.17, 0.17	85.5	89
Grapes	0			103
	1	0.18, 0.19	93.5	92
	3	0.18, 0.18	91	89
	6	0.17, 0.18	88.5	83
	12	0.17, 0.17	85.5	80
	18	0.2, 0.19	96.5	97
	24	0.16, 0.16	81	85

Table 53 Stability of cyantraniliprole metabolite IN-J9Z38 residues in plant matrices spiked at 0.2 mg/kg and stored at -20 ± 10 °C

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Apples	0			95.5
	1	0.2, 0.19	96.5	102.5
	3	0.17, 0.17	85	85
	6	0.16, 0.15	77	83.5
	12	0.15, 0.16	79.5	73
	18	0.16, 0.16	80.5	89.5
	24	0.17, 0.17	85	85
Peanuts	0			88.5
	1	0.18, 0.17	86.5	103
	2	0.15, 0.16	78.5	82
	3	0.14, 0.15	72	94
	6	0.15, 0.13	75	77
	12	0.14, 0.14	70.5	73
	18	0.14, 0.15	76	92.5
	24	0.15, 0.17	80.5	90
Dried beans	0			88.5
	1	0.19, 0.16	88	92
	3	0.18, 0.17	86	87
	6	0.14, 0.12	72	80.5
	12	0.15, 0.14	72.5	73
	18	0.16, 0.16	78.5	88
	24	0.18, 0.18	91	105.5
Potatoes	0			92
	1	0.17, 0.17	84.5	87.5
	3	0.18, 0.19	93.5	94.5
	6	0.14, 0.15	74	77.5
	12	0.16, 0.17	83	80.5
	18	0.18, 0.18	90	94
	24	0.16, 0.16	81.5	82.5
Grapes	0			102
	1	0.18, 0.18	88.5	88
	3	0.18, 0.18	89.5	86.5
	6	0.16, 0.17	81.5	80
	12	0.17, 0.16	80.5	73
	18	0.18, 0.18	89.5	92
	24	0.18, 0.17	86.5	93

Table 54 Stability of cyantraniliprole metabolite IN-JCZ38 residues in plant matrices spiked at 0.2 mg/kg and stored at -20 ± 10 °C

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Apples	0			99
	1	0.18, 0.18	89.5	97.5
	3	0.17, 0.18	86	88
	6	0.16, 0.17	81.5	86
	12	0.16, 0.16	81	76.5
	18	0.17, 0.17	86.5	91.5
	24	0.18, 0.18	90.5	93
Peanuts	0			88.5
	1	0.13, 0.12	62.5	94.5
	2	0.15, 0.15	75.5	88.5
	3	0.13, 0.12	62	98
	6	0.14, 0.13	66.5	82
	12	0.12, 0.11	59	78
	18	0.11, 0.12	58	89.5
	24	0.11, 0.097	51.5	86.5
Dried beans	0			92.5
	1	0.19, 0.18	92	92.5
	3	0.17, 0.17	86.5	90
	6	0.16, 0.14	76.5	89.5
	12	0.14, 0.14	70.5	76.5
	18	0.17, 0.17	86.5	97
	24	0.14, 0.14	71.5	89.5
Potatoes	0			94.5
	1	0.18, 0.18	90.5	94
	3	0.19, 0.19	96	98
	6	0.16, 0.16	80.5	91
	12	0.16, 0.16	81	85.5
	18	0.19, 0.2	95.5	97.5
	24	0.17, 0.17	86.5	92.5
Grapes	0			106
	1	0.17, 0.18	86	86
	3	0.18, 0.19	93.5	91
	6	0.17, 0.17	85	85
	12	0.16, 0.16	80	76
	18	0.18, 0.18	89.5	92.5
	24	0.19, 0.18	92	100

Table 55 Stability of cyantraniliprole metabolite IN-K7H19 residues in plant matrices spiked at 0.2 mg/kg and stored at -20 ± 10 °C

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Apples	0			99
	1	0.18, 0.18	91	96.5
	3	0.16, 0.18	85	86.5
	6	0.16, 0.16	81	83.5
	12	0.16, 0.18	85	79
	18	0.17, 0.17	84	90.5
	24	0.19, 0.19	94	96
Peanuts	0			90
	1	0.12, 0.1	55.5	92
	2	0.14, 0.14	70.5	89.5
	3	0.12, 0.1	55	98.5
	6	0.13, 0.12	63	82.5
	12	0.12, 0.11	56	77.5
	18	0.097, 0.097	49	85.5
	24	0.087, 0.072	39.5	76

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Dried beans	0			93
	1	0.18, 0.17	87	87.5
	3	0.17, 0.17	84.5	90
	6	0.16, 0.14	76	89.5
	12	0.14, 0.15	73	78.5
	18	0.19, 0.19	94	103.5
	24	0.2, 0.21	103.5	111.5
Potatoes	0			97.5
	1	0.17, 0.18	88	89
	3	0.19, 0.18	93	95
	6	0.16, 0.16	79	92
	12	0.17, 0.17	83.5	85
	18	0.17, 0.18	88.5	92
	24	0.18, 0.17	87.5	91.5
Grapes	0			107
	1	0.17, 0.18	87.5	87
	3	0.18, 0.19	93	92
	6	0.16, 0.17	82.5	83
	12	0.18, 0.18	91.5	83.5
	18	0.18, 0.18	90	92
	24	0.19, 0.19	93.5	96.5

Table 56 Stability of cyantraniliprole metabolite IN-MLA84 residues in plant matrices spiked at 0.2 mg/kg and stored at -20 ± 10 °C

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Apples	0			92
	1	0.19, 0.17	88.5	95
	3	0.16, 0.17	83.5	86
	6	0.15, 0.15	74	80
	12	0.15, 0.16	78	77
	18	0.17, 0.16	81.5	90
	24	0.16, 0.16	79	82
Peanuts	0			90
	1	0.16, 0.15	78	97
	2	0.17, 0.17	86	88
	3	0.15, 0.15	75	100
	6	0.15, 0.14	72.5	75
	12	0.13, 0.13	63.5	68c
	18	0.14, 0.16	74.5	96
	24	0.14, 0.16	75	90
Dried beans	0			87
	1	0.18, 0.16	86	86
	3	0.17, 0.17	84	84
	6	0.15, 0.13	72	74
	12	0.14, 0.14	70	75
	18	0.16, 0.16	80.5	86
	24	0.2, 0.19	97.5	113
Potatoes	0			86
	1	0.16, 0.17	82.5	87
	3	0.18, 0.18	88.5	92
	6	0.17, 0.18	88	85
	12	0.15, 0.16	77.5	80
	18	0.18, 0.19	93.5	94
	24	0.15, 0.15	74	75
Grapes	0			98
	1	0.16, 0.17	81	77
	3	0.18, 0.18	89	91
	6	0.15, 0.16	78	82
	12	0.16, 0.16	80	76
	18	0.18, 0.17	87.5	88
	24	0.17, 0.16	81	83

Table 57 Stability of cyantraniliprole metabolite IN-MYX98 residues in plant matrices spiked at 0.2 mg/kg and stored at -20 ± 10 °C

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Apples	0			106
	1	0.18, 0.18	89	97
	3	0.17, 0.18	87	90.5
	6	0.17, 0.17	85.5	87
	12	0.19, 0.19	94.5	83
	18	0.22, 0.23	112.5	106
	24	0.22, 0.21	107	97.5
Peanuts	0			102
	1	0.14, 0.14	70	93
	2	0.16, 0.16	80	90.5
	3	0.14, 0.14	72	101
	6	0.16, 0.15	79	84.5
	12	0.16, 0.15	77	80.5
	18	0.16, 0.18	85.5	99.5
	24	0.14, 0.12	67	81
Dried beans	0			99
	1	0.19, 0.17	88	90.5
	3	0.18, 0.17	87.5	94
	6	0.17, 0.15	81	90
	12	0.17, 0.17	84	83.5
	18	0.24, 0.24	121	114
	24	0.14, 0.15	73	71
Potatoes	0			103
	1	0.17, 0.18	85.5	89.5
	3	0.19, 0.19	96.5	96
	6	0.18, 0.18	89.5	93
	12	0.19, 0.19	95.5	90
	18	0.22, 0.23	112	103.5
	24	0.2, 0.2	101.5	95
Grapes	0			111
	1	0.16, 0.17	83	84
	3	0.19, 0.19	94	96.5
	6	0.18, 0.19	91	89
	12	0.19, 0.19	96.5	83.5
	18	0.23, 0.23	114.5	109.5
	24	0.23, 0.22	112	105.5

Table 58 Stability of cyantraniliprole metabolite IN-N7B69 residues in plant matrices spiked at 0.2 mg/kg and stored at -20 ± 10 °C

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Apples	0			105.5
	1	0.19, 0.18	92	97
	3	0.17, 0.17	87	90.5
	6	0.17, 0.17	83.5	88
	12	0.18, 0.19	92.5	85
	18	0.18, 0.18	90	96.5
	24	0.18, 0.19	92.5	100
Peanuts	0			97.5
	1	0.14, 0.13	68.5	93.5
	2	0.15, 0.16	77.5	88
	3	0.14, 0.14	70.5	99.5
	6	0.15, 0.13	69	77
	12	0.15, 0.15	75.5	81
	18	0.13, 0.14	67	78.5
	24	0.11, 0.081	46.5	67

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Dried beans	0			96.5
	1	0.18, 0.16	85	88
	3	0.18, 0.18	89.5	94
	6	0.15, 0.13	71	83
	12	0.17, 0.17	86	86.5
	18	0.23, 0.23	117	119.5
	24	0.17, 0.18	86	89.5
Potatoes	0			104.5
	1	0.17, 0.17	85	91
	3	0.19, 0.2	98.5	101
	6	0.16, 0.16	78	86.5
	12	0.19, 0.2	97.5	99.5
	18	0.17, 0.14	77.5	79
	24	0.16, 0.17	82	91
Grapes	0			116
	1	0.17, 0.17	84.5	84.5
	3	0.19, 0.2	97.5	95.5
	6	0.17, 0.17	86	87
	12	0.19, 0.2	98.5	85.5
	18	0.19, 0.2	97	98.5
	24	0.2, 0.2	99.5	105.5

Table 59 Stability of cyantraniliprole metabolite IN-N5M09 residues in plant matrices spiked at 0.2 mg/kg and stored at -20 ± 10 °C

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Apples	0			97
	1	0.18, 0.18	90	92
	3	0.17, 0.18	87.5	89
	6	0.16, 0.17	84	87
	12	0.16, 0.18	84.5	79.5
	18	0.19, 0.19	95.5	97
	24	0.2, 0.2	102	100
Peanuts	0			88
	1	0.16, 0.16	80.5	94
	2	0.19, 0.19	93.5	95
	3	0.15, 0.15	76	96.5
	6	0.15, 0.14	72.5	79.5
	12	0.14, 0.14	71	77
	18	0.15, 0.16	79.5	96
	24	0.15, 0.15	75.5	92
Dried beans	0			88
	1	0.18, 0.16	84.5	89
	3	0.18, 0.17	86	91
	6	0.15, 0.13	72	89.5
	12	0.14, 0.14	70	78.5
	18	0.18, 0.17	87.5	101.5
	24	0.16, 0.16	79	96.5
Potatoes	0			91.5
	1	0.17, 0.17	86	89.5
	3	0.19, 0.19	94.5	99
	6	0.18, 0.17	87	83.5
	12	0.17, 0.17	84	86.5
	18	0.2, 0.2	100.5	101
	24	0.17, 0.19	91	97.5

Commodity	Storage interval (months)	Residues remaining (mg/kg)	% Residues remaining	Procedural recovery (%)
Grapes	0			102.5
	1	0.16, 0.16	80	80
	3	0.18, 0.19	91	90
	6	0.16, 0.18	87	86.5
	12	0.17, 0.16	84	79
	18	0.2, 0.2	99	97.5
	24	0.21, 0.2	100.5	102.5

Animal matrices

The stability of residues in animal matrices during frozen storage (at ca. -80 °C) was measured in the both milk and egg matrices as part of the cattle feeding study, reported by Ward & Vance, 2011 [Ref: DP-27180] in support of analyses conducted as part of the cattle and hen feeding studies

Cyantraniliprole and its seven metabolites (IN-HGW87, IN-J9Z38, IN-JCZ38, IN-K7H19, IN-MLA84, IN-MYX98, and IN-N7B69) were shown to be stable for at least 3 months in milk and eggs. Storage stability testing was not performed for residues in other cow or hen tissues given that all analysis was carried out within 30 days of sampling.

Table 60 Stability of cyantraniliprole and metabolite residues in milk stored at -80 °C

Analyte	% Residues remaining		Procedural recovery (%)
	Day 0	Day 99	
Cyantraniliprole	96	99	100
IN-HGW87	102	113	108
IN-J9Z38	94	69	77
IN-JCZ38	90	93	96
IN-K7H19	98	99	100
IN-MLA84	93	56	58
IN-MYX98	103	98	96
IN-N7B69	116	87	93

Table 61 Stability of cyantraniliprole and metabolite residues in eggs stored at -80 °C

Analyte	% Residues remaining		Procedural recovery (%)
	Day 0	Day 99	
Cyantraniliprole	98	101	100
IN-HGW87	99	104	96
IN-J9Z38	98	84	85
IN-JCZ38	92	91	93
IN-K7H19	95	95	95
IN-MLA84	103	81	73
IN-MYX98	105	98	97
IN-N7B69	109	79	81

USE PATTERNS

Information on GAP in Canada, Columbia, Malaysia, New Zealand, Vietnam and West Africa was provided to the Meeting. Proposed uses in Australia, Europe, and USA that are currently being progressed under an OECD Joint Review exercise and in Brazil, China and India were also provided but are not reported.

Cyantraniliprole is intended for use to control of larval stages of lepidopteran insects, thrips, aphids, and some other chewing and sucking insects in a wide range of fruit and vegetable crops, tree crops and oil seed crops as foliar applications and as seed treatments (potato seed pieces, oil seed crops) and as pre-plant soil 'in-furrow' treatments (potatoes and brassica vegetables).

Table 62 Registered uses of cyantraniliprole (foliar applications)

Crop (Group)	Country	Application				Max/season		PHI (days)	Comments
		kg ai/ha	g ai/hL	water L/ha	RTI (days)	no	kg ai/ha		
Pome fruits (002)									
Pome fruit	Canada	0.05–0.15		min 450	7	4	0.45	3	
Stone fruits (003)									
Stone fruit	Canada	0.05–0.15		min 450	7	4	0.45	3	
Bush berries (004B)									
Bush berries	Canada	0.05–0.15		200 50 (air)	5–7	4	0.45	3	
Bulb vegetables (009)									
Bulb vegetables	Canada	0.1–0.15		200 50 (air)	5	4	0.45	1	
Onions (bulb)	Columbia	0.1–0.125				2	0.3	1	
Welsh onion	Columbia	0.1–0.125				2	0.3	1	
Brassica (cole or cabbage) vegetables (010)									
Brassica vegetables	Canada	0.025–0.15		100 50 (air)	5–7	4	0.45	1	
Fruiting vegetables, Cucurbits (011)									
Cucurbit vegetables	Canada	0.025–0.15		100 50 (air)	5–7	4	0.45	1	
Cucumber	Malaysia	0.075–0.1	10–13	750	7	3		1	
Fruiting Vegetables, other than Cucurbits (012)									
Fruiting Vegetables, (except Cucurbits)	Canada	0.025–0.15		100 50 (air)	5–14	4	0.45	1	
Tomatoes	Malaysia	0.075–0.1	10–13	750	7	3		1	
Eggplant (Brinjal)	Malaysia	0.04–0.01	5–13	750	7	3		1	
Chili pepper	Malaysia	0.04–0.1	5–13	750	7	3		1	
Leafy vegetables (including Brassica leafy vegetables) (013)									
Leafy vegetables Brassica vegetables	Canada	0.025–0.15		100 50 (air)	5–7	4	0.45	1	
Legume vegetables (014)									
Long bean	Malaysia	0.04–0.075	5–10	750	7	2		1	
Root and tuber vegetables (016)									
Tuber & corm vegetables	Canada	0.1–0.15		100 50 (air)	5–14	4	0.45	7	
Potato	Canada	0.05–0.15		100 50 (air)	7–14	4	0.45	7	
Stalk and stem vegetables (017)									
Leafy vegetables	Canada	0.025–		100	5–7	4	0.45	1	includes celery

Crop (Group)	Country	Application				Max/season		PHI (days)	Comments
		kg ai/ha	g ai/hL	water L/ha	RTI (days)	no	kg ai/ha		
		0.15		50 (air)					
Cereal grains (020)									
Rice	Vietnam	0.05–0.1		500–600				5	
Tree nuts (022)									
Tree nuts	Canada	0.05–0.1		min 450	7	4	0.45	5	
Oilseed (023)									
Oil seed group	Canada	0.025–0.1		100 50 (air)	7	4	0.11	7	includes rape seed, sunflower
Cotton	CILSS	0.05		150	14	3	0.15	7	
Seeds for beverages and sweets (024)									
Coffee	Columbia	0.125–0.175	50–70	50 ml/tree		1	0.3	28	based on 5000 trees/ha @ 2.5–3.5 g ai/100 trees
Miscellaneous Fodder and Forage crops (052)									
Fodder brassicas	New Zealand	0.015			14–21	3		28 (stock)	with surfactant

Canada: GAP includes a general recommendation to not apply cyantraniliprole following a soil or seed treatment of a Group 28 Insecticide (including cyantraniliprole).

CILSS: Regional (Sahel) group, of countries—Benin, Côte d'Ivoire, Gambia, Guinea Bissau, Mauritania, Senegal, Togo, Burkina Faso, Mali, Niger, Chad and Cape Verde.

Table 63 Registered uses of cyantraniliprole (soil and seed treatments)

Crop (Group)	Country	Application				Max/season		Comments
		form	type	rate	kg ai/ha	no	kg ai/ha	
Brassica (cole or cabbage) vegetables (010)								
Brassica vegetables	Canada	200SC	furrow		0.15–0.2	1	0.2	Band spray in-furrow
Brassica vegetables	Canada	200SC	drench	45 mL drench solution/plant	0.15–0.2	1		At transplanting
Brassica vegetables	Canada	200SC	surface		0.15–0.2	1		5 cm band spray at planting with soil incorporation by irrigation
Leafy vegetables (including Brassica leafy vegetables) (013)								
Leafy vegetables Brassica vegetables	Canada	200SC	furrow		0.15–0.2	1	0.2	Band spray in-furrow
Leafy vegetables Brassica vegetables	Canada	200SC	drench	45 mL drench solution/plant	0.15–0.2	1		At transplanting
Leafy vegetables Brassica vegetables	Canada	200SC	surface		0.15–0.2	1		5 cm band spray at planting with soil incorporation by irrigation
Root and tuber vegetables (016)								
Potato	Canada	200SC	seed	9 g ai/100 kg seed	0.2 (equiv)	1	0.3	Based on sowing rate of 2200 kg seed/ha
Potato	Canada	200SC	furrow	1.35–1.8 g ai/100 m row	0.15–0.2 (equiv)	1		Band spray in-furrow to cover seed pieces Based on 90 cm row spacing

Crop (Group)	Country	Application				Max/season		Comments
		form	type	rate	kg ai/ha	no	kg ai/ha	
Oilseed (023)								
Oilseed rape rapeseed Oilseed mustard	Canada	625SC	seed	0.3– 1.0 kg ai/100 kg seed				

Canada: GAP includes a general recommendation to not apply any subsequent soil or foliar treatments of a Group 28 Insecticide (including cyantraniliprole).

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised field trials involving foliar, drip irrigation or seed treatment applications of cyantraniliprole to the following crops.

Group	Crop	Countries	Table no
Citrus	Orange	Brazil, USA, Europe	64–67
	Mandarin	Europe	68
	Grapefruit	USA	69
	Lemons	USA	70–71
Pome fruit	Apple	Europe, Nth America	72–73
	Pear	Europe, Nth America	74–75
Stone fruit	Apricot,	Europe	76
	Cherry	Nth America	77
	Peach	Nth America, Europe	78–79
	Plum	Nth America, Europe	80–81
Small fruit	Blueberry	Nth America	82
	Grape	Europe	83
Other fruit	Olive	Europe	84
	Pomegranate	India	85
Bulb vegetables	Onion, bulb	North America	86
	Spring onion		87
Brassica vegetables	Broccoli	Nth America	88
	Cauliflower	Nth America	89
	Cabbage	Nth America	90
Cucurbits	Cucumber	Nth America, Europe, Australia	91–94
	Summer squash	Nth America, Europe, Australia	95–98
	Melon	Nth America, Europe, Australia	99–102
Fruiting vegetables	Tomato	Nth America, Europe, Australia	103–107
	Peppers	Nth America, Europe, Australia	108–113
Leafy vegetables	Head lettuce	Nth America, Europe	114–119
	Leaf lettuce	Nth America, Europe	120–125
	Lamb's lettuce	Europe	126–127
	Spinach	USA	128–129
	Mustard greens	USA	130
	Scarole	Europe	131–134
Legume vegetables	Common bean	Europe	135–136

Group	Crop	Countries	Table no
Tuber vegetables	Potato	North America, Europe	137–139
Stem vegetables	Celery	Nth America	140–141
Cereals	Rice	China	142
Tree nuts	Almond	USA	143
	Pecan	USA	144
Oilseeds	Cotton	Australia, Nth America	145–146
	Oil-seed rape	Australia, Nth America	147–148
	Sunflower	North America	149
Others	Coffee	Brazil	150

The supervised trials were well documented with laboratory and field reports. Laboratory reports included method validation including procedural recoveries with spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analyses or duration of residue sample storage were also provided. Although trials included control plots, no control data are recorded in the tables unless residues in control samples exceeded the LOQ. In such cases, the residues found are noted as “c=nn mg/kg” in the Reference and Comments columns. Residue data are recorded unadjusted for recovery.

Results from replicated field plots are presented as individual values. When residues were not detected they are shown as ND. Residues and application rates have been reported as provided in the study reports, although the results from trials used for the estimation of maximum residue levels (underlined) have been rounded to two significant digits (or if close to the LOQ, rounded to one significant digit) in the Appraisal.

In some trials, samples were taken just before the final application and then, again on the same day after the spray had dried. In the data tables the notation for these two sampling times is '-0' and '0' respectively.

When multiple applications were made to a crop, the application rate, spray concentration and spray volume were not always identical from one application to the next. In most trials, the actual treatment rates were within 10% of the listed ‘target’ application rates, but if not, the actual treatment rates are listed.

The analytical methods used in the field trials were capable of analysing both cyantraniliprole and from 1 to 7 metabolites. In most cases, residues of these metabolites were not detected (LOD of 0.003 mg/kg in most trials) or in some cases were reported at levels below the LOQ of 0.01 mg/kg. Where metabolite residues were present at levels above the LOQ, these values are recorded in the following tables using the abbreviations listed below:

M1	IN-J9Z38	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-3,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarbonitrile
M2	IN-MYX98	3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-[(hydroxymethyl)amino]carbonyl]-6-methylphenyl]-1 <i>H</i> -pyrazole-5-carboxamide
M3	IN-N7B69	3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-(hydroxymethyl)-6-[(methylamino)carbonyl]phenyl]-1 <i>H</i> -pyrazole-5-carboxamide

M4	IN-MLA84	2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]-1,4-dihydro-8-methyl-4-oxo-6-quinazolinecarbonitrile
M5	IN-JCZ38	4-[[[3-Bromo-1-(3-chloro-2-pyridinyl)-1 <i>H</i> -pyrazol-5-yl]carbonyl]amino]- <i>N</i> '3',5-dimethyl-1,3-benzenedicarboxamide
M6	IN-N5M09	6-Chloro-4-methyl-11-oxo-11 <i>H</i> -pyrido[2,1- <i>b</i>]quinazoline-2-carbonitrile
M7	IN-F6L99	3-Bromo- <i>N</i> -methyl-1 <i>H</i> -pyrazole-5-carboxamide

Citrus fruits

Results from supervised trials from Brazil, Europe and USA on oranges, grapefruit, lemons and mandarins were provided to the Meeting.

Brazil

In four Brazilian trials on oranges, one plot was treated with two soil drench applications of cyantraniliprole (200 g ai/L SC), 30 days apart, using 1.4 g ai in 200 mL water/tree (equivalent to 0.7 kg ai/ha for a tree density of 500 trees/ha) and a second plot was treated with two foliar applications of cyantraniliprole (100 g/L OD) using 0.3 kg ai/ha in 1500 L water/ha. No adjuvants were used.

Samples were frozen within 4 hours of sampling, stored at –20 °C for up to 84 days before whole fruit analysis for cyantraniliprole and metabolite IN-J9Z38 using an adaptation of method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 108% (cyantraniliprole) and 99% (IN-J9Z38) in samples spiked with 0.01 and 0.1 mg/kg.

North America

In trials conducted in the USA on oranges, grapefruit and lemons, three foliar applications of 0.15 kg ai/ha cyantraniliprole (SE formulation) were applied at 7 day intervals, either as high volume, concentrate or ultra-low-volume treatments, with adjuvant added. Band treatment plots also included in three trial sites, where band spray applications (200 SC formulation) were made on one side of the tree rows, targeting 950 mL spray solution per tree.

Duplicate samples were frozen within 5 hours of sampling, stored at –20 °C for up to 5 months 12 months for Test 2 peel) before extraction and analysis of pulp and peel for cyantraniliprole and metabolites (within 46 days of extraction) using an adaptation of method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries in peel and pulp were 91–96% (cyantraniliprole) and 75–110% (metabolites) in samples spiked with 0.01, 0.1 and 1.0 mg/kg (peel). Whole fruit residues were calculated from the pulp and peel analysis results.

Europe

In trials conducted in Europe on oranges and mandarins, 2–3 foliar applications of 0.15 kg ai/ha cyantraniliprole (SE formulation) were applied at 7 day intervals, either as high volume or concentrate treatments, with added surfactant.

Samples were stored at –18 °C for up to 12 months before extraction and analysis of pulp and peel for cyantraniliprole and six metabolites (within 7 days of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries in peel and pulp were 88–98% (cyantraniliprole) and 80–102% (metabolites) in samples spiked with 0.01, 0.1 and 1.0 mg/kg (peel). Whole fruit residues were calculated from the pulp and peel analysis results.

Table 64 Residues in oranges from supervised trials in Brazil involving soil drench applications of cyantraniliprole (OD formulation)

ORANGE Country, year Location (variety)	Application				RTI (days)	DAT, (days)	Matrix	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha ^a	g ai/tree	water (mL/tree)				cyantraniliprole	metabolites	
Jaguaruna, SP Brazil, 2010 (Valencia)	2	0.7	1.4	200	28	7 14 21 28	whole fruit	ND ND ND ND		BRI-09/10-014 Test A (357 trees/ha)
Conchal, SP Brazil, 2010 (Valencia)	2	0.7	1.4	200	28	7 14 21 28	whole fruit	ND < 0.01 ND ND		BRI-09/10-014 Test B (357 trees/ha)
Botucatu (Valencia)	2	0.7	1.4	200	28	21	whole fruit	ND		BRI-09/10-014 Test C (332 trees/ha)
Espirito Santo do Pinhal, SP Brazil, 2010 (Valencia)	2	0.7	1.4	200	28	21	whole fruit	< 0.01		BRI-09/10-014 Test D (446 trees/ha)

^a Calculated application rate/ha based on a planting density of 500 trees/ha

Table 65 Residues in oranges from supervised trials in Brazil involving foliar applications of cyantraniliprole (SC formulation)

ORANGE Country, year Location (variety)	Application				RTI (days)	DAT, (days)	Matrix	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)				cyantraniliprole	metabolites	
Jaguaruna, SP Brazil, 2010 (Valencia)	2	0.3	20	1500	28	7 14 21 28	whole fruit	0.15 0.05 0.05 0.04		BRI-09/10-014 Test A (357 trees/ha)
Conchal, SP Brazil, 2010 (Valencia)	2	0.3	21	1430	28	7 14 21 28	whole fruit	0.62 0.33 0.33 0.23		BRI-09/10-014 Test B (357 trees/ha)
Botucatu Brazil, 2010 (Valencia)	2	0.3	23	1330	28	21	whole fruit	0.1		BRI-09/10-014 Test C (332 trees/ha)
Espirito Santo do Pinhal, SP Brazil, 2010 (Valencia)	2	0.3	21	1430	28	21	whole fruit	0.23		BRI-09/10-014 Test D (446 trees/ha)

Table 66 Residues in oranges from supervised trials in the USA involving foliar applications of cyantraniliprole (SE formulation)

ORANGE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Clermont, FL USA, 2009 (Hamlin)	3	0.15	535	28	7	1	peel pulp whole	0.37, 0.19 0.033, 0.028 0.19, 0.11	0.28 0.03 0.15		DP-27554 Test 01
Clermont, FL USA, 2009 (Mid Sweet)	3	0.15	535	28	7	1	peel pulp whole	0.56, 0.69 0.054, 0.074 0.31, 0.38	0.63 0.064 0.35		DP-27554 Test 02
Mascotte, FL USA, 2009 (Valencia—Early)	3	0.15	535	28	7	1	peel pulp whole	0.54, 0.39 0.08, 0.092 0.31, 0.24	0.46 0.086 0.28		DP-27554 Test 03
Oviedo, FL USA, 2009 (Navel)	3	0.15	11	1400	7	1	peel pulp whole	0.36, 0.36 0.053, 0.039 0.17, 0.17	0.36 0.046 0.17		DP-27554 Test 04
Oviedo, FL USA, 2009 (Hamlin)	3	0.15	11	1400	7	1	peel pulp whole	0.27, 0.14 0.026, 0.029 0.15, 0.085	0.21 0.027 0.12		DP-27554 Test 05
Mims, FL USA, 2009 (Hamlin)	3	0.15	20	700	7	1	peel pulp whole	0.48, 0.64 0.036, 0.043 0.26, 0.35	0.56 0.04 0.3		DP-27554 Test 06
Holopaw, FL USA, 2009 (Valencia)	3	0.15	21	700	7	1	peel pulp whole	0.34, 0.47 0.041, 0.045 0.18, 0.24	0.41 0.043 0.21		DP-27554 Test 07
Chuluota, FL USA, 2009 (Hamlin)	3	0.15	11	1400	7	1	peel pulp whole	0.69, 0.7 0.081, 0.092 0.37, 0.4	0.7 0.086 0.39		DP-27554 Test 08
Alamo, TX USA, 2009 (Valencia)	3	0.15	25	610	7	1	peel pulp whole	0.86, 0.91 0.071, 0.066 0.22, 0.23	0.88 0.069 0.22		DP-27554 Test 09
Sanger, CA USA, 2009 (Fisher)	3	0.15	25	610	7	1	peel pulp whole	0.23, 0.28 0.016, 0.02 0.087, 0.11	0.25 0.018 0.098	M1=0.01	DP-27554 Test 10
Sanger, CA USA, 2009 (Campbell)	3	0.15	25	610	7	1	peel pulp whole	0.45, 0.35 0.017, 0.01 0.14, 0.1	0.4 0.013 0.12		DP-27554 Test 14
Sanger, CA USA, 2009 (Navel)	3	0.15	8	1870	7	1	peel pulp whole	0.21, 0.21 0.038, 0.035 0.1, 0.1	0.21 0.036 0.1		DP-27554 Test 25
Sanger, CA USA, 2009 (Washington Navel)	3	0.15	0.01	1550	7	1	peel pulp whole	0.7, 0.64 0.019, 0.024 0.2, 0.2	0.67 0.021 0.2		DP-27554 Test 26

M1: Average residues of metabolite IN-J9Z38 reported in peel

Table 67 Residues in oranges from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation)

ORANGE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Andalucia Spain, 2010 (Navelina)	2	0.15	0.01	1500	7	-0	peel	0.27			DP-27716 Test 14 Orange
							pulp	0.023			
							whole	0.093			
						0	peel	0.33			
							pulp	0.017			
							whole	0.11			
						1	peel	0.074			
							pulp	0.021			
							whole	0.036			
						3	peel	0.84			
							pulp	0.012			
							whole	0.26			
Andalucia Spain, 2010 (Navelina)	2	0.15	0.01	1500	7	-0	peel	0.24			DP-27716 Test 15 Orange
							pulp	0.012			
							whole	0.067			
						0	peel	0.56			
							pulp	0.046			
							whole	0.17			
						1	peel	0.73			
							pulp	0.034			
							whole	0.18			
						3	peel	0.56			
							pulp	ND			
							whole	0.13			
Kostaki Greece, 2010 (Salustiana)	2	0.15	0.01	1500	7	7	peel	0.26			DP-27716 Test 08 Orange
							pulp	0.023			
							whole	0.09			

ORANGE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Sicily Italy, 2010 (Tarocco)	2	0.15	0.01	1500	7	-0	peel	0.49			DP-27716 Test 16 Orange
							pulp	ND			
							whole	0.1			
						0	peel	0.96			
							pulp	0.011			
							whole	0.21			
						1	peel	1.2			
							pulp	0.01			
							whole	0.26			
						3	peel	0.73			
							pulp	ND			
							whole	0.15			
Tortosa Spain, 2009 (Navelina)	2	0.15	0.01	1500	7	-0	peel	0.28			DP-27716 Test 06 Orange
							pulp	0.018			
							whole	0.091			
						0	peel	0.53			
							pulp	0.041			
							whole	0.17			
						1	peel	0.51			
							pulp	0.032			
							whole	0.16			
						3	peel	0.47			
							pulp	0.032			
							whole	0.15			
Xerta Spain, 2010 (Navelate)	2	0.15	0.01	1500	7	7	peel	0.54			DP-27716 Test 07 Orange
							pulp	0.016			
							whole	0.13			
Kostaki Greece, 2009 (Salustiana)	3	0.15	0.01	1500	7	-0	peel	0.65			DP-27716 Test 01 Orange
							pulp	0.043			
							whole	0.23			
						1	peel	0.79			
							pulp	0.041			
							whole	0.26			

ORANGE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Sicily Italy, 2009 (Tarocco)	3	0.15	0.01	1500	7	-0	peel	0.85			DP-27716 Test 02 Orange
							pulp	0.004			
							whole	0.2			
	1						peel	0.9			
							pulp	0.007			
							whole	0.23			

Table 68 Residues in mandarins from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation)

MANDARIN Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Andaluci Spain, 2009 (Clementina)	2	0.15	0.01	1500	7	-0	peel	0.37			DP-27716 Test 04 Mandarin
							pulp	0.01			
							whole	0.079			
						0	peel	0.6			
							pulp	0.025			
							whole	0.14			
						1	peel	0.78			
							pulp	ND			
							whole	0.17			
						3	peel	0.61			
							pulp	0.008			
							whole	0.15			
Andalucia, Spain, 2010 (Clementina)	2	0.15	0.01	1500	7	-0	peel	0.56			DP-27716 Test 11 Mandarin
							pulp	0.041			
							whole	0.16			
						0	peel	1.2		M1=0.013	
							pulp	0.086			
							whole	0.35			
						1	peel	1.0		M1=0.013	
							pulp	0.063			
							whole	0.3			
						3	peel	0.73			
							pulp	0.026			
							whole	0.22			
						7	peel	0.54		M1=0.011	
							pulp	0.028			
							whole	0.16			

MANDARIN Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Kostaki Greece, 2010 (Nova)	2	0.15	0.01	1500	7	7	peel pulp whole	0.54 0.017 0.14		M1=0.01	DP-27716 Test 09 Mandarin
Sant Jordi Spain, 2010 (Ortanike)	2	0.15	0.03	510		-0	peel pulp whole	0.24 0.023 0.073			DP-27716 Test 10 Mandarin
						0	peel pulp whole	0.54 0.11 0.19			
						1	peel pulp whole	0.67 ND 0.15			
						3	peel pulp whole	0.74 0.035 0.19			
						7	peel pulp whole	0.55 0.033 0.16			
Sicily Italy, 2010 (Clementine Comune)	2	0.15	0.01	1500	7	-0	peel pulp whole	0.58 0.004 0.17			DP-27716 Test 12 Mandarin
						0	peel pulp whole	1.4 0.014 0.39			
						1	peel pulp whole	0.9 0.007 0.25			
						3	peel pulp whole	1.2 0.009 0.33			
						7	peel pulp whole	0.81 0.006 0.23			

MANDARIN Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Sicily Italy, 2010 (Nova)	2	0.157	0.01	1560	7	-0	peel	0.57			DP-27716 Test 13 Mandarin
							pulp	0.006			
							whole	0.13			
						0	peel	1.0			
							pulp	0.013			
							whole	0.24			
						1	peel	1.1			
							pulp	0.043			
							whole	0.29			
						3	peel	0.84			
							pulp	0.009			
							whole	0.2			
						7	peel	0.64			
							pulp	0.008			
							whole	0.16			
Tivenys Spain, 2009 (Nules)	2	0.15	0.03	500	7	-0	peel	1.5			DP-27716 Test 05 Mandarin
							pulp	0.06			
							whole	0.42			
						0	peel	1.6			
							pulp	0.1			
							whole	0.49			
						1	peel	1.9			
							pulp	0.07			
							whole	0.51			
						3	peel	2.0			
							pulp	0.09			
							whole	0.56			
						7	peel	2.7		M1=0.01	
							pulp	0.03			
							whole	0.71			
Kostaki Greece, 2009 (Clementine)	3	0.15	0.01	1500	7	-0	peel	1.1		M1=0.01	DP-27716 Test 03 Mandarin
							pulp	0.08			
							whole	0.38			
						1	peel	1.1		M1=0.014	
							pulp	0.2			
							whole	0.47			

M1: Average residues of metabolite IN-J9Z38 reported in peel

Table 69 Residues in grapefruit from supervised trials in the USA involving foliar applications of cyantraniliprole (SE formulation)

GRAPEFRUIT Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Mims, FL USA, 2009 (White Marsh)	3	0.15	21	700	7	1	peel pulp whole	0.35, 0.34 0.022, 0.019 0.14, 0.14	0.35 0.021 0.14		DP-27554 Test 11
Oviedo, FL USA, 2009 (Flame)	3	0.15	11	1400	7	1	peel pulp whole	0.41, 0.43 0.028, 0.037 0.18, 0.2	0.42 0.032 0.19		DP-27554 Test 12
Holopaw, FL USA, 2009 (White)	3	0.15	10	1500	7	1	peel pulp whole	0.77, 0.67 0.043, 0.055 0.33, 0.3	0.72 0.049 0.31		DP-27554 Test 13
Alamo, TX USA, 2009 (Rio Red)	3	0.15	6	2400	7	1	peel pulp whole	0.45, 0.28 0.032, 0.019 0.11, 0.21	0.36 0.026 0.16	M1=0.015	DP-27554 Test 15
Elderwood, CA USA, 2009 Duncan	3	0.15	32	470	7	1	peel pulp whole	0.26, 0.18 0.035, 0.03 0.11, 0.076	0.22 0.033 0.091		DP-27554 Test 16
Sanger, CA USA, 2009 (Rio Red)	3	0.15	0.025	620	7	1	peel pulp whole	0.32, 0.29 0.02, 0.039 0.12, 0.12	0.3 0.029 0.12		DP-27554 Test 17
Sanger, CA USA, 2009 (Marsh White)	3	0.15	0.01	1560	7	1	peel pulp whole	0.31, 0.34 0.012, 0.016 0.11, 0.13	0.33 0.014 0.12		DP-27554 Test 18

M1: Average residues of metabolite IN-J9Z38 reported in peel

Table 70 Residues in lemons from supervised trials in the USA involving foliar applications of cyantraniliprole (SE formulation).

LEMON Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Newman, CA USA, 2009/2010 (Lisbon)	3	0.15	8	1870	7	1	peel pulp whole	0.42, 0.44 0.11, 0.11 0.21, 0.22	0.43 0.11 0.21		DP-27554 Test 19
Sanger, CA USA, 2009 (Lisbon)	3	0.15	25	610	7	1	peel pulp whole	0.3, 0.45 0.022, 0.024 0.13, 0.2	0.37 0.023 0.16		DP-27554 Test 20
Sanger, CA USA, 2009 (Frost Lisbon)	3	0.15	10	1560	7	1	peel pulp whole	0.62, 0.63 0.068, 0.057 0.31, 0.3	0.63 0.063 0.3		DP-27554 Test 21
Sanger, CA USA, 2009/2010 (Eureka)	3	0.15	33	470	7	1	peel pulp whole	0.34, 0.39 0.069, 0.071 0.18, 0.2	0.36 0.07 0.19		DP-27554 Test 22
Sanger, CA USA, 2009 (Lizbon 8A)	3	0.16	8	1870	7	1	peel pulp whole	0.32, 0.39 0.059, 0.066 0.14, 0.17	0.35 0.063 0.16		DP-27554 Test 23
Elderwood, CA USA, 2009 (Lizbon)	3	0.15	32	470	7	1	peel pulp whole	0.24, 0.42 0.037, 0.077 0.11, 0.21	0.33 0.057 0.16		DP-27554 Test 24

Table 71 Residues in lemons from supervised trials in the USA involving soil band applications of cyantraniliprole (200 SC formulation)

LEMON Location Country, year (variety)	Application					DAT (days)	Cyantraniliprole Residues (mg/kg)				Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	water L/tree		peel	pulp	whole fruit	metabolites	
Sanger, CA USA, 2009/2010 (Eureka)	1	0.45	117	390	0.95	1 7 14	< 0.01 ND ND	ND ND ND	< 0.01 ND ND		DP-27554 Test 22
Sanger, CA USA, 2009 (Lizbon 8A)	1	0.45	0.16	280	0.95	1 7 14	ND < 0.01 ND	ND ND ND	ND < 0.01 ND		DP-27554 Test 23
Elderwood, CA USA, 2009 (Lizbon)	1	0.45	0.17	260	0.95	1 7 14	ND ND ND	ND ND ND	ND ND ND		DP-27554 Test 24

Pome fruits

Results from supervised trials from Europe and North America on apples and pears were provided to the Meeting.

North America

In trials conducted in North America on apples and pears, three foliar applications of 0.15 kg ai/ha cyantraniliprole (SE formulation) were applied at 7 day intervals, either as high volume or concentrate airblast applications, with adjuvant added (except in the processing study trials).

Duplicate samples were stored at –20 °C for up to 7 months before analysis (within 76 days of extraction) for cyantraniliprole and six metabolites using analytical method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 93–97% (cyantraniliprole) and 83–102% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Europe

In trials conducted in Europe on apples and pears, two foliar applications of 6–15 g ai/hL cyantraniliprole (SE or WG formulations) were applied at 7 day intervals, either as high volume or concentrate treatments, with and without added adjuvant. These trials included a number of reverse decline studies, where different plots were treated at staggered intervals so that the sampling dates coincided with normal commercial harvest.

Samples were stored at –18 °C for up to 4–5 months before analysis of whole fruit for cyantraniliprole and 6–7 metabolites (within 2–24 hours after extraction) using analytical method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 90–94% (cyantraniliprole) and 88–99% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Table 72 Residues in apples from supervised trials in North America involving foliar applications of cyantraniliprole (SE formulation)

APPLE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Beldenville, WI USA, 2009 (Connell Red)	3	0.15	31	490	7	3 7	whole fruit	0.13, 0.13 0.08, 0.12	<u>0.13</u> 0.099		DP-27438 Trial 20

APPLE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Berwick, NS, CAN, 2009 (Coatland)	3	0.15	34	450	6, 9	3 7	whole fruit	0.086, 0.056 0.066, 0.052	<u>0.071</u> 0.059		DP-27438 Test 02
Branchton, ON, CAN, 2009 (Northern Spy)	3	0.15	12	1260	7	3 7	whole fruit	0.2, 0.21 0.19, 0.17	<u>0.21</u> 0.18		DP-27438 Trial 05
Cana, VA USA, 2009 (Yellow Delicious)	3	0.15	27	560	7	3 7	whole fruit	0.25, 0.26 0.29, 0.21	<u>0.26</u> 0.25		DP-27438 Trial 04
Centralia, IL USA, 2009 (Golden Delicious)	3	0.15	38	400	7, 6	3 7	whole fruit	0.2, 0.16 0.13, 0.13	<u>0.18</u> 0.13		DP-27438 Trial 08
Conklin, MI USA, 2009 (Golden Delicious)	3	0.15	8	1900	4, 7	3 7	whole fruit	0.15, 0.19 0.099, 0.12	<u>0.17</u> 0.11		DP-27438 Trial 16
Ephrata, WA USA, 2009 (Red Delicious)	3	0.15	7	1880	7	3 7	whole fruit	0.31, 0.27 0.26, 0.27	<u>0.29</u> 0.27		DP-27438 Trial 10
Hart, MI USA, 2009 (Golden Delicious)	3	0.15	30	500	7	3 7	whole fruit	0.31, 0.31 0.29, 0.31	<u>0.31</u> 0.3		DP-27438 Trial 07
Hood River, OR USA, 2009 (Gingergold)	3	0.15	8	1900	7	3 6	whole fruit	0.15, 0.16 0.1, 0.089	<u>0.15</u> 0.096		DP-27438 Trial 13
Hood River, OR USA, 2009 (Jonagold)	3	0.15	13	550	7	3 7	whole fruit	0.046, 0.057 0.072, 0.055	0.052 <u>0.064</u>		DP-27438 Trial 15
North Rose, NY USA, 2009 (Ida Red)	3	0.15	7	2100	7, 6	3 8	whole fruit	0.15, 0.086 0.073, 0.072	<u>0.12</u> 0.072		DP-27438 Trial 03
Payette, ID USA, 2009 (Early Spur Rome)	3	0.15	13	1180	7	3 7	whole fruit	0.23, 0.28 0.17, 0.13	<u>0.26</u> 0.15		DP-27438 Trial 14
Perry, UT USA, 2009 (Gala)	3	0.15	8	2000	7	3 7	whole fruit	0.13, 0.17 0.11, 0.12	<u>0.15</u> 0.12		DP-27438 Trial 11
Sanger, CA USA, 2009 (Pink Lady)	3	0.15	32	480	7	3 7	whole fruit	0.072, 0.062 0.094, 0.11	0.067 <u>0.1</u>		DP-27438 Trial 12
Santa Maria, CA USA, 2009 (Starkrimson)	3	0.15	7	2250	6	3 7	whole fruit	0.1, 0.15 0.14, 0.12	<u>0.13</u> 0.13		DP-27438 Test 01
Wyoming, IL USA, 2009 (Imperial Gala)	3	0.15	12	1290	7	-0 0 1 3 6	whole fruit	0.066, 0.097 0.16, 0.18 0.2, 0.17 0.16, 0.15 0.12, 0.16	0.081 0.17 0.19 <u>0.16</u> 0.14		DP-27438 Trial 06

Table 73 Residues in apples from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation unless specified)

APPLE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Bentley, Suffolk, UK South, 2010 (Spartan)	2	0.045	6	750	6–8	–0 0 7 14 27 55	whole fruit	0.042 0.06 0.052 0.041 0.02 ND			DP-27714 Test 21 [reverse decline]
KR Groesbeek, Limburg, Netherlands, 2010 (Elstar)	2	0.05	6	900	6–8	–0 0 7 14 28 56	whole fruit	0.034 0.13 0.06 0.041 0.026 0.015			DP-27714 Test 32 [reverse decline]
Dommartin, Rhone Alpes, S France, 2010 (Golden)	2	0.06	15	400	6	8	whole fruit	0.011			DP-27714 Test 30
Herlies, NordPas de Calais, N France, 2010 (Elstar)	2	0.06	15	400	7	7	whole fruit	0.058			DP-27714 Test 17
Herlies, NordPas de Calais, N France, 2010 (Jonagored)	2	0.06	6	1000	6–7	–0 0 7 13 28 55	whole fruit	0.039 0.14 0.052 0.042 0.013 ND			DP-27714 Test 25 [reverse decline]
Thurins, Rhone Alpes, S France, 2010 (Braeburn)	2	0.06	6	1000	6–8	–0 0 7 15 28 56	whole fruit	0.025 0.059 0.027 0.052 0.021 0.005			DP-27714 Test 23 [reverse decline]
Calatorao, Aragon Spain, 2009 (Starking)	2	0.07	5	1400	10	0 0 1 3 7 14	whole fruit	0.05 0.12 0.13 0.06 0.1 0.07			S09-01572 Test 04 [400 WG]
Meauzac, Midi Pyrénées S. France, 2010 (Pink Lady)	2	0.07	5	1400	10	0 1 3 7 14	whole fruit	0.06 0.07 0.04 0.04 <LOQ			S10-01052 Test 04 [400 WG]
Meauzac, Midi Pyrénées S. France, 2010 (Pink Lady)	2	0.07 (adjuvant)	5	1400	10	0 1 3 7 14	whole fruit	0.12 0.12 0.07 0.08 0.09			S10-01052 Test 04 [400 WG]

APPLE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Fuilla, Languedoc Roussillon S. France, 2010 (Golden)	2	0.075	5	1500	10	0 1 3 7 14	whole fruit	0.07 0.12 0.08 0.03 0.05			S10-01052 Test 03 [400 WG]
Hechthausen, Lower Saxony, Germany, 2009 (Delba)	2	0.075	5	1500	11	0 0 1 3 7 14	whole fruit	0.05 0.17 0.15 0.18 0.1 0.08			S09-01571 Test 02 [400 WG]
Heidelberg, BadenWürttemberg Germany, 2010 (Gala)	2	0.075	5	1500	10	0 1 3 7 14	whole fruit	0.08 0.07 0.06 0.05 0.03			S10-01051 Test 01
Heidelberg, BadenWürttemberg Germany, 2010 (Gala)	2	0.075 (adjuvant)	5	1400	10	0 1 3 7 14	whole fruit	0.1 0.07 0.04 0.03 0.02			S10-01051 Test 01 [400 WG]
Innenheim, Alsace N. France, 2009 (Elstar)	2	0.075	5	1500	10	0 1 3 7 14	whole fruit	0.1 0.09 0.08 0.06 0.03			S09-01571 Test 01 [400 WG]
Languedoc Roussillon S. France, 2010 (Golden)	2	0.075 (adjuvant)	5	1500	10	0 1 3 7 14	whole fruit	0.13 0.17 0.08 0.04 0.08			S10-01052 Test 03 [400 WG]
Ressen, Gelderland Netherlands, 2010 (var)	2	0.075	6	1260	7	7	whole fruit	0.045			DP-27714 Test 22
Stotzheim, Alsace N. France, 2010 (Ambassy)	2	0.075	5	1400	10	0 1 3 7 14	whole fruit	0.16 0.13 0.09 0.04 0.04			S10-01051 Test 02 [400 WG]
Stotzheim, Alsace N. France, 2010 (Ambassy)	2	0.075 (adjuvant)	5	1500	10	0 1 3 7 14	whole fruit	0.12 0.1 0.09 0.08 0.02			S10-01051 Test 02 [400 WG]
Castelnaudary, Languedoc Roussillon S. France, 2009 (Fuji)	2	0.08	5	1600	10	0 1 3 7 14	whole fruit	0.04 0.03 0.02 0.01 0.02			S09-01572 Test 03 [400 WG]

APPLE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Arbeca, Catalunya, N Spain, 2010 (Golden)	2	0.11	7.6	1500	7	-0 0 7 14 28 56	whole fruit	0.051 0.11 0.079 0.087 0.11 0.025			DP-27714 Test 26 [reverse decline]
Monleale, Piemonte, Italy, 2010 (Stark)	2	0.11	7.6	1500	7	-0 0 7 14 29 56	whole fruit	0.094 0.11 0.13 0.076 0.015 0.017			DP-27714 Test 24 [reverse decline]
Nea Trapezounda, Central Macedonia, Greece, 2010 (Fuji)	2	0.11	7.6	1500	7	7	whole fruit	0.12			DP-27714 Test 18
Calatorao, Aragon Spain, 2009 (Starking)	2	0.125	8.3	1500	10	0 0 1 3 7 14	whole fruit	0.12 0.22 0.13 0.21 0.19 0.1			S09-01572 Test 04 [400 WG]
Calatorao, Aragon Spain, 2009 (Starking)	2	0.125 (adjuvant)	8.3	1500	10	0 0 1 3 7 14	whole fruit	0.06 0.33 0.2 0.23 0.28 0.21			S09-01572 Test 04 [400 WG]
Castelnaudary, Languedoc Roussillon S. France, 2009 (Fuji)	2	0.125	8.6	1600	10	0 1 3 7 14	whole fruit	0.12 0.06 0.04 0.03 0.02			S09-01572 Test 03 [400 WG]
Castelnaudary, Languedoc Roussillon S. France, 2009 (Fuji)	2	0.125 (adjuvant)	8.3	1500	10	0 1 3 7 14	whole fruit	0.06 0.05 0.04 0.02 0.02			S09-01572 Test 03 [400 WG]
Hechthausen, Lower Saxony, Germany, 2009 (Delba)	2	0.125	8.3	1500	11	0 0 1 3 7 14	whole fruit	0.08 0.38 0.31 0.39 0.26 0.16			S09-01571 Test 02 [400 WG]
Hechthausen, Lower Saxony, Germany, 2009 (Delba)	2	0.125 (adjuvant)	8.3	1500	11	0 0 1 3 7 14	whole fruit	0.09 0.29 0.27 0.23 0.22 0.13			S09-01571 Test 02 [400 WG]

APPLE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Innenheim, Alsace N. France, 2009 (Elstar)	2	0.125	8.6	1600	10	0 1 3 7 14	whole fruit	0.24 0.14 0.17 0.13 0.08			S09-01571 Test 01 [400 WG]
Innenheim, Alsace N. France, 2009 (Elstar)	2	0.125 (adjuvant)	8.3	1500	10	0 1 3 7 14	whole fruit	0.18 0.18 0.18 0.09 0.09			S09-01571 Test 01 [400 WG]

Table 74 Residues in pears from supervised trials in North America involving foliar applications of cyantraniliprole (SE formulation)

PEAR Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Alton, NY USA, 2009 (Clapps Favorite)	3	0.15	13	1100	6, 7	3 7	whole fruit	0.21, 0.24 0.18, 0.15	<u>0.23</u> 0.16		DP-27438 Trial 17
Beamsville, ON CAN, 2009 (D'Anjou)	3	0.15	15	1000	7	3 7	whole fruit	0.078, 0.074 0.058, 0.071	<u>0.077</u> 0.065		DP-27438 Trial 18
Ephrata, WA USA, 2009 (Bartlett)	3	0.15	32	470	7, 8	3 7	whole fruit	0.56, 0.6 0.45, 0.46	<u>0.58</u> 0.45		DP-27438 Trial 26
Ephrata, WA USA, 2009 (Concord)	3	0.15	32	470	7	3 7	whole fruit	0.39, 0.48 0.37, 0.39	<u>0.44</u> 0.38		DP-27438 Trial 25
Hood River, OR USA, 2009 (Bartlett)	3	0.15	27	550	7	3 6	whole fruit	0.13, 0.11 0.12, 0.12	<u>0.12</u> 0.12		DP-27438 Trial 24
Hood River, OR USA, 2009 (Red Clapp)	3	0.15	7	2200	7	3 6	whole fruit	0.13, 0.15 0.11, 0.098	<u>0.14</u> 0.1		DP-27438 Trial 23
Lindsay, CA USA, 2009 (Olympic)	3	0.15	9	1700	7	3 8	whole fruit	0.16, 0.14 0.14, 0.17	0.15 <u>0.16</u>		DP-27438 Trial 21
Marysville, CA USA, 2009 (Bartlett)	3	0.15	11	1400	7	3 7	whole fruit	0.54, 0.3 0.39, 0.3	<u>0.42</u> 0.35		DP-27438 Trial 22
Shelby, MI USA, 2009 (Bartlett)	3	0.15	31	500	7	3 7	whole fruit	0.42, <u>0.65</u> 0.59, 0.54	0.54 <u>0.56</u>		DP-27438 Trial 19
Simcoe, ON CAN, 2009 (Bartlett)	3	0.15	26	600	7	3 7	whole fruit	0.1, 0.09 0.034, 0.049	<u>0.095</u> 0.042		DP-27438 Trial 09

Table 75 Residues in pears from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation)

PEAR Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Bentley, Suffolk, UK South, 2010 (Conference)	2	0.045	6	750	6–8	–0 0 7 14 27 55	whole fruit	0.025 0.056 0.075 0.052 0.044 0.01			DP-27714 Test 31 [reverse decline]
Dommartin, Rhone Alpes, S France, 2010 (William)	2	0.06	6	1000	6–8	–0 0 6 14 28 55	whole fruit	0.038 0.084 0.081 0.033 0.02 0.013			DP-27714 Test 34 [reverse decline]
Herlies, NordPas de Calais, N France, 2010 (Angelys)	2	0.06	6	1000	6–7	–0 0 7 13 28 55	whole fruit	0.03 0.083 0.021 0.019 0.008 0.004			DP-27714 Test 33 [reverse decline]
Herlies, NordPas de Calais, N France, 2010 (Comice)	2	0.06	15	400	7	7	whole fruit	0.13			DP-27714 Test 28
Höhnstedt, SaxonyAnhalt, Germany, 2010 (Williams)	2	0.06	6	1000	8	7	whole fruit	0.063			DP-27714 Test 19
KR Groesbeek, Limburg, Netherlands, 2009 (Conference)	2	0.06	7.5	800	7	7	whole fruit	0.055			DP-27714 Test 10
Le Marne, Rhone Alpes, S France, 2010 (Packham)	2	0.06	15	400	6	7	whole fruit	0.081			DP-27714 Test 20
Elne, Languedoc Roussillon S. France, 2010 (Williams)	2	0.07	5	1400	10	0 1 3 7 14	whole fruit	0.12 0.1 0.13 0.11 0.06			S10-01054 Test 07 [400 WG]
Altedo Bologna Italy, 2010 (Decana)	2	0.075	5	1500	10	0 1 3 7 14	whole fruit	0.13 0.13 0.1 0.1 0.05			S10-01054 Test 08 [400 WG]

PEAR Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Altedo Bologna Italy, 2010 (Decana)	2	0.075 (adjuvant)	5	1500	10	0 1 3 7 14	whole fruit	0.12 0.13 0.09 0.04 0.05			S10-01054 Test 08 [400 WG]
Bradfield Combust, Suffolk UK South, 2009 (Conference)	2	0.075	7.5	1000	6-9	-0 0 7 13 27 56	whole fruit	0.068 0.11 0.076 0.12 0.022 0.015			DP-27714 Test 14 [Reverse decline]
Calatorao, Aragon Spain, 2009 (Conference)	2	0.075	5	1500	10	0 0 1 3 7 14	whole fruit	0.03 0.11 0.12 0.11 0.04 0.05			S09-01574 Test 08 [400 SG]
Elne, Languedoc Roussillon S. France, 2010 (Williams)	2	0.075 (adjuvant)	5	1500	10	0 1 3 7 14	whole fruit	0.15 0.15 0.01 0.1 0.03			S10-01054 Test 07 [400 WG]
Elne, Languedoc Roussillon S. France, 2009 (Williams)	2	0.075	5	1500	10	0 1 3 7 14	whole fruit	0.04 0.04 0.02 0.02 0.02			S09-01574 Test 07 [400 WG]
Herlies, NordPas de Calais, N France, 2009 (Conference)	2	0.075	19	400	6	9	whole fruit	0.11			DP-27714 Test 09
Herlies, NordPas de Calais, N France, 2009 (Angelys)	2	0.075	7.5	1000	5-7	-0 0 5 12 26 54	whole fruit	0.027 0.044 0.019 0.029 0.01 ND			DP-27714 Test 13 [Reverse decline]
Jork, Lower Saxony Germany, 2009 (Condo)	2	0.075	5	1500	10	0 0 1 3 7 14	whole fruit	0.02 0.13 0.13 0.08 0.05 0.04			S09-01573 Test 06 [400 WG]
Neuenschleuse, Niedersachsen Germany, 2010 (Hollandische Zuckerbirne)	2	0.075 (adjuvant)	5	1500	10	0 1 3 7 14	whole fruit	0.16 0.13 0.14 0.08 0.03			S10-01053 Test 05 [400 WG]

PEAR Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Stotzheim, Alsace N. France, 2009 (Williams)	2	0.075	5	1500	10	0 1 3 7 14	whole fruit	0.06 0.04 0.03 0.02 0.02			S09-01573 Test 05 [400 WG]
Stotzheim, Alsace N. France, 2010 (Williams)	2	0.075	5	1500	10	0 1 3 7 14	whole fruit	0.12 0.16 0.08 0.04 0.03			S10-01053 Test 06 [400 WG]
Stotzheim, Alsace N. France, 2010 (Williams)	2	0.075 (adjuvant)	5	1500	10	0 1 3 7 14	whole fruit	0.19 0.12 0.08 0.05 0.04			S10-01053 Test 06 [400 WG]
Vergers des 4 Loups, Lot en Garonne, S France, 2009 (Passe Ciassome)	2	0.075	7.5	1000	6–8	–0 0 7 13 27 55	whole fruit	0.031 0.044 0.06 0.035 0.018 0.006			DP-27714 Test 15 [Reverse decline]
Dommartin, Rhône Alpes, S France, 2009 (William)	2	0.076	19	410	7	7	whole fruit	0.092			DP-27714 Test 12
Ablass, Saxony, Germany, 2010 (Williams)	2	0.08	6	1300	7	–0 0 7 14 28 56	whole fruit	0.04 0.097 0.042 0.029 0.023 0.004			DP-27714 Test 27 [reverse decline]
Neuenschleuse, Niedersachsen Germany, 2010 (Hollandische Zuckerbirne)	2	0.08	5	1600	10	0 1 3 7 14	whole fruit	0.08 0.06 0.08 0.06 0.01			S10-01053 Test 05 [400 WG]
Agia Triada, Central Macedonia, Greece, 2009 (Kristalia)	2	0.11	7.5	1450	7	7	whole fruit	0.099			DP-27714 Test 11
Akrolimni, Central Macedonia, Greece, 2010 (Williams)	2	0.11	7.6	1500	7	7	whole fruit	0.18			DP-27714 Test 29

PEAR Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Bellvis, Catalunya, N Spain, 2010 (Ercolini)	2	0.11	7.6	1500	7	-0 0 7 14 28 56	whole fruit	0.095 0.17 0.16 0.11 0.045 0.009			DP-27714 Test 36 [reverse decline]
Bellvis, Catalunya, N Spain, 2009 (Conference)	2	0.11	7.5	1500	7-8	-0 0 7 14 29 55	whole fruit	0.12 0.26 0.15 0.071 0.067 0.017			DP-27714 Test 16 [Reverse decline]
Carpi, Emilia Romagna, Italy, 2010 (William)	2	0.11	7.6	1500	7	-0 0 7 14 28 56	whole fruit	0.037 0.1 0.048 0.032 0.057 0.004			DP-27714 Test 35 [reverse decline]
Calatorao, Aragon Spain, 2009 (Conference)	2	0.125	8.3	1500	10	0 0 1 3 7 14	whole fruit	0.02 0.2 0.19 0.08 0.09 0.03			S09-01574 Test 08 [400 SG]
Calatorao, Aragon Spain, 2009 (Conference)	2	0.125 (adjuvant)	8.3	1500	10	0 0 1 3 7 14	whole fruit	0.07 0.13 0.29 0.16 0.09 0.13			S09-01574 Test 08 [400 SG]
Elne, Languedoc Roussillon S. France, 2009 (Williams)	2	0.125	8.3	1500	10	0 1 3 7 14	whole fruit	0.08 0.08 0.02 0.02 0.05			S09-01574 Test 07 [400 WG]
Elne, Languedoc Roussillon S. France, 2009 (Williams)	2	0.125 (adjuvant)	8.3	1500	10	0 1 3 7 14	whole fruit	0.15 0.08 0.07 0.06 0.04			S09-01574 Test 07 [400 WG]
Jork, Lower Saxony Germany, 2009 (Condo)	2	0.125	8.3	1500	10	0 0 1 3 7 14	whole fruit	0.04 0.24 0.17 0.18 0.11 0.12			S09-01573 Test 06 [400 WG]

PEAR Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)	RTI (days)			cyantraniliprole	mean	metabolites	
Jork, Lower Saxony Germany, 2009 (Condo)	2	0.125 (adjuvant)	8.3	1500	10	0 0 1 3 7 14	whole fruit	0.06 0.21 0.26 0.17 0.16 0.11			S09-01573 Test 06 [400 WG]
Stotzheim, Alsace N. France, 2009 (Williams)	2	0.125	8.3	1500	10	0 1 3 7 14	whole fruit	0.09 0.06 0.07 0.06 0.04			S09-01573 Test 05 [400 WG]
Stotzheim, Alsace N. France, 2009 (Williams)	2	0.125 (adjuvant)	8.3	1500		0 1 3 7 14	whole fruit	0.09 0.07 0.06 0.07 0.04			S09-01573 Test 05 [400 WG]

Stonefruit

Results from supervised trials from Europe and North America on peaches, plums and cherries were provided to the Meeting.

North America

In trials conducted in North America, three foliar applications of 0.15 kg ai/ha cyantraniliprole (SE formulation) were applied at 7 day intervals, either as high volume (1000–2000 L/ha) or concentrate (100–800 L/ha) airblast applications, with adjuvant added.

Duplicate samples were stored at –20 °C for up to 7 months before analysis of flesh (within 101 days of extraction) for cyantraniliprole and six metabolites using analytical method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 100–104% (cyantraniliprole) and 91–109% (metabolites) in samples spiked with 0.01, 0.1, 0.5 and/or 2 mg/kg. Residues in whole fruit were calculated from the flesh residue results and the relative flesh:stone weights.

Europe

In trials conducted in Europe on apricots, peaches and plums, two foliar applications of 0.15 kg ai/ha (10–30 g ai/hL) cyantraniliprole (SE or WG formulations) were applied 7 days apart, using 500–1500 L/ha, with and without added adjuvant. These trials included a number of reverse decline studies, where different plots were treated at staggered intervals so that the sampling dates coincided with normal commercial harvest.

Samples were stored at –18 °C for up to 9 months before analysis for cyantraniliprole and six to seven metabolites (within 1–23 days after extraction) using analytical method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 82–96% (cyantraniliprole) and 79–96% (metabolites) in samples spiked with 0.01, 0.1 and 0.5 or 1.0 mg/kg. Residues in whole fruit were calculated from residues measured in the flesh, and the relative weights of flesh and stones.

Table 76 Residues in apricots from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation)

APRICOT Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Mandalo Greece, 2009 (Bebeku)	2	0.15	10	1500	8	7	flesh whole fruit	0.36 0.34		M1=0.01 M1=0.01	DP-27717 Test 02
La Granja d'Escarp Spain, 2010 (Pinkoot)	2	0.15	30	500		-0	flesh	0.17			DP-27717 Test 04 [reverse decline]
						0		0.17			
						7		0.34			
						14		0.25			
						28		0.19			
						56		0.065			
						-0	whole fruit	0.16			
						0		0.16			
						7		0.32			
						14		0.24			
						28		0.18			
						56		0.062			
						7	whole fruit	0.08			
						15		0.064			
						21		0.058			
						34		0.048			
						63		0.012			
						7	whole fruit	0.08			
						15		0.064			
						21		0.058			
						34		0.048			
						63		0.012			
Seros Spain, 2010 (Traver)	2	0.15	10	1500		7	flesh	0.083			DP-27717 Test 09 [reverse decline]
						15	flesh	0.066			
						21		0.06			
						34		0.05			
						63		0.012			
						7	whole fruit	0.08			
						15		0.064			
						21		0.058			
						34		0.048			
						63		0.012			
						7	whole fruit	0.08			
						15		0.064			
						21		0.058			
						34		0.048			
						63		0.012			

M1: Residues of metabolite IN-J9Z38

Table 77 Residues in cherries from supervised trials in North America involving foliar applications of cyantraniliprole (SE formulation).

CHERRY Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Denair, CA USA, 2009 Sweet Cherry (Bing)	3	0.15	10	1500	7, 8	3	flesh	0.32, 0.4	0.36	M1=0.03	DP-27437 Trial 28
						7		0.31, 0.36	0.34	M1=0.04	
						3	whole fruit	0.28, 0.35	<u>0.32</u>	M1=0.03	
						7		0.28, 0.32	0.3	M1=0.04	
Hart, MI USA, 2009 Tart Cherry (Montmorency)	3	0.15	28	500	7	3	flesh	0.99, 0.79	0.89		DP-27437 Trial 26
						7		0.75, 0.91	0.83		
						3	whole fruit	0.89, 0.71	<u>0.8</u>		
						7		0.66, 0.81	0.74		

CHERRY Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Hood River, OR USA, 2009 Sweet Cherry (Selah)	3	0.15	26	600	7	3	flesh	0.37, 0.29	0.33		DP-27437 Trial 29
						7		0.21, 0.19	0.2		
						3	whole	0.33, 0.26	<u>0.3</u>		
						7	fruit	0.19, 0.17	0.18		
Orefield, PA USA, 2009 Tart Cherry (Montmorency)	3	0.15	6	2300	7, 6	3	flesh	1.1, 0.87	0.96	M1=0.01	DP-27437 Test 23
						7		0.96, 0.95	0.96	M1=0.01	
						3	whole	1.0, 0.8	<u>0.9</u>	M1=0.01	
						7	fruit	0.87, 0.87	0.87	M1=0.01	
Pentwater, MI USA, 2009 Tart Cherry (Montmorency)	3	0.15	30	500	7	3	flesh	3.9, 3.6	3.8	M1=0.03	DP-27437 Trial 25
						7		1.3, 3.1	2.2	M1=0.03 + M2=0.01	
						3	whole	<u>3.5</u> , 3.2	<u>3.4</u>	M1=0.02	
						7	fruit	1.2, 2.9	2.1	M1=0.03	
Perry, UT USA, 2009 Tart Cherry (Montmorency)	3	0.15	7	2000	6, 7	3	flesh	1, 0.93	0.98	M1=0.05	DP-27437 Trial 27
						7		1, 0.73	0.88	M1=0.05	
						3	whole	0.92, 0.85	<u>0.89</u>	M1=0.05	
						7	fruit	0.92, 0.67	0.8	M1=0.05	
Ridgeville, ON, Canada, 2009 Tart Cherry (Montmorency)	3	0.15	12	1200	7, 6	3	flesh	0.93, 0.93	0.93	M1=0.04	DP-27437 Trial 24
						7		0.72, 0.83	0.77	M1=0.04	
						3	whole	0.67, 0.72	<u>0.7</u>	M1=0.03	
						7	fruit	0.58, 0.65	0.62	M1=0.03	

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

Table 78 Residues in peaches from supervised trials in North America involving foliar applications of cyantraniliprole (SE formulation)

PEACH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Alexandria, LA USA, 2009 (June Prince)	3	0.15	9	1750	7	3	flesh	0.17, 0.17	0.17	M1=0.01	DP-27437 Trial 06
						7		0.18, 0.22	0.2	M1=0.015	
						3	whole	0.16, 0.16	0.16		
						7	fruit	0.17, 0.21	<u>0.19</u>	M1=0.01	
Branchton, ON Canada, 2009 (Reliance)	3	0.15	13	1200	7	3	flesh	0.16, 0.21	0.19		DP-27437 Trial 07
						7		0.15, 0.11	0.13		
						3	whole	0.13, 0.18	<u>0.16</u>		
						7	fruit	0.13, 0.1	0.12		
Clanton, AL USA, 2009 (Bounty)	1+ 2	0.15+ 0.15	120+ 60	120+ 250	7	3	flesh	0.47, 0.66	0.56		DP-27437 Trial 04
						7		0.32, 0.4	0.36		
						3	whole	0.43, 0.58	<u>0.51</u>		
						7	fruit	0.3, 0.38	0.34		

PEACH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Hart, MI USA, 2009 (Baby Gold)	3	0.15	30	500	7	3	flesh	1.4, 0.47	0.94	M1=0.01	DP-27437 Trial 08
						7		0.44, 0.67	0.56		
						3	whole	<u>1.2</u> , 0.41	<u>0.81</u>		
						7	fruit	0.4, 0.61	0.51		
Hickman, CA USA, 2009 (Summerset)	3	0.15	23	650	6, 7	3	flesh	0.31, 0.39	0.35		DP-27437 Trial 10
						7		0.35, 0.33	0.34		
						3	whole	0.3, 0.37	<u>0.34</u>		
						7	fruit	0.34, 0.32	0.33		
Hondo, TX USA, 2009 (Tex Royal)	3	0.15	35	450	7	3	flesh	0.73, 0.47	0.6	M1=0.02 M1=0.03	DP-27437 Trial 09
						6		0.85, 0.93	0.89		
						3	whole	0.66, 0.43	0.55	M1=0.02 M1=0.03	
						6	fruit	0.75, 0.82	<u>0.79</u>		
Live Oak, CA USA, 2009 (Halfords)	3	0.15	23	650	7	3	flesh	0.41, 0.27	0.34		DP-27437 Trial 11
						7		0.11, 0.1	0.1		
						3	whole	0.34, 0.22	<u>0.28</u>		
						7	fruit	0.09, 0.09	0.09		
Madera, CA USA, 2009 (Springcrest)	3	0.15	11	1400	7	-0	flesh	0.17, 0.17	0.17		DP-27437 Trial 12
						0		0.25, 0.27	0.26		
						1		0.29, 0.21	0.25		
						3		0.22, 0.17	0.19		
						7		0.2, 0.15	0.18		
						-0	whole	0.15, 0.15	0.15		
						0	fruit	0.22, 0.24	0.23		
						1		0.26, 0.19	0.23		
						3		0.2, 0.15	<u>0.18</u>		
						7		0.18, 0.13	0.16		
Monetta, SC USA, 2009 (Red Globe)	3	0.15	20	700	7	3	flesh	0.25, 0.22	0.23		DP-27437 Trial 03
						7		0.18, 0.19	0.18		
						3	whole	0.19, 0.18	<u>0.19</u>		
						7	fruit	0.16, 0.15	0.16		
Oliver, BC, Canada, 2009 (Red Haven)	3	0.15	15	1000	6	3	flesh	0.33, 0.52	0.42	M1=0.01	DP-27437 Trial 13
						6		0.34, 0.31	0.32		
							whole	0.3, 0.47	<u>0.39</u>		
							fruit	0.3, 0.28	0.29		
Orefield, PA, USA, 2009 (Glen Glo)	3	0.15	8	1800	6, 8	3	flesh	0.27, 0.23	0.25		DP-27437 Trial 01
						7		0.24, 0.21	0.23		
						3	whole	0.24, 0.21	<u>0.23</u>		
						7	fruit	0.22, 0.19	0.21		
Pikeville, NC, USA, 2009 (New Haven)	3	0.15	13	1200	7, 6	3	flesh	0.52, 0.47	0.49	M1=0.02 M1=0.02	DP-27437 Trial 02
						6		0.37, 0.46	0.41		
						3	whole	0.47, 0.42	<u>0.45</u>	M1=0.02 M1=0.02	
						6	fruit	0.33, 0.41	0.37		

PEACH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Ridge Spring, SC USA, 2009 (Contender)	3	0.15	24	630	7	3	flesh	0.3, 0.23	0.27		DP-27437 Trial 05
						7		0.13, 0.2	0.17		
						3	whole	0.27, 0.21	<u>0.24</u>		
						7	fruit	0.12, 0.19	0.16		

M1: Average residues of metabolite IN-J9Z38

Table 79 Residues in peaches from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation)

PEACH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Altedo Italy, 2009 (Red Coast)	2	0.075	5	1500	7	0	whole fruit	0.07			S09-01576 Test 04a 400 WG
						1		0.13			
						3		0.08			
						7		0.06			
						14		0.04			
Barbiano Italy, 2010 (Big top)	2	0.075	5	1500	7	0	whole fruit	0.12			S10-01055 Test 2a 400 WG
						1		0.07			
						3		0.05			
						7		0.05			
						14		0.02			
Calatorao Spain, 2009 (Miraflores)	2	0.075	5	1500	7	0	whole fruit	0.08			S09-01576 Test 03a 400 WG
						0		0.13			
						1		0.13			
						3		0.13			
						7		0.13			
Calatorao Spain, 2009 (Sudanell)	2	0.075	5	1500	7	14	whole fruit	0.05			S09-01576 Test 02a 400 WG
						0		0.06			
						0		0.13			
						1		0.12			
						3		0.12			
Corbère S France, 2010 (Corindon)	2	0.075	5	1500	7	7	whole fruit	0.09			S10-01055 Test 1a 400 WG
						14		0.05			
						0		0.32			
						1		0.31			
						3		0.24			
Corbère S. France, 2009 (Corindon)	2	0.075	5	1500	7	7	whole fruit	0.13			S09-01576 Test 01a 400 WG
						14		0.1			
						0		0.02			
						1		0.12			
						3		0.11			
El Coronil Spain, 2010 (Red Robin)	2	0.075	5	1500	7	7	whole fruit	0.05			S10-01055 Test 4a 400 WG
						14		0.08			
						0		0.29			
						1		0.19			
						3		0.16			
						7		0.1			
						14		0.05			

PEACH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Valdelacalzada Spain, 2010 (Spring lady)	2	0.075	5	1500	7	0 1 3 7 14	whole fruit	0.48 0.23 0.1 0.13 0.09			S10-01055 Test 3a 400 WG
Barbiano Italy, 2010 (Big top)	2	0.125	8.3	1500	7	0 1 3 7 14	whole fruit	0.2 0.19 0.17 0.1 0.04			S10-01055 Test 2b 400 WG
Corbère S France, 2010 (Corindon)	2	0.125	8.3	1500	7	0 1 3 7 14	whole fruit	0.39 0.63 0.5 0.26 0.21			S10-01055 Test 1b 400 WG
El Coronil Spain, 2010 (Red Robin)	2	0.125	8.3	1500	7	0 1 3 7 14	whole fruit	0.42 0.26 0.37 0.26 0.09			S10-01055 Test 4b 400 WG
Valdelacalzada Spain, 2010 (Spring lady)	2	0.125	8.3	1500	7	0 1 3 7 14	whole fruit	0.48 0.34 0.28 0.18 0.14			S10-01055 Test 3b 400 WG
Barbiano Italy, 2010 (Big top)	2	0.125+ surfact	8.3	1500	7	0 1 3 7 14	whole fruit	0.19 0.18 0.15 0.11 0.06			S10-01055 Test 2c 400 WG
Corbère S France, 2010 (Corindon)	2	0.125+ surfact	8.3	1500	7	0 1 3 7 14	whole fruit	0.56 0.29 0.25 0.35 0.14			S10-01055 Test 1c 400 WG
El Coronil Spain, 2010 (Red Robin)	2	0.125+ surfact	8.3	1500	7	0 1 3 7 14	whole fruit	0.3 0.25 0.36 0.22 0.1			S10-01055 Test 4c 400 WG
Valdelacalzada Spain, 2010 (Spring lady)	2	0.125+ surfact	8.3	1500	7	0 1 3 7 14	whole fruit	0.59 0.35 0.33 0.21 0.17			S10-01055 Test 3c 400 WG
Alcarras Spain 2009 (Romestart)	2	0.15	10	1500	6	7	flesh whole fruit	0.2 0.19		M1=0.01 M1=0.01	DP-27717 Test 01

PEACH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Altedo Italy, 2009 (Red Coast)	2	0.15	10	1500	7	0 1 3 7 14	whole fruit	0.11 0.2 0.14 0.19 0.14			S09-01576 Test 04b 400 WG
Calatorao Spain, 2009 (Miraflores)	2	0.15	10	1500	7	0 0 1 3 7 14	whole fruit	0.12 0.2 0.35 0.3 0.19 0.15			S09-01576 Test 03b 400 WG
Calatorao Spain, 2009 (Sudanell)	2	0.15	10	1500	7	0 0 1 3 7 14	whole fruit	0.17 0.47 0.49 0.23 0.19 0.29			S09-01576 Test 02b 400 WG
Corbère S. France, 2009 (Corindon)	2	0.15	10	1500	7	0 1 3 7 14	whole fruit	0.19 0.36 0.12 0.08 0.1			S09-01576 Test 01b 400 WG
Galatades Greece, 2010 (Katerina)	2	0.15	10	1500		7	flesh whole fruit	0.3 0.28		M1=0.01 M1=0.01	DP-27717 Test 05
Lizac S France, 2009 (Plat)	2	0.15	10	1500		7	flesh whole fruit	0.023 0.02			DP-27717 Test 06
Poulariot S France, 2010 (Plat Sweetcap)	2	0.15	15	1000		-0 0 6 14 28 56 -0 0 6 14 28 56	flesh whole fruit	0.034 0.055 0.032 0.026 0.035 0.014 0.031 0.05 0.029 0.024 0.032 0.013			DP-27717 Test 07 [reverse decline]

PEACH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Volpedo Italy, 2010 (Cresthaven)	2	0.15	10	1500		-0	flesh	0.089			DP-27717 Test 08 [reverse decline]
						0		0.31			
						7		0.14			
						15		0.058			
						29		0.078			
						56		0.027			
						-0	whole fruit	0.081			
						0		0.28			
						7		0.13			
						15		0.053			
						29		0.07			
						56		0.024			
Volpedo Italy, 2009 (Cresthaven)	2	0.15	10	1500	5-7	-0	flesh	0.096			DP-27717 Test 03 [reverse decline]
						0		0.18			
						7		0.18			
						14		0.13			
						28		0.074			
						56		0.046			
						-0	whole fruit	0.092			
						0		0.17			
						7		0.17			
						14		0.12			
						28		0.07			
						56		0.044			
Altado Italy, 2009 (Red Coast)	2	0.15+ surfact	10	1500	7	0	whole fruit	0.15			S09-01576 Test 04c 400 WG
						1		0.31			
						3		0.16			
						7		0.18			
						14		0.14			
Calatorao Spain, 2009 (Miraflores)	2	0.15+ surfact	10	1500	7	0	whole fruit	0.18			S09-01576 Test 03c 400 WG
						0		0.16			
						1		0.34			
						3		0.21			
						7		0.31			
Calatorao Spain, 2009 (Sudanell)	2	0.15+ surfact	10	1500	7	14	whole fruit	0.16			S09-01576 Test 02c 400 WG
						0		0.15			
						0		0.33			
						1		0.54			
						3		0.29			
Corbère S. France, 2009 (Corindon)	2	0.15+ surfact	10	1500	7	7	whole fruit	0.25			S09-01576 Test 01c 400 WG
						14		0.14			
						0		0.2			
						1		0.13			
						3		0.09			
						7		0.11			
						14		0.12			

M1: Residues of metabolite IN-J9Z38

Table 80 Residues in plums from supervised trials in North America involving foliar applications of cyantraniliprole (SE formulation)

PLUM Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Beamville, ON, Canada, 2009 (Vibrant V70034)	3	0.15	26	600	6, 7	3 7	flesh	0.065, 0.077 0.061, 0.057	0.07 0.06		DP-27437 Trial 15
						3 7	whole fruit	0.06, 0.07 0.06, 0.05	<u>0.07</u> 0.06		
Conklin, MI USA, 2009 (Vision)	3	0.15	7	2000	7	3 7	flesh	0.23, 0.17 0.17, 0.14	0.2 0.15		DP-27437 Trial 14
						3 7	whole fruit	0.22, 0.16 0.16, 0.14	<u>0.19</u> 0.15		
Hughson, CA USA, 2009 (French Plum)	3	0.15	11	1300	7	3 7	flesh	0.3, 0.26 0.29, 0.3	0.28 0.29		DP-27437 Trial 16
						3 7	whole fruit	0.28, 0.24 0.27, 0.28	0.26 <u>0.28</u>		
Live Oak, CA USA, 2009 (French)	3	0.15	9	1700	7	3 7	flesh	0.043, 0.046 0.046, 0.055	0.04 0.05		DP-27437 Trial 20
						3 7	whole fruit	0.041, 0.044 0.043, 0.052	0.04 <u>0.05</u>		
Madera, CA USA, 2009 (Fortune)	3	0.15	23	650	7	2 7	flesh	0.065, 0.063 0.059, 0.062	0.06 0.06		DP-27437 Trial 17
						2 7	whole fruit	0.063, 0.059 0.056, 0.058	<u>0.06</u> 0.06		
Madera, CA USA, 2009 (Red Beauty)	3	0.15	23	650	6	3 7	flesh	0.028, 0.035 0.028, 0.028	0.03 0.03		DP-27437 Trial 18
						3 7	whole fruit	0.026, 0.032 0.025, 0.025	<u>0.03</u> 0.03		
Monmouth, OR USA, 2009 (Moyer)	3	0.15	10	1500	6, 7	3 7	flesh	0.059, 0.073 0.06, 0.051	0.07 0.06		DP-27437 Trial 22
						3 7	whole fruit	0.056, 0.07 0.058, 0.049	<u>0.06</u> 0.05		
Payette, ID USA, 2009 (Empress)	3	0.15	11	1400	6, 7	3 7	flesh	0.13, 0.13 0.11, 0.12	0.13 0.12		DP-27437 Trial 21
						3 7	whole fruit	0.12, 0.12 0.11, 0.11	<u>0.12</u> 0.11		
Sanger, CA USA, 2009 (Santa Rosa)	3	0.15	12	1250	7	3 7	flesh	0.043, 0.06 0.073, 0.048	0.05 0.06		DP-27437 Trial 19
						3 7	whole fruit	0.037, 0.054 0.067, 0.045	0.05 <u>0.06</u>		

Table 81 Residues in plums from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation)

PLUM Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Calatorao Spain, 2009 (Anaspar)	2	0.075	5	1500	7	0	whole fruit	0.01			S09-01578 Test 10a 400 WG
						0		0.02			
						1		0.03			
						3		0.01			
						7		0.01			
						14		0.01			
Dirmstein Germany, 2010 (Czadczaks Schöne)	2	0.075	5	1500	7	0	whole fruit	0.33			S10-01056 Test 6a 400 WG
						1		0.02			
						3		0.03			
						7		0.02			
						14		0.01			
Innenheim N France, 2010 (Quetsches d'Alsace)	2	0.075	5	1500	7	0	whole fruit	0.12			S10-01056 Test 7a 400 WG
						1		0.12			
						3		0.12			
						7		0.09			
						14		0.06			
Innenheim N. France, 2009 (Quetsche)	2	0.075	5	1500	7	0	whole fruit	0.13			S09-01577 Test 05a 400 WG
						1		0.15			
						3		0.14			
						7		0.13			
						14		0.11			
Jork Germany, 2010 (Bühler)	2	0.075	5	1500	7	0	whole fruit	< 0.01			S10-01056 Test 5a 400 WG
						1		< 0.01			
						3		ND			
						7		ND			
						14		ND			
Moissac S. France, 2009 (Royal)	2	0.075	5	1500	7	0	whole fruit	0.06			S09-01578 Test 09a 400 WG
						1		0.03			
						3		0.03			
						7		0.02			
						14		0.02			
Ortenberg Germany, 2009 (Presenta)	2	0.075	5	1500	7	0	whole fruit	< 0.01			S09-01577 Test 08a 400 WG
						0		0.01			
						1		0.03			
						3		0.02			
						7		0.01			
						14		0.01			
Quatretonda La Costera Spain, 2010 (Black Diamond)	2	0.075	5	1500	7	0	whole fruit	0.02			S10-01057 Test 10a 400 WG
						1		0.02			
						3		< 0.01			
						7		< 0.01			
						14		< 0.01			
Saint Aignan S France, 2010 (Golden Japan)	2	0.075	5	1500	7	0	whole fruit	ND			S10-01057 Test 9a 400 WG
						1		ND			
						3		ND			
						7		ND			
						14		ND			

PLUM Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Stade Germany, 2009 (Schoneberger)	2	0.075	5	1500	7	0	whole fruit	0.02			S09-01577 Test 07a 400 WG
						0		0.06			
						1		0.06			
						3		0.06			
						7		0.04			
						14		0.02			
Stotzheim N France, 2010 (Elena)	2	0.075	5	1500	7	0	whole fruit	0.06			S10-01056 Test 8a 400 WG
						1		0.07			
						3		0.09			
						7		0.06			
						14		0.03			
Stotzheim N. France, 2009 (Elena)	2	0.075	5	1500	7	0	whole fruit	0.08			S09-01577 Test 06a 400 WG
						1		0.1			
						3		0.11			
						7		0.1			
						14		0.08			
Dirmstein Germany, 2010 (Czadczaks Schöne)	2	0.125	8.3	1500	7	0	whole fruit	0.15			S10-01056 Test 6b 400 WG
						1		0.08			
						3		0.07			
						7		0.04			
						14		0.04			
Innenheim N France, 2010 (Quetsches d'Alsace)	2	0.125	8.3	1500	7	0	whole fruit	0.25			S10-01056 Test 7b 400 WG
						1		0.22			
						3		0.23			
						7		0.15			
						14		0.12			
Jork Germany, 2010 (Bühler)	2	0.125	8.3	1500	7	0	whole fruit	0.02			S10-01056 Test 5b 400 WG
						1		< 0.01			
						3		< 0.01			
						7		< 0.01			
						14		ND			
Quatretonda La Costera Spain, 2010 (Black Diamond)	2	0.125	8.3	1500	7	0	whole fruit	0.04			S10-01057 Test 10b 400 WG
						1		0.02			
						3		0.02			
						7		0.02			
						14		0.02			
Saint Aignan S France, 2010 (Golden Japan)	2	0.125	8.3	1500	7	0	whole fruit	ND			S10-01057 Test 9b 400 WG
						1		ND			
						3		ND			
						7		ND			
						14		ND			
Stotzheim N France, 2010 (Elena)	2	0.125	8.3	1500	7	0	whole fruit	0.18			S10-01056 Test 8b 400 WG
						1		0.16			
						3		0.16			
						7		0.1			
						14		0.08			
Dirmstein Germany, 2010 (Czadczaks Schöne)	2	0.125+ surfact	8.3	1500	7	0	whole fruit	0.05			S10-01056 Test 6c 400 WG
						1		0.23			
						3		0.15			
						7		0.11			
						14		0.09			

PLUM Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Innenheim N France, 2010 (Quetsches d'Alsace)	2	0.125+ surfact	8.3	1500	7	0 1 3 7 14	whole fruit	0.43 0.34 0.37 0.18 0.17			S10-01056 Test 7c 400 WG
Jork Germany, 2010 (Bühler)	2	0.125+ surfact	8.3	1500	7	0 1 3 7 14	whole fruit	0.03 0.01 0.02 0.01 0.02			S10-01056 Test 5c 400 WG
Quatretonda La Costera Spain, 2010 (Black Diamond)	2	0.125+ surfact	8.3	1500	7	0 1 3 7 14	whole fruit	0.06 0.06 0.06 0.07 0.05			S10-01057 Test 10c 400 WG
Saint Aignan S France, 2010 (Golden Japan)	2	0.125+ surfact	8.3	1500	7	0 1 3 7 14	whole fruit	< 0.01 ND ND ND ND			S10-01057 Test 9c 400 WG
Stotzheim N France, 2010 (Elena)	2	0.125+ surfact	8.3	1500	7	0 1 3 7 14	whole fruit	0.21 0.24 0.27 0.12 0.17			S10-01056 Test 8c 400 WG
Calatorao Spain, 2009 (Anaspar)	2	0.15	10	1500	7	0 0 1 3 7 14	whole fruit	0.02 0.09 0.06 0.04 0.05 0.06			S09-01578 Test 10b 400 WG
Innenheim N. France, 2009 (Quetsche)	2	0.15	10	1500	7	0 1 3 7 14	whole fruit	0.33 0.4 0.32 0.26 0.3			S09-01577 Test 05b 400 WG
Moissac S. France, 2009 (Royal)	2	0.15	10	1500	7	0 1 3 7 14	whole fruit	0.1 0.1 0.08 0.06 0.06			S09-01578 Test 09b 400 WG
Ortenberg Germany, 2009 (Presenta)	2	0.15	10	1500	7	0 0 1 3 7 14	whole fruit	0.01 0.07 0.05 0.02 0.03 0.05			S09-01577 Test 08b 400 WG
Stade Germany, 2009 (Schoneberger)	2	0.15	10	1500	7	0 0 1 3 7 14	whole fruit	0.05 0.11 0.12 0.15 0.07 0.03			S09-01577 Test 07b 400 WG

PLUM Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Stozheim N. France, 2009 (Elena)	2	0.15	10	1500	7	0 1 3 7 14	whole fruit	0.17 0.17 0.13 0.11 0.19			S09-01577 Test 06b 400 WG
Calatorao Spain, 2009 (Anaspar)	2	0.15+ surfact	10	1500	7	0 0 1 3 7 14	whole fruit	0.04 0.13 0.13 0.13 0.08 0.08			S09-01578 Test 10c 400 WG
Innenheim N. France, 2009 (Quetsche)	2	0.15+ surfact	10	1500	7	0 1 3 7 14	whole fruit	0.57 0.59 0.51 0.42 0.49			S09-01577 Test 05c 400 WG
Moissac S. France, 2009 (Royal)	2	0.15+ surfact	10	1500	7	0 1 3 7 14	whole fruit	0.19 0.17 0.14 0.23 0.16			S09-01578 Test 09c 400 WG
Ortenberg Germany, 2009 (Presenta)	2	0.15+ surfact	10	1500	7	0 0 1 3 7 14	whole fruit	0.04 0.17 0.17 0.13 0.1 0.03			S09-01577 Test 08c 400 WG
Stade Germany, 2009 (Schoneberger)	2	0.15+ surfact	10	1500	7	0 0 1 3 7 14	whole fruit	0.07 0.17 0.23 0.21 0.12 0.09			S09-01577 Test 07c 400 WG
Stozheim N. France, 2009 (Elena)	2	0.15+ surfact	10	1500	7	0 1 3 7 14	whole fruit	0.3 0.39 0.45 0.31 0.17			S09-01577 Test 06c 400 WG

Blueberries

In trials conducted on blueberries in North America, three foliar applications of 0.15 kg ai/ha cyantraniliprole (SE formulation) were applied at 4–7 day intervals, using between 200 and 650 L/ha (with one trial at 50 L/ha), with adjuvant added.

Duplicate samples were stored at –20 °C for up to 6 months before analysis (within 23 days of extraction) for cyantraniliprole and six metabolites using analytical method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 101–104% (cyantraniliprole) and 95–109% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Table 82 Residues in blueberries from supervised trials in North America involving foliar applications of cyantraniliprole (SE formulation)

BLUEBERRY Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Aldergrove, BC, CAN, 2009 (Briggitta)	3	0.15	34	440	6, 5	3	berries	0.53, 0.5	0.52		AAFC09-025R Trial 268
East Gove, NS, CAN, 2009 (Wild Clones)	3	0.15	50	300	5, 4	3	berries	1.9, 2.0	2.0		AAFC09-025R Trial 264
Frelighsburg, QC, CAN, 2009 (Bluecrop)	3	0.15	50	300	6, 4	3	berries	0.73, 0.87	0.8		AAFC09-025R Trial 266 early treatments
Frelighsburg, QC, CAN, 2009 (Bluecrop)	3	0.15	50	300	5	4	berries	0.64, 0.85	0.75		AAFC09-025R Trial 267 late treatments
Kinston NC, USA, 2009 (Blue Haven)	3	0.15	330	47	5	3	berries	0.61, 0.43	0.52		DP-27971 Trial 02
Rawdon, NS, CAN, 2009 (Wild Clones)	3	0.15	50	300	5, 4	3	berries	1.4, 1.6	1.5	M1=0.01 M2=0.01	AAFC09-025R Trial 261 early treatments
Rawdon, NS, CAN, 2009 (Wild Clones)	3	0.15	50	300	4, 3	4	berries	0.37, 0.46	0.42	M1=0.02 M2=0.01	AAFC09-025R Trial 263 late treatments
Scotland, ON, CAN, 2009 (Duke)	3	0.15	75	200	6, 4	0 4 7 10	berries	1.0, 1.1 0.47, 0.55 0.31, 0.3 0.25, 0.23	1.1 0.51 0.31 0.24		AAFC09-025R Trial 265
Sheffield Mills, NS, CAN, 2009 (Wild Clones)	3	0.15	50	300	5, 6	0 2 7 8	berries	0.74, 0.58 0.66, 0.55 0.22, 0.25 0.19, 0.18	0.66 0.60 0.23 0.19	M1=0.01 M1=0.01	AAFC09-025R Trial 262
Wetumpka, AL USA, 2009 (Tifblue)	3	0.15	24	630	7, 8	3	berries	1.5, 1.5	1.5	M1=0.01 M2=0.01	DP-27971 Trial 01

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

Grapes

In trials on wine grapes conducted in Europe, two foliar applications of 0.12–0.15 kg ai/ha cyantraniliprole (SE formulation) were applied at 14 day intervals, using 1500 L/ha (300 L/ha in two trials), with no added adjuvant. These trials were reverse decline studies, where treatments were applied at staggered intervals to align the sampling times with the commercial harvest date.

Samples were stored at –18 °C for up to 10 months before analysis of berries (within 5 days of extraction) for cyantraniliprole and six metabolites using analytical method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 92–94% (cyantraniliprole) and 88–96% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Table 83 Residues in grapes from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation)

GRAPES Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Boxted UK, 2010 (Baccus)	2	0.12	8	1500	14–15	–0 0 10 22 29 56	grapes	0.053 0.13 0.096 0.059 0.039 0.034			DP-27718 Trial 19 [reverse decline]
Höhnstedt Germany, 2010 (Müller- Thurgau)	2	0.12	8	1500	14	–0 0 10 21 28 56	grapes	0.033 0.34 0.11 0.14 0.12 0.045			DP-27718 Trial 20 [reverse decline]
Kesten Germany, 2010 (Riesling)	2	0.12	8	1500	14–15	–0 0 10 21 28 56	grapes	0.16 0.23 0.24 0.22 0.21 0.12			DP-27718 Trial 21 [reverse decline]
La Roche Vineuse N France, 2010 (Gamay)	2	0.12	40	300	13–15	–0 0 10 21 28 56	grapes	0.061 0.13 0.16 0.16 0.047 0.047			DP-27718 Trial 15 [reverse decline]
Miradolo Terme Italy, 2009 (Bonarda)	2	0.12	8	1500	13–14	–0 0 10 21 28 56	grapes	0.45 0.99 0.8 0.63 0.45 0.21			DP-27718 Trial 16 [reverse decline]
Veldenzen Germany, 2010 (Müller- Thurgau)	2	0.12	8	1500	13–15	–0 0 10 21 28 56	grapes	0.22 0.64 0.49 0.19 0.22 0.14			DP-27718 Trial 22 [reverse decline]
Verdu Spain, 2010 (Macabeu)	2	0.12	8	1500	13–14	–0 0 10 21 28 56	grapes	0.06 0.16 0.48 0.14 0.19 0.056			DP-27718 Trial 18 [reverse decline]
Verdu Spain, 2010 (Ull de Liebre)	2	0.12	8	1500	14	–0 0 10 21 28 56	grapes	0.13 0.4 0.13 0.19 0.074 0.024			DP-27718 Trial 17 [reverse decline]

GRAPES Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Villie Morgon S France, 2010 (Gamay)	2	0.12	8	1500	13–15	–0 0 10 21 28 56	grapes	0.021 0.073 0.071 0.036 0.028 0.032			DP-27718 Trial 14 [reverse decline]
Guimera Spain, 2009 (Tempranillo)	2	0.15	10	1500	13–14	–0 0 10 21 28 56	grapes	0.062 0.065 0.21 0.18 0.079 0.077			DP-27718 Trial 07 [reverse decline]
Höhnstedt Germany, 2009 (Gutedel)	2	0.15	10	1500	14	–0 0 10 21 28 56	grapes	0.29 0.42 0.33 0.27 0.15 0.17			DP-27718 Trial 03 [reverse decline]
Kato Milia Greece, 2009 (Muscat)	2	0.15	10	1500	14	–0 0 10 21 28 56	grapes	0.14 0.32 0.28 0.076 0.11 0.029			DP-27718 Trial 01 [reverse decline]
Kato Milia Greece, 2010 (Muscat)	2	0.15	10	1500	14	–0 0 10 21 28 56	grapes	0.15 0.33 0.41 0.31 0.18 0.071			DP-27718 Trial 13 [reverse decline]
Marfaux N France, 2009 (Chardonnay)	2	0.15	50	300	14–15	–0 0 10 21 28 56	grapes	0.023 0.071 0.07 0.034 0.04 0.047			DP-27718 Trial 08 [reverse decline]
Mersea Island UK, 2009 (Reichensteiner)	2	0.15	10	1500	14	–0 0 10 21 28 56	grapes	0.11 0.23 0.3 0.16 0.16 0.1			DP-27718 Trial 04 [reverse decline]
Miradolo Terme Italy, 2009 (Bonarda)	2	0.15	10	1500	13–15	–0 0 10 21 28 56	grapes	0.34 0.65 0.56 0.48 0.67 0.63			DP-27718 Trial 06 [reverse decline]

GRAPES Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Veldenz Germany, 2009 (Kerner)	2	0.15	10	1500	13–15	–0	grapes	0.16			DP-27718 Trial 05 [reverse decline]
						0		0.46			
						10		0.36			
						21		0.3			
						28		0.68			
						56		0.19			
Villie Morgon S France, 2009 (Gamay)	2	0.15	10	1500	14	–0	grapes	0.05			DP-27718 Trial 02 [reverse decline]
						0		0.24			
						10		0.14			
						21		0.11			
						28		0.096			
						56		0.05			

Olives

In trials on olives conducted in Europe, two foliar applications of 0.15 kg ai/ha cyantraniliprole (SE formulation) were applied at 10 day intervals, using 2000 or 3000 L/ha with added adjuvant.

After the olive samples were weighed and the stoned removed in the field, flesh samples were stored at –18 °C for up to 17 months before analysis (within 7 days of extraction) for cyantraniliprole and six metabolites using analytical method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 88–94% (cyantraniliprole) and 86–108% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg. Whole fruit residues were calculated from the relative flesh:stone weights.

Table 84 Residues in olives from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation)

OLIVES Location Country, year (variety)	Application					DAT (days)	Residues (mg/kg)				Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)		cyantraniliprole		metabolites		
							flesh	whole fruit	flesh	whole fruit	
Agios Mamas Greece, 2009 (Chondrolia Chalkidikis)	2	0.15	7.5	2000	9	14	0.47	0.36	M1=0.013	M1=0.01	DP-27709 Trial 1
Aguadulce Spain, 2010 (Hojiblanca)	2	0.15	5	3000	10	14	0.3	0.25			DP-27709 Trial 10
Aguadulce Spain, (Hojiblanca)	2	0.15	7.5	2000	14	−0	0.17	0.11	M1=0.012		DP-27709 Trial 4
						0	0.53	0.34			
						3	0.53	0.35			
						7	0.64	0.41			
						14	0.41	0.26			
Bardolino Italy, 2009 (Casaliva)	2	0.15	7.5	2000	9	−0	0.39	0.26			DP-27709 Trial 3
						0	0.84	0.53			
						3	0.18	0.14			
						7	0.19	0.13			
						14	0.3	0.21			
Bardolino Italy, 2010 (Leccino)	2	0.15	5	3100	13	14	0.39	0.27			DP-27709 Trial 9

OLIVES Location Country, year (variety)	Application					DAT (days)	Residues (mg/kg)				Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)		cyantraniliprole		metabolites		
							flesh	whole fruit	flesh	whole fruit	
Fuente de Piedra Spain, 2010 (Hojiblanca)	2	0.15	5	3000	9	−0	0.26	0.2	M1=0.1 M1=0.02	M1=0.075 M1=0.015	DP-27709 Trial 6
						0	0.82	0.57			
						3	0.62	0.47			
						7	0.54	0.41			
						14	0.63	0.47			
Nea Skion, Greece, 2010 (Chondroelia Chalkidikis)	2	0.15	5	3000	11	−0	0.29	0.21	M1=0.011 M1=0.013	M1=0.1	DP-27709 Trial 5
						0	0.64	0.44			
						3	0.49	0.36			
						7	0.41	0.31			
						14	0.27	0.21			
Venterol S France, 2010 (Tanche)	2	0.15	5	3000	10	14	0.66	0.38			DP-27709 Trial 7
Venterol S France, (Tanche)	2	0.15	7.5	2000	11	−0	0.85	0.49			DP-27709 Trial 2
						0	2.3	1.4			
						3	2.4	1.5			
						7	2.3	1.3			
						14	1.9	1.1			

M1: Residues of metabolite IN-J9Z38

Pomegranate

In trials on pomegranates conducted in India, two to five foliar applications of 0.075–0.18 kg ai/ha cyantraniliprole (OD formulation) were applied at 10 day intervals, using 400–1000 L/ha with added adjuvant

Samples were stored at –20 °C for up to 1 month before analysis for cyantraniliprole and the IN-J9Z38 metabolite using analytical method DP-15736, with reported LOQs of 0.005 mg/kg. Average concurrent recoveries were 83–93% (cyantraniliprole) and 85–92% (IN-J9Z38) in samples spiked with 0.005, 0.025 and 0.05 mg/kg.

Table 85 Residues in pomegranates from supervised trials in India involving foliar applications of cyantraniliprole (OD formulation)

POMEGRANATE Location Country, year (variety)	Application					DAT (days)	Cyantraniliprole residues (mg/kg)				Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)		rind (parent)	rind M1	seed	juice	
Raichur India, 2011	2	0.075	12.5–19	400– 600	10	0	0.05		ND	ND	DP-1104829 Trial 1
						1	0.03	0.03	ND	ND	
						3	0.006		ND	ND	
						5	ND		ND	ND	
Raichur India, 2011	2	0.09	15–23	400– 600	10	0	0.07		ND	ND	DP-1104829 Trial 1
						1	0.03	M1=0.035	ND	ND	
						3	0.008		ND	ND	
						5	ND		ND	ND	
Raichur India, 2011	2	0.18	30–45	400– 600	10	0	0.14		ND	ND	DP-1104829 Trial 1
						1	0.07	M1=0.065	ND	ND	
						3	0.01		ND	ND	
						5	ND		ND	ND	

POMEGRANATE Location	Application					DAT (days)	Cyantraniliprole residues (mg/kg)					Reference & Comments
Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)		rind (parent)	rind M1	seed	juice		
Medhak India, 2011	3	0.075	7.5	1000	10	0 1 3 5	0.04 0.03 0.005 ND	M1=0.02	ND ND ND ND	ND ND ND ND	DP-1104829 Trial 3	
Medhak India, 2011	3	0.09	9	1000	10	0 1 3 5	0.05 0.02 0.006 ND	M1=0.02	ND ND ND ND	ND ND ND ND	DP-1104829 Trial 3	
Medhak India, 2011	3	0.18	18	1000	10	0 1 3 5	0.09 0.04 0.009 ND	M1=0.04	ND ND ND ND	ND ND ND ND	DP-1104829 Trial 3	
Rahuri India, 2011	5	0.075	15	500	10	0 1 3 5	0.07 0.05 0.01 ND	M1=0.02	ND ND ND ND	ND ND ND ND	DP-1104829 Trial 2	
Trichy India 2011	5	0.075	12.5	600	10	0 1 3 5	0.06 0.03 0.01 ND		ND ND ND ND	ND ND ND ND	DP-1104829 Trial 4	
Rahuri India, 2011	5	0.09	18	500	10	0 1 3 5	0.08 0.06 0.01 ND	M1=0.03	ND ND ND ND	ND ND ND ND	DP-1104829 Trial 2	
Trichy India 2011	5	0.09	15	600	10	0 1 3 5	0.08 0.03 0.01 ND		ND ND ND ND	ND ND ND ND	DP-1104829 Trial 4	
Rahuri India, 2011	5	0.18	36	500	10	0 1 3 5	0.17 0.12 0.03 ND	M1=0.05 M1=0.02	ND ND ND ND	ND ND ND ND	DP-1104829 Trial 2	
Trichy India 2011	5	0.18	30	600	10	0 1 3 5	0.16 0.06 0.03 ND	M1=0.02 M1=0.01	ND ND ND ND	ND ND ND ND	DP-1104829 Trial 4	

M1: Residues of metabolite IN-J9Z38

Bulb vegetables

Onion, bulb, Spring onion

In trials conducted in North America on dry bulb onions and on green onions, three foliar applications of 0.15 kg ai/ha cyantraniliprole (OD formulation) were applied at 4–6 day intervals, using 300–400 L/ha, with adjuvant added. In one trial on green onions, an additional plot was treated with two soil treatments of 0.23 kg ai/ha cyantraniliprole (SC formulation) applied through the drip-line irrigation system, 7 days apart using about 100 L/ha, without added surfactant.

Duplicate samples of dry onion bulbs and green onion plants (without roots) were stored frozen at –20 °C for up to 1 year before analysis for cyantraniliprole and six metabolites (within 55 days of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent

recoveries were 92% (cyantraniliprole) and 81–97% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Table 86 Residues in bulb onions from supervised trials in North America involving foliar applications of cyantraniliprole (OD formulation)

ONION, BULB Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Arlington, WI USA, 2009 (Yellow Stuttgarten)	3	0.15	38	400	6, 4	1	bulb	0.03, 0.02	0.02		DP-27436 WI09
Freeville, NY USA, 2009 (EX 18368)	3	0.15	42–46	350–320	5, 4	1	bulb	0.01, 0.02	0.01		DP-27436 NY09
Harrow, ON CAN, 2009 (Joliet)	3	0.15	50	300	4, 5	1	bulb	0.03, 0.03	0.03		DP-27436 ON06
Harrow, ON CAN, 2009 (Pulsar)	3	0.15	50	300	4, 5	1	bulb	0.02, 0.02	0.02		DP-27436 ON07
Las Cruces, NM USA, 2009 (NuMex Freedom)	3	0.15	53–44	290–380	4	1	bulb	0.01, 0.02	0.015		DP-27436 NM15
Parma, ID USA, 2009 (Granero)	3	0.15	47	330	6	1	bulb	ND, ND	ND		DP-27436 ID10
Salem, OR USA, 2009 (Red Bull)	3	0.15	42	380	4	1	bulb	ND, ND	ND		DP-27436 OR13
Ste-Clotilde, QC CAN, 2009 (Champlain)	3	0.15	39	370	5, 6	1 4 10 15	bulb	< 0.01, < 0.01 ND, ND ND, ND ND, ND	<u>< 0.01</u> ND ND ND		DP-27436 QC02
Ste-Clotilde, QC CAN, 2009 (Ricochet)	3	0.15	41	370	5, 6	1	bulb	< 0.01, < 0.01	< 0.01		DP-27436 QC03
Westlaco, TX USA, 2009 (Sweet Sunrise)	3	0.15	40	390	5, 6	1	bulb	0.02, 0.02	0.02		DP-27436 TX07

Table 87 Residues in spring onions (green onion) from supervised trials in North America involving foliar applications of cyantraniliprole (OD formulation) or soil (dripline) treatments (SC formulation)

SPRING ONION Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Willard, OH USA, 2009 (Feast)	3	0.15	47	320	4	1	trimmed plant	0.71, 0.55	0.63		DP-27436 OH11
Westlaco, TX USA, 2009 (Sweet Sunrise)	3	0.15	39	390	4	1	trimmed plant	4.1, 4.1	<u>4.1</u>	M1=0.016 M2=0.01 M3=0.08	DP-27436 TX28
						3		1.4, 1.4	1.4	M1=0.014 M3=0.09	
						7		0.84, 0.85	0.85	M2=0.01 M3=0.04	
						13		0.16, 0.16	0.16	M3=0.04	
Charleston, SC USA, 2009 (Red Baron Bunching)	3	0.15	43	350	4, 5	1	trimmed plant	1.6, 1.6	1.6	M3=0.024	DP-27436 SC08
Salinas, CA USA, 2009 (White Spear)	3	0.15	36	420	5, 6	1	trimmed plant	0.35, 0.42	0.38		DP-27436 CA118
Ste-Clotilde, QC CAN, 2009 (Tokyo Long White)	3	0.15	42	370	6	1	trimmed plant	1.3, 1.4	1.3		DP-27436 QC04
Westlaco, TX USA, 2009 (Sweet Sunrise)	2	0.225	24	94	7	1 3 7 13	trimmed plant	0.04, 0.03 0.03, 0.03 0.05, 0.06 0.06, 0.05	0.03 0.03 0.05 0.05		DP-27436 TX28 Soil dripline treatment

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

M3: Average residues of metabolite IN-N7B69

Brassica vegetables

In trials conducted in North America on broccoli, cauliflower and head cabbage, two or three foliar applications of 0.15 kg ai/ha cyantraniliprole (OD and SE formulations) were applied at 4–6 day intervals, using 200–500 L/ha, with adjuvant added. In several trials, separate plots were also treated with the equivalent of 0.2 kg ai/ha as a soil injection (soil shank) treatment at planting (without added surfactant).

Duplicate samples of broccoli florets, cauliflower heads, cabbage heads (including wrapper leaves) and trimmed cabbage heads (washed after removing the wrapper leaves) were stored at –20 °C for up to 8 months before extraction and analysis for cyantraniliprole and six metabolites (within 5 months of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 90–94% (cyantraniliprole) and 80–103% (metabolites) in samples spiked with 0.01, 0.05, 0.1 and 1.0 mg/kg.

Table 88 Residues in broccoli from supervised trials in North America involving two or three foliar applications of cyantraniliprole (OD formulation unless specified)

BROCCOLI Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Guadalupe, CA, USA, 2008 (Bay Meadows) Broccoli	2	0.15	65	230	5	1	florets	0.15, 0.15	0.15		DP-25641 Trial 1
Santa Maria, CA, USA, 2008 (Green Magic) Broccoli/	2	0.15	54	280	5	1	florets	0.28, 0.23	0.26		DP-25641 Trial 2
Terra Bella, CA, USA, 2008-09 (Heritage) Broccoli/	2	0.15	73	210	5	1	florets	0.61, 0.54	0.58		DP-25641 Trial 3
Terra Bella, CA, USA, 2008-09 (Heritage) Broccoli/	2	0.15	73	210	5	-0 0 1 3 5	florets	0.12, 0.13 0.4, 0.63 0.57, 0.34 0.4, 0.24 0.19, 0.23	0.13 0.52 0.45 0.32 0.21		DP-25641 Trial 3
Albany, OR, USA, 2009 (Arcadia) Broccoli/	3	0.15	53	280	5	1	florets	0.59, 0.42	0.51		DP-25641 Trial 17
Branchton, ON, CAN, 2009 (Windsor) Broccoli/	3	0.15	50	300	5	1	florets	0.73, 0.91	0.82	M1=0.01	DP-25641 Trial 14
Branchton, ON, CAN, 2009 (Windsor) Broccoli/	3	0.15	50	300	5	1	florets	0.8, 0.77	0.79	M1=0.015	DP-25641 Trial 14 [100 SE]
Conklin, MI, USA, 2009 (Everest) Broccoli/	3	0.15	53	280	5	1	florets	1.1, 1	1.0	M1=0.02	DP-25641 Trial 16
Conklin, MI, USA, 2009 (Everest) Broccoli/	3	0.15	53	280	5	1	florets	1.1, 1.1	1.1	M1=0.02	DP-25641 Trial 16 [100 SE]
Delavan, WI, USA, 2009 (Patron) Broccoli/	3	0.15	75	200	5	1	florets	0.56, 0.62	0.59		DP-25641 Trial 15
Delavan, WI, USA, 2009 (Patron) Broccoli/	3	0.15	75	200	5	1	florets	0.43, 0.51	0.47		DP-25641 Trial 15 [100 SE]
Guadalupe, CA, USA, 2008 (Bay Meadows) Broccoli	3	0.15	65	230	6, 5	1	florets	0.23, 0.21	0.22		DP-25641 Trial 1

BROCCOLI Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Santa Maria, CA, USA, 2008 (Green Magic) Broccoli/	3	0.15	54	280	5	1	florets	0.3, 0.26	0.28		DP-25641 Trial 2
Terra Bella, CA, USA, 2008-09 (Heritage) Broccoli/	3	0.15	73	210	5	1	florets	0.46, 0.92	0.69		DP-25641 Trial 3
Wyoming, IL, USA, 2009 (Premium Crop) Broccoli/	3	0.15	75	200	5, 4	1	florets	0.51, 0.59	0.55		DP-25641 Trial 13 [100 OD]
Wyoming, IL, USA, 2009 (Premium Crop) Broccoli/	3	0.15	75	200	5, 4	1	florets	0.59, 0.62	0.61		DP-25641 Trial 13 [100 SE]
Terra Bella, CA, USA, 2008-09 (Heritage) Broccoli/	1+ 1+ 1	0.2 (soil) 0.1+ 0.15	97 49 73	210 210	116 5	1	florets	0.49, 0.47	0.48		DP-25641 Trial 3 soil inject at planting+ 2 foliar sprays

M1: Average residues of metabolite IN-J9Z38

Soil injection (shank) treatment rate was 2.13 g ai/100 m of row

Table 89 Residues cauliflowers from supervised trials in North America involving two or three foliar applications of cyantraniliprole (OD formulation)

CAULIFLOWER Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Santa Maria, CA, USA, 2008 (Apex) Cauliflower/	2	0.15	54	280	5	1	flower-head	0.006, 0.012	0.01		DP-25641 Trial 4
Terra Bella, CA, USA, 2008 (Symphony) Cauliflower/	2	0.15	70	220	5	1	flower-head	0.12, 0.14	0.13		DP-25641 Trial 5
Santa Maria, CA, USA, 2008 (Apex) Cauliflower/	3	0.15	54	280	5	1	flower-head	0.007, 0.009	0.01		DP-25641 Trial 4
Terra Bella, CA, USA, 2008 (Symphony) Cauliflower/	3	0.15	70	220	5	1	flower-head	0.079, 0.086	0.08		DP-25641 Trial 5

Table 90 Residues in cabbages from supervised trials in North America involving two or three foliar applications of cyantraniliprole (OD formulation)

CABBAGE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Bradenton, FL, USA, 2008 (Copenhagen) Cabbage/	2	0.15	50	300	5	1	head trimmed	0.22, 0.22 0.016, 0.013	0.22 0.01		DP-25641 Trial 06
King City, CA, USA, 2008 (Romanov) Cabbage/	2	0.15	65	230	5	1	head trimmed	0.72, 0.64 0.024, 0.005	0.68 0.01		DP-25641 Trial 8
Porterville, CA, USA, 2008 (Supreme Vantage) Cabbage/	2	0.15	70	220	5	1	head	0.82, 0.54	0.68		DP-25641 Trial 9
Raymondville, TX, USA, 2008 (Cheers) Cabbage/	2	0.15	40	380	5	1	head trimmed	0.46, 0.28 0.027, 0.01	0.37 0.02		DP-25641 Trial 7
Alton, NY, USA, 2009 (Fario) Cabbage/	3	0.15	53	280	5	1	heads	0.68, 0.74	0.71		DP-25641 Trial 18
Bradenton, FL, USA, 2008 (Copenhagen) Cabbage/	3	0.15	50	300	5	1	head trimmed	0.29, 0.28 0.035, 0.097	<u>0.29</u> 0.07		DP-25641 Trial 06
Branchton, ON, CAN, 2009 (Red Dynasty) Cabbage/	3	0.15	52	290	4, 5	1	heads	0.78, 0.94	0.86		DP-25641 Trial 21
Carlyle, IL, USA, 2009 (Stonehead) Cabbage/	1+ 1+ 1	0.15	46 52 72	340 290 220	5	1	heads	0.42, 0.52	0.47		DP-25641 Trial 20
Conklin, MI, USA, 2009 (Megaton) Cabbage/	3	0.15	53	280	5	1	heads	0.38, 0.45	0.42		DP-25641 Trial 23
Corvallis, OR, USA, 2009 (Late Flat Dutch) Cabbage/	3	0.15	53	280	5, 4	1	heads	0.3, 0.34	0.32		DP-25641 Trial 24
Delavan, WI, USA, 2009 (Vantage Point) Cabbage/	3	0.15	70	220	5, 6	1	heads	0.36, 0.27	0.32		DP-25641 Trial 22
King City, CA, USA, 2008 (Romanov) Cabbage/	3	0.15	70	220	5	1	head trimmed	0.64, 0.67 0.007, 0.006	<u>0.65</u> 0.01		DP-25641 Trial 8

CABBAGE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Porterville, CA, USA, 2008 (Supreme Vantage) Cabbage/	3	0.15	70	220	5	1	head	0.66, 0.47	0.56		DP-25641 Trial 9
Raymondville, TX, USA, 2008 (Cheers) Cabbage/	3	0.15	40	380	5	1	head trimmed	0.6, 0.54 0.028, 0.015	<u>0.57</u> 0.02		DP-25641 Trial 7
Seven Springs, NC, USA, 2009 (Early Jersey Wakefield) Cabbage/	3	0.15	70	220	6, 4	1	heads	0.93, <u>0.98</u>	0.95	M1=0.01	DP-25641 Trial 19
Porterville, CA, USA, 2008 (Supreme Vantage) Cabbage/	1+ 1+ 1	0.2 (soil) 0.1 0.15	110 47 70	190 220 220	69 5	1DAA 3	head	0.59, 0.4	0.49		DP-25641 Trial 9 soil inject at planting+ 2 foliar sprays

M1: Average residues of metabolite IN-J9Z38

Soil injection (shank) treatment rate was 2.13 g ai/100 m of row

Trimmed=cabbage heads without wrapper leaves

Fruiting vegetable, Cucurbits

Results from supervised trials from Australia, Europe and North America on cucumber, summer squash and melons were provided to the Meeting.

North America

In trials conducted in North America on cucumber, melons and summer squash, two or three foliar applications of 0.15 kg ai/ha cyantraniliprole (OD formulation) were applied at 5–7 day intervals, using 200–500 L/ha with adjuvant added. Soil treatment plots were also included in three trial sites, where two soil treatments of 0.15 kg ai/ha cyantraniliprole (SC formulation) were applied through drip-line irrigation systems (adjusted to pH 4–5, with no added adjuvant).

Duplicate samples were stored at –20 °C for up to 9 months before analysis of whole fruit or pulp and peel for cyantraniliprole and six metabolites analysis (within 70 days of extraction) using an adaptation of method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 90–94% (cyantraniliprole) and 82–100% (metabolites) in samples spiked with 0.01, 0.1, 0.2 and 0.6 mg/kg.

Europe

In trials conducted in Europe on melons, cucumbers and summer squash (courgettes), two applications of 0.09 kg ai/ha cyantraniliprole (OD formulation) were applied to field crops using 800 L/ha or four applications of 0.12 kg ai/ha cyantraniliprole (OD formulation) using 1200 L/ha were applied to crops grown under protection. The retreatment intervals in all trials was 7 days and all foliar treatments included added surfactant. Soil treatment plots were also included in a number of trial sites, where 2–4 soil treatments of 0.075–0.1 kg ai/ha cyantraniliprole (SC formulation) were applied through the drip-line irrigation systems, with no added adjuvants.

Samples were stored at -18°C for up to 8 months before analysis of whole fruit or pulp and peel for cyantraniliprole and six metabolites analysis (within 10 days of extraction) using an adaptation of method DP-15736, with reported LOQs of 0.01 mg/kg. For melons, the peel and pulp (minus seeds) weights were used to calculate whole fruit residues. Average concurrent recoveries were 91–101% (cyantraniliprole) and 93–104% (metabolites) in samples spiked with 0.01, 0.1, and 0.5 mg/kg.

Australia

In trials conducted in Australia on rockmelons, cucumbers and summer squash (zucchini), two applications of 0.05, 0.075 and 0.15 kg ai/ha cyantraniliprole (OD formulation) were applied to field crops using 400 L/ha. The retreatment intervals in all trials was 7 days and all treatments included added surfactant.

Samples were stored at -20°C for up to 6 months before analysis of whole fruit for cyantraniliprole and six metabolites analysis (within 1 day of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 76–77% (cyantraniliprole) and 75–92% (metabolites) in samples spiked with 0.01–2.0 mg/kg.

Table 91 Residues in field cucumbers from supervised trials in the USA with cyantraniliprole as foliar applications (OD formulation) or applied via dripline irrigation systems (SC formulation)

CUCUMBER Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference& Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Hinton, OK USA, 2008 (Poinsett 76)	2	0.15	75	200	5	1	whole fruit	0.037, 0.035	0.036		DP-25642 Trial 3
Oviedo, FL USA, 2008 (Park's Bush Whopper II)	2	0.15	53	280	5	1	whole fruit	0.032, 0.034	0.033		DP-25642 Trial 1
Clewiston, FL USA, 2009 (Speedway)	2	0.16	58	260	5	1	whole fruit	0.1, 0.12	0.11		DP-25642 Trial 2
(Branchton, ON, Canada, 2009) (Thunder)	3	0.15	75	200	5, 4	1	whole fruit	0.026, 0.032	0.029		DP-25642 Trial 15
(Corvallis, OR USA, 2009 (Genuine F1)	3	0.15	54	280	5	1	whole fruit	0.027, 0.02	0.023		DP-25642 Trial 18
Carlyle, IL USA, 2009 (Talladega)	3	0.15	65	230	5	1	whole fruit	0.082, 0.057	0.07		DP-25642 Trial 14
Conklin, MI USA, 2009 (Dasher II)	3	0.15	68	220	5	1	whole fruit	0.1, 0.13	0.12		DP-25642 Trial 17
Delavan, WI USA, 2009 (Marketmore 76)	3	0.15	75	200	5	1	whole fruit	0.019, 0.024	0.021		DP-25642 Trial 16
Elko, SC USA, 2009 (Talladega)	3	0.15	75	200		1	whole fruit	0.038, 0.052	0.045		DP-25642 Trial 13

CUCUMBER Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference& Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Hinton, OK USA, 2008 (Poinsett 76)	3	0.15	75	200	5, 7	1	whole fruit	0.042, 0.049	0.045		DP-25642 Trial 3
Oviedo, FL USA, 2008 (Park's Bush Whopper II)	3	0.15	53	280	5, 4	1	whole fruit	0.02, 0.016	0.018		DP-25642 Trial 1
Seven Springs, NC USA, 2009 (Ashley)	3	0.15	60	250	5	1	whole fruit	0.039, 0.044	0.041		DP-25642 Trial 12
Clewiston, FL USA, 2009 (Speedway)	2+ 1	0.16 0.115	58+ 50	260+ 230	5	1	whole fruit	0.2, 0.12	0.16		DP-25642 Trial 2
Clewiston, FL USA, 2009 (Speedway)	2+ 1	0.15 0.15	4.4 60	3400 250	7 7	-0 0 1 3 5 6	whole fruit	ND, ND 0.086, 0.095 0.058, 0.12 0.044, 0.053 0.055, 0.064 0.048, 0.048	ND 0.09 0.089 0.049 0.06 0.048		DP-25642 Trial 2 2 drip applications (2.3 g ai/100m row) + 1 foliar spray

Table 92 Residues in field cucumbers from supervised trials in Europe with cyantraniliprole as foliar applications (OD formulation) or applied via dripline irrigation systems (SC formulation)

[illegible]

CUCUMBER Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Torrevecchia Pia Italy, 2009 (Gemini)	2	0.075	3.8	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-27711 Test 05 200 SC soil dripline irrigation

Table 93 Residues in cucumbers from supervised trials in Australia involving foliar applications of cyantraniliprole (OD formulation)

CUCUMBER Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Bowen, QLD Australia, 2009 (Gremlin) Cucumber	2	0.05	0.0125	400	7	-0 1	whole fruit	0.01 0.05			DP-31413 Site 2
Bowen, QLD Australia, 2009 (Gremlin) Cucumber	2	0.075	0.019	400	7	-0 1	whole fruit	0.04 0.09			DP-31413 Site 2
Bowen, QLD Australia, 2009 (Gremlin) Cucumber	2	0.15	0.0375	400	7	-0 1	whole fruit	0.08 0.22			DP-31413 Site 2

Table 94 Residues in protected cucumbers from supervised trials in Europe with cyantraniliprole as foliar applications (OD formulation) or applied via dripline irrigation systems (SC formulation)

CUCUMBER Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Oirlo Netherlands, 2009 (Cratos) Cucumber	4	0.12	10	1200	7	1	whole fruit	0.089			DP-28201 Test 01
Nea Magnisia Greece, 2009 (Gallileo) Cucumber	4	0.12	10	1200	7	1	whole fruit	0.053			DP-28201 Test 02

CUCUMBER Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Castenray Netherlands, 2009 (Sheilla) Cucumber	4	0.12	10	1200	6–8	–0 0 1 3 7 14	whole fruit	0.11 0.12 0.11 0.091 0.13 0.18			DP-28201 Test 05
Puente del Rio Spain, 2009 (Estrada) Cucumber	4	0.12	10	1200	7–8	–0 0 1 3 7 14	whole fruit	0.019 0.076 0.077 0.18 0.044 0.013			DP-28201 Test 06
Castenray Netherlands, 2009 (Sheilla)	4	0.1	5	2000	6–8	–0 0 1 3 7 14	whole fruit	0.015 0.01 0.003 0.009 0.019 0.019			DP-28201 Test 05 200 SC soil dripline irrigation
Puente del Rio Spain, 2009 (Estrada)	4	0.1	5	2000	7–8	–0 0 1 3 7 14	whole fruit	ND ND ND ND ND ND			DP-28201 Test 06 200 SC soil dripline irrigation

Table 95 Residues in summer squash from supervised trials in North America with cyantraniliprole as foliar applications (OD formulation) or applied via dripline irrigation systems (SC formulation)

SUMMER SQUASH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Fresno, CA USA, 2008 (Jackpot F1)	2	0.15	54	280	5	1	whole fruit	0.074, 0.1	0.089		DP-25642 Trial 11
Oviedo, FL USA, 2008 (Early Summer Crookneck)	2	0.15	52	290	5	1	whole fruit	0.14, 0.086	0.11		DP-25642 Trial 9
Porterville, CA USA, 2008 (Early Summer Yellow Crookneck)	2	0.15	38	400	6	1	whole fruit	0.1, 0.083	0.094		DP-25642 Trial 10

SUMMER SQUASH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Alton, NY USA, 2009 (Meteor)	3	0.15	54	280	5	1	whole fruit	0.059, 0.06	0.059		DP-25642 Trial 19
Branchton, ON Canada, 2009 (Senator)	3	0.15	75	200	5	1	whole fruit	0.012, 0.01	0.011		DP-25642 Trial 22
Conklin, MI USA, 2009 (Spineless Beauty) Zucchini	3	0.15	50	300	5, 7	1	whole fruit	0.093, 0.067	0.08		DP-25642 Trial 23
Corvallis, OR USA, 2009 (Noche)	3	0.15	53	280	5	1	whole fruit	0.05, 0.055	0.053		DP-25642 Trial 24
Fresno, CA USA, 2008 (Jackpot F1)	3	0.15	54	280	5	1	whole fruit	0.1, 0.12	0.11		DP-25642 Trial 11
Oviedo, FL USA, 2008 (Early Summer Crookneck)	3	0.15	52	290	5, 4	1	whole fruit	0.091, 0.084	0.088		DP-25642 Trial 9
Porterville, CA USA, 2008 (Early Summer Yellow Crookneck)	3	0.15	38	400	6, 4	1	whole fruit	< 0.01, 0.06	0.034		DP-25642 Trial 10
Seven Springs, NC USA, 2009 (Yellow Straight-Neck)	3	0.15	60	250	5	1	whole fruit	0.071, 0.072	0.072		DP-25642 Trial 20
Wyoming, IL USA, 2009) (Spineless Beauty F1) Zucchini	3	0.15	75	200	5	1	whole fruit	0.044, 0.041	0.043		DP-25642 Trial 21
Porterville, CA USA, 2008 (Early Summer Yellow Crookneck)	2+ 1	0.15 0.15	1.5 38	10200 400	7	1	whole fruit	0.031, 0.029	0.03		DP-25642 Trial 10 2 drip applications (2.3 g ai/100m row) + 1 foliar spray

Table 96 Residues in field summer squash from supervised trials in Europe with cyantraniliprole as foliar applications (OD formulation) or applied via dripline irrigation systems (SC formulation)

SUMMER SQUASH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
St Vincent S France, 2009 (Mirza) Courgette	2	0.09	11	800	8	1	whole fruit	< 0.01 ND ND			DP-27711 Test 04
Nea Magnisia Greece, 2009 (Ezra) Courgette	2	0.09	11	800	6	1	whole fruit	0.025			DP-27711 Test 06
Le Mas Rillier S France, 2009 (Mirza) Courgette	2	0.09	11	800	6	-0 0 1 3 7	whole fruit	< 0.01 0.046 0.022 0.014 0.025			DP-27711 Test 09
Los Palacios Spain, 2009 (Amalia) Courgette	2	0.09	11	800	6	-0 0 1 3 7	whole fruit	< 0.01 0.054 0.039 < 0.01 < 0.01			DP-27711 Test 10
Perea Greece, 2010 (Unspecified) Courgette	2	0.09	11	800	8	1	whole fruit	0.1			DP-27711 Test 14
Mediglia Italy, 2010 (Unspecified) Courgette	2	0.09	11	800	7	1	whole fruit	0.1			DP-27711 Test 15
Aguadulce Spain, 2010 (Unspecified) Courgette	2	0.09	11	800	7	1	whole fruit	< 0.01			DP-27711 Test 16
Le Mas Rillier S France, 2009 (Mirza)	2	0.075	3.8	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-27711 Test 09 (soil dripline)
Los Palacios Spain, 2009 (Amalia) Courgette	2	0.075	3.8	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-27711 Test 10 (soil dripline)
Nea Magnisia Greece, 2009 (Ezra)	2	0.075	3.8	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-27711 Test 06 (soil dripline)

SUMMER SQUASH Location	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
St Vincent S France, 2009 (Mirza)	2	0.075	3.8	2000	8	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-27711 Test 04 (soil dripline)

Table 97 Residues in summer squash (zucchini) from supervised trials in Australia involving foliar applications of cyantraniliprole (OD formulation)

SUMMER SQUASH Location	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Bowen, QLD Australia, 2009 (Crowbar) Zucchini	2	0.05	0.0125	400	7	-0 1	whole fruit	0.02 0.04			DP-31413 Site 3
Bowen, QLD Australia, 2009 (Crowbar) Zucchini	2	0.075	0.019	400	7	-0 1	whole fruit	0.02 0.05			DP-31413 Site 3
Bowen, QLD Australia, 2009 (Crowbar) Zucchini	2	0.15	0.0375	400	7	-0 1	whole fruit	0.07 0.15			DP-31413 Site 3

Table 98 Residues in protected summer squash from supervised trials in Europe with cyantraniliprole as foliar applications (OD formulation) or applied via dripline irrigation systems (SC formulation)

SUMMER SQUASH Location	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Dirillo Italy, 2009 (Richgreen) Courgette	4	0.12	10	1200	7	1	whole fruit	0.22			DP-28201 Test 03
Berja Spain, 2009 (Otelo) Courgette	4	0.12	10	1200	7	1	whole fruit	0.033			DP-28201 Test 04
Mediglia Italy, 2009 (President) Courgette	4	0.12	10	1200	7	-0 0 1 3 7 14	whole fruit	ND 0.051 0.035 0.015 0.005 ND			DP-28201 Test 07

SUMMER SQUASH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Utrera Spain, 2009 (Nieves) Courgette	4	0.12	10	1200	6-7	-0 0 1 3 7 14	whole fruit	0.022 0.084 0.08 0.07 0.059 0.021			DP-28201 Test 08
Puente del Rio Spain, 2009 (Sinatra) Courgette	4	0.12	10	1200	7-8	-0 0 1 3 7 14	whole fruit	0.016 0.051 0.06 ND 0.008 ND			DP-28201 Test 09
Mediglia Italy, 2009 (President)	4	0.1	5	2000	7	-0 0 1 3 7 14	whole fruit	ND ND ND ND ND ND			DP-28201 Test 07 (soil dripline)
Puente del Rio Spain, 2009 (Sinatra)	4	0.1	5	2000	7-8	-0 0 1 3 7 14	whole fruit	0.004 ND ND 0.004 ND ND			DP-28201 Test 09 (soil dripline)
Utrera Spain, 2009 (Nieves)	4	0.1	5	2000	6-7	-0 0 1 3 7 14	whole fruit	ND ND ND ND ND ND			DP-28201 Test 08 (soil dripline)

Table 99 Residues in melons from supervised trials in North America with cyantraniliprole as foliar applications (OD formulation) or applied via dripline irrigation systems (SC formulation).

MELON Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Fresno, CA USA, 2008 (Athena) Cantaloupe	2	0.15	54	280	5	1	flesh skin whole fruit	ND, ND 0.22, 0.22 0.075, 0.091	ND 0.22 0.083		DP-25642 Trial 6
Hinton, OK USA, 2008 (PMR 45) Cantaloupe	2	0.15	80	200	6	1	flesh skin whole fruit	ND, ND 0.17, 0.13 0.106, 0.085	ND 0.15 0.095		DP-25642 Trial 4
Paso Robles, CA USA, 2008 (Hale's Best) Cantaloupe	2	0.15	50	300	5	1	flesh skin whole fruit	ND, ND 0.35, 0.24 0.12, 0.088	ND 0.3 0.11		DP-25642 Trial 8

MELON Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Porterville, CA USA, 2008 (Hale's Best Jumbo) Cantaloupe	2	0.15	38	400	5	1	flesh skin whole fruit	ND, ND 0.12, 0.096 0.061, 0.049	ND 0.11 0.055		DP-25642 Trial 5
Porterville, CA USA, 2008 (Honeydew)	2	0.15	60	250	5	1	flesh skin whole fruit	< 0.01, < 0.01 0.035, 0.054 0.03, 0.049	< 0.01 0.044 0.04		DP-25642 Trial 7
Branchton, ON Canada, 2009 (Primo) Cantaloupe	3	0.15	75	200	5	1	flesh skin whole fruit	< 0.01, < 0.01 0.22, 0.18 0.12, 0.098	< 0.01 0.2 <u>0.11</u>		DP-25642 Trial 27
Conklin, MI USA, 2009 (Aphrodite VIP (8793)) Cantaloupe	3	0.15	52	290	5	1	flesh skin whole fruit	ND, ND 0.17, 0.19 0.096, 0.11	ND 0.18 <u>0.1</u>		DP-25642 Trial 28
Fresno, CA USA, 2008 (Athena) Cantaloupe	3	0.15	54	280	5	1	flesh skin whole fruit	< 0.01, ND 0.3, 0.093 0.14, 0.039	< 0.01 0.2 <u>0.087</u>		DP-25642 Trial 6
Hinton, OK USA, 2008 (PMR 45) Cantaloupe	3	0.15	80	200	6, 4	1	flesh skin whole fruit	ND, ND 0.23, 0.25 0.15, 0.16	ND 0.24 <u>0.15</u>		DP-25642 Trial 4
Paso Robles, CA USA, 2008 (Hale's Best) Cantaloupe	3	0.15	50	300	5, 4	1	flesh skin whole fruit	ND, ND 0.54, 0.43 0.18, 0.15	ND 0.48 <u>0.17</u>		DP-25642 Trial 8
Porterville, CA USA, 2008 (Hale's Best Jumbo) Cantaloupe	3	0.15	38	400	5	1	flesh skin whole fruit	ND, ND 0.19, 0.21 0.081, 0.1	ND 0.2 <u>0.09</u>		DP-25642 Trial 5
Porterville, CA USA, 2008 (Honeydew)	3	0.15	60	250	5	1	flesh skin whole fruit	< 0.01, < 0.01 0.046, 0.023 0.058, 0.024	< 0.01 0.034 <u>0.041</u>		DP-25642 Trial 7
Seven Springs, NC USA, 2009 (Hales Best Jumbo) Cantaloupe	3	0.15	37	400	4, 6	1	flesh skin whole fruit	ND, ND 0.13, 0.12 0.05, 0.047	ND 0.13 <u>0.048</u>		DP-25642 Trial 25
Wyoming, IL USA, 2009 (Atlantis F1) Muskmelon	3	0.15	68	220	5	1	flesh skin whole fruit	ND, ND 0.12, 0.15 0.072, 0.095	ND 0.14 <u>0.084</u>		DP-25642 Trial 26

MELON Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Porterville, CA USA, 2008 (Hale's Best Jumbo) Cantaloupe	2+ 1	0.15 0.15	1.47 38	10200 400	7 7	1	flesh skin whole fruit	ND, ND 0.039, 0.045 0.022, 0.024	ND 0.042 0.023		DP-25642 Trial 5 2 drip applicatio ns (4.2 g ai/100m row) + 1 foliar spray

Table 100 Residues in outdoor melons from supervised trials in Europe with cyantraniliprole as foliar applications (OD formulation) or applied via dripline irrigation systems (SC formulation)

MELON Location Country, year (variety)	Application					DAT (days)	Cyantraniliprole Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)		whole fruit	peel	pulp	
Svoronos Greece, 2009 (Lavigal) Melon	2	0.09	11	800	6	1	0.069	0.12	ND	DP-27711 Test 01
Casteldidone Italy, 2009 (Sogno) Melon	2	0.09	11	800	8	1	0.041	0.093	ND	DP-27711 Test 02
Puerto Serrano Spain, 2009 (Anasta) Cantaloupe Melon	2	0.09	11	800	7	1	0.05	0.12	ND	DP-27711 Test 03
Villamartin Spain, 2009 (Alonso) Cantaloupe Melon	2	0.09	11	800	7	-0 0 1 3 7	0.039 0.051 0.015 0.039 0.046	0.086 0.11 0.031 0.096 0.12	ND < 0.01 ND ND ND	DP-27711 Test 07
Los Palacios Spain, 2009 (Linord) Melon	2	0.09	11	800	6	-0 0 1 3 7	0.016 0.021 0.016 0.03 0.013	0.042 0.058 0.04 0.076 0.035	ND ND ND ND ND	DP-27711 Test 08
Svoronos Greece, 2009 (Lavigal)	2	0.075	3.8	2000	7	-0 0 1 3 7	ND ND ND ND ND	ND ND ND ND ND	ND ND ND ND ND	DP-27711 Test 01 (soil dripline)
Casteldidone Italy, 2009 (Sogno)	2	0.075	3.8	2000	7	-0 0 1 3 7	ND ND ND ND ND	ND ND ND ND ND	ND ND ND ND ND	DP-27711 Test 02 (soil dripline)

MELON Location Country, year (variety)	Application					DAT (days)	Cyantraniliprole Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)		whole fruit	peel	pulp	
Puerto Serrano Spain, 2009 (Anasta) Cantaloupe	2	0.075	3.8	2000	7	–0	ND	ND	ND	DP-27711 Test 03 (soil dripline)
						0	ND	ND	ND	
						1	ND	ND	ND	
						3	ND	ND	ND	
						7	ND	ND	ND	
Villamartin Spain, 2009 (Alonso) Cantaloupe	2	0.075	3.8	2000	8	–0	ND	ND	ND	DP-27711 Test 07 (soil dripline)
						0	ND	ND	ND	
						1	ND	ND	ND	
						3	ND	ND	ND	
						7	ND	ND	ND	
Los Palacios Spain, 2009 (Linord)	2	0.075	3.8	2000	7	–0	ND	ND	ND	DP-27711 Test 08 (soil dripline)
						0	ND	ND	ND	
						1	ND	ND	ND	
						3	ND	ND	ND	
						7	ND	ND	ND	

Table 101 Residues in melons (rockmelon) from supervised trials in Australia involving foliar applications of cyantraniliprole (OD formulation)

MELON Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Bowen, QLD Australia, 2009 (Northern Sky) Rockmelon	2	0.05	0.0125	400	7	0	whole fruit	0.08			DP-31413 Site 1
						1		0.06			
						7		0.02			
						14		ND			
						21		ND			
Bowen, QLD Australia, 2009 (Northern Sky) Rockmelon	2	0.075	0.019	400	7	0	whole fruit	0.18			DP-31413 Site 1
						1		0.1			
						7		0.03			
						14		< 0.01			
						21		ND			

Table 102 Residues in protected melons from supervised trials in Europe with cyantraniliprole as foliar applications (OD formulation) or applied via irrigation dripline systems (SC formulation)

MELON Location Country, year (variety)	Application					DAT (days)	Cyantraniliprole residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)		whole fruit	peel	pulp	
Contrada Randello Italy, 2009 (Cabrero) Melon	4	0.12	10	1200	7	1	0.044	0.066	ND	DP-28186 Test 01

MELON Location Country, year (variety)	Application					DAT (days)	Cyantraniliprole residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)		whole fruit	peel	pulp	
Contada Randello Italy, 2009 (Cabrero) Melon	4	0.12	10	1200	7	1	0.06	0.11	ND	DP-28186 Test 02
Svoronos Greece, 2009 (Lavigas) Melon	4	0.12	10	1200	6–8	1	0.031	0.064	ND	DP-28186 Test 03
Mea Magnisia Greece, 2009 (Galia F1) Melon	4	0.12	10	1200	7	1	0.038	0.068	ND	DP-28186 Test 04
Mezin S France, 2009 (Charentais) Melon	4	0.12	10	1200	6–8	–0	0.038	0.068	< 0.01	DP-28186 Test 05
						0	0.1	0.19	ND	
						1	0.035	0.083	ND	
						3	0.05	0.13	ND	
						7	0.029	0.069	ND	
						14	0.034	0.06	ND	
Adra Spain, 2009 (Valverde) Melon	4	0.12	10	1200	6–7	–0	0.048	0.13	ND	DP-28186 Test 07
						0	0.07	0.18	ND	
						1	0.078	0.21	ND	
						3	0.077	0.2	ND	
						7	0.018	0.054	ND	
						14	0.059	0.17	ND	
Adra Spain, 2009 (Galia) Melon	4	0.12	10	1200	6–7	–0	0.023	0.079	ND	DP-28186 Test 08
						0	0.026	0.08	ND	
						1	0.049	0.14	ND	
						3	0.064	0.21	ND	
						7	0.005	0.013	ND	
						14	0.019	0.053	ND	
Adra Spain, 2009 (Cantaloupe) Melon	4	0.12	10	1200		–0	0.051	0.13	ND	DP-28186 Test 09
						0	0.066	0.17	ND	
						1	0.096	0.24	ND	
						3	0.062	0.16	ND	
						7	0.035	0.072	ND	
						14	0.024	0.056	< 0.01	
Mezin S France, 2009 (Charentais)	4	0.1	5	2000	6–8	–0	ND	ND	ND	DP-28186 Test 05 (soil dripline)
						0	ND	ND	ND	
						1	ND	ND	ND	
						3	ND	ND	ND	
						7	< 0.01	0.012	ND	
						14	ND	ND	ND	
Adra Spain, 2009 (Valverde)	4	0.1	5	2000	6–7	–0	ND	ND	ND	DP-28186 Test 07 (soil dripline) May–Jun
						0	ND	ND	ND	
						1	ND	ND	ND	
						3	ND	ND	ND	
						7	ND	ND	ND	
						14	ND	ND	ND	

MELON Location Country, year (variety)	Application					DAT (days)	Cyantraniliprole residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)		whole fruit	peel	pulp	
Adra Spain, 2009 (Galia)	4	0.1	5	2000	6–7	–0	ND	ND	ND	DP-28186 Test 08 (soil dripline) May–Jun
						0	ND	ND	ND	
						1	ND	ND	ND	
						3	ND	< 0.01	ND	
						7	ND	ND	ND	
						14	ND	ND	ND	
Adra Spain, 2009 (Cantaloupe)	4	0.1	5	2000		–0	ND	0.004	ND	DP-28186 Test 09 (soil dripline) October
						0	ND	ND	ND	
						1	ND	ND	ND	
						3	ND	ND	ND	
						7	ND	ND	ND	
						14	ND	ND	ND	

Fruiting vegetables, other than Cucurbits

Results from supervised trials from Australia, Europe and North America on tomatoes and peppers were provided to the Meeting.

North America

In trials conducted in North America on field tomatoes and peppers (bell and non-bell), two or three foliar applications of 0.15 kg ai/ha cyantraniliprole (OD formulation) were applied at 4–6 day intervals, using 200–500 L/ha, with adjuvant added. Soil treatment plots were also included in three trial sites, where two soil treatments of 0.15 kg ai/ha cyantraniliprole (SC formulation) were applied through drip-line irrigation systems (adjusted to pH 4–5, with no added adjuvant).

Duplicate samples of fruit were stored at –20 °C for up to 8 months before extraction and analysis for cyantraniliprole and six metabolites (within 3 months of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 88–92% (cyantraniliprole) and 83–99% (metabolites) in samples spiked with 0.01–1.0 mg/kg and also 4 mg/kg for tomatoes.

Europe

In trials conducted in Europe on protected sweet peppers, chilli peppers and tomatoes, four applications of 10 g ai/hL cyantraniliprole were applied using 1200 L/ha as foliar sprays (OD formulation) or four applications of 5 g ai/hL using 2000 L/ha as soil treatments (SC formulation), applied through the dripline irrigation systems. The retreatment intervals in all trials was 7 days and all foliar treatments included added surfactant.

In outdoor tomatoes, sweet and chilli peppers in Southern Europe, two foliar applications of 0.09 kg ai/ha cyantraniliprole (OD formulation) were applied using 800 L water/ha at 6–7 day intervals with added surfactant.

Samples were stored at –18 °C for up to 8 months before extraction and analysis for cyantraniliprole and six metabolites analysis (within 7 days of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 75–101% (cyantraniliprole) and 77–101% (metabolites) in samples spiked with 0.01, 0.1, 1.0 and 5.0 (peppers) mg/kg.

Australia

In trials conducted in Australia on outdoor tomatoes and sweet peppers (capsicums), two foliar applications of 0.05, 0.075 or 0.15 kg ai/ha cyantraniliprole (OD formulation) were applied 7 days apart to separate plots using 400 L water/ha with added surfactant.

Table 103 Residues in field tomatoes from supervised trials in North America involving two or three foliar applications of cyantraniliprole (OD formulation)

[illegible]

TOMATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Alton, NY USA, 2009 (Polbig F1) Tomato/	3	0.15	53	280	5, 6	1	whole fruit	0.091, 0.072	0.082		DP-25643 Trial 20
Bradenton, FL USA, 2008 (FL-47) Tomato/	3	0.15	34	450	5	1	whole fruit	0.037, 0.045	0.041		DP-25643 Trial 1
Branchton, ON, CAN 2009 (9909) Tomato/	3	0.15	60	250	4, 5	1	whole fruit	0.075, 0.096	0.086		DP-25643 Trial 22
Conklin, MI USA, 2009 (Supersweet 100 VF) Tomato (Cherry)/	3	0.15	50	300	5	1	whole fruit	0.2, 0.14	0.17		DP-25643 Trial 28
Delavan, WI USA, 2009 (Rutgers) Tomato/	3	0.15	75	200	7, 4	1	whole fruit	0.063, 0.078	0.071		DP-25643 Trial 25
Fresno, CA USA, 2008 (H8004) Tomato/	3	0.15	53	290	5	1	whole fruit	0.12, 0.16	0.14		DP-25643 Trial 8
Fresno, CA USA, 2008 (H8004) Tomato/	3	0.15	53	280	5	1	whole fruit	0.055, 0.06	0.058		DP-25643 Trial 9
Hickman, CA USA, 2008 (6368) Tomato/	3	0.15	53	280	5	1	whole fruit	0.16, 0.17	0.16		DP-25643 Trial 10
Huron, CA USA, 2008 (Sun 6117) Tomato/	3	0.15	39	390	5	1	whole fruit	0.08, 0.053	0.067		DP-25643 Trial 6
Lemore, CA USA, 2008 (Shady Lady) Tomato/	3	0.15	41	360	5	1	whole fruit	0.14, 0.15	0.14		DP-25643 Trial 4
Oviedo, FL USA, 2008 (Burpee Big Boy) Tomato/	3	0.15	53	280	5, 4	1	whole fruit	0.052, 0.041	0.046		DP-25643 Trial 2

TOMATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Paso Robles, CA USA, 2008 (Red Cherry) Tomato/	3	0.15	53	290	5	1	whole fruit	<u>0.28</u> , 0.25	0.26		DP-25643 Trial 7
Richland, IA USA, 2009 (Supersweet) Tomato (Cherry)/	3	0.15	66	220	6, 5	1	whole fruit	0.081, 0.062	0.072		DP-25643 Trial 26
Rockville, IN USA, 2009 (Mountain Spring) Tomato/	3	0.15	48	310	5	1	whole fruit	0.066, 0.05	0.058		DP-25643 Trial 24
San Ardo, CA USA, 2008 (Shady Lady) Tomato/	3	0.15	55	270	5	1	whole fruit	0.076, 0.054	0.065		DP-25643 Trial 3
Seven Springs, NC USA, 2009 (Rutgers) Tomato/	1+ 2	0.15	59 73	250 210	5	1	whole fruit	0.086, 0.066	0.076		DP-25643 Trial 21
Sparta, MI USA, 2009 (Sunoma) Tomato (Roma)/	3	0.15	50	300	5	1	whole fruit	0.099, 0.088	0.093		DP-25643 Trial 29
Verona, WI USA, 2009 (Red Defender) Tomato/	3	0.15	57	260	5	1	whole fruit	0.094, 0.11	0.1		DP-25643 Trial 27
Porterville, CA USA, 2008 (Sun 6117) Tomato/	1+ 2	0.15 0.15	66 77	230 200		1	whole fruit	0.08, 0.074	0.077		DP-25643 Trial 5
Caryle, IL USA, 2009 (Burpee Big Boy) Tomato/	1+ 1+ 1	0.15 0.15 0.15	60 58 44	250 260 340	5	1	whole fruit	0.14, 0.091	0.12		DP-25643 Trial 23
San Ardo, CA USA, 2008 (Shady Lady) Tomato/	2+ 1	0.15 (soil) 0.15	2 54	7700 280	7	1	whole fruit	0.044, 0.052	0.048		DP-25643 Trial 3 2 soil dripline + 1 foliar

Soil (dripline irrigation) treatment rate of 2.7 g ai/100 metres of row

Table 1 Residues in field tomatoes from supervised trials in Europe involving foliar applications of cyantraniliprole (OD formulation)

TOMATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Perea Greece, 2009 (Meteor) Tomato/	2	0.09	11	800	7	1	whole fruit	ND			DP-27712 Test 05
Fiorenzuola d'Arda Italy, 2009 (Heinz 690) Tomato/	2	0.09	11	800	7	1	whole fruit	0.079			DP-27712 Test 06
Aguadulce Spain, 2009 (Manitu) Tomato/	2	0.09	11	800	7	1	whole fruit	0.018			DP-27712 Test 07
Les Massonnes S France, 2009 (Perfect Peel) Tomato	2	0.09	11	800	7	-0 0 1 3	whole fruit	0.038 0.071 0.077 0.068			DP-27712 Test 12
Villalba del Alcor Spain, 2009 (Lidia) Tomato/	2	0.09	11	800	6	-0 0 1 3	whole fruit	0.013 < 0.01 0.02 0.01			DP-27712 Test 13

Table 105 Residues in field tomatoes from supervised trials in Australia involving foliar applications of cyantraniliprole (OD formulation)

TOMATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Bowen, QLD Australia, 2009 (Danika) Tomato	2	0.05	0.0125	400	7	0 1 7 14 21	whole fruit	0.11 0.09 0.03 ND ND			DP-31520 Site 1
Bowen, QLD Australia, 2009 (Danika) Tomato	2	0.075	0.019	400	7	0 1 7 14 21	whole fruit	0.19 0.16 0.09 0.02 ND			DP-31520 Site 1
Bowen, QLD Australia, 2009 (Pinacle) Tomato	2	0.05	0.0125	400	7	0 1	whole fruit	ND 0.01			DP-31520 Site 2

TOMATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Bowen, QLD Australia, 2009 (Pinnacle) Tomato	2	0.075	0.019	400	7	0 1	whole fruit	0.01 0.02			DP-31520 Site 2
Bowen, QLD Australia, 2009 (Pinnacle) Tomato	2	0.15	0.0375	400	7	0 1	whole fruit	0.01 0.03			DP-31520 Site 2

Table 106 Residues in protected tomatoes from supervised trials in Europe involving soil (drip irrigation) applications of cyantraniliprole (SC formulation)

TOMATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Birac Sur Trec S France, 2009 (Carnegie) Tomato	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28187 Test 09 [SC soil drip]
Mediglia Italy, 2009 (Naram) Tomato	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28187 Test 05 [SC soil drip]
Puente del Rio Spain, 2009 (HA 04077) Tomato	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28187 Test 06 [SC soil drip]
Wellerlooi Netherlands, 2009 (Capricia RZ) Tomato	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	< 0.01 ND 0.02 ND 0.029, ND			DP-28187 Test 07 [SC soil drip]
Wellerlooi Netherlands, 2009 (Capricia RZ) Tomato	4	0.1	5	2000	6-8	-0 0 1 3 7	whole fruit	0.003 ND 0.005 0.007 0.01			DP-28187 Test 10 [SC soil drip]
Nea Magnisia Greece, 2009 (Winner F1) Cherry Tomato	4	0.1	5	2000	7, 8	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28187 Test 08 [SC soil drip]

TOMATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Puente del Rio Spain, 2009 (Sirtaki) Cherry Tomato	4	0.1	5	2000	7, 8	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28187 Test 11 [SC soil drip]
La Mojonera Spain, 2009 (Foster) Cherry Tomato	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND 0.008 ND			DP-28187 Test 12 [SC soil drip]

Table 107 Residues in protected tomatoes from supervised trials in Europe involving foliar applications of cyantraniliprole (OD formulation)

TOMATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Birac Sur Trec S France, 2009 (Carnegie) Tomato/ Indoor	4	0.12	10	1200	7	-0 0 1 3 7	whole fruit	0.038 0.058 0.053 0.049 0.053			DP-28187 Test 09
La Mojonera Spain, 2009 (Ikram) Tomato/ Indoor	4	0.12	10	1200	7	1	whole fruit	0.14			DP-28187 Test 04
Mediglia Italy, 2009 (Naram) Tomato/ Indoor	4	0.12	10	1200	7, 6	1	whole fruit	0.072			DP-28187 Test 05
Nea Magnisia Greece, 2009 (Optima) Tomato/ Indoor	4	0.12	10	1200	7	1	whole fruit	0.043			DP-28187 Test 01
Puente del Rio Spain, 2009 (HA 04077) Tomato/ Indoor	4	0.12	10	1200	7	1	whole fruit	0.18			DP-28187 Test 06
Vittoria Italy, 2009 (Arawak) Tomato/ Indoor	4	0.12	10	1200	7	1	whole fruit	0.14			DP-28187 Test 03

TOMATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Vittoria Italy, 2009 (Rovente) Tomato/ Indoor	4	0.12	10	1200	7	1	whole fruit	0.18			DP-28187 Test 02
Wellerlooi Netherlands, 2009 (Capricia RZ) Tomato/ Indoor	4	0.12	10	1200	7	1	whole fruit	0.15			DP-28187 Test 07
Wellerlooi Netherlands, 2009 (Capricia RZ) Tomato/ Indoor	4	0.12	10	1200	6–8	–0 0 1 3 7	whole fruit	0.14 0.26 0.19 0.18 0.22			DP-28187 Test 10
Nea Magnisia Greece, 2009 (Winner F1) Cherry Tomato/ Indoor	4	0.12	10	1200	7	1	whole fruit	0.14			DP-28187 Test 08
Puente del Rio Spain, 2009 (Sirtaki) Cherry Tomato/ Indoor	4	0.12	10	1200	7, 8	–0 0 1 3 7	whole fruit	0.095 0.68 0.57 0.62 ND			DP-28187 Test 11
La Mojonera Spain, 2009 (Foster) Cherry Tomato/ Indoor	4	0.12	10	1200	7	–0 0 1 3 7	whole fruit	0.099 0.16 0.42 0.16 0.17			DP-28187 Test 12
Belfeld Netherlands, 2009 (Cabbricia) Cherry Tomato/ Indoor	4	0.12	10	1200	7	–0 0 1 3 7	whole fruit	0.42 0.49 0.59 0.44 0.41			DP-28187 Test 13
Caphan France, 2009 (Amoroso) Cherry Tomato/ Indoor	4	0.1	5	2000	6, 7	–0 0 1 3 7	whole fruit	0.35 0.49 0.37 0.4 0.36			DP-28187 Test 14

Table 108 Residues in sweet peppers from supervised trials in North America involving two or three foliar applications of cyantraniliprole (OD formulation)

PEPPERS, SWEET Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Arroyo Grande, CA USA, 2008 (Crusader) Bell Pepper/	2	0.15	70 64	220 240	5	1	whole fruit	0.031, 0.052	0.041		DP-25643 Trial 15
Bradenton, FL USA, 2008 (Camelot) Bell Pepper/	2	0.15	38	390	5	1	whole fruit	0.14, 0.14	0.14		DP-25643 Trial 11
Fresno, CA USA, 2008 (Indra) Bell Pepper/	2	0.15	53	280	5	1	whole fruit	0.19, 0.2	0.2		DP-25643 Trial 14
Raymondville, TX USA, 2008 (Camelot) Bell Pepper/	2	0.15	40	380	5	1	whole fruit	0.17, 0.12	0.15		DP-25643 Trial 12
San Ardo, CA USA, 2008 (Moody) Bell Pepper/	2	0.15	53	290	4	1	whole fruit	0.11, 0.097	0.1		DP-25643 Trial 13
Bradenton, FL USA, 2008 (Camelot) Bell Pepper/	3	0.15	38	390	5	1	whole fruit	0.26, 0.23	0.24		DP-25643 Trial 11
Branchton, ON CAN, 2009 (Permit) Bell Pepper/	3	0.15	73	210	6	1	whole fruit	0.082, 0.068	0.075		DP-25643 Trial 32
Carlyle, IL USA, 2009 (California Wonder) Bell Pepper/	3	0.15	68	230	5	1	whole fruit	0.1, 0.064	0.082		DP-25643 Trial 31
Conklin, MI USA, 2009 (Aristotle X3R) Bell Pepper/	3	0.15	52	290	5	1	whole fruit	0.074, 0.061	0.067		DP-25643 Trial 34
Delavan, WI USA, 2009 (Keystone) Bell Pepper/	3	0.15	76	200	5	1	whole fruit	0.033, 0.03	0.032		DP-25643 Trial 33
Fresno, CA USA, 2008 (Indra) Bell Pepper/	3	0.15	53	280	5	1	whole fruit	0.28, 0.28	0.28		DP-25643 Trial 14

PEPPERS, SWEET Location	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
Country, year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Raymondville, TX USA, 2008 (Camelot) Bell Pepper/	3	0.15	40	380	5	1	whole fruit	0.22, 0.2	0.21		DP-25643 Trial 12
San Ardo, CA USA, 2008 (Moody) Bell Pepper/	3	0.15	53	290	4, 5	1	whole fruit	0.12, 0.17	0.15		DP-25643 Trial 13
Seven Springs, NC USA, 2009 (California Wonder) Bell Pepper/	1+ 2	0.15 0.15	59 73	250 210	5	1	whole fruit	0.066, 0.05	0.058		DP-25643 Trial 30
Verona, WI USA, 2009 (King Arthur) Bell Pepper/	2+ 1	0.15 0.15	42 57	370 260	6, 5	1	whole fruit	0.078, 0.071	0.074		DP-25643 Trial 35
Arroyo Grande, CA USA, 2008 (Crusader) Bell Pepper/	1+ 1+ 1	0.15 0.15 0.14	70 64 58	220 240 240	5	1	whole fruit	0.046, 0.042	0.044		DP-25643 Trial 15
Bradenton, FL USA, 2008 (Camelot) Bell Pepper/	2+ 1	0.15 (soil) 0.15	4 39	3800 380	7	1	whole fruit	0.088, 0.095	0.092		DP-25643 Trial 11 2 soil dripline + 1 foliar

Soil (dripline irrigation) treatment rate was 2.3 g ai/100 metres of row

Table 109 Residues in non-bell peppers from supervised trials in North America involving two or three foliar applications of cyantraniliprole (OD formulation)

PEPPERS Location	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
Country, year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Fresno, CA USA, 2008 (Jalafuego NonBell Pepper/	2	0.15	53	280	5	1	whole fruit	0.39, 0.34	0.36		DP-25643 Trial 18
Paso Robles, CA USA, 2008 (Jalapeno NonBell Pepper/	2	0.15	51	290	5	1	whole fruit	0.19, 0.28	0.24		DP-25643 Trial 19

PEPPERS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Porterville, CA USA, 2008 (Anaheim TMR 23) NonBell Pepper/	2+ 1	0.15 (soil) 0.15	0.74 39	20400 380	7	1	whole fruit	0.21, 0.15	0.18		DP-25643 Trial 17 2 soil dripline + 1 foliar

Soil (dripline irrigation) treatment rate was 2.3 g ai/100 metres of row

Table 110 Residues in field peppers from supervised trials in Europe involving foliar applications of cyantraniliprole (OD formulation)

PEPPERS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Poirino Italy, 2009 (Corno di Cramagnola) Pepper/	2	0.09	11	800	7	1	whole fruit	0.077			DP-27712 Test 01
Los Palacios Spain, 2009 (Negrillo) Pepper/	2	0.09	11	800	7	1	whole fruit	0.096			DP-27712 Test 02
Chalkidona Greece, 2009 (Raiko) Pepper/	2	0.09	11	800	7	1	whole fruit	0.081			DP-27712 Test 03
Clairac S France, 2009 (Alléla) Pepper/	2	0.09	11	800	7	-0 0 1 3	whole fruit	0.062 0.067 0.068 0.059			DP-27712 Test 08
Villalba del Alcor Spain, 2009 (Italico) Pepper/	2	0.09	11	800	6	-0 0 1 3	whole fruit	0.031 0.09 0.066 0.047			DP-27712 Test 09
Contrada Gelso Bianco Italy, 2009 (Pyros) Hot pepper/	2	0.09	11	800	7	1	whole fruit	0.82			DP-27712 Test 04
Perea Greece, 2009 (Magnisia) Hot pepper	2	0.09	11	800	7	-0 0 1 3	whole fruit	0.13 0.35 0.32 0.23			DP-27712 Test 10
Utrera Spain, 2009 (Fire Flame) Hot pepper	2	0.09	11	800	7	-0 0 1 3	whole fruit	0.19 0.61 0.59 0.58			DP-27712 Test 11

PEPPERS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Contrada Gelso, Bianco, Sicily Italy, 2010 (Not specified) Hot pepper	2	0.09	11	800	7	-0 0 1 3	whole fruit	0.13			DP-27712 Test 14
Aguadulce Spain 2010 (Not specified) Hot pepper	2	0.09	11	800	7	1	whole fruit	0.24			DP-27712 Test 15

Table 111 Residues in field sweet peppers from supervised trials in Australia involving foliar applications of cyantraniliprole (OD formulation)

PEPPER Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Bowen, QLD Australia, 2009 (Warlock) Capsicum	2	0.05	0.0125	400	7	0 1	whole fruit	ND < 0.01			DP-31520 Site 3
Bowen, QLD Australia, 2009 (Warlock) Capsicum	2	0.075	0.019	400	7	0 1	whole fruit	ND 0.02			DP-31520 Site 3
Bowen, QLD Australia, 2009 (Warlock) Capsicum	2	0.15	0.0375	400	7	0 1	whole fruit	0.01 0.02			DP-31520 Site 3

Table 112 Residues in protected sweet and chilli peppers from supervised trials in Europe involving involving soil (drip irrigation) applications of cyantraniliprole (SC formulation)

PEPPERS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Los Palacios, Andalucia, Spain, 2008 (Palermo) Pepper	2	0.1	5	2000	7	-0 0 1 3 7 14	whole fruit	ND ND ND ND ND ND			DP-23885 Test 03a [soil dripline]

PEPPERS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Los Palacios, Andalucia, Spain, 2008 (Palermo) Pepper	2	0.1	5	2000	7	-0 0 1	whole fruit	ND ND ND			DP-23885 Test 03b [soil dripline]
NK Belfeld Netherlands, 2008 (Sensation) Sweet Pepper	2	0.1	5	2000	8	-0 0 1 3 7 14	whole fruit	ND ND ND ND ND 0.009			DP-23885 Test 01a [soil dripline]
NK Belfeld Netherlands, 2008 (Sensation) Sweet Pepper	2	0.1	5	2000	8	-0 0 1	whole fruit	ND ND ND			DP-23885 Test 01b [soil dripline]
Berja Spain, 2009 (Melchor) Pepper	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	0.007 0.005 0.006 0.008 0.008			DP-28188 Test 05 [soil dripline]
El Puente del Rio Spain, 2009 (California Rojo) Pepper	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28188 Test 11 [soil dripline]
El Puente del Rio Spain, 2009 (Italico) Pepper	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	0.005 0.005 ND 0.007 0.006			DP-28188 Test 12 [soil dripline]
El Puente del Rio Spain, 2009 (Lamullo) Pepper/	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	0.004 0.004 0.005 0.004 0.004			DP-28188 Test 04 [soil dripline]
Los Palacios, Andalucia, Spain, 2008 (Palermo) Pepper	4	0.1	5	2000	7	-0 0 1 3 7 14	whole fruit	ND ND ND ND ND ND			DP-23885 Test 03c [soil dripline]
Los Palacios, Andalucia, Spain, 2008 (Palermo) Pepper	4	0.1	5	2000	7	-0 0 1	whole fruit	ND ND ND			DP-23885 Test 03d [soil dripline]

PEPPERS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
NE Meterik Netherlands, 2009 (Spider) Pepper	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND 0.003 ND			DP-28118 Test 01 [soil dripline]
Nea Magnisia Greece, 2009 (Raikon) Pepper	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	0.007 0.006 0.007 0.006 0.011			DP-28118 Test 02 [soil dripline]
NK Belfeld Netherlands, 2008 (Sensation) Sweet Pepper	4	0.1	5	2000	6-8	-0 0 1 3 7 14	whole fruit	0.009 0.007 0.006 0.006 0.006 ND			DP-23885 Test 01c [soil dripline]
NK Belfeld Netherlands, 2008 (Sensation) Sweet Pepper	4	0.1	5	2000	6-8	-0 0 1	whole fruit	ND 0.079 0.004			DP-23885 Test 01d [soil dripline]
NK Belfeld Netherlands, 2009 (Ferrari) Pepper	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND 0.004 ND ND ND			DP-28118 Test 10 [soil dripline]
Pact S France, 2009 (Minerva) Pepper	4	0.1	5	2000	6-8	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28118 Test 09 [soil dripline]
Poirino Italy, 2009 (Sienor) Pepper/	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28118 Test 03 [soil dripline]
Chalkidona Greece, 2009 (Local "Magnisias") Hot pepper/	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND 0.004 0.007			DP-28118 Test 06 [soil dripline]
NM Grashoek Netherlands, 2009 (Midal) Hot pepper/	4	0.1	5	2000	6-8	-0 0 1 3 7	whole fruit	0.004 0.007 0.006 0.007 0.007			DP-28118 Test 07 [soil dripline]

PEPPERS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Contrada Sughero Torto Italy, 2009 (Romitol) Hot pepper/	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28118 Test 08 [soil dripline]
Pact S France, 2009 (Capel Hot) Hot pepper/	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28118 Test 13 [soil dripline]
Berja Spain, 2009 (Fire flame) Hot pepper/	4	0.1	5	2000	7	-0 0 1 3 7	whole fruit	ND ND ND ND ND			DP-28118 Test 14 [soil dripline]

Table 113 Residues in protected peppers from supervised trials in Europe involving foliar applications of cyantraniliprole (OD formulation)

PEPPERS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
K Belfeld Netherlands, 2008 (Sensation) Sweet Pepper	2	0.12	10	1200	8	-0 0 1 3 7 14	whole fruit	0.023 0.081 0.071 0.03 0.032 0.053			DP-23885 Test 01a
Los Palacios, Andalucia, Spain, 2008 (Palermo) Pepper	2	0.12	10	1200	7	-0 0 1 3 7 14	whole fruit	0.24 0.47 0.35 0.41 0.31 0.24			DP-23885 Test 03a
Los Palacios, Andalucia, Spain, 2008 (Palermo) Pepper	2	0.12	10	1200	7	-0 0 1	whole fruit	0.21 0.51 0.31			DP-23885 Test 03b
NK Belfeld Netherlands, 2008 (Sensation) Sweet Pepper	2	0.12	10	1200	6	-0 0 1	whole fruit	0.010 0.057 0.051			DP-23885 Test 01b
Berja Spain, 2009 (Melchor) Pepper	4	0.12	10	1200	7	1	whole fruit	0.076			DP-28118 Test 05

PEPPERS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
El Puente del Rio Spain, 2009 (California Rojo) Pepper	4	0.12	10	1200	7	-0 0 1 3 7	whole fruit	0.063 0.14 0.13 0.13 0.12			DP-28118 Test 11
El Puente del Rio Spain, 2009 (Italico) Pepper	4	0.12	10	1200	7	-0 0 1 3 7	whole fruit	0.12 0.16 0.15 0.1 0.094			DP-28118 Test 12
El Puente del Rio Spain, 2009 (Lamullo) Pepper	4	0.12	10	1200	7	1	whole fruit	0.096			DP-28118 Test 04
NE Meterik Netherlands, 2009 (Spider) Pepper	4	0.12	10	1250	7	1	whole fruit	0.13			DP-28118 Test 01
Nea Magnisia Greece, 2009 (Raikon) Pepper/	4	0.12	10	1200	7	1	whole fruit	0.14			DP-28118 Test 02
NK Belfeld Netherlands, 2009 (Ferrari) Pepper	4	0.12	10	1200	7	-0 0 1 3 7	whole fruit	0.13 0.13 0.17 0.17 0.11			DP-28118 Test 10
Pact S France, 2009 (Minerva) Pepper	4	0.12	10	1200	6-8	1	whole fruit	0.12 0.2 0.12 0.13 0.16			DP-28118 Test 09
Poirino Italy, 2009 (Sienor) Pepper	4	0.12	10	1200	7	1	whole fruit	0.12			DP-28118 Test 03
Chalkidona Greece, 2009 (Local "Magnisias") Hot pepper	4	0.12	10	1200	7	1	whole fruit	0.12			DP-28118 Test 06
NM Grashoek Netherlands, 2009 (Midal) Hot pepper	4	0.12	10	1200	6-8	1	whole fruit	1			DP-28118 Test 07

PEPPERS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Contrada Sughero Torto Italy, 2009 (Romitol) Hot pepper	4	0.12	10	1200	7	1	whole fruit	0.86			DP-28118 Test 08
Pact S France, 2009 (Capel Hot) Hot pepper	4	0.12	10	1200	7	-0 0 1 3 7	whole fruit	0.26 0.14 0.34 0.12 0.24			DP-28118 Test 13
Berja Spain, 2009 (Fire flame) Hot pepper	4	0.12	10	1200	7	-0 0 1 3 7	whole fruit	0.27 0.17 0.12 0.16 0.17			DP-28118 Test 14

Leafy vegetables

Results from supervised trials from Australia, Europe and North America on lettuce, spinach, Lamb's lettuce and scarole were provided to the Meeting.

North America

In trials conducted in North America on head and leaf lettuce and spinach, two or three foliar applications of 0.15 kg ai/ha cyantraniliprole (OD formulation) were applied at 5 day intervals, using 200–500 L/ha, with adjuvant added. Soil treatment plots were also included at several trial sites, either as a soil shank (in furrow) treatment of 0.2 kg ai/ha (SC formulation) at planting or two soil treatments of 0.15 kg ai/ha cyantraniliprole (SC formulation) applied through drip-line irrigation systems (adjusted to pH 4–5, with no added adjuvant).

Duplicate samples of spinach and lettuce leaves, lettuce heads (trimmed/washed and also with wrapper leaves) and celery (with tops and also trimmed/washed) were stored at –20 °C for up to 9 months before extraction and analysis for cyantraniliprole and six metabolites (within 3 months of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 96–98% (cyantraniliprole) and 80–106% (metabolites) in samples spiked with 0.01–5.0 mg/kg and up to 10 mg/kg in celery and 17 mg/kg in spinach.

In trials conducted in the USA on mustard greens, two or three foliar applications of 0.15 kg ai/ha cyantraniliprole (OD and SE formulations) were applied at 4–6 day intervals, using 200–500 L/ha, with adjuvant added. In several trials, separate plots were also treated with the equivalent of 0.2 kg ai/ha as a soil injection (soil shank) treatment at planting (without added surfactant).

Duplicate samples were stored at –20 °C for up to 8 months before extraction and analysis for cyantraniliprole and six metabolites (within 5 months of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 90–94% (cyantraniliprole) and 80–103% (metabolites) in samples spiked with 0.01 to 25 mg/kg.

Europe

In trials conducted in Europe on protected head lettuce, leaf (open head) lettuce, Lamb's lettuce and scarole, two to three applications of 3.7–10 g ai/hL cyantraniliprole were applied using 750–800 L/ha (0.078–0.096 kg ai/ha) as foliar sprays (OD formulation) or three to four applications of 0.075–

0.1 kg ai/ha using 2000 L/ha as soil treatments (SC formulation), applied through the dripline irrigation systems. The retreatment intervals in all trials was 7 days and no added surfactants were included.

In outdoor head lettuce, leaf (open head) lettuce, Lamb's lettuce and scarole in Southern Europe, three foliar applications of 0.078 kg ai/ha cyantraniliprole (OD formulation) were applied using 800 L water/ha (5 g ai/hL) or three soil treatments (SC formulation) were applied through the dripline irrigation systems at a rate equivalent to 0.1 kg ai/ha. The retreatment intervals in all trials was 7 days and no added surfactants were included.

Samples were stored at -18°C for up to 7 months before extraction and analysis for cyantraniliprole and six metabolites analysis (within 7 days of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 88–102% (cyantraniliprole) and 83–95% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg and also 2 and 10 mg/kg cyantraniliprole and 0.5 mg/kg IN-J9Z38 metabolite in leaf lettuce.

Table 114 Residues in field head lettuce from supervised trials in North America involving soil applications (SC formulation) at planting or through dripline irrigation systems (with foliar applications—OD formulation)

LETTUCE HEAD Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Conklin, MI USA, 2009 Head Lettuce Skyline)	1	0.15	0.74	20400		0 3 7	heads	ND, ND ND, ND < 0.01, < 0.01	ND ND < 0.01		DP-25644 Trial 27 [by drip irrigation]
Conklin, MI USA, 2009 Head Lettuce Skyline)	2	0.15	0.74	20400	7	-0 0 3 7	heads	< 0.01, < 0.01 < 0.01, < 0.01 0.01, < 0.01 < 0.01, < 0.01	< 0.01 < 0.01 < 0.01 < 0.01		DP-25644 Trial 27 [by drip irrigation]
Porterville, CA USA, 2008 Head Lettuce/ Vandenberg)	1+ 1+ 1	0.2 0.1 0.15	97 42 62	200 240 240	73 5	1	heads	0.017, 0.017	0.017		DP-25644 Trial 2 1 soil shank treatment + 2 foliar sprays
Conklin, MI USA, 2009 Head Lettuce Skyline)	2+ 1	0.15 0.15	0.74 52	20400 290	7	-0 1	heads	< 0.01, < 0.01 1, 0.81	< 0.01 0.91		DP-25644 Trial 27 [2 by drip irrigation + 1 foliar]

Soil (shank) treatment rate at planting of 1.5 g ai/100 metres of row (Trial 2)

Soil (dripline irrigation) treatment rate of 1.1 g ai/100 metres of row (Trial 27)

Table 115 Residues in field head lettuce from supervised trials in Europe involving soil (drip irrigation) applications of cyantraniliprole (SC formulation)

LETTUCE HEAD Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M2	M4	

LETTUCE HEAD Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M2	M4	
L'Aldea Spain, 2009 (Maravilla)	3	0.1	5	2000		−0 0 1 3	heads	0.013 0.017 0.013 0.013				DP-27713 Test 05
Lorgies S France, 2009 (Altadis)	3	0.1	5	2010		−0 0 1 3	heads	ND 0.021 0.009 0.006				DP-27713 Test 06
Nea Magnisia Greece, 2009 (Verdunna)	3	0.1	5	2000		7 −0 0 1 3	heads	0.032 0.12 0.12 0.13				DP-27713 Test 07

Table 116 Residues in field head lettuce from supervised trials in North America involving two or three foliar applications of cyantraniliprole (OD formulation unless specified)

LETTUCE HEAD Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Bradenton, FL USA, 2008 (Iceberg)	2	0.15	36	420	5	1	heads trimmed	0.68, 0.75 0.21, 0.21	0.71 0.21		DP-25644 Trial 1
Greenfield, CA USA, 2008 (Telluride)	2	0.15	54	280	5	1	heads trimmed	0.023, 0.045 0.009, 0.018	0.034 0.014		DP-25644 Trial 5
Guadalupe, CA USA, 2008 (Durango)	2	0.15	54	280	5	1	heads trimmed	2.1, 2.9 0.046, 0.027	2.5 0.036	M2=0.01	DP-25644 Trial 4
Porterville, CA USA, 2008 (Vandenberg)	2	0.15	60	250	5	1	heads	0.018, 0.013	0.016		DP-25644 Trial 3
Porterville, CA USA, 2008 Head Lettuce/ Vandenberg)	2	0.15	62	240	5	1	heads	0.016, 0.022	0.019		DP-25644 Trial 2
Santa Maria, CA USA, 2008 (Quest)	2	0.15	65	230	5	1	heads	1.3, 1.1	1.2		DP-25644 Trial 6
Alton, NY USA, 2009 (Ithaca MTO)	3	0.15	40	380	5	1	heads	1.8, 1.9	1.8	M1=0.01	DP-25644 Trial 23

LETTUCE HEAD	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Alton, NY USA, 2009 (Ithaca MTO)	3	0.15	40	380	5	1	heads	1.2, 1.9	1.5		DP-25644 Trial 23 [100 SE]
Bradenton, FL USA, 2008 (Iceberg)	3	0.15	36	420	5	1	heads trimmed	1.6, 1.7 0.6, 0.6	<u>1.6</u> 0.6	M1=0.02	DP-25644 Trial 1
Conklin, MI USA, 2009 Skyline)	3	0.15	50	300	5	1	heads	1.6, 1.7	1.7		DP-25644 Trial 27
Conklin, MI USA, 2009 Skyline)	3	0.15	50	300	5	1	heads	2.2, 2	2.1	M4=0.01	DP-25644 Trial 27 [100 SE]
Delavan, WI USA, 2009 (Sun Devil)	3	0.15	73	210	5	1	heads	0.2, 0.16	0.18		DP-25644 Trial 26
Delavan, WI USA, 2009 (Sun Devil)	3	0.15	73	210	5	1	heads	0.18, 0.16	0.17		DP-25644 Trial 26 [100 SE]
Fitchburg, WI USA, 2009 (Summertime)	3	0.15	60	250	5	1	heads	0.17, 0.16	0.16		DP-25644 Trial 24
Fitchburg, WI USA, 2009 (Summertime)	3	0.15	60	250	5	1	heads	0.12, 0.15	0.13		DP-25644 Trial 24 [100 SE]
Greenfield, CA USA, 2008 (Telluride)	3	0.15	54	280	5	1	heads trimmed	0.56, 0.95 0.004, ND	0.75 ND		DP-25644 Trial 5
Guadalupe, CA USA, 2008 (Durango)	3	0.15	53	290	5	1	heads trimmed	2.9, 2.6 0.008, 0.012	<u>2.7</u> 0.01	M1=0.01 M2=0.02	DP-25644 Trial 4
Porterville, CA USA, 2008 (Vandenberg)	3	0.15	60	250	5	1	heads	0.021, 0.015	0.018		DP-25644 Trial 3
Porterville, CA USA, 2008 Head Lettuce/ Vandenberg)	3	0.15	62	240	5	1	heads	0.05, 0.12	0.084		DP-25644 Trial 2
Princeton, ON CAN, 2009 (Mighty Joe)	3	0.15	72	210	5	1	heads	0.39, 0.89	0.64		DP-25644 Trial 25
Princeton, ON CAN, 2009 (Mighty Joe)	3	0.15	72	210	5	1	heads	0.53, 0.46	0.5		DP-25644 Trial 25 [100 SE]
Santa Maria, CA USA, 2008 (Quest)	3	0.15	65	230	5	1	heads	1.1, 1.5	1.3	M2=0.01	DP-25644 Trial 6

LETTUCE HEAD Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Canby, OR USA, 2009 (Sniper)	1+ 1+ 1	0.15 0.14 0.16	53 52 54	290 270 300	5	1	heads	0.5, 0.56	0.53		DP-25644 Trial 28
Canby, OR USA, 2009 (Sniper)	2+ 1	0.15 0.17	54 53	280 310	5	1	heads	0.85, 0.82	0.83		DP-25644 Trial 28 [100 SE]

Trimmed=washed after outer leaves were removed

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

M4: Average residues of metabolite IN-MLA84

Table 117 Residues in field head lettuce from supervised trials in Europe involving 3 foliar applications of cyantraniliprole (OD formulation)

LETTUCE HEAD Location	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments
Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M2	M4	
L'Aldea Spain, 2009 (Maravilla)	3	0.08	9.8	800		−0 0 1 3	heads	0.092 0.64 0.5 0.16				DP-27713 Test 05
Lorgies S France, 2009 (Altadis)	3	0.08	9.8	830		−0 0 1 3	heads	0.062 0.15 0.045 0.037				DP-27713 Test 06
Nea Magnisia Greece, 2009 (Verdunna)	3	0.08	9.8	800		−0 0 1 3	heads	0.37 2.8 2.4 2.3	0.02 0.03 0.02 0.02		0.02 0.02 0.02 0.01 0.02	DP-27713 Test 07

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

M4: Average residues of metabolite IN-MLA84

Table 118 Residues in protected head lettuce from supervised trials in Europe involving soil (drip irrigation) applications of cyantraniliprole (SC formulation)

LETTUCE HEAD	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments	
Location Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M2	M4	
Azzano S. Paolo Italy, 2008 (Loira)	2	0.07	3.7	2000	8, 7	−0 0 1 3 7 14	heads	< 0.01, 0.031 < 0.01, < 0.01 ND, 0.01 0.048 0.017 < 0.01				DP-21415 Test 02

LETTUCE HEAD	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments
Location Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M2	M4	
Los Palacios Spain, 2008 (Filipu)	2	0.07	3.7	2000	7	−0 0 1 3 7 14	heads	ND, 0.026 < 0.01, 0.019 0.017, 0.013 0.017 0.021 0.013				DP-21415 Test 03
Lucenay France, 2009 (Dedale)	3	0.1	5	2000	7	−0 0 1 3	heads	0.02 0.012 0.006 0.034				DP-28200 Test 10
Utrera Spain, 2009 (Iceberg)	3	0.1	5	2000	7	−0 0 1 3	heads	0.009 0.007 0.009 0.008				DP-28200 Test 09
Azzano S. Paolo Italy, 2008 (Loira)	4	0.07	3.7	2000	7–6	−0 0 1 3 7 14	heads	< 0.01, 0.01 < 0.01, 0.024 < 0.01, ND < 0.01 0.011 0.011				DP-21415 Test 02
Los Palacios Spain, 2008 (Filipu)	4	0.07	3.7	2000	8–6	−0 0 1 3 7 14	heads	0.041, 0.071 0.053, 0.067 0.052, 0.028 0.055 0.049 0.013				DP-21415 Test 03

Table 119 Residues in protected head lettuce from supervised trials in Europe involving foliar applications of cyantraniliprole (SC formulation)

LETTUCE HEAD	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
Location Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites		
									M1	M4	
Los Palacios Spain, 2008 (Filipu)	2				7	−0 0 1 3 7 14	heads	1.5, 0.56 2.0, 0.92 2.3, 0.13 1.9 1.4 ND			DP-21415 Test 03
Azzano S. Paolo Italy, 2008 (Loira)	2	0.1	13	750	7, 6	−0 0 1 3 7 14	heads	1.1, 2.9 4.9, 6.1 4.1, 7.4 3.6 3.6 2.6	0.04 0.04, 0.03 0.04, 0.02 0.05 0.05 0.02	0.03 0.02, 0.01 0.03, 0.02 0.02 0.02 0.02	DP-21415 Test 02
Azzano San Paolo Italy, 2009 (Nacre)	3	0.08	9.7	820	6, 8	−0 0 1 3	heads	0.95 3.1 2.9 2.7	0.01 0.02 0.01	0.01 0.02 0.01	DP-28200 Test 01

LETTUCE HEAD	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
Location Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites		
									M1	M4	
Chalkidona Greece, 2009 (Sonia)	3	0.08	9.8	800	7	-0 0 1 3	heads	2.9 6.4 6.3 5.6	0.02 0.03 0.03 0.02	0.01 0.02 0.02 0.02	DP-28200 Test 02
Lucenay France, 2009 (Dedale)	3	0.08	9.8	780	7	-0 0 1 3	heads	1.4 2 2 3	0.01 0.02 0.02 0.02	0.01 0.01 0.01 0.01	DP-28200 Test 10
Utrera Spain, 2009 (Iceberg)	3	0.08	9.8	810	7	-0 0 1 3	heads	0.006 0.009 0.009 0.006			DP-28200 Test 09

M1: Average residues of metabolite IN-J9Z38

M4: Average residues of metabolite IN-MLA84

Table 120 Residues in field leaf lettuce from supervised trials in North America involving soil applications (SC formulation) at planting or through dripline irrigation systems (with foliar applications-OD formulation)

LETTUCE LEAF	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
Location Country, year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Conklin, MI USA, 2009 (Bergam's Green)	1	0.15	0.74	20400		0 3 7	leaves	ND, ND 0.015, 0.015 0.028, 0.022	ND 0.015 0.025		DP-25644 Trial 33 [drip irrigation]
Conklin, MI USA, 2009 (Bergam's Green)	2	0.15	0.74	20400	7	-0 0 3 7	leaves	0.028, 0.022 0.025, 0.032 0.023, 0.028 0.016, 0.015	0.025 0.028 0.026 0.016		DP-25644 Trial 33 [drip irrigation]
Fresno, CA USA, 2008 (Big Star)	1+ 1+ 1	0.2 0.1 0.15	107 36 54	190 280 280	68 5	1	leaves	1, 1.1	1.1		DP-25644 Trial 12 1 soil shank treatment + 2 foliar sprays
Conklin, MI USA, 2009 (Bergam's Green)	2+ 1	0.15 0.15	0.74 51	20400 290	7 7	-0 1	leaves	0.016, 0.015 1.8, 1.6	0.016 1.7		DP-25644 Trial 33 [2 by drip irrigation + 1 foliar]

Soil (shank) treatment rate of 1.5 g ai/100 metres of row (Trial 12)

Soil (dripline irrigation) treatment rate of 1.1 g ai/100 metres of row (Trial 27)

Table 121 Residues in field leaf (open head) lettuce from supervised trials in Europe involving soil (drip irrigation) applications of cyantraniliprole (SC formulation)

LETTUCE LEAF Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments	
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites				
									M1	M2	M4		
Utrera Spain, 2009 (Filipus)	3	0.1	5	2000		−0 0 1 3	leaves	0.007 0.007 0.01 0.016				DP-27713 Test 01	
Mediglia Italy, 2009 (Canasta)	3	0.1	5	2000		−0 0 1 3	leaves	ND 0.006 ND 0.004				DP-27713 Test 02	
Lorgies France, 2009 (Kytare)	3	0.1	5	2030		−0 0 1 3	leaves	0.02 0.05 0.016 0.011				DP-27713 Test 03	
Chalkidona Greece, 2009 (Simson)	3	0.1	5	2000		−0 0 1 3	leaves	0.004 0.005 0.004 0.009				DP-27713 Test 04	

Table 122 Residues in field leaf lettuce from supervised trials in North America involving two or three foliar applications of cyantraniliprole (OD formulation)

LETTUCE LEAF	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
Location Country, year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Bradenton, FL USA, 2008 (Oak Leaf)	2	0.15	36	430	5	1	leaves	1.3, 0.95	1.1		DP-25644 Trial 7
Fresno, CA USA, 2008 (Big Star)	2	0.15	54	280	5	−0 0 1 3 5	leaves	0.28, 0.25 2.9, 3.0 2, 2.2 1.5, 1.2 0.74, 0.59	0.27 3.0 2.1 1.3 0.67	M1=0.01	DP-25644 Trial 12
King City, CA USA, 2008 (“454”)	2	0.15	40	380	5	1	leaves	4.9, 3.8	4.4	M1=0.01 M2=0.02 M4=0.01	DP-25644 Trial 10
King City, CA USA, 2008 (Sunbelt)	2	0.15	65	230	5	1	leaves	0.42, 0.58	0.5		DP-25644 Trial 11
Porterville, CA USA, 2008 (Buttercrunch)	2	0.15	63	240	5	1	leaves	4.6, 3.9	4.2	M1=0.01	DP-25644 Trial 9
Porterville, CA USA, 2008 (Tehema)	2	0.15	410	37	5	1	leaves	3.6, 4.7	4.2	M1=0.02 M2=0.03 M4=0.04	DP-25644 Trial 8

LETTUCE LEAF	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Alton, NY USA, 2009 (Harmony)	3	0.15	53	280	5	1	leaves	2.7, 3.1	2.9	M1=0.02 M2=0.01 M4=0.02	DP-25644 Trial 29a
Alton, NY USA, 2009 (Harmony)	3	0.15	53	280	5	1	leaves	3, 3.3	3.2	M1=0.01 M2=0.01 M4=0.01	DP-25644 Trial 29b [100 SE]
Bradenton, FL USA, 2008 (Oak Leaf)	3	0.15	35	430	5	1	leaves	1.1, 1.4	1.2		DP-25644 Trial 7
Conklin, MI USA, 2009 (Bergam's Green)	3	0.15	51	300	5	1	leaves	1.9, 2	1.9	M4=0.02	DP-25644 Trial 33a
Conklin, MI USA, 2009 (Bergam's Green)	3	0.15	51	300	5	1	leaves	2.5, 2.5	2.5		DP-25644 Trial 33b [100 SE]
Corvallis, OR USA, 2009 (Waldmanns Green)	3	0.15	53	280	5	1	leaves	4.2, 3.5	3.9	M1=0.02 M2=0.01 M4=0.03	DP-25644 Trial 34a
Corvallis, OR USA, 2009 (Waldmanns Green)	3	0.15	53	280	5	1	leaves	5.8, 4.8	5.3	M1=0.02 M2=0.02 M4=0.03	DP-25644 Trial 34b [100 SE]
Delavan, WI USA, 2009 (Salad Bowl)	3	0.15	73	210	5	1	leaves	7.4, 6.3	6.8	M1=0.02 M2=0.02 M4=0.02	DP-25644 Trial 32a
Delavan, WI USA, 2009 (Salad Bowl)	3	0.15	75	200	5	1	leaves	7.7, 5.2	6.4	M1=0.02 M2=0.02 M4=0.01	DP-25644 Trial 32b [100 SE]
Fresno, CA USA, 2008 (Big Star)	3	0.15	54	280	5	-0 1	leaves	0.74, 0.59 2.6, 2.1	0.67 <u>2.4</u>		DP-25644 Trial 12
King City, CA USA, 2008 ("454")	3	0.15	40	380	5	1	leaves	3, 3.6	3.3	M1=0.01 M4=0.02	DP-25644 Trial 10
King City, CA USA, 2008 (Sunbelt)	3	0.15	70	220	5	1	leaves	1.4, 0.92	1.1		DP-25644 Trial 11
Porterville, CA USA, 2008 (Buttercrunch)	3	0.15	63	240	5	1	leaves	1.9, 2.2	2.1	M1=0.01	DP-25644 Trial 9
Porterville, CA USA, 2008 (Tehema)	3	0.15	410	37	5	1	leaves	4, 3.9	4.0	M1=0.01 M2=0.02 M4=0.04	DP-25644 Trial 8
Princeton, ON CAN, 2009 (Summer Star)	1+ 1+ 1	0.15 0.15 0.14	76 71 73	200 220 200	5 4	1	leaves	2.2, 2.5	2.4		DP-25644 Trial 31a

LETTUCE LEAF Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Princeton, ON CAN, 2009 (Summer Star)	3	0.16 0.15 0.14	76 74 73	200 200 200	5 4	1	leaves	2.3, 2.5	2.4		DP-25644 Trial 31b [100 SE]
Carlyle, IL USA, 2009 (Loose Leaf Oakleaf)	1+ 1+ 1	0.15 0.15 0.15	45 50 72	340 300 200	5	1	leaves	5, 5.8	5.4	M1=0.03 M2=0.02 M4=0.06	DP-25644 Trial 30a
Carlyle, IL USA, 2009 (Loose Leaf Oakleaf)	1+ 1+ 1	0.15 0.15 0.15	46 50 72	330 300 200	5	1	leaves	6.3, 7.4	6.8	M1=0.04 M2=0.02 M4=0.05	DP-25644 Trial 30b [100 SE]

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

M4: Average residues of metabolite IN-MLA84

Table 123 Residues in field leaf (open head) lettuce from supervised trials in Europe involving three foliar applications of cyantraniliprole (OD formulation)

LETTUCE LEAF Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M2	M4	
Utrera Spain, 2009 (Filipus)	3	0.08	9.8	800		-0 0 1 3	leaves	0.27 0.49 0.94 0.4				DP-27713 Test 01
Mediglia Italy, 2009 (Canasta)	3	0.08	9.8	800		-0 0 1 3	leaves	0.047 0.69 0.5 0.41			0.01	DP-27713 Test 02
Lorgies France, 2009 (Kytare)	3	0.08	9.8	810		-0 0 1 3	leaves	0.14 0.42 0.18 0.088			0.01 0.01	DP-27713 Test 03
Chalkidona Greece, 2009 (Simson)	3	0.08	9.8	810		-0 0 1 3	leaves	0.054 0.91 0.81 0.49	0.01		0.01	DP-27713 Test 04

M1: Average residues of metabolite IN-J9Z38

M4: Average residues of metabolite IN-MLA84

Table 124 Residues in protected leaf (open head) lettuce from supervised trials in Europe involving soil (drip irrigation) applications of cyantraniliprole (SC formulation)

LETTUCE LEAF Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites	

LETTUCE LEAF Location	Application					DAT (days)	Matrix	Residues (mg/kg)		Reference & Comments
Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites	
Treviolo Italy, 2009 (Gentile)	3	0.1	5	2000	7	-0 0 1 3	leaves	0.01 0.008 0.032 0.083		DP-28820 Test 11
Utrera Spain, 2009 (Filipu)	3	0.1	5	2000	7	-0 0 1 3	leaves	0.011 0.011 0.007 0.18		DP-28200 Test 12
Lleida Spain, 2009 (Inverna)	3	0.1	5	2000	8, 6	-0 0 1 3	leaves	0.012 0.014 0.009 0.009		DP-28200 Test 13

Table 125 Residues in protected leaf (open head) lettuce from supervised trials in Europe involving foliar applications of cyantraniliprole (SC formulation)

LETTUCE LEAF Location	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites		
									M1	M4	
Nea Magnisia Greece, 2009 (Bera)	3	0.08	9.8	800	7	-0 0 1 3	leaves	2.5 4.4 4.4 4.9	0.01 0.02 0.02 0.02	0.02 0.02 0.01 0.02	DP-28200 Test 03
Lucenay France, 2009 (Kidam)	3	0.08	9.8	800	7	-0 0 1 3	leaves	1.9 4 4.6 3.6	0.03 0.05 0.07 0.06	0.01 0.02 0.03 0.02	DP-28200 Test 04
Treviolo Italy, 2009 (Gentile)	3	0.08	9.8	800	7	-0 0 1 3	leaves	0.28 2.4 1.6 1.1	0.01 0.01 0.01	0.02 0.02 0.02 0.01	DP-28200 Test 11
Utrera Spain, 2009 (Filipu)	3	0.08	9.8	810	7	-0 0 1 3	leaves	0.022 1.1 0.49 0.012			DP-28200 Test 12
Lleida Spain, 2009 (Inverna)	3	0.08	9.8	800	8, 6	-0 0 1 3	leaves	0.12 0.8 0.78 0.12			DP-28200 Test 13

M1: Average residues of metabolite IN-J9Z38

M4: Average residues of metabolite IN-MLA84

Table 126 Residues in protected Lamb's lettuce from supervised trials in Europe involving soil (drip irrigation) applications of cyantraniliprole (SC formulation)

LAMB'S LETTUCE Location	Application					DAT (days)	Matrix	Residues (mg/kg)		Reference & Comments
Country, year	no	kg ai/ha	g ai/hL	water	RTI			cyantraniliprole	metabolites	

(variety)				L/ha	(days)				M1		
Treviolo Italy, 2009 (Macholong)	3	0.1	5	2000	6, 7	–0 0 1 3	leaves	0.025 0.015 0.19 0.016	0.01		DP-28200 Test 14
Azzano San Paolo Italy, 2009 (Tropi)	3	0.1	5	2000	6, 8	–0 0 1 3	leaves	0.055 0.064 0.057 0.078	0.01 0.01		DP-28200 Test 15
Lleida Spain, 2009 (Verte de Cambrai)	3	0.1	5	2000	7, 6	–0 0 1 3	leaves	0.025 0.099 0.045 0.034			DP-28200 Test 16

Table 127 Residues in protected Lamb's lettuce from supervised trials in Europe involving foliar applications of cyantraniliprole (SC formulation).

LAMB'S LETTUCE Location	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments
Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M2	M4	
Cadreita Spain, 2009 (Trophy)	3	0.08	9.8	810	8, 6	–0 0 1 3	leaves	2.8 5.3 4.9 4.9	0.11 0.12 0.12 0.14		0.06 0.06 0.06 0.07	DP-28200 Test 05
Dommartin France, 2010 (Gala)	3	0.08	9.7	790	7	–0 0 1 3	leaves	3 4.4 3.7 3.7	0.02 0.03 0.03 0.03			DP-28200 Test 06
Treviolo Italy, 2009 (Macholong)	3	0.08	9.7	800	6, 7	–0 0 1 3	leaves	4.7 3.6 6.9 6.5	0.07 0.08 0.09 0.06	0.01 0.02 0.02 0.02	0.02 0.02 0.03 0.02	DP-28200 Test 14
Azzano San Paolo Italy, 2009 (Tropi)	3	0.08	9.7	790	6, 8	–0 0 1 3	leaves	4 8 6.6 7.4	0.09 0.14 0.14 0.17	0.01 0.01 0.01	0.05 0.07 0.06 0.08	DP-28200 Test 15
Lleida Spain, 2009 (Verte de Cambrai)	3	0.08	9.8	800	7, 6	–0 0 1 3	leaves	0.37 4 1.7 0.73	0.01 0.03 0.02 0.02			DP-28200 Test 16

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

M4: Average residues of metabolite IN-MLA84

Table 128 Residues in spinach from supervised trials in the USA involving soil applications at planting or through dripline irrigation systems (with foliar applications).

SPINACH Location	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
Country, year (variety)	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	

SPINACH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Conklin, MI USA, 2009 Spinach (Melody)	1	0.15	0.59	25500		0 3 7	leaves	< 0.01, < 0.01 < 0.01, < 0.01 < 0.01, < 0.01	< 0.01 < 0.01 < 0.01		DP-25644 Trial 38 [by drip irrigation]
Conklin, MI USA, 2009 Spinach (Melody)	1+ 1	0.15 0.15	0.59 0.74	25500 20400	7	-0 0 3 7	leaves	< 0.01, < 0.01 < 0.01, < 0.01 0.01, < 0.01 < 0.01, < 0.01	< 0.01 < 0.01 < 0.01 < 0.01		DP-25644 Trial 38 [by drip irrigation]
Terra Bella, CA USA, 2008 Spinach (Shasta)	1+ 1+ 1	0.2 0.1 0.15	97 46 71	210 230 220	51 5	1	leaves	6.7, 6.8	6.7	M1=0.05 M2=0.18	DP-25644 Trial 20 [1 soil shank treatment + 2 foliar sprays]
Conklin, MI USA, 2009 Spinach (Melody)	1+ 1+ 1	0.15 0.15 0.15	0.59 0.74 51	25500 20400 300	7 7	-0 1	leaves	< 0.01, < 0.01 6.7, 6.8	< 0.01 6.8	M1=0.03 M2=0.08	DP-25644 Trial 38 2 [by drip irrigation + 1 foliar]

Soil (shank) treatment rate of 1.5 g ai/100 metres of row (Trial 20)

Soil (dripline irrigation) treatment rate of 1.1 g ai/100 metres of row (Trial 38)

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

Table 129 Residues in spinach from supervised trials in the USA involving two or three foliar applications of cyantraniliprole (OD formulation)

SPINACH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
King City, CA USA, 2008 Spinach/	2	0.15	60	250	6	1	leaves	3.1, 3.9	3.5	M1=0.02 M2=0.31	DP-25644 Trial 22
Raymondville, TX USA, 2008 Spinach (Melody)	2	0.15	40	380	5	1	leaves	14, 13	13.0	M1=0.07 M2=0.29	DP-25644 Trial 19
Santa Maria, CA USA, 2008 Spinach (Mizano)	2	0.15	54	280	5	1	leaves	3.5, 3.2	3.4	M1=0.04 M2=0.07	DP-25644 Trial 21
Terra Bella, CA USA, 2008 Spinach (Shasta)	2	0.15	70	220	5	1	leaves	8.2, 8.9	8.5	M1=0.05 M2=0.2	DP-25644 Trial 20

SPINACH Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Alton, NY USA, 2009 Spinach (Lombardia)	3	0.15	40	380	5	1	leaves	5.8, 4	4.9	M1=0.07 M2=0.24 M4=0.02	DP-25644 Trial 35
Conklin, MI USA, 2009 Spinach (Melody)	3	0.15	51	290	6, 4	1	leaves	4.5, 4.7	4.6	M1=0.03 M2=0.26 M4=0.01	DP-25644 Trial 38
Corvallis, OR USA, 2009 Spinach (Tiger Cat)	3	0.15	53	280	5	1	leaves	4, 4.3	4.2	M1=0.03 M2=0.22	DP-25644 Trial 40
Jerome, ID USA, 2009 Spinach (Unipack 151)	3	0.15	76	200	7, 5	1	leaves	5.7, 6	5.8	M1=0.03 M2=0.1	DP-25644 Trial 39
Marengo, IL USA, 2009 Spinach (Bloomsdale Long Standing)	3	0.15	66	230	5	1	leaves	10, 10	10	M1=0.09 M2=0.48 M3=0.01 M4=0.06	DP-25644 Trial 37
Raymondville, TX USA, 2008 Spinach (Melody)	3	0.15	40	380	5	1	leaves	13, 13	13	M1=0.09 M2=0.4 M3=0.01 M4=0.01	DP-25644 Trial 19
Santa Maria, CA USA, 2008 Spinach (Mizano)	3	0.15	54	280	5	1	leaves	4, 4.2	4.1	M1=0.05 M2=0.13	DP-25644 Trial 21
Seven Springs, NC USA, 2009 Spinach (Hybrid 7)	3	0.15	65	230	5, 6	1	leaves	4.9, 4.6	4.7	M1=0.04 M2=0.15 M4=0.01	DP-25644 Trial 36
Terra Bella, CA USA, 2008 Spinach (Shasta)	3	0.15	70	220	5	1	leaves	7.9, 8.4	8.2	M1=0.09 M2=0.33 M4=0.01	DP-25644 Trial 20
King City, CA USA, 2008 Spinach/	2+ 1	0.15 0.15	60 62	250 240	6 5	1	leaves	3.6, 4	3.8	M1=0.02 M2=0.14	DP-25644 Trial 22

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

M3: Average residues of metabolite IN-N7B69

M4: Average residues of metabolite IN-MLA84

Table 130 Residues in mustard greens from supervised trials in the USA involving two or three foliar applications of cyantraniliprole (OD formulation)

MUSTARD GREENS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
King City, CA, USA, 2008 (Mizuna) Mustard Greens/	2	0.15	60	250	6	1	leaves	4.3, 4.7	4.5	M1=0.01 M2=0.03 M4=0.03 M5=0.015	DP-25641 Trial 11
Raymondville, TX, USA, 2008 (Florida Broadleaf) Mustard Greens/	2	0.15	40	380	5	1	leaves	9.5, 11	10	M1=0.05 M2=0.05 M4=0.06 M5=0.02	DP-25641 Trial 10
Terra Bella, CA, USA, 2008 (Southern Giant Curled) Mustard Greens/	2	0.15	70	220	5	1	leaves	4.2, 5.2	4.7	M1=0.03 M2=0.01 M4=0.05	DP-25641 Trial 12
Alton, NY, USA, 2009 (Pizzo) Mustard Greens/	3	0.15	53	280	4, 6	1	leaves	2.2, 2.5	2.4	M1=0.02 M2=0.01 M4=0.02 M5=0.01	DP-25641 Trial 25
Chula, GA, USA, 2009 (Southern Giant Curled) Mustard Greens/	3	0.15	53	290	5	1	leaves	6.4, 5.6	6.0	M1=0.04 M2=0.02 M4=0.04 M5=0.01	DP-25641 Trial 28
Conklin, MI, USA, 2009 (Green Wave) Mustard Greens/	3	0.15	50	300	5	1	leaves	7.4, 6.8	7.1	M1=0.03 M2=0.03 M4=0.03 M5=0.01	DP-25641 Trial 31
Corvallis, OR, USA, 2009 (Green Wave) Mustard Greens/	3	0.15	54	280	5	1	leaves	6.1, 5.5	5.8	M1=0.02 M2=0.02 M4=0.03 M5=0.01	DP-25641 Trial 32
King City, CA, USA, 2008 (Mizuna) Mustard Greens/	3	0.15	60	250	5, 6	1	leaves	2.9, 4.9	3.9	M1=0.01 M2=0.03 M4=0.03 M5=0.015	DP-25641 Trial 11
Newberry, FL, USA, 2009 (Southern Giant Curled) Mustard Greens/	3	0.15	70	220	5, 6	1	leaves	6.8, 9.1	8.0	M1=0.06 M2=0.02 M4=0.09 M5=0.02	DP-25641 Trial 29
North Rose, NY, USA, 2009 (Savanna) Mustard Greens/	3	0.15	53	290	5	1	leaves	3.6, 3.1	3.4	M1=0.02 M2=0.02 M4=0.07 M5=0.02	DP-25641 Trial 26
Raymondville, TX, USA, 2008 (Florida Broadleaf) Mustard Greens/	3	0.15	40	380	5	1	leaves	14, 13	13	M1=0.07 M2=0.07 M3=0.01 M4=0.12 M5=0.04	DP-25641 Trial 10

MUSTARD GREENS Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Seven Springs, NC, USA, 2009 (Southern Giant Curled) Mustard Greens/	3	0.15	59	260	5	1	leaves	20, 17	19	M1=0.22 M2=0.08 M3=0.02 M4=0.23 M5=0.11	DP-25641 Trial 27
Terra Bella, CA, USA, 2008 (Southern Giant Curled) Mustard Greens/	3	0.15	70	220	5	1	leaves	5.4, 5.7	5.5	M1=0.04 M2=0.02 M4=0.1 M5=0.02	DP-25641 Trial 12
Washington, LA, USA, 2009 (Florida Broadleaf) Mustard Greens/	3	0.15	70	220	5	1	leaves	4.5, 9.9	7.2	M1=0.12 M2=0.05 M4=0.19 M5=0.03	DP-25641 Trial 30
Terra Bella, CA, USA, 2008 (Southern Giant Curled) Mustard Greens/	1+ 1+ 1	0.2 (soil) 0.1 0.15	97 47 70	200 220 220	— 5	1	leaves	3.0, 3.3	3.1	M1=0.02 M2=0.03	DP-25641 Trial 12 soil inject at planting+ 2 foliar sprays

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

M3: Average residues of metabolite IN-N7B69

M4: Average residues of metabolite IN-MLA84

M5: Average residues of metabolite IN-JCZ38

Soil injection (shank) treatment rate was 1.8 g ai/100 metres of row

Table 131 Residues in field scarole from supervised trials in Europe involving soil (drip irrigation) applications of cyantraniliprole (SC formulation)

SCAROLE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M2	M4	
Lorgies S France, 2009 (Sacha)	3	0.1	5	2010		–0 0 1 3	leaves	ND 0.09 0.006 ND				DP-27713 Test 08
Chalkidona Greece, 2009 (Full Heart)	3	0.1	5	2000		–0 0 1 3	leaves	0.017 0.076 0.05 0.036				DP-27713 Test 09
Torrevecchia Pia Italy, 2009 (Samoa)	3	0.1	5	2000		–0 0 1 3	leaves	0.011 ND 0.005 0.036				DP-27713 Test 10

Table 132 Residues in field scarole from supervised trials in Europe involving three foliar applications of cyantraniliprole (OD formulation)

SCAROLE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments	
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)				cyantraniliprole	metabolites			
										M1	M2		M4
Lorgies S France, 2009 (Sacha)	3	0.08	9.8	810		-0 0 1 3	leaves	0.083 0.12 0.056 0.059				DP-27713 Test 08	
Chalkidona Greece, 2009 (Full Heart)	3	0.08	9.8	800		-0 0 1 3	leaves	0.21 3.3 4.3 2.4	0.01 0.01		0.01	DP-27713 Test 09	
Torrevecchia Pia Italy, 2009 (Samoa)	3	0.08	9.8	810		-0 0 1 3	leaves	0.65 1.4 1.2 0.66	0.01		0.01 0.01 0.02 0.01	DP-27713 Test 10	

M1: Average residues of metabolite IN-J9Z38

M4: Average residues of metabolite IN-MLA84

Table 133 Residues in protected scarole from supervised trials in Europe involving soil (drip irrigation) applications of cyantraniliprole (SC formulation)

SCAROLE Location	Application					DAT (days)	Matrix	Residues (mg/kg)		Reference & Comments
Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites	
Utrera Spain, 2009 (Tosca)	3	0.1	5	2000	7	−0 0 1 3	leaves	0.01 0.02 0.014 0.022		DP-28200 Test 17
Roncoferraro Italy, 2009 (Nuance)	3	0.1	5	2000	6, 7	−0 0 1 3	leaves	0.032 0.1 0.091 0.015		DP-28200 Test 18
Lleida Spain, 2009 (Zigal)	3	0.1	5	2000	7	−0 0 1 3	leaves	0.035 0.011 0.022 0.025		DP-28200 Test 19

Table 134 Residues in protected scarole from supervised trials in Europe involving foliar applications of cyantraniliprole (SC formulation)

SCAROLE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites		
									M1	M4	
Dommartin France, 2010 (Natadia)	3	0.08	9.7	820	7	-0 0 1 3	leaves	1.4 3.4 2.7 2.2		0.01 0.02 0.01 0.01	DP-28200 Test 07

SCAROLE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments	
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M4		
Los Palacios Spain, 2009 (Seychel)	3	0.08	9.7	820	7	–0	leaves	0.8	0.01	0.01	DP-28200 Test 08	
								2.2		0.02		
						1		1.3		0.01		
						3		1.8		0.01		0.02
Utrera Spain, 2009 (Tosca)	3	0.08	9.7	810	7	–0	leaves	1.6	0.01	0.03	DP-28200 Test 17	
						0		4.3		0.01		0.04
						1		5.3		0.01		0.02
						3		3.3				
Roncoferraro Italy, 2009 (Nuance)	3	0.08	9.7	800	6, 7	–0	leaves	1.8	0.02	0.02	DP-28200 Test 18	
						0		3.4		0.02		0.03
						1		2.8		0.01		0.02
						3		2.1				0.02
Lleida Spain, 2009 (Zigal)	3	0.08	9.8	800	7	–0	leaves	0.1			DP-28200 Test 19	
						0		0.91				
						1		1.3				
						3		0.19				

M1: Average residues of metabolite IN-J9Z38

M4: Average residues of metabolite IN-MLA84

Legume vegetables

In trials conducted in Europe on common beans in the field and grown under protection, two applications of 0.09 kg ai/ha cyantraniliprole (OD formulation) were applied 7 days apart, using 800 L spray mix/ha with added surfactants in the protected crops but not in the field crops.

Samples of pods (with seeds) and foliage (leaves and stems) were stored at –18 °C for up to 7 months before extraction and analysis for cyantraniliprole and six metabolites analysis (within 2 days of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 90–106% (cyantraniliprole) and 84–93% (metabolites) in samples spiked with 0.01, 0.1, 0.2, 0.6 and 1.0 mg/kg and also 8 mg/kg cyantraniliprole in foliage.

Table 135 Residues in field common beans from supervised trials in Europe involving two foliar applications of cyantraniliprole (OD formulation)

COMMON BEAN Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments	
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites				
									M1	M2	M4		
Lleida Spain, 2009 (Festival)	2	0.09	11	820	7	1	foliage pods	4.9 0.22	0.14		0.05	DP-27710 Test 01	
Palioura Greece, 2009 (Magirus)	2	0.09	11	800	7	1	foliage pods	5.5 0.16	0.02	0.02		DP-27710 Test 02	
Herlies N France, 2009 (Arras)	2	0.09	11	780	7	1	foliage pods	2.0 0.19	0.01			DP-27710 Test 03	

COMMON BEAN Location	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments		
Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites					
									M1	M2	M4			
Emilia Romagna Italy, 2009 (Flavio)	2	0.09	11	810	7	-0	foliage	0.31	0.02			DP-27710 Test 04		
						0		4.9					0.01	
						1		1.7					0.01	
						3		1.8					0.01	
						-0	pods	0.023						
						0		0.27						
						1		0.13						
						3		0.12						
Tayrac S France, 2009 (Banga)	2	0.09	11	800	8	-0	foliage	0.22	0.02		0.01	DP-27710 Test 05		
						0		7.1					0.05	0.01
						1		4.3					0.05	0.01
						3		1.9					0.03	
						-0	pods	0.062						
						0		0.75					0.01	
						1		0.54					0.01	
						3		0.36					0.01	

Foliage=leaves and stems (without pods)

Pods includes seeds

M1: Residues of metabolite IN-J9Z38

M2: Residues of metabolite IN-MYX98

M3: Residues of metabolite IN-N7B69

Table 136 Residues in protected common beans from supervised trials in Europe involving two foliar applications of cyantraniliprole (OD formulation)

COMMON BEAN	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments
Location Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M2	M4	
Chiclana de la Frontera Spain, 2009 (Emerite)	2	0.09	12	790	7	−0 0 1 3 7 14	Pods	0.052 0.14 0.17 0.13 0.1 0.043				DP-21413 Test 08
La Sentiu de Sio Spain, 2008 (Nuria)	2	0.1	12	830	7	−0 0 1 3 7 14	Pods	0.029 0.044 0.12 0.099 0.023 0.016				DP-21413 Test 02
La Sentiu de Sio Spain, 2009 (Kilie)	2	0.1	12	820	7	1	Pods	0.42				DP-21413 Test 07
Nea Magnisia Greece, 2009 (Trebona)	2	0.1	12	800	7	1	Pods	0.14				DP-21413 Test 06

COMMON BEAN	Application					DAT (days)	Matrix	Residues (mg/kg)				Reference & Comments
Location Country, year (variety)	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	metabolites			
									M1	M2	M4	
Palefito Greece, 2008 (Trebona)	2	0.1	12	800	7	−0 0 1 3 7 14	Pods	0.058 0.19 0.16 0.063 0.067 0.021				DP-21413 Test 04
Roncoferraro Italy, 2008 (Bronco)	2	0.1	12	800	7	−0 0 1 3 7 14	Pods	0.13 0.49 0.36 0.19 0.22 0.11				DP-21413 Test 01
Roncoferraro Italy, 2009 (Slankette)	2	0.1	12	820	7	1	Pods	0.44	0.02			DP-21413 Test 05
St Chamond S France, 2008 (Hemerite)	2	0.1	12	810	7	−0 0 1 3 7 14	Pods	0.27 0.94 0.81 0.81 0.55 0.45	0.01			DP-21413 Test 03
St Chamond S France, 2009 (Hemerite)	2	0.1	12	810	7	1	Pods	0.16				DP-21413 Test 09

M1: Residues of metabolite IN-J9Z38

Tuber vegetables

In trials conducted with cyantraniliprole on potatoes in North America, plots were treated with either a pre-planting seed treatment (FS formulation) followed by one late season foliar spray (OD formulation) or with three late season foliar spray applications (OD formulation). Potato seed was treated with 13.5 g ai cyantraniliprole/100 kg of seed (equivalent to 0.15 kg ai/ha based on 2200 kg seed/ ha) and the foliar application was 0.15 kg ai/ha with added surfactant.

In several trials, additional plots were treated with three late season foliar applications of an SE formulation of cyantraniliprole (with added surfactant) or with a pre-plant in-furrow soil treatment (0.3 kg ai/ha, SC formulation) followed by a single late season foliar spray application (0.15 kg ai/ha, OD formulation).

Samples of tubers were stored at -20 °C for up to 11 months before analysis (within 3 months after extraction) for cyantraniliprole and eight metabolites using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 95% (cyantraniliprole) and 97–102% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Table 137 Residues in potato tubers from supervised trials in North America involving three foliar applications of cyantraniliprole (OD or 100 SE formulations)

POTATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Alton, NY USA, 2009 (Superior)	3	0.15	40	370	4, 6	6	tubers	< 0.01, < 0.01	< 0.01		DP-27583 Test 01
Alton, NY USA, 2009 (Superior)	3	0.15	40	370	4, 6	6	tubers	< 0.01, < 0.01	< 0.01		DP-27583 Test 01 [100 SE]
Berwick, NS CAN, 2009 (Goldrush)	3	0.15	36	420	6, 4	8	tubers	0.02, 0.016	0.018		DP-27583 Test 04
Fort Saskatchewan, AB CAN, 2009 (Yukon gold)	3	0.15	50	300	5	7	tubers	ND, < 0.01	ND		DP-27583 Test 21
Gardner, ND USA, 2009 (Gold Rush)	3	0.15				7	tubers	< 0.01, < 0.01	< 0.01		DP-27583 Test 12
Germansville, PA USA, 2009 (Reba)	1+ 2	0.14 0.15	50 50	330 300	5, 4	7	tubers	ND, < 0.01	ND		DP-27583 Test 02
Inglisville, NS CAN, 2009 (Superior)	3	0.15	36	420	6, 5	8	tubers	0.011, 0.01	0.011		DP-27583 Test 05
Jerome, ID USA, 2009 (Norland)	3	0.15	79	190	7	7	tubers	ND, ND	ND		DP-27583 Test 14
Jerome, ID USA, 2009 (Russet Burbank)	3	0.15	80	190	4, 5	7	tubers	ND, ND	ND		DP-27583 Test 18
Merritt, BC CAN, 2009 (Russet Burbank)	3	0.15	30	490	5	6	tubers	0.021, 0.018	0.02		DP-27583 Test 16
Merritt, BC CAN, 2009 (Russet Burbank)	3	0.15	30	490	5	6	tubers	0.021, 0.021	0.021		DP-27583 Test 16 [100 SE]
Merritt, BC CAN, 2009 (Russet Burbank)	3	0.15	63	240	5	7	tubers	< 0.01, < 0.01	< 0.01		DP-27583 Test 17
New Glasgow, PE CAN, 2009 (Gold Rush)	3	0.15	73	200	6	7	tubers	< 0.01, < 0.01	< 0.01		DP-27583 Test 07

POTATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
New Glasgow, PE CAN, 2009 (Yukon Gold)	3	0.14 0.15	73 73	200 190	6	7	tubers	ND, ND	ND		DP-27583 Test 06
North Rose, NY USA, 2009 (Superior)	3	0.16	80	190	5	7	tubers	ND, ND	ND		DP-27583 Test 03
Northwood, ND USA, 2009 (Pontiac)	3	0.15	79	190	5, 7	7	tubers	ND, ND	ND		DP-27583 Test 11
Oviedo, FL USA, 2009 Fall application (Red Chieftain)	3	0.15	55	280	4	7	tubers	< 0.01, < 0.01	< 0.01		DP-27583 Test 09
Oviedo, FL USA, 2009 Fall application (Red Chieftain)	3	0.15	54	280	4	7	tubers	< 0.01, < 0.01	< 0.01		DP-27583 Test 09 [100 SE]
Oviedo, FL USA, 2009 Spring application (Red Pontiac)	3	0.15	53	280	4	6	tubers	0.033, 0.034	0.034		DP-27583 Test 09
Oviedo, FL USA, 2009 Spring application (Red Pontiac)	3	0.15	53	280	4	6	tubers	0.035, 0.026	0.03		DP-27583 Test 09 [100 SE]
Payette, ID USA, 2009 (Russet Norkatah)	3	0.15	64	230	5	7	tubers	ND, < 0.01	ND		DP-27583 Test 20
Portage la Prairie, MB CAN, 2009 (Umatilla Russet)	3	0.15	74	200	5, 6	8	tubers	ND, ND	ND		DP-27583 Test 10
Richland, IA USA, 2009 (Kennebec)	3	0.15	77	190	4, 5	7	tubers	ND, ND	ND		DP-27583 Test 13
Sanger, CA USA, 2009 (Red La Soda)	3	0.15	37	400	5	7	tubers	ND, ND	ND		DP-27583 Test 15
Seven Springs, NC USA, 2009 (Red Pontiac)	3	0.15	71	220	6, 4	7	tubers	< 0.01, < 0.01	< 0.01		DP-27583 Test 08

POTATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Seven Springs, NC USA, 2009 (Red Pontiac)	3	0.15	70	200	6, 4	7	tubers	< 0.01, < 0.01	< 0.01		DP-27583 Test 08 [100 SE]

Table 138 Residues in potato tubers from supervised trials in North America involving seed treatment (or in-furrow) plus one foliar applications of cyantraniliprole

POTATO Location Country, year (variety)	Application				DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	g ai/ 100 kg seed	kg ai/ha	water L/ha			cyantraniliprole	mean	metabolites	
Alton, NY USA, 2009 (Superior)	1+ 1	13.5	0.15	370	6	tubers	0.037, < 0.01	0.023	M1=0.01	DP-27583 Test 01
Germansville, PA USA, 2009 (Reba)	1+ 1	13.5	0.15	300	7	tubers	0.027, 0.027	0.027	M1=0.01	DP-27583 Test 02
North Rose, NY USA, 2009 (Superior)	1+ 1	13.5	0.15	190	7	tubers	ND, ND	ND		DP-27583 Test 03
Berwick, NS CAN, 2009 (Goldrush)	1+ 1	13.5	0.15	420	8	tubers	0.019, 0.027	0.023		DP-27583 Test 04
Inglisville, NS CAN, 2009 (Superior)	1+ 1	13.5	0.15	420	8	tubers	0.052, 0.052	0.052		DP-27583 Test 05
New Glasgow, PE CAN, 2009 (Yukon Gold)	1+ 1	13.5	0.15	200	7	tubers	< 0.01, 0.011	0.01	M1=0.01	DP-27583 Test 06
New Glasgow, PE CAN, 2009 (Gold Rush)	1+ 1	13.5	0.15	200	7	tubers	0.028, 0.033	0.031	M1=0.03	DP-27583 Test 07
Seven Springs, NC USA, 2009 (Red Pontiac)	1+ 1	13.5	0.15	220	7	tubers	0.11	0.11	M1=0.02	DP-27583 Test 08
Oviedo, FL USA, 2009 Fall (Red Chieftain)	1+ 1	13.5	0.15	280	7	tubers	0.012, 0.011	0.011		DP-27583 Test 09
Portage la Prairie, MB CAN, 2009 (Umatilla Russet)	1+ 1	13.5	0.15	200	8	tubers	< 0.01 (3)	< 0.01		DP-27583 Test 10
Northwood, ND USA, 2009 (Pontiac)	1+ 1	13.5	0.15	370	7	tubers	ND, 0.021, < 0.01	< 0.01		DP-27583 Test 11

POTATO Location Country, year (variety)	Application				DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	g ai/ 100 kg seed	kg ai/ha	water L/ha			cyantraniliprole	mean	metabolites	
Gardner, ND USA, 2009 (Gold Rush)	1+ 1	13.5	0.15	190	7	tubers	0.019, 0.021, 0.019	0.02		DP-27583 Test 12
Richland, IA USA, 2009 (Kennebec)	1+ 1	13.5	0.15	190	7	tubers	< 0.01, < 0.01	< 0.01		DP-27583 Test 13
Jerome, ID USA, 2009 (Norland)	1+ 1	13.5	0.15	190	7	tubers	< 0.01, ND	< 0.01		DP-27583 Test 14
Sanger, CA USA, 2009 (Red La Soda)	1+ 1	13.5	0.15	400	7	tubers	0.014, < 0.01	0.01		DP-27583 Test 15
Merritt, BC CAN, 2009 (Russet Burbank)	1+ 1	13.5	0.15	490	6	tubers	0.035, 0.11	0.072		DP-27583 Test 16
Payette, ID USA, 2009 (Ranger Russet)	1+ 1	13.5	0.15	240	7	tubers	ND, < 0.01	< 0.01		DP-27583 Test 17
Jerome, ID USA, 2009 (Russet Burbank)	1+ 1	13.5	0.15	190	7	tubers	< 0.01, 0.05	0.028		DP-27583 Test 18
Ephrata, WA USA, 2009 (Ranger Russet)	1+ 1	13.5	0.15	190	-0 0 1 5 7	tubers	ND, ND ND, < 0.01 ND, < 0.01 ND, ND ND, ND	ND ND ND ND ND		DP-27583 Test 19
Payette, ID USA, 2009 (Russet Norkatah)	1+ 1	13.5	0.15	230	7	tubers	0.01, < 0.01	< 0.01		DP-27583 Test 20
Fort Saskatchewan, AB CAN, 2009 (Yukon gold)	1+ 1	13.5	0.15	300	7	tubers	0.012, 0.016	0.014		DP-27583 Test 21
Ephrata, WA USA, 2009 (Ranger Russet)	1+ 1	in furrow foliar	0.32 0.15	140 190	7	tubers	ND, ND	ND		DP-27583 Test 19

M1: Average residues of metabolite IN-J9Z38

Note: Second sample from Test site 8 reported high residues (cyantraniliprole 3.1 ppm) attributed to the selection of a treated seed piece

In trials conducted with cyantraniliprole on potatoes in Europe, plots were treated with two foliar applications of cyantraniliprole (OD formulation) with and without added surfactant. Targeted application rates were 0.01 kg ai/ha or 0.08 kg ai/ha, applied about 7 days apart using 450–500 L water/ha.

Samples of tubers were stored at -18 °C for up to 8 months before analysis (within 2 days after extraction) for cyantraniliprole and six metabolites using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 97% (cyantraniliprole) and 88–101% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Table 140 Residues in potato tubers from supervised trials in Europe involving foliar applications of cyantraniliprole (OD formulation)

POTATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Ballencrieff Mains UK North, 2008 (Maris Piper)	2	0.01	2.2	410	7	0 0 7 14	tuber	ND ND ND ND			DP-21414 Test 5a
Ballencrieff Mains UK, 2008 (Maris Piper)	2	0.08	18	460	7	0 0 7 14	tuber	ND ND ND ND			DP-21414 Test 5b (with surfactant)
Castello de Farfanya Spain, 2008 (Kenebec)	2	0.01	2.2	470	7	0 0 7 14	tuber	ND ND ND ND			DP-21414 Test 8a
Castello de Farfanya Spain, 2008 (Kenebec)	2	0.08	18	440	7	0 0 7 14	tuber	ND ND ND ND			DP-21414 Test 8b (with surfactant)
Cervesina Italy, 2008 (Dejsy)	2	0.01	2.2	450	7	14	tuber	ND			DP-21414 Test 6a
Cervesina Italy, 2008 (Dejsy)	2	0.08	18	450	7	14	tuber	ND			DP-21414 Test 6b (with surfactant)
Douai N France, 2008 (Marabella)	2	0.01	2.2	460	7	0 0 7 14	tuber	ND ND ND ND			DP-21414 Test 1a
Douai N France, 2008 (Marabella)	2	0.08	18	450	7	0 0 7 14	tuber	ND ND ND ND			DP-21414 Test 1b (with surfactant)
Galatades Greece, 2008 (Spunta)	2	0.01	2.2	460	7	14	tuber	ND			DP-21414 Test 7a
Galatades, Greece, 2008 (Spunta)	2	0.08	18	470	7	14	tuber	ND			DP-21414 Test 7b (with surfactant)
Herlies N France, 2008 (Bintje)	2	0.01	2.2	450	8	14	tuber	ND			DP-21414 Test 2a
Herlies N France, 2008 (Bintje)	2	0.08	18	470	8	14	tuber	ND			DP-21414 Test 2b (with surfactant)
Le Mas Riller S France, 2008 (Mona Lisa)	2	0.01	2.2	460	7	0 0 7 14	tuber	ND ND ND ND			DP-21414 Test 10a
Le Mas Riller S France, 2008 (Mona Lisa)	2	0.08	18	460	7	0 0 7 14	tuber	ND ND ND ND			DP-21414 Test 10b (with surfactant)

POTATO Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Motterwitz Germany, 2008 (Secura)	2	0.01	2.2	430	7	14	tuber	ND			DP-21414 Test 3a
Motterwitz Germany, 2008 (Secura)	2	0.08	18	470	7	14	tuber	ND			DP-21414 Test 3b (with surfactant)
Prušánky Czech Republic, 2008 (Impala)	2	0.01	2.2	470	8	14	tuber	ND			DP-21414 Test 4a
Prušánky Czech Republic, 2008 (Impala)	2	0.08	18	450	8	14	tuber	ND			DP-21414 Test 4b (with surfactant)
Tora Spain, 2008 (Kenebec)	2	0.01	2.2	470	8	14	tuber	ND			DP-21414 Test 9a
Tora Spain, 2008 (Kenebec)	2	0.08	18	460	8	14	tuber	ND			DP-21414 Test 9b (with surfactant)

Stalk and stem vegetables

In trials conducted in the USA on celery, two or three foliar applications of 0.15 kg ai/ha cyantraniliprole (OD formulation) were applied at 5 day intervals, using 200–500 L/ha, with adjuvant added. Soil treatment plots were also included at several trial sites, either as a soil shank (in furrow) treatment of 0.2 kg ai/ha (SC formulation) at planting or two soil treatments of 0.15 kg ai/ha cyantraniliprole (SC formulation) applied through drip-line irrigation systems (adjusted to pH 4–5, with no added adjuvant).

Duplicate samples of celery (with tops and also trimmed/washed) were stored at –20 °C for up to 9 months before extraction and analysis for cyantraniliprole and six metabolites (within 3 months of extraction) using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 96–98% (cyantraniliprole) and 80–106% (metabolites) in samples spiked with 0.01–10 mg/kg.

Table 140 Residues in celery from supervised trials in North America involving soil applications at planting or through dripline irrigation systems (with foliar applications)

CELERY Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Sparta, MI USA, 2009 Celery (Sabroso)	1	0.15	0.42	36000		0 3 7	with tops	ND, ND ND, ND ND, ND	ND ND ND		DP-25644 Trial 45 [by drip irrigation]
Sparta, MI USA, 2009 Celery (Sabroso)	2	0.15	0.42	36000	7	–0 0 3 7	with tops	ND, ND ND, ND ND, < 0.01 ND, ND	ND ND ND ND		DP-25644 Trial 45 [by drip irrigation]

CELERY Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Porterville, CA USA, 2008 Celery (Challenger)	1+ 1+ 1	0.2 0.1 0.15	97 41 62	210 240 240	77 5	1	with tops	3, 4.1	3.5	M1=0.02	DP-25644 Trial 14 [1 soil shank treatment + 2 foliar sprays]
Sparta, MI USA, 2009 Celery (Sabroso)	2+ 1	0.15 0.15	0.42 47	36000 320	7 7	-0 1	with tops	ND, ND 1.1, 0.98	ND 1.0		DP-25644 Trial 45 2 [by drip irrigation + 1 foliar]

Soil (shank) treatment rate of 2 g ai/100 metres of row (Trial 14)

Soil (dripline irrigation) treatment rate of 1.5 g ai/100 metres of row (Trial 45)

M1: Average residues of metabolite IN-J9Z38

Table 141 Residues in celery from supervised trials in North America involving two or three foliar applications of cyantraniliprole (OD formulation)

CELERY Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Bradenton, FL USA, 2008 Celery (Tall Utah)	2	0.15	36	420	5	1	with tops	5.3, 5.7	5.5	M1=0.03 M2=0.02	DP-25644 Trial 13
						1	trimmed	4.4, 3.5	4.0	M1=0.02 M2=0.01	
Porterville, CA USA, 2008 Celery (Challenger)	2	0.15	62	240	5	1	with tops	4.4, 5.5	5	M1=0.02	DP-25644 Trial 14
Santa Maria, CA USA, 2008 Celery (Conquistador)	2	0.15	54	280	5	1	with tops	1, 0.84	0.92		DP-25644 Trial 15
Fresno, CA USA, 2008 Celery (Command)	2	0.15	54	280	5	1	with tops	2.1, 1.7	1.9	M1 =.02	DP-25644 Trial 16
Guadalupe, CA USA, 2008 Celery (Conquistador)	2	0.15	64	230	5	1	with tops trimmed	1.5, 1.0 0.7, 0.76	1.3 0.73		DP-25644 Trial 17

CELERY Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
King City, CA USA, 2008 Celery (G15)	2	0.15	51	290	6	1	with tops trimmed	0.62, 0.73 0.34, 0.46	0.68 0.4		DP-25644 Trial 18
Bradenton, FL USA, 2008 Celery (Tall Utah)	3	0.15	37	430	5	1	with tops trimmed	8.8, 9.5 4.2, 5.4	<u>9.1</u> 4.8	M1=0.04 M2=0.03 M1=0.02 M2=0.01	DP-25644 Trial 13
Branchton, ON CAN, 2009 Celery (Florida 683)	3	0.15	74	200	5, 6	1	with tops	2.4, 2.2	2.3	M1=0.02	DP-25644 Trial 42
Delavan, WI USA, 2009 Celery (XP266)	3	0.15	70	220	5	1	with tops	2.1, 1.9	2.0	M1=0.02	DP-25644 Trial 43
Fitchburg, WI USA, 2009 Celery (Tango)	3	0.15	60	250	5	1	with tops	0.31, 0.24	0.28	M1=0.01	DP-25644 Trial 41
Fresno, CA USA, 2008 Celery (Command)	3	0.15	54	280	5	1	with tops	2.3, 2.6	2.5	M1=0.02	DP-25644 Trial 16
Guadalupe, CA USA, 2008 Celery (Conquistador)	3	0.15	66	230	5	1	with tops trimmed	0.37, 1.7 0.81, 0.97	<u>1.1</u> 0.89		DP-25644 Trial 17
King City, CA USA, 2008 Celery (G15)	2+ 1	0.15 0.16	51 52	290 300	6 5	1	with tops trimmed	0.9, 0.57 0.45, 0.29	<u>0.73</u> 0.37		DP-25644 Trial 18
Porterville, CA USA, 2008 Celery (Challenger)	3	0.15	62	240	5	1	with tops	6.3, 5.1	5.7	M1=0.02	DP-25644 Trial 14
Richland, IA USA, 2009 Celery (Conquistador Pelleted)	3	0.15	74	210	5	1	with tops	4.7, 4.8	4.7	M1=0.04 M2=0.01	DP-25644 Trial 44
Santa Maria, CA USA, 2008 Celery (Conquistador)	3	0.15	54	280	5	1	with tops	1, 1.1	1.0		DP-25644 Trial 15

CELERY Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	kg ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Sparta, MI USA, 2009 Celery (Sabroso)	3	0.15	47	320	5	1	with tops	1.2, 1.2	1.2	M1=0.02	DP-25644 Trial 45

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

Cereals

In three trials on rice, conducted in China, cyantraniliprole (OD formulation) was applied two or three times as foliar sprays, using either 0.1 kg ai/ha or 0.15 kg ai/ha, with a 7 day retreatment interval. No adjuvants were used.

Samples of threshed brown rice, hulls and straw (leaves and stalks) were stored at -20 °C until analysed for cyantraniliprole and the metabolite IN-J9Z38 using an aqueous acetonitrile extraction and LC-MS/MS analysis method based on method DP-15736. The reported LOQs for cyantraniliprole were 0.01 mg/kg in grain and 0.05 mg/kg in hulls and straw, and the LOQs for IN-J9Z38 were 0.02 mg/kg in grain and 0.1 mg/kg in hulls and straw. Average concurrent recoveries were 78-103% (cyantraniliprole) and 79-102% (IN-J9Z38) in samples spiked with 0.01, 0.05, 0.1, 1.0 mg/kg and also 2.0 mg/kg ((IN-J9Z38).

Table 142 Residues in rice grain and hulls from supervised trials in China involving foliar applications of cyantraniliprole (100 FC formulation)

RICE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	M1	
Hangzhou Zhejiang China 2011 (Xiu Shui 009)	2	0.1			7	7	grain	< 0.01		< 0.02	CL-2010-026 Site 1-11
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	0.67		0.1	
						14		0.37		< 0.1	
						21		0.43		< 0.1	
						7	straw	< 0.05		0.21	
						14		< 0.05		0.12	
						21		< 0.05		< 0.1	
Hangzhou Zhejiang China, 2010 (Xiu Shui 009)	2	0.1			7	7	grain	< 0.01		< 0.02	CL-2010-026 Site 1-10
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	3.3		0.28	
						14		4.3		0.35	
						21		2.3		0.2	
						7	straw	0.67		0.29	
						14		1.4		0.28	
						21		1.1		0.2	

RICE Location Country, year (variety)	Application				DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha			cyantraniliprole	mean	M1	
Hunan, Changsha China, 2010 (Yue You 712)	2	0.1			7	7	grain	< 0.01	< 0.02	CL-2010-026 Site 2-10
						14		< 0.01	< 0.02	
						21		< 0.01	< 0.02	
						7	hulls	0.99	< 0.1	
						14		1.1	< 0.1	
						21		0.92	< 0.1	
						7	straw	< 0.05	< 0.01	
						14		0.083	< 0.01	
						21		0.057	< 0.01	
Hunan, Changsha China, 2011 (Yue You 712)	2	0.1			7	7	grain	< 0.01	< 0.02	CL-2010-026 Site 2-11
						14		< 0.01	< 0.02	
						21		< 0.01	< 0.02	
						7	hulls	1.4	< 0.1	
						14		1.4	< 0.1	
						21		1.6	< 0.1	
						7	straw	0.15	< 0.1	
						14		0.098	< 0.1	
						21		0.18	< 0.1	
Jinan, Shandong China, 2010 (Xin Dao 16)	2	0.1			7	7	grain	< 0.01	< 0.02	CL-2010-026 Site 3-10
						14		< 0.01	< 0.02	
						21		< 0.01	< 0.02	
						7	hulls	0.46	< 0.1	
						14		0.38	< 0.1	
						21		0.32	< 0.1	
						7	straw	0.27	< 0.1	
						14		0.14	< 0.1	
						21		0.4	< 0.1	
Jinan, Shandong China, 2011 (Xin Dao 16)	2	0.1			7	7	grain	< 0.01	< 0.02	CL-2010-026 Site 3-11
						14		< 0.01	< 0.02	
						21		< 0.01	< 0.02	
						7	hulls	0.081	< 0.1	
						14		0.092	< 0.1	
						21		0.57	< 0.1	
						7	straw	0.2	< 0.1	
						14		0.13	< 0.1	
						21		0.075	< 0.1	

RICE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	M1	
Hangzhou Zhejiang China 2011 (Xiu Shui 009)	2	0.15			7	7	grain	0.023		< 0.02	CL-2010-026 Site 1-11
						14		0.016		< 0.02	
						21		0.01		< 0.02	
						7	hulls	1.7		0.21	
						14		1.2		0.2	
						21		0.95		0.17	
						7	straw	0.12		0.5	
						14		0.063		0.46	
						21		0.075		0.16	
Hangzhou Zhejiang China, 2010 (Xiu Shui 009)	2	0.15			7	7	grain	0.02		< 0.02	CL-2010-026 Site 1-10
						14		0.013		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	7.5		0.92	
						14		12		0.76	
						21		3.4		0.41	
						7	straw	1.1		0.46	
						14		3.7		0.47	
						21		1.9		0.31	
Hunan, Changsha China, 2010 (Yue You 712)	2	0.15			7	7	grain	< 0.01		< 0.02	CL-2010-026 Site 2-10
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	1.4		< 0.1	
						14		2.2		< 0.1	
						21		1.5		< 0.1	
						7	straw	0.37		< 0.1	
						14		0.33		< 0.1	
						21		0.17		< 0.1	
Hunan, Changsha China, 2011 (Yue You 712)	2	0.15			7	7	grain	0.07		< 0.02	CL-2010-026 Site 2-11
						14		0.029		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	8.2		< 0.1	
						14		6.8		< 0.1	
						21		2.2		< 0.1	
						7	straw	0.42		< 0.1	
						14		1.1		< 0.1	
						21		0.13		< 0.1	

RICE Location Country, year (variety)	Application				DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha			cyantraniliprole	mean	M1	
Jinan, Shandong China, 2010 (Xin Dao 16)	2	0.15			7	7	grain	< 0.01	< 0.02	CL-2010-026 Site 3-10
						14		< 0.01	< 0.02	
						21		< 0.01	< 0.02	
						7	hulls	0.92	< 0.1	
						14		0.18	0.1	
						21		0.14	< 0.1	
						7	straw	0.31	< 0.1	
						14		0.33	0.1	
						21		< 0.05	< 0.1	
Jinan, Shandong China, 2011 (Xin Dao 16)	2	0.15			7	7	grain	< 0.01	< 0.02	CL-2010-026 Site 3-11
						14		< 0.01	< 0.02	
						21		< 0.01	< 0.02	
						7	hulls	< 0.05	< 0.1	
						14		< 0.05	< 0.1	
						21		< 0.05	< 0.1	
						7	straw	0.25	< 0.1	
						14		0.18	< 0.1	
						21		0.079	< 0.1	
Hangzhou Zhejiang China 2011 (Xiu Shui 009)	3	0.1			7	7	grain	< 0.01	< 0.02	CL-2010-026 Site 1-11
						14		< 0.01	< 0.02	
						21		< 0.01	< 0.02	
						7	hulls	1.2	0.18	
						14		0.71	0.16	
						21		0.42	0.096	
						7	straw	< 0.05	0.24	
						14		0.095	0.24	
						21		< 0.05	< 0.1	
Hangzhou Zhejiang China, 2010 (Xiu Shui 009)	3	0.1			7	7	grain	0.01	< 0.02	CL-2010-026 Site 1-10
						14		< 0.01	< 0.02	
						21		< 0.01	< 0.02	
						7	hulls	4.6	0.55	
						14		3.7	0.52	
						21		1.7	0.37	
						7	straw	0.78	0.34	
						14		1.9	0.24	
						21		1.4	0.16	

RICE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	M1	
Hunan, Changsha China, 2010 (Yue You 712)	3	0.1			7	7	grain	< 0.01		< 0.02	CL-2010-026 Site 2-10
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	0.87		< 0.1	
						14		1.1		< 0.1	
						21		1.4		< 0.1	
						7	straw	0.085		< 0.1	
						14		0.058		< 0.1	
						21		< 0.05		< 0.1	
						7	grain	0.018		< 0.02	CL-2010-026 Site 2-11
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
Hunan, Changsha China, 2011 (Yue You 712)	3	0.1			7	7	grain	0.018		< 0.02	
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	4.0		< 0.1	
						14		2.5		0.11	
						21		1.6		< 0.1	
						7	straw	0.68		< 0.1	
						14		0.4		< 0.1	
						21		0.35		< 0.1	
Jinan, Shandong China, 2010 (Xin Dao 16)	3	0.1			7	7	grain	< 0.01		< 0.02	CL-2010-026 Site 3-10
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	0.55		< 0.1	
						14		0.71		< 0.1	
						21		0.57		< 0.1	
						7	straw	0.26		< 0.1	
						14		0.44		0.13	
						21		0.28		< 0.1	
Jinan, Shandong China, 2011 (Xin Dao 16)	3	0.1			7	7	grain	< 0.01		< 0.02	CL-2010-026 Site 3-11
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	< 0.05		< 0.1	
						14		0.16		< 0.1	
						21		0.13		< 0.1	
						7	straw	0.34		0.18	
						14		0.2		< 0.1	
						21		0.12		< 0.1	

RICE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	M1	
Hangzhou Zhejiang China 2011 (Xiu Shui 009)	3	0.15			7	7	grain	0.041		< 0.02	CL-2010-026 Site 1-11
						14		0.022		< 0.02	
						21		0.012		< 0.02	
						7	hulls	2.3		0.33	
						14		2.4		0.3	
						21		0.95		0.19	
						7	straw	< 0.05		0.36	
						14		< 0.05		0.59	
						21		0.12		0.39	
Hangzhou Zhejiang China, 2010 (Xiu Shui 009)	3	0.15			7	7	grain	0.035		< 0.02	CL-2010-026 Site 1-10
						14		0.019		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	12		1.4	
						14		11		0.6	
						21		9.9		0.84	
						7	straw	1.8		0.59	
						14		4.1		0.43	
						21		3.0		0.51	
Hunan, Changsha China, 2010 (Yue You 712)	3	0.15				7	grain	< 0.01		< 0.02	CL-2010-026 Site 2-10
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	1.6		< 0.1	
						14		1.8		< 0.1	
						21		2.1		0.1	
						7	straw	0.58		< 0.1	
						14		0.51		< 0.1	
						21		0.36		< 0.1	
Hunan, Changsha China, 2011 (Yue You 712)	3	0.15				7	grain	0.039		< 0.02	CL-2010-026 Site 2-11
						14		0.025		< 0.02	
						21		0.019		< 0.02	
						7	hulls	6.2		< 0.1	
						14		4.1		< 0.1	
						21		2.4		< 0.1	
						7	straw	0.55		< 0.1	
						14		0.26		< 0.1	
						21		0.33		< 0.1	

RICE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	M1	
Jinan, Shandong China, 2010 (Xin Dao 16)	3	0.15				7	grain	< 0.01		< 0.02	CL-2010-026 Site 3-10
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	1.2		< 0.1	
						14		0.21		< 0.1	
						21		0.66		< 0.1	
						7	straw	1.3		0.12	
						14		0.33		< 0.1	
						21		< 0.05		< 0.1	
Jinan, Shandong China, 2011 (Xin Dao 16)	3	0.15				7	grain	< 0.01		< 0.02	CL-2010-026 Site 3-11
						14		< 0.01		< 0.02	
						21		< 0.01		< 0.02	
						7	hulls	< 0.05		< 0.1	
						14		< 0.05		< 0.1	
						21		< 0.05		< 0.1	
						7	straw	0.35		0.11	
						14		0.24		< 0.1	
						21		0.18		< 0.1	

M1: Residues of metabolite IN-J9Z38

Tree nuts

In trials conducted in the USA on almonds and pecans, three foliar (airblast) treatments of 0.15 kg ai/ha cyantraniliprole (OD formulation) were applied at about 7 day intervals using either high volume (1000–3000 L/ha), concentrate (100–800 L/ha) or ultra-low-volume (50 L/ha) sprays, all with adjuvant added. An additional soil (shank) injection side dressing treatment was included in one trial.

Duplicate samples of nutmeat and hulls were stored at –20 °C for up to 6 months before analysis (within 37 days of extraction) for cyantraniliprole and six metabolites using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries in peel and pulp were 81–93% (cyantraniliprole) and 76–97% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Table 143 Residues in almonds from supervised trials in the USA involving foliar applications of cyantraniliprole (OD or SE formulations)

ALMOND Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
(Turlock, CA USA, 2009) (Butte)	3	0.15	26	580	7, 6	5	nutmeat	0.012, 0.012	<u>0.012</u>		DP-27446 Trial 01
							hulls	4.5, 4.6	4.6	M1=0.03 M2=0.01	
Kerman, CA USA, 2009 (Non-Pareil)	3	0.15	32	470	7	5	nutmeat	0.009, 0.01	<u>0.009</u>		DP-27446 Trial 02
							hulls	2.0, 1.7	1.9	M1=0.01	

PECAN Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Pearsall, TX USA, 2009 (Wichita)	1	0.46	490	90		57	nutmeat	ND, ND	ND		DP-27446 Trial 12 [200 SC soil injection]

Oilseed crops

In trials conducted with cyantraniliprole on cotton in the USA, plots were treated with three late season foliar sprays (OD formulation) at a rate of 0.15 kg ai/ha, using 200–500 L water/ha, with added surfactant. In one trial, an additional plot was treated with a pre-plant in-furrow soil treatment (0.2 kg ai/ha, SC formulation) followed by two late season foliar spray applications (0.1–0.15 kg ai/ha, OD formulation).

Samples of cotton seed and cotton gin byproducts were stored at –20 °C for up to 8 months before extraction and analysed within 3 months after extraction for cyantraniliprole and eight metabolites using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 75–76% (cyantraniliprole) and 69–120% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg and also 1.0 and 1.6 mg/kg in cotton seed.

Table 145 Residues in cotton from supervised trials in the USA involving three foliar applications of cyantraniliprole (OD formulation)

COTTON SEED Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Cheneyville, LA USA, 2009 (Phytogen 485WRF)	3	0.16	77	200	7, 6	–0 0 5 7	seed	0.28, 0.2 0.63, 0.58 0.2, 0.14 0.17, 0.2	0.24 0.6 0.17 0.18	M1=0.02 M1=0.02 M1=0.02 M1=0.03	DP-27565 Trial 02
East Bernard, TX USA, 2009 (DP0924 B2F)	3	0.15	77	200	8, 6	–0 0 1 5 7	seed	0.27, 0.33 0.94, 0.66 0.63, 0.89 0.56, 0.82 0.26, 0.26	0.3 0.8 0.76 0.69 0.26	M1=0.05 M1=0.05 M1=0.05 M1=0.07 M1=0.06	DP-27565 Trial 05
Edmonson, TX USA, 2009 (DP 924)	3	0.15	96	160	8, 6	7	seed gin trash	0.83, 1.2 4.3, 5.7	0.99 5	 M1=0.02 M2=0.03	DP-27565 Trial 08
Fisk, MO USA, 2009 (DP 164 B2RF)	3	0.15	80	190	8	8	seed	0.023, 0.027	0.025		DP-27565 Trial 03
Hickman, CA USA, 2009 (Pima)	3	0.15	40	370	7	8	seed	0.2, 0.2	0.2		DP-27565 Trial 11
Hinton, OK USA, 2009 (FM1740B2F)	3	0.15	72	200	8, 9	9	seed gin trash	0.18, 0.13 2.6, 2.6	0.16 2.6	 M1=0.03 M2=0.01	DP-27565 Trial 07

COTTON SEED Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Larned, KS USA, 2009 (Delta Pine)	3	0.15	71	210	7	8	seed	0.27, 0.32	0.29	M1=0.01	DP-27565 Trial 06
Levelland, TX USA, 2009 (9063 B2F)	3	0.15	63	230	7	8	seed gin trash	0.11, 0.12 3.5, 3.5	0.12 3.5	M1=0.07 M2=0.02	DP-27565 Trial 09
Madera, CA USA, 2009 (Acala Riata RR)	3	0.15	64	230	7, 6	7	seed	0.15, 0.12	0.14		DP-27565 Trial 12
Newport, AR USA, 2009 (DP 164 B2RF)	3	0.15	80	190	7	7	seed	0.045, 0.025	0.035		DP-27565 Trial 04
Sanger, CA USA, 2009 (PHY 725 RF Acala)	1+ 2	0.15	54 37	290 400	6 8	7	seed	0.24, 0.21	0.22		DP-27565 Trial 13
Seven Springs, NC USA, 2009 (ST 4554B2RF)	3	0.15	63	240	7	8	seed	0.011, 0.013	0.012		DP-27565 Trial 01
Uvalde, TX USA, 2009 (DP6167 B2RF)	3	0.15	62	230	7	6	seed gin trash	0.1, 0.14 2.8, 2.6	0.12 2.7	M1=0.07 M2=0.01	DP-27565 Trial 10
Larned, KS USA, 2009 (Delta Pine)	1+ 1+ 1	0.19 0.1 0.15	110 48 72	180 210 210	146 7	8	seed	0.16, 0.14	0.15		DP-27565 Trial 06 [soil inject+ 2 foliar]

M1: Average residues of metabolite IN-J9Z38

M2: Average residues of metabolite IN-MYX98

In trials conducted in Australia on cotton, two foliar applications of 0.06 or 0.12 kg ai/ha cyantraniliprole (SE formulations) were applied at 7 day intervals using 120 L water/ha, with added adjuvant. Several of these trials were reverse decline studies, where different plots were treated at staggered intervals so that the sampling dates co-incided with normal commercial harvest.

Samples were stored at –20 °C for up to 1 month before analysis of forage (leaves, stems etc), seeds and field trash for cyantraniliprole and six metabolites (within 4 days after extraction) using analytical method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 95–99% (cyantraniliprole) and 77–101% (metabolites) in samples spiked with 0.01–2.0 mg/kg.

Table 146 Residues in cotton from supervised trials in Australia involving two foliar applications of cyantraniliprole (SE formulation)

COTTONSEED Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Boggabilla, NSW Australia, 2010 (Sicot 71 BRF)	2	0.06	0.05	120	7	7	forage	0.39		M1=0.01	DP-31410 Site 1 [Reverse decline]
						14		0.23		M1=0.01	
						21		0.08			
						28		0.03			
						7	seed	ND			
						14		ND			
						21		ND			
						28		ND			
						7	field trash	1.18		M1=0.05	
						14		0.59		M1=0.03	
						21		0.19			
						28		0.11			
Brookstead, QLD Australia, 2010 (Sicot 71 BRF)	2	0.06	0.05	120	7	14	forage	0.28		M1=0.02	DP-31410 Site 3
						14	seed	ND			
						14	field trash	0.74		M1=0.04	
Toobeah, QLD Australia, 2010 (Sicot 71 BRF)	2	0.06	0.05	120	7	14	forage	0.15		M1=0.01	DP-31410 Site 2
						14	seed	ND			
						14	field trash	0.34		M1 =0.02	
Boggabilla, NSW Australia, 2010 (Sicot 71 BRF)	2	0.12	0.1	120	7	7	forage	0.68		M1=0.03	DP-31410 Site 1 [Reverse decline]
						14		0.38		M1=0.01	
						21		0.12			
						28		0.09			
						7	seed	ND			
						14		ND			
						21		ND			
						28		ND			
						7	field trash	1.85		M1=0.08	
						14		1.01		M1=0.04	
						21		0.47		M1=0.02	
						28		0.16			
Brookstead, QLD Australia, 2010 (Sicot 71 BRF)	2	0.12	0.1	120	7	14	forage	0.43		M1=0.02	DP-31410 Site 3
						14	seed	ND			
						14	field trash	1.22		M1=0.04	
Toobeah, QLD Australia, 2010 (Sicot 71 BRF)	2	0.12	0.1	120	7	14	forage	0.27		M1=0.02	DP-31410 Site 2
						14	seed	ND			
						14	field trash	0.76		M1=0.02	

M1: Average residues of metabolite IN-J9Z38

Rape seed

In trials conducted with cyantraniliprole on oil-seed rape (canola) in North America, plots were treated with three late season foliar sprays (OD formulation) at a rate of 0.15 kg ai/ha, using 200–500 L water/ha, with added surfactant. In several trials, seed treated with cyantraniliprole FS formulation) at a rate required to achieve an application rate about 0.08 kg ai/ha planted and the plots were also treated with two late season foliar spray applications (0.15 kg ai/ha, OD formulation).

Seed samples were stored at -20 °C for up to 6.5 months before extraction and analysed within 4 months after extraction for cyantraniliprole and six metabolites using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 92% (cyantraniliprole) and 85–99% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg and also 1.0 mg/kg cyantraniliprole in cotton seed.

Table 147 Residues in oil-seed rape from supervised trials in North America involving foliar applications of cyantraniliprole (OD formulation), with and without the use of cyantraniliprole-treated seed

OILSEED RAPE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Alvena, SK CAN, 2009 (RR 7145)	3	0.15	75	200		7	seed	0.24, 0.3	0.27	M1=0.02	DP-27582 Test 10
Blaine Lake, SK CAN, 2009 (Dekalb 7145 RR)		0.15	74	200	7	7	seed	0.25, 0.33	0.29	M1=0.01	DP-27582 Trial 16
Brandon, MB CAN, 2009 (Invigor 5030)	3	0.15	60	250	7	7	seed	0.18, 0.16	0.17		DP-27582 Test 09
Carberry, MB CAN, 2009 (D3151)	3	0.15	60	250	7, 6	6	seed	0.054, 0.065	0.059		DP-27582 Test 07
Carrington, ND USA, 2009 (Pioneer D3151)	3	0.15	54	280	7	7	seed	0.017, 0.017	0.017		DP-27582 Test 04
Ephrata, WA USA, 2009 (7145 RR)	3	0.15	73	210	7	7	seed	0.087, 0.08	0.084	M1=0.01	DP-27582 Test 05
Ft. Saskatchewan, AB CAN, 2009 (1818 Roundup Ready)	3	0.15	50	300	7	7	seed	0.13, 0.12	0.12		DP-27582 Trial 12
Ft. Saskatchewan, AB CAN, 2009 (Liberty 1141)	3	0.15	50	300	7, 6	7	seed	0.057, 0.066	0.061		DP-27582 Trial 11
Geneva, MN USA, 2009 (Pioneer 45H21)	3	0.15	79	190	6, 7	8	seed	0.027, 0.016	0.021		DP-27582 Test 02
Jerome, ID USA, 2009 (D3151)	2+ 1	0.15	76 80	200 190	6 8	7	seed	0.29, 0.34	0.32		DP-27582 Test 06
Justice, MB CAN, 2009 (D3151)	3	0.15	60	250	7, 6	6	seed	0.022, 0.023	0.022		DP-27582 Test 08

OILSEED RAPE Location	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Lamont, AB CAN, 2009 (Invigor 8440)	3	0.15	50	300	6, 7	7	seed	0.14, 0.21	0.18		DP-27582 Trial 13
St. Marcsur Richelieu, QC CAN, 2009 (Pioneer D3150)	3	0.15	50	300	6, 9	1	seed	0.17, 0.16	0.16		DP-27582 Trial 03
Stephens, GA USA, 2009 (Sumner)	1+	0.15	51	290	7	7	seed	0.017, 0.022	0.019		DP-27582 Test 01
	1+	0.15	62	240							
	1	0.14	70	210							
Wakaw, SK CAN, 2009 (RR 7145)	3	0.15	75	200	7	7	seed	0.066, 0.047	0.057		DP-27582 Trial 17
Waldheim, SK CAN, 2009 (Dekalb 7145 RR)	3	0.15	75	200	7	7	seed	0.57, 0.65	0.61	M1=0.02	DP-27582 Trial 15
Westlock, AB CAN, 2009 (Roundup Ready 1818)	3	0.15	50	300	7, 6	7	seed	0.07, 0.07	0.07	M1=0.01	DP-27582 Trial 14
Carberry, MB CAN, 2009 (D3151)	1+	0.08+				6	seed	0.029, 0.032	0.031		DP-27582 Test 07 [with treated seed]
	1+	0.07	29	250	7						
	2	0.15	60	250	6						
Carrington, ND USA, 2009 (Pioneer D3151)	1+	0.08+				7	seed	0.015, 0.016	0.015		DP-27582 Test 04 [with treated seed]
	1+	0.07	25	280	7						
	2	0.15	54	280	7						
Jerome, ID USA, 2009 (D3151)	1+	0.08+				7	seed	0.21, 0.22	0.21		DP-27582 Test 06 [with treated seed]
	1+	0.07	37	200	6						
	1+	0.15	74	200	8						
	1	0.16	80	190							
Justice, MB CAN, 2009 (D3151)	1+	0.08+				6	seed	0.048, 0.047	0.047		DP-27582 Test 08 [with treated seed]
	1+	0.07	29	250	7						
	2	0.15	60	250	6						
St. Marcsur Richelieu, QC CAN, 2009 (Pioneer D3150)	1+	0.08+				1	seed	0.11, 0.13	0.12		DP-27582 Trial 03 [with treated seed]
	1+	0.07	24	310	6						
	2	0.15	50	300	9						

M1: Average residues of metabolite INJ9Z38

In trials conducted in Australia on oilseed rape, single foliar applications of 0.015 or 0.03 kg ai/ha cyantraniliprole (SE formulations) were applied using about 100 L water/ha, with added adjuvant. One of these trials was a reverse decline study, where different plots were treated at staggered intervals so that the sampling dates co-incided with normal commercial harvest.

Samples, fodder (remaining straw/trash) and processed oil were stored at -20 °C for up to 3 months before extraction for analysis of seeds, trash and oil for cyantraniliprole and six metabolites (within 4 days after extraction) using analytical method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 91–102% (cyantraniliprole) and 75–102% (metabolites) in samples spiked with 0.01–2.0 mg/kg.

Table 148 Residues in oilseed rape from supervised trials in Australia involving foliar applications of cyantraniliprole (SE formulation)

OILSEED RAPE Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Welshpool, WA Australia, 2009	1	0.015	15	100		7	seed	ND			DP-31412 Site 1 [Reverse decline]
						14		ND			
						21		ND			
						28		ND			
						7	fodder	0.15			
						14		0.06			
						21		0.02			
						28		ND			
						7	oil	ND			
						14		ND			
						21		ND			
						28		ND			
Tranmere, SA Australia, 2009	1	0.015	15	100		14	seed	ND			DP-31412 Site 2
						14	fodder	0.38		M1=0.01	
						14	oil	ND			
Young, NSW Australia, 2009	1	0.015	15	100		14	seed	ND			DP-31412 Site 3
						14	fodder	0.08			
						14	oil	ND			
Tranmere, SA Australia, 2009	1	0.03	30	100		14	seed	< 0.01			DP-31412 Site 2
						14	fodder	0.57		M1=0.03	
						14	oil	ND			
Young, NSW Australia, 2009	1	0.03	30	100		14	seed	ND			DP-31412 Site 3
						14	fodder	0.21		M1=0.01	
						14	oil	ND			

M1: Average residues of metabolite INJ9Z38

Sunflower

In trials conducted with cyantraniliprole on sunflowers in North America, plots were treated with three late season foliar sprays (OD formulation) at a rate of 0.15 kg ai/ha, using 200–500 L water/ha, with added surfactant.

Seed samples were stored at -20 °C for up to 6.5 months before extraction and analysed within 4 months after extraction for cyantraniliprole and six metabolites using method DP-15736,

with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 92% (cyantraniliprole) and 85–99% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg and also 1.0 mg/kg cyantraniliprole in cotton seed.

Table 149 Residues in sunflower seed from supervised trials in North America involving foliar applications of cyantraniliprole (OD formulation)

SUNFLOWER Location Country, year (variety)	Application					DAT (days)	Matrix	Residues (mg/kg)			Reference & Comments
	no	kg ai/ha	g ai/hL	water L/ha	RTI (days)			cyantraniliprole	mean	metabolites	
Atlantic, IA USA, 2009 (Sunflower/ 8007 Millborn)	3	0.15	80	190	7	7	seed	0.069, 0.065	0.067		DP-27582 Trial 19
Brookdale, MB CAN, 2009 (Sunflower/ 6946)	3	0.15	60	250	7, 6	6	seed	0.36, 0.28	0.32		DP-27582 Trial 25
Carrington, ND USA, 2009 (Sunflower/ Pioneer)	3	0.15	54	280	5, 7	7	seed	0.068, 0.1	0.085		DP-27582 Trial 20
Hinton, OK USA, 2009 (Sunflower/ 8N453DM)	3	0.15	63	240	8, 9	5	seed	0.06, 0.059	0.059		DP-27582 Trial 24
Jamestown, ND USA, 2009 (Sunflower/ IS 8048)	3	0.15	80	190	7	7	seed	0.03, 0.049	0.039		DP-27582 Trial 22
Montpelier, ND USA, 2009 (Sunflower/ IS 8048)	1+ 2	0.16 0.15	83 80	190 190	7	7	seed	0.026, 0.031	0.028		DP-27582 Trial 23
Neepawa, MB CAN, 2009 (Sunflower/ Jaguar)	3	0.15	60	250	7, 6	6	seed	0.092, 0.093	0.092		DP-27582 Trial 26
Stafford, KS USA, 2009 (Sunflower/ Pioneer 63M61)	2+ 1	0.15 0.16	71 75	210	7	7	seed	0.045, 0.082	0.064		DP-27582 Trial 18
Velda, ND USA, 2009 (Sunflower/ 8N835CL)	3	0.15	80	190	8, 7	7	seed	0.14, 0.15	0.14		DP-27582 Trial 21

Coffee

In Brazilian trials on coffee, plots was treated with two soil drench applications of cyantraniliprole (SC formulation), 30 days apart, using from 0.01–0.06 g ai/100 mL/plant to achieve the equivalent of 0.2 kg ai/ha/treatment, followed by two late season foliar applications of 0.175 kg ai/ha cyantraniliprole (OD formulation), 30 days apart, using 400–600 L water/ha with no added adjuvants. In two trials, additional plots received only the two late season foliar sprays.

Samples of beans were dried at room temperature and manually peeled, with the dried beans being stored frozen until analysis for cyantraniliprole and the metabolite IN-J9Z38 using method DP-15736, with reported LOQs of 0.01 mg/kg. Average concurrent recoveries were 93% (cyantraniliprole) and 88% (IN-J9Z38) in samples spiked with 0.01 and 1.0 mg/kg.

Table 150 Residues in coffee beans from supervised trials in Brazil involving soil drench (SC formulation) and foliar applications of cyantraniliprole (OD formulation)

COFFEE Country, year Location (variety)	Application				RTI (days)	DAT, (days)	Matrix	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	g ai/hL	water (L/ha)				cyantraniliprole	metabolites	
Campinas SP Brazil, 2011	2	0.175	35	500		7 28	beans	< 0.01 <u>≤ 0.01</u>		BRI- 10/11-008 Test A
Monte Santo de Minas Brazil, 2011	2	0.175	29	600		7 28	beans	0.02 <u>0.02</u>		BRI- 10/11-008 Test F
Cabo Verde Brazil, 2011	2+2	0.2 (soil) 0.175	0.5 35	0.1L/plant 500	30	7 28	beans	0.03 <u>0.01</u>		BRI- 10/11-008 Test C
Campinas SP Brazil, 2011	2+2	0.2 (soil) 0.175	0.5 35	0.1L/plant 500	30	7 14 28 35 45 60	beans	0.02 0.01 < 0.01 < 0.01 < 0.01 ND		BRI- 10/11-008 Test A
Espirito Santo do Pinhal SP Brazil, 2011	2+2	0.2 (soil) 0.175	0.6 35	0.1L/plant 500	30	7 14 28 35	beans	0.01 < 0.01 <u>≤ 0.01</u> < 0.01		BRI- 10/11-008 Test B
Indianopolis Brazil, 2011	2+2	0.2 (soil) 0.175	0.7 29	0.1L/plant 600	30	7 28 45 60	beans	< 0.01 <u>≤ 0.01</u> < 0.01 < 0.01		BRI- 10/11-008 Test G
Lohdrina Brazil 2011	2+2	0.2 (soil) 0.175	0.5 44	0.1L/plant 400	30	7 14 28 35	beans	< 0.01 < 0.01 <u>ND</u> <u>ND</u>		BRI- 10/11-008 Test I
Monte Santo de Minas Brazil, 2011	2+2	0.2 (soil) 0.175	0.4 29	0.1L/plant 600	30	7 28	beans	0.01 0.01		BRI- 10/11-008 Test F
Pardinho – SP Brazil, 2011	2+2	0.2 (soil) 0.175	0.6 30	0.1L/plant 580	30	7 28	beans	0.02 <u>≤ 0.01</u>		BRI- 10/11-008 Test D
Restinga – SP Brazil, 2011	2+2	0.2 (soil) 0.175	0.2 29	0.1L/plant 600	30	7 14 28 35	beans	< 0.01 < 0.01 <u>≤ 0.01</u> < 0.01		BRI- 10/11-008 Test E

FATE OF RESIDUES IN STORAGE AND PROCESSING

High temperature hydrolysis

In a study reported by Lowrie, 2005 [Ref: DP-16989], the high-temperature hydrolysis of [¹⁴C]-cyantraniliprole in buffered solutions of pH 4, 5, and 6 was investigated to simulate representative processing conditions: pasteurization at 90 °C for 20 minutes in pH 4 solution; baking, brewing, or boiling at 100 °C for 60 minutes in pH 5 solution; and sterilization at 120 °C for 20 minutes in pH 6 solution.

Solutions of [CN-¹⁴C]-cyantraniliprole and [PC-¹⁴C]-cyantraniliprole were incubated at 90, 100, and 120 °C at pH 4, 5, and 6, respectively, using aqueous citrate buffer and samples analyzed

after 20 min. (pH 4 and 6) and 1 h (pH 5) by LSC and HPLC. Identification of parent and transformation products was by co-chromatography and the identifications made were confirmed using LC-MS analysis. The limit of quantification (LOQ) for both labelled forms was 1% AR.

Cyantraniliprole was susceptible to hydrolysis with IN-J9Z38 being the significant hydrolysis product, making up about 4–5% AR under conditions representative of pasteurization (20 minutes at 90 °C and pH 4) and 12–14% AR under sterilisation conditions (20 minutes at 120 °C and pH 6). Under conditions reflecting baking, brewing, or boiling (60 minutes at 100 °C and pH 5) levels of IN-J9Z38 were lower, at 4–6% AR with IN-F6L99 and IN-N5M09 making up a further 5–8% AR. Minor components were detected but represented < 1% AR.

Table 151 Distribution of radioactivity for [CN-¹⁴C]-cyantraniliprole in citrate buffer solutions—high temperature hydrolysis (% radioactivity)

Component	pH 4		pH 5		pH 6	
	Control	90 °C	Control	100 °C	Control	120 °C
Cyantraniliprole (parent)	97.54	90.56	96.73	74.54	96.92	93.58
IN-J9Z38	0.69	4.40	1.14	11.51	0.92	6.21
IN-N5M09	ND	1.90	ND	8.41	ND	ND
Others ^a	ND	0.70	0.32	3.39	0.47	1.64
Apparatus wash	0.77	0.84	0.80	0.74	0.74	0.68
Total % recovery	99.00	98.40	98.99	98.59	98.92	102.11

Table 152 Distribution of radioactivity for [PC-¹⁴C]-cyantraniliprole in citrate buffer solutions—high temperature hydrolysis (% radioactivity)

Component	pH 4		pH 5		pH 6	
	Control	90 °C	Control	100 °C	Control	120 °C
Cyantraniliprole	97.00	89.23	94.71	75.12	98.43	91.49
IN-J9Z38	0.14	5.36	1.05	13.64	0.36	3.71
IN-F6L99	ND	1.71	ND	5.33	ND	0.12
Other peaks	0.80	1.70	1.33	4.04	1.26	2.14
Total	97.94	97.99	97.09	98.12	100.05	97.46

Potatoes

In three field trials conducted in North America and reported by Thiel, 2010 [Ref: DP-27583], bulk samples of tubers were taken from plots planted with cyantraniliprole-treated seed pieces (13.5 g ai/100 kg seed) and treated with a single foliar application of 0.15 kg ai/ha cyantraniliprole (OD formulation), with added surfactant, 7 days before harvest.

Samples were shipped under ambient conditions to the processing facility where samples were processed to potato flakes, potato waste, peeled potatoes, potato chips, wet peel, culls, fries, cooking water, unpeeled boiled potatoes, and unpeeled microwaved potatoes.

Tubers were washed for 5 minutes and representative samples were batch steam peeled, batch scrubbed for 20 seconds and further processed into flake processing and french fries. The collected peel was hydraulically pressed and blended with the cut trim waste to derive the wet potato waste sample.

A representative sample of steam-peeled potatoes were cut into slabs, batch spray-washed in cold tap water for 30 seconds to remove free starch, precooked at 70–77 °C for 20 minutes in a steam jacketed kettle and cooled to less than 32 °C for 20 minutes. The cooled potato slabs were then steam-cooked at 94–100 °C for 40 minutes and mixed with an emulsion of pre-weighed food additives. The cooked mash was then hand fed onto a drum dryer to produce a thin sheet of potato flake which was then hammer-milled to give the final potato flakes sample.

An additional representative sample of steam-peeled potatoes were pre-cooked in 54 °C water for 40 minutes and then cut into 3/16" strips using a french fry cutter. After cutting, the strips were spray-washed for 30 seconds to remove free starch, blanched in 79–85 °C water for 5 minutes and then dipped in a solution of 0.5% sodium acid pyrophosphate and 0.5% dextrose for 30 seconds at 71–74 °C. The strips were then air dried (75 °C) to reduce the moisture content of the strips by about 15% and par-fried in vegetable oil for 45–50 seconds at 188–191 °C. After frying, the fried strips were drained to remove excess oil and placed in the freezer for rapid (12 minute) cooling before being labelled and placed back into freezer storage for subsequent analysis.

Potato chips were prepared from the washed potatoes by batch peeling and slicing the peeled potatoes into thin 16mm slices. The sliced potatoes were placed in a tub of hot water to remove free starch, drained and fried at 163–191 °C frying oil for 90 seconds. After draining and salting, samples were labelled and stored frozen for subsequent analysis.

For producing unpeeled boiled potatoes, washed potatoes were quartered and boiled in water until an internal temperature of 88–92 °C was achieved. Once the desired temperature was reached, the unpeeled boiled potato fraction was removed from the water and packaged, labelled and placed into frozen storage.

For producing unpeeled microwaved potatoes, the quartered potatoes were placed into the commercial microwave oven and microwaved in 5 minute increments until an internal temperature of 88–92 °C was achieved. After the desired temperature was reached, the unpeeled microwaved potato fraction was packaged, labelled and placed into frozen storage.

Tubers and processed fractions were stored at –20 °C for up to 9 months before analysis (within 3 months of extraction) for cyantraniliprole and eight metabolites using LC/MS/MS method DP-15736. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 91–95% (cyantraniliprole) and 79–113% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Residues of cyantraniliprole were detected at up to 0.02 mg/kg in fresh tubers, less than 0.01 mg/kg in wet peel and unpeeled microwaved potatoes and were not detectable in all other samples tested. The IN-JZ38 metabolite was also measured at < 0.01 mg/kg in tubers and wet peel, but was not detectable in other matrices. Residues of the other metabolites (IN-JCZ38, IN-K7H19, IN-MLA84, IN-MYX98, IN-N7B69, IN-N5M09, and IN-F6L99) were not detected in tubers or in processed fractions.

Table 153 Residues in potato tubers and processed products from supervised trials in North America involving a seed treatment plus one foliar application of cyantraniliprole

POTATO Study ID	Matrix	Cyantraniliprole	IN-JZ38	Total	
		mg/kg	mg/kg	mg/kg	PF
DP-27583 Test 10	tubers	< 0.01 (3)	ND	< 0.01	–
	flakes	ND	ND	ND	–
	waste	ND	ND	ND	–
	peeled tubers	ND	ND	ND	–
	chips	ND	ND	ND	–
	wet peel	< 0.01	< 0.01	< 0.02	–
	culls	< 0.01	ND	< 0.01	–
	fries	ND	ND	ND	–
	cooking water	ND	ND	ND	–
	unpeeled, boiled	ND	ND	ND	–
	unpeeled mwaved	< 0.01	ND	< 0.01	–

POTATO Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total	
		mg/kg	mg/kg	mg/kg	PF
DP-27583 Test 11	tubers	0.02, <u>< 0.01</u> , ND	ND	< 0.01	–
	flakes	ND	ND	ND	–
	waste	ND	ND	ND	–
	peeled tubers	ND	ND	ND	–
	chips	ND	ND	ND	–
	wet peel	< 0.01	< 0.01	< 0.02	–
	culls	0.01	ND	< 0.01	–
	fries	ND	ND	ND	–
	cooking water	ND	ND	ND	–
	unpeeled, boiled	ND	ND	ND	–
	unpeeled m'waved	ND	ND	ND	–
DP-27583 Test 12	tubers	0.02, <u>0.02</u> , 0.02	< 0.01	<u>0.03</u>	
	flakes	ND	ND	ND	0.1
	waste	ND	ND	ND	0.1
	peeled tubers	ND	ND	ND	0.1
	chips	ND	ND	ND	0.1
	wet peel	0.02	0.05	0.07	2.3
	culls	0.02	< 0.01	< 0.03	1.0
	fries	ND	ND	ND	0.1
	cooking water	ND	ND	ND	0.1
	unpeeled, boiled	ND	ND	ND	0.1
	unpeeled m'waved	< 0.01	ND	< 0.01	0.33

For calculation purposes, where the residue in the processed commodity was reported as ND (< LOD), a value of 0.003 mg/kg was used and where residues were above the LOD but below the LOQ, a value of 0.01 mg/kg was used. In both cases, the PF was expressed as “less than” (e.g. < 0.01). Where residues of IN-J9Z38 are below the LOQ in the RAC, a value of 0.01 has been used to calculate ‘total’ residues.

Spinach

The effects of cooking on residues of cyantraniliprole in spinach were investigated by Carringer & Vogl, 2010 [Ref: DP-25644]. Bulk samples of spinach were taken from three field trials in the USA, one day after the last of three foliar applications of 0.15 kg ai/ha cyantraniliprole (OD formulation), applied at 5–6 day intervals with added surfactant.

At each of the three field sites about 400 g spinach leaves were added to 3 L boiling water in a large pot and boiled in the uncovered pot for approximately 15 minutes, stirring as needed to keep the leaves submerged under the water. The cooked spinach was removed and squeezed to remove as much water as possible.

Fresh and cooked leaves and the cooking water were stored at –20 °C for up to 8 months before analysis (within 10 weeks of extraction) for cyantraniliprole and eight metabolites using LC/MS/MS method DP-15736. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 87–98% (cyantraniliprole) and 73–103% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Residues of the IN-J9Z38, IN-MLA84 and IN-N5M09 metabolites increased significantly during the cooking process, with IN-J9Z38 being the predominant residue in cooked spinach. Residues of the other metabolites (IN-MYX98, IN-N7B69, IN-JCZ38 and IN-F6L99) decreased and the metabolite IN-K7H19 was not detected in any samples.

Table 154 Residues in fresh and cooked spinach from supervised trials in North America involving three foliar applications of cyantraniliprole (OD formulation)

SPINACH Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total		Other metabolites (mg/kg)					
		mg/kg	mg/kg	mg/kg	PF	M2	M3	M4	M5	M6	M7
DP-25644 Trial 35	fresh leaves	4.6	0.07	5.3		0.24	< 0.01	0.02	< 0.01	ND	ND
	cooked leaves	0.8	3.5	4.3	0.81	0.01	ND	0.09	ND	0.02	< 0.01
	water	0.03	0.25	0.28	0.05	ND	ND	0.02	ND	ND	< 0.01
DP-25644 Trial 36	fresh leaves	5.3	0.04	5.7		0.15	< 0.01	0.01	ND	< 0.01	ND
	cooked leaves	0.86	5.8	6.7	1.3	ND	ND	0.19	ND	0.04	< 0.01
	water	0.24	0.22	0.46	0.08	ND	ND	0.01	ND	ND	< 0.01
DP-25644 Trial 37	fresh leaves	10	0.1	10.1		0.43	0.01	0.05	< 0.01	< 0.01	< 0.01
	cooked leaves	0.9	9.2	10.1	1.0	< 0.01	ND	0.35	ND	0.09	0.015
	water	0.18	0.45	0.63	0.06	ND	ND	0.06	ND	< 0.01	0.011

M2: Residues of metabolite IN-MYX98

M3: Residues of metabolite IN-N7B69

M4: Residues of metabolite IN-MLA84

M5: Residues of metabolite IN-JCZ38

M6: Residues of metabolite IN-N5M09

M7: Residues of metabolite IN-F6L99

Tomatoes

Processing studies on tomatoes were reported by Carringer & Vogl, 2009 [Ref: DP-25645]. In three field trials in the USA, involving three foliar applications of 0.3 kg ai/ha cyantraniliprole (OD formulation), applied at 5 day intervals, with added surfactant, bulk samples were taken one day after the last application and shipped under ambient conditions to the processing facility where samples were processed to washed tomatoes, peeled tomatoes, sun-dried tomatoes, canned tomatoes, juice, wet pomace, dried pomace, paste, and puree.

Canned tomatoes were prepared by spray-rinsing the field samples with high pressure warm water (68–74 °C) for 30 seconds and boiling the rinsed tomatoes for about a minute to crack the skin prior to removal and peeled by hand before packing in cans with a teaspoon of salt. The cans were steam heated for about 10 minutes to achieve a temperature of about 80 °C, sealed, cooked in a boiling water bath for about 15 minutes and cooled in cold tap water.

Sun-dried tomatoes were prepared from the rinsed samples by removing the cores and stems, quartering the fruit and spreading them with the peel down on a tray for drying to a moisture content of < 16%.

Washed tomato samples were prepared by batch soaking a representative sample of the field tomatoes in a 5 g/L solution of sodium hydroxide at about 52–60 °C for 3 minutes and then spray-rinsing with high pressure warm water (68–74 °C) for 30 seconds.

Pomace samples were prepared by crushing the washed tomatoes in a hammermill and then rapidly heating the crush to about 79–85 °C for 15–30 seconds (hot break) before separation into pomace and juice. The wet pomace was pressed and the recovered press juice was combined with the fresh juice from the pulper/finisher. A representative sample of the wet pomace was then bin-dried to less than 10% moisture.

Fresh juice was heated to not more than 82 °C in the steam jacketed kettle and an aliquot was vacuum-evaporated to produce puree with the addition of 1% salt and the Brix level adjusted to 12.0–13.0° by the addition of water. The puree was heated to 82–88 °C, canned, sealed and cooked in a boiling water bath for about 15 minutes at 96–100 °C and then cooled under running cold tap water

Fresh juice was also vacuum-evaporated to paste with the addition of 0.5–1.0% salt and the Brix level adjusted to 24.0–33° by the addition of water. The puree was heated to 82–88 °C, canned, sealed and cooked in a boiling water bath for about 15 minutes at 96–100 °C and then cooled under running cold tap water.

An aliquot of the paste was also diluted with hot water, mixed with 0.5%–1.0% salt and the Brix level adjusted to about 4.5–5.5°, to produce juice. This juice was then heated to about 85 °C, canned, sealed and cooked in a boiling water bath for about 15 minutes at 96–100 °C and then cooled in cold tap water.

Processed samples were stored at or below -17 °C for up to 7 months before analysis (within about 2 weeks of extraction) for cyantraniliprole and eight metabolites using LC/MS/MS method DP-15736. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 76–102% (cyantraniliprole) and 70–117% (metabolites) in samples spiked with 0.01 to 2.0 mg/kg.

Cyantraniliprole was the predominant residue in processed tomato products, with significant residues of the IN-J9Z38 metabolite also found in wet and dry pomace. In the wet and dry pomace, paste and sun-dried tomato samples, low levels (up to 0.04 mg/kg) of IN-MYX98, IN-MLA84 or IN-N5M09 were reported. Residues of the other metabolites (IN-N7B69, IN-K7H19 and IN-JCZ38) were not detected in any samples.

Table 155 Residues in fresh and processed tomatoes from supervised trials in North America involving three foliar applications of cyantraniliprole (OD formulation)

TOMATO Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total		Other metabolites (mg/kg)			
		mg/kg	mg/kg	mg/kg	PF	M2	M4	M6	M7
DP-25645 Trial 1	fresh (field)	0.13	ND	0.13		ND	ND	ND	ND
	washed	0.02	ND	0.02	0.15	ND	ND	ND	ND
	peeled	< 0.01	ND	< 0.01	< 0.08	ND	ND	ND	ND
	sun-dried	0.45	0.03	0.48	3.7	ND	ND	ND	ND
	canned	ND	ND	ND	< 0.02	ND	ND	ND	ND
	juice	< 0.01	< 0.01	< 0.02	< 0.15	ND	ND	ND	ND
	wet pomace	0.08	0.05	0.13	1.0	ND	< 0.01	ND	ND
	dry pomace	0.23	0.18	0.41	3.2	ND	0.01	< 0.01	ND
	paste	0.03	0.05	0.08	0.62	ND	ND	< 0.01	< 0.01
	puree	0.02	0.01	0.03	0.23	ND	ND	ND	ND
DP-25645 Trial 2	fresh (field)	0.2	< 0.01	0.21		ND	ND	ND	ND
	washed	0.05	< 0.01	< 0.06	< 0.29	ND	ND	ND	ND
	peeled	0.02	ND	0.02	0.1	ND	ND	ND	ND
	sun-dried	0.73	0.07	0.8	3.8	ND	< 0.01	< 0.01	< 0.01
	canned	< 0.01	ND	< 0.01	< 0.05	ND	ND	ND	ND
	juice	0.03	0.01	0.04	0.19	ND	ND	ND	ND
	wet pomace	0.29	0.17	0.46	2.2	ND	0.02	< 0.01	ND
	dry pomace	0.5	0.35	0.85	4.0	ND	0.04	0.01	ND
	paste	0.12	0.06	0.18	0.86	ND	ND	< 0.01	< 0.01
	puree	0.07	0.02	0.09	0.43	ND	ND	ND	ND
DP-25645 Trial 3	fresh (field)	0.12	ND	0.12		ND	ND	ND	ND
	washed	0.02	ND	0.02	0.17	ND	ND	ND	ND
	peeled	< 0.01	ND	< 0.01	< 0.08	ND	ND	ND	ND
	sun-dried	0.34	0.02	0.36	3.0	< 0.01	< 0.01	ND	ND
	canned	< 0.01	ND	< 0.01	< 0.08	ND	ND	ND	ND
	juice	0.01	< 0.01	< 0.02	< 0.17	ND	ND	ND	ND
	wet pomace	0.06	0.03	0.09	0.75	ND	ND	ND	ND
	dry pomace	0.12	0.08	0.2	1.7	ND	ND	< 0.01	ND
	paste	0.08	0.04	0.12	1.0	ND	ND	< 0.01	< 0.01
	puree	0.02	0.01	0.03	0.25	ND	ND	ND	ND

M2: Residues of metabolite IN-MYX98

M4: Residues of metabolite IN-MLA84

M6: Residues of metabolite IN-N5M09

M7: Residues of metabolite IN-F6L99

For calculation purposes, where the residue in the processed commodity was reported as ND (< LOD), a value of 0.003 mg/kg was used and where residues were above the LOD but below the LOQ, a value of 0.01 mg/kg was used. In both cases, the PF was expressed as “less than” (e.g. < 0.01). Where residues of IN-J9Z38 are below the LOQ in the RAC, a value of 0.01 has been used to calculate ‘total’ residues.

Oranges

In three field trials on oranges conducted in North America and reported by Rice, 2010 [Ref: DP-27554], plots were treated 7 days apart with three late season foliar applications of 0.15 kg ai/ha

cyantraniliprole (OD formulation) with added surfactant and bulk samples of fruit were taken 1 day after the last application for processing.

The samples were shipped under ambient conditions to the processing facility where samples were processed to juice, wet pulp, dry pulp, meal, molasses, marmalade, oil, and canned oranges.

Juice was prepared from batch-washing field oranges by scarifying the fruit in a Hobart Peeler for 45 seconds, collecting the oil-water emulsion and passing it through a 180 μm screen to remove flavedo fragments before separating the oil fraction through a cream separator and then an IEC centrifuge. The residual emulsion was then frozen, thawed and centrifuged to collect the remaining oil.

Juice extracted from the scarified oranges was transferred to a pulper/finisher and passed through an approximately 1.2 mm screen to remove the rag and seeds. Peel from the juice extraction process was shredded and combined with scarified flavedo fragments and the residual pulp from the juice extraction to generate wet peel. Lime (about 95% CaO) was mixed with this wet peel and the limed peel was pressed to obtain press liquor which was then vacuum-evaporated to produce molasses.

An aliquot of the wet pulp was also dried to below 10% moisture and hammer-milled to produce the dry pulp sample, with further milling producing the meal sample.

Washed oranges were also peeled, segmented, mixed with a light syrup (Brix 14.0–18.0 °) and canned, with the sealed cans being cooked in a boiling water bath for about 15 minutes at 96–100 °C and cooled with tap water.

For marmalade, the rinds from washed oranges were chipped in a food processor and cooked for 20 minutes and the chopped pulp (without seeds) was mixed with 20% w/w water and cooked for 45 minutes. The cooked rind and pulp (with about 45 mL lemon juice and 1.5 kg sugar added per kg) was then boiled for 3 minutes, pectin was added and the mixture was boiled for a further 2 minutes. After standing for 1–2 minutes, the finished marmalade was packed in sterilised jars for subsequent analysis.

Fruit and processed fractions were stored at -20 °C for up to 8 months before analysis (within 7 weeks of extraction) for cyantraniliprole and eight metabolites using LC/MS/MS method DP-15736. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 81–96% (cyantraniliprole) and 64–101% (metabolites) in samples spiked with 0.01, 0.1 and 0.2 mg/kg.

The storage stability of frozen samples was also evaluated as part of this study. Whole fruit were cut in half and one-half of each fruit comprising each whole fruit incurred residue sample was pooled, homogenized, and extracted for analysis to provide an initial residue value for incurred residue stability determinations for this high-acid content commodity. The other half of these fruit were homogenized per sample and analyzed ten months later, to complete a ten-month incurred residue storage stability determination for orange fruit. Residues of cyantraniliprole after 10 months storage were 79, 88, and 128% of the initial residues in three composite samples.

Cyantraniliprole was the predominant residue in processed orange products, with residues concentrating in oil. Significant residues of the IN-J9Z38 metabolite were also in oil and other matrices, together with trace levels of the IN-N5M09 metabolite in oil. Residues of the other metabolites (IN-N7B69, IN-MYX98, IN-MLA84, IN-N5M09 IN-K7H19, IN-F6L99 and IN-JCZ38) were not detected in any samples.

Table 156 Residues in fresh and processed oranges from supervised trials in North America involving three foliar applications of cyantraniliprole (OD formulation)

ORANGE Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total		Other metabolites (mg/kg)
		mg/kg	mg/kg	mg/kg	PF	
DP-27554 Trial 8	oranges	0.13	ND	0.13		M6=< 0.01
	juice	< 0.01	ND	< 0.01	0.08	
	wet pulp	0.05	< 0.01	0.06	0.46	
	dry pulp	0.11	0.01	0.12	0.92	
	meal	0.1	< 0.01	0.11	0.85	
	molasses	ND	0.09	0.09	0.69	
	marmalade	< 0.01	< 0.01	< 0.02	< 0.15	
	oil	0.81	0.25	1.1	8.5	
	canned	ND	ND	ND	< 0.02	
DP-27554 Trial 25	oranges	0.09	ND	0.09		
	juice	ND	ND	ND	< 0.03	
	wet pulp	0.02	ND	0.02	0.22	
	dry pulp	0.02	< 0.01	< 0.03	< 0.33	
	meal	0.02	ND	0.02	0.22	
	molasses	ND	0.03	0.03	0.33	
	marmalade	ND	ND	ND	< 0.03	
	oil	0.21	0.048	0.26	2.9	
	canned	ND	ND	ND	< 0.03	
DP-27554 Trial 26	oranges	0.17	ND	0.17		
	juice	ND	ND	ND	< 0.02	
	wet pulp	0.04	ND	0.04	0.24	
	dry pulp	0.07	0.01	0.08	0.47	
	meal	0.07	0.01	0.08	0.47	
	molasses	ND	0.1	0.1	0.59	
	marmalade	ND	< 0.01	< 0.01	< 0.06	
	oil	1.4	0.08	1.5	8.8	
	canned	< 0.01	ND	< 0.01	< 0.06	

M6: Residues of metabolite IN-N5M09

For calculation purposes, where the residue in the processed commodity was reported as ND (< LOD), a value of 0.003 mg/kg was used and where residues were above the LOD but below the LOQ, a value of 0.01 mg/kg was used. In both cases, the PF was expressed as “less than” (e.g. < 0.01). Where residues of IN-J9Z38 are below the LOQ in the RAC, a value of 0.01 has been used to calculate ‘total’ residues.

Apples

In three field trials on apples conducted in North America and reported by Thiel, 2010 [Ref: DP-27438], plots were treated 7 days apart with three late season foliar applications of 0.15 kg ai/ha cyantraniliprole (SE formulation) with added surfactant and bulk samples of fruit were harvested 3 day after the last application for processing.

Samples were shipped under ambient conditions to the processing facility where samples were processed to washed apples, puree, canned apples, frozen apples, juice, wet pomace, dry pomace, and sauce.

To produce juice, fresh apples were ground in a hammer-mill and the wet mash was pressed to 2200–3000 psi for at least 5 minutes to extract the juice, leaving the wet pomace. A representative sample of the wet pomace was also dried for 1–4 hours using hot air at 60–88 °C, to achieve a moisture content of 10% or less.

Apple sauce was prepared from peeled, cored and diced apples by heating in a kettle with added water (approximately 25% by weight) at about 70 °C for 45 minutes and mashing to produce puree. Further heating at 82–93 °C for 6–10 hours allowed excess moisture to evaporate, producing

apple sauce. Apple slices were also prepared from peeled, cored and sliced (6–7 mm) fruit by heating to about 70 °C for 20 minutes, resulting in cooked slices in syrup.

Peeled and cored apples were also cut into sliced to 3 mm slices and dehydrated at 65–70 °C for 20–24 hours to achieve a moisture content of about 10%.

Fruit and processed fractions were stored at -20 °C for up to 8 months before analysis (within 11 weeks of extraction) for cyantraniliprole and eight metabolites using LC/MS/MS method DP-15736. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 91–101% (cyantraniliprole) and 81–109% (metabolites) in samples spiked with 0.01, 0.1 and 1.0 mg/kg.

Cyantraniliprole was the predominant residue in processed apple products, with residues concentrating in the dry pomace. Significant residues of the IN-J9Z38 metabolite were present in sauce and to a lesser extent in dry pomace. Residues of IN-N5M09 and IN-F6L99 were also found at levels up to 0.07 mg/kg in sauce. Residues of the other metabolites (IN-N7B69, IN-MYX98, IN-MLA84, IN-K7H19 and IN-JCZ38) were not detected in any samples.

Table 157 Residues in fresh and processed apples from supervised trials in the USA involving foliar applications of cyantraniliprole (SE formulation)

APPLE Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total		Other metabolites (mg/kg)	
		mg/kg	mg/kg	mg/kg	PF	M6	M7
DP-27438 Trial 3	fruit	0.08	ND	0.08		ND	ND
	washed	0.05	ND	0.05	0.63	ND	ND
	puree	0.08	ND	0.08	1.0	ND	ND
	canned	0.01	ND	0.01	0.13	ND	ND
	frozen	0.12	ND	0.12	1.5	ND	ND
	juice	0.03	ND	0.03	0.38	ND	ND
	wet pomace	0.08	ND	0.08	1.0	ND	ND
	dry pomace	0.3	< 0.01	0.31	3.9	ND	ND
	sauce	0.13	0.06	0.19	2.4	0.014	< 0.01
DP-27438 Trial 10	fruit	0.26	ND	0.26		ND	ND
	washed	0.15	ND	0.15	0.58	ND	ND
	puree	0.23	ND	0.23	0.88	ND	ND
	canned	0.01	ND	0.01	0.04	ND	ND
	frozen	0.25	ND	0.25	0.96	ND	ND
	juice	0.05	ND	0.05	0.19	ND	ND
	wet pomace	0.31	ND	0.31	1.2	ND	ND
	dry pomace	0.68	0.02	0.7	2.7	ND	ND
	sauce	0.21	0.35	0.56	2.2	0.053	0.04
DP-27438 Trial 14	fruit	0.26	ND	0.26		ND	ND
	washed	0.12	ND	0.12	0.46	ND	ND
	puree	0.34	ND	0.34	1.3	ND	ND
	canned	0.03	< 0.01	0.04	0.15	ND	ND
	frozen	0.16	ND	0.16	0.62	ND	ND
	juice	0.08	ND	0.08	0.31	ND	ND
	wet pomace	0.2	ND	0.2	0.77	ND	ND
	dry pomace	0.52	0.01	0.53	2.0	ND	ND
	sauce	0.36	0.35	0.71	2.7	0.07	0.036

M6: Residues of metabolite IN-N5M09

M7: Residues of metabolite IN-F6L99

For calculation purposes, where the residue in the processed commodity was reported as ND (< LOD), a value of 0.003 mg/kg was used and where residues were above the LOD but below the LOQ, a value of 0.01 mg/kg was used. In both cases, the PF was expressed as “less than” (e.g. < 0.01). Where residues of IN-J9Z38 are below the LOQ in the RAC, a value of 0.01 has been used to calculate ‘total’ residues.

Plums

In three field trials on plums conducted in North America and reported by Thiel, 2010 [Ref: DP-27437], plots were treated 7 days apart with three late season foliar applications of 0.15 kg ai/ha cyantraniliprole (SE formulation) with added surfactant and bulk samples of fruit were taken 3 day after the last application for processing.

Samples were shipped under ambient conditions to the processing facility where the plums were stored for up to three days at about 6 °C before processing. The plums were sliced in half, the stones were removed and the pitted plums, on dehydrator trays, were dried at 130°–150 °C for about 14 to 18 hours to produce dried prunes, with a moisture content of 15–18%.

Plums and dried prunes were stored at –20 °C for up to 9 months before analysis (within 15 weeks of extraction) for cyantraniliprole and eight metabolites using LC/MS/MS method DP-15736. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 101–104% (cyantraniliprole) and 92–109% (metabolites) in samples spiked with 0.01, 0.1, 0.2 and 0.5 mg/kg.

Cyantraniliprole was the predominant residue in dried prunes, found a levels up to twice those in plums (without stones). Residues of the IN-J9Z38 metabolite were also found in the dried prunes, with IN-N5M09 and IN-F6L99 also found at levels up to 0.01 mg/kg. Residues of the other metabolites (IN-N7B69, IN-MYX98, IN-MLA84, IN-K7H19 and IN-JCZ38) were not detected in any samples.

Table 158 Residues in plums and dried prunes from supervised trials in North America involving foliar applications of cyantraniliprole (SE formulation)

PLUM Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total		Other metabolites (mg/kg)	
		mg/kg	mg/kg	mg/kg	PF	M6	M7
DP-27437 Trial 14	plum flesh	<u>0.18</u>	ND	0.18		ND	ND
	dried prunes	0.35	0.01	0.36	2.0	ND	ND
DP-27437 Trial 16	plum flesh	<u>0.24</u>	< 0.01	0.25		ND	ND
	dried prunes	0.37	0.04	0.41	1.6	< 0.01	< 0.01
DP-27437 Trial 20	plum flesh	<u>0.04</u>	ND	0.04		ND	ND
	dried prunes	0.05	ND	0.05	1.3	ND	ND

M6: Residues of metabolite IN-N5M09

M7: Residues of metabolite IN-F6L99

For calculation purposes, where the residue in the processed commodity was reported as ND (< LOD), a value of 0.003 mg/kg was used and where residues were above the LOD but below the LOQ, a value of 0.01 mg/kg was used. In both cases, the PF was expressed as “less than” (e.g. < 0.01). Where residues of IN-J9Z38 are below the LOQ in the RAC, a value of 0.01 has been used to calculate ‘total’ residues.

Cotton seed

In three field trials on cotton conducted in North America and reported by Thiel, 2010 [Ref: DP-27565], plots were treated 7 days apart with three late season foliar applications of 0.75 kg ai/ha cyantraniliprole (OD formulation) with added surfactant and bulk samples of cotton seed were taken 7 day after the last application for processing.

Ginned cotton seed samples were saw-delinted to remove most of the remaining lint, the hulls were cracked using a roller mill and screened (4–5 mm mesh) to separate out the kernels. After adjusting the kernel moisture content to 12–13.5%, the kernel material was heated to 80–90 °C for 30 minutes, flaked in a roller mill and steam extruded (93–121 °C) to form collets (pellets) which were then dried for 30–40 minutes at 66–82 °C prior to solvent extraction.

Flakes and collets were soaked in hexane at 49–60 °C for 30 minutes (1st cycle) and then 15 minutes each (2nd and 3rd cycles) with the miscella (crude oil and hexane) from each cycle being drained off and combined with the residual hexane from the final extraction (at about 95 °C). The combined miscella was passed through a vacuum evaporator (91–96 °C) to remove the hexane, leaving the raw oil solvent extract. This crude oil was refined by mixing with sodium hydroxide (16 °

Baume) in a water bath, first at 20–24 °C then at 63–67 °C before centrifuging to separate the oil from the soapstock.

Samples of delinted seed were also cold-pressed using a Komet expeller and the crude oil obtained by mechanical pressing was filtered and alkali-refined to produce refined cold-pressed oil.

Samples were shipped under frozen conditions to the processing facility where they were processed to cottonseed raw oil, cottonseed refined oil, cottonseed meal, cottonseed hull, cottonseed raw oil (cold press), cottonseed refined oil (cold press), and cottonseed meal (cold press).

The processing samples were stored at -20 °C for up to 8 months before analysis (within 13 weeks of extraction) for cyantraniliprole and eight metabolites using LC/MS/MS method DP-15736. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 75–114% (cyantraniliprole) and 65–120% (metabolites) in samples spiked with 0.01–1.0 mg/kg.

Cyantraniliprole was the predominant residue in the processed fractions, with residues of the IN-J9Z38 metabolite also present in most oil fractions. Residues of the other metabolites (IN-N7B69, IN-MYX98, IN-MLA84, IN-N5M09, IN-F6L99, IN-K7H19 and IN-JCZ38) were not detected in any samples.

Table 159 Residues in raw and processed cotton seed from supervised trials in the USA involving three foliar applications of cyantraniliprole (OD formulation)

COTTON SEED Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total		Other metabolites (mg/kg)	
		mg/kg	mg/kg	mg/kg	PF	M6	M7
DP-27565 Trial 4	cottonseed	<u>0.52</u>	< 0.01	<u>0.53</u>		ND	ND
	raw oil (solvent extr)	0.02	< 0.01	0.03	0.06	ND	ND
	refined oil (solvent extr)	ND	0.02	0.02	0.04		
	meal (solvent extr)	0.05	ND	0.05	0.09		
	hulls	0.17	< 0.01	0.18	0.34		
	raw oil (cold press)	0.16	ND	0.16	0.3		
	refined oil (cold press)	ND	0.02	0.02	0.04		
	meal (cold press)	0.06	ND	0.06	0.11		
DP-27565 Trial 10	cottonseed	<u>0.71</u>	0.02	<u>0.73</u>		ND	ND
	raw oil (solvent extr)	0.017	0.016	0.03	0.04	< 0.01	< 0.01
	refined oil (solvent extr)	ND	0.02	0.02	0.03		
	meal (solvent extr)	0.01	< 0.01	< 0.02	< 0.03		
	hulls	0.25	0.02	0.27	0.37		
DP-27565 Trial 13	cottonseed	<u>1.6</u>	0.01	<u>1.6</u>		ND	ND
	raw oil (solvent extr)	0.05	0.07	0.12	0.08	ND	ND
	refined oil (solvent extr)	ND	0.08	0.08	0.05		
	meal (solvent extr)	0.06	0.02	0.08	0.05		
	hulls	0.42	< 0.01	< 0.43	< 0.27		
	raw oil (cold press)	0.34	< 0.01	< 0.34	< 0.21		
	refined oil (cold press)	ND	0.07	0.07	0.04		
	meal (cold press)	0.11	ND	0.11	0.07		

M6: Residues of metabolite IN-N5M09

M7: Residues of metabolite IN-F6L99

For calculation purposes, where the residue in the processed commodity was reported as ND (< LOD), a value of 0.003 mg/kg was used and where residues were above the LOD but below the LOQ, a value of 0.01 mg/kg was used. In both cases, the PF was expressed as “less than” (e.g. < 0.01). Where residues of IN-J9Z38 are below the LOQ in the RAC, a value of 0.01 has been used to calculate ‘total’ residues.

Olives

In three field trials on olives conducted in Europe and reported by Haigh & Cairns, 2011[Ref: DP-27709], plots were treated about 10 days apart with two late season foliar applications of 5 g ai/hL (0.15 kg ai/ha) cyantraniliprole (OD formulation) without added surfactant and bulk samples of olives were taken 14 day after the last application for processing.

Samples were shipped under ambient conditions to the processing facility within 1 day of sampling and were immediately processed to canned olives, raw and refined oil. The fresh whole olives were washed by immersion, drained and placed in a brine solution (220 g salt/2 L/kg olives) and allowed to soak for 30 days at room temperature and stirred daily before being stored for 60 days at 5–10 °C. The olives in brine were then canned (500 g olives with 250 g brine) and sterilised for 10 minutes at 115–120 °C.

For oil production, the fresh olives were hammer-milled and the resulting pulp was mixed and heated for about 30 minutes in a thermo-malaxer with the addition of boiling water and centrifuged to separate the oil/margines/water from the solid cake. The liquid phase was left to settle and the floating oil was decanted, with one portion being filtered to produce raw (virgin) oil and the other portion used to obtain refined oil.

The raw (unfiltered) oil was mixed with 115 g/L soda, heated in an oven at 60–70 °C for at least 30 minutes and the oil decanted from the sediment (soap) and filtered to give refined oil.

The processed samples were stored at –20 °C for up to 5 months before analysis (within 1 week of extraction) for cyantraniliprole and six metabolites using LC/MS/MS method DP-15736. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 84–103% (cyantraniliprole) and 87–107% (metabolites) in samples spiked with 0.01–1.0 mg/kg.

Cyantraniliprole was the predominant residue in the processed fractions, with levels concentrating in oil. Residues of the IN-J9Z38 metabolite were also measured in canned olives and trace residues (< 0.01 mg/kg) of IN-N5M09 and IN-F6L99 were also detected in canned olives and IN-MYX98 and IN-JCZ38 in oil. Residues of the other metabolites (IN-N7B69, IN-MLA84 and IN-K7H19) were not detected in any samples.

Table 160 Residues in processed olives and olive oil from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation)

OLIVE Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total		Other metabolites (mg/kg)			
		mg/kg	mg/kg	mg/kg	PF	M2	M5	M6	M7
DP-27709 Trial 7	whole fruit	<u>0.55</u>	ND	<u>0.55</u>		ND	ND		
	canned fruit	0.22	0.12	0.34	0.62	ND	ND	< 0.01	< 0.01
	olive flesh	0.93	< 0.01	0.94	1.7	ND	ND		
	canned flesh	0.34	0.18	0.52	0.95	ND	ND	< 0.01	< 0.01
	raw oil	0.92	< 0.01	0.93	1.7	ND	ND	ND	ND
	refined oil	0.69	< 0.01	0.7	1.3	ND	ND	ND	ND
DP-27709 Trial 9	whole fruit	<u>0.26</u>	ND	<u>0.26</u>		ND	ND		
	canned fruit	0.1	0.05	0.15	0.58	ND	ND	ND	ND
	olive flesh	0.45	< 0.01	0.46	1.8	ND	ND		
	canned flesh	0.16	0.09	0.25	0.96	ND	ND	ND	ND
	raw oil	0.31	0.01	0.32	1.2	ND	ND	ND	ND
	refined oil	0.17	0.04	0.21	0.81	ND	ND	ND	ND

OLIVE Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total		Other metabolites (mg/kg)			
		mg/kg	mg/kg	mg/kg	PF	M2	M5	M6	M7
DP-27709 Trial 10	whole fruit	0.29	< 0.01	0.3		ND	ND		
	canned fruit	0.04	0.02	0.06	0.2	ND	ND	ND	ND
	olive flesh	0.45	< 0.01	0.46	1.5	ND	ND	< 0.01	
	canned flesh	0.14	0.07	0.21	0.7	ND	ND	< 0.01	ND
	raw oil	0.16	0.02	0.18	0.6	ND	ND	ND	ND
	refined oil	0.06	0.06	0.12	0.4	< 0.01	< 0.01	ND	ND

M2: Residues of metabolite IN-MYX98

M5: Residues of metabolite IN-JCZ38

M6: Residues of metabolite IN-N5M09

M7: Residues of metabolite IN-F6L99

For calculation purposes, where the residue in the processed commodity was reported as ND (< LOD), a value of 0.003 mg/kg was used and where residues were above the LOD but below the LOQ, a value of 0.01 mg/kg was used. In both cases, the PF was expressed as "less than" (e.g. < 0.01). Where residues of IN-J9Z38 are below the LOQ in the RAC, a value of 0.01 has been used to calculate 'total' residues.

Grapes

In three field trials on wine grapes conducted in Europe and reported by Aitken, 2011 [Ref: DP-27718], plots were treated about 14 days apart with two late season foliar applications of 0.15 kg ai/ha) cyantraniliprole (OD formulation) by either high volume (1500 L/ha) or concentrate (300 L/ha) applications without added surfactant and bulk samples of grapes were taken 14 days after the last application for processing.

Samples were shipped under ambient conditions to the processing facility where samples were processed to stems, must, must deposit, wet pomace, lees, dry pomace, alcoholic fermentation (AF) Wine, malolactic fermentation (MF) Wine, bottled wine, grape juice and raisins.

For wine, grape samples were crushed and stemmed with an electric crusher/stemmer and sub samples taken for storage and analysis. For red wine, potassium metabisulphite (0.06–0.08 g/L) was added to the crushed grapes (must) and dry active yeast (0.1 g/L) added to initiate alcoholic fermentation. For white wine, potassium metabisulphite (0.12 g/L) and pectolytic enzymes were added to the must, which was then allowed to settle for 24 hours, decanted and the yeast was added to initiate alcoholic fermentation. The remaining wet pomace was sub-sampled for subsequent analysis and the wet pomace was also oven-dried at about 60 °C for two days to produce dry pomace.

At the end of the fermentation period, when the wine density had stabilised, the red wine was decanted and the solids were pressed to extract the remaining wine from the wet pomace. The wet pomace and the 'alcoholic fermentation' wine (AF wine) were sub-sampled for subsequent analysis and the wet pomace was also oven-dried at about 60 °C for two days to produce dry pomace. The white wine was separated from the lees and de-acidified by the addition of potassium bicarbonate.

Both the red and white 'AF wine' was then subjected to malolactic fermentation in the absence of air at ambient temperature by the addition of lactic bacteria and on completion, potassium metabisulphite was added. After settling for 4 days, the 'after malolactic fermentation' wine (MF wine) was separated from the lees and the wine was further clarified by the addition of gelatine (0.1 g/L) and potassium metabisulphite (0.04 g/L). After cool storage, the wine was racked and pressure-filtered (cellulose filter plate—2.5 µm pore) under nitrogen and 0.1 g/L potassium metabisulphite added to protect against oxidation.

Grape juice was prepared from the fresh grape samples by removing the stems and manually crushing the berries. After the addition of pectolytic enzymes, the crush was heated to 50 °C, put in jars and sterilised for 2 hours at 45–60 °C before being water-pressed to separate the juice and pomace. The juice was then clarified (5 minutes at about 80 °C), cool stored, racked and pressure-filtered under nitrogen and pasteurised for 1 minute at +85 °C.

Raisins were produced by oven-drying the bunch samples at 60 °C until the weight of the dried grapes was less than 35% of the initial weight and the stems were then removed by hand.

The processed samples were stored at –18 °C for up to 21 months before analysis (within 5 days of extraction) for cyantraniliprole and six metabolites using LC/MS/MS method DP-15736. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 72–111% (cyantraniliprole) and 71–111% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Cyantraniliprole was the predominant residue in the processed fractions, with levels concentrating in the pomace and in raisins. Residues of the IN-J9Z38 metabolite were also measured in dry pomace, lees and juice, with trace levels (< 0.01 mg/kg) also found in wine and raisins. Low levels of IN-N5M09, IN-MYX98 and IN-F6L99 were also detected in pomace and juice. Residues of the other metabolites (IN-N7B69, IN-MLA84, IN-JCZ38 and IN-K7H19) were not detected in any samples.

Table 161 Residues in grapes and processed fractions from supervised trials in Europe involving foliar applications of cyantraniliprole (SE formulation)

GRAPE Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total		Other metabolites (mg/kg)		
		mg/kg	mg/kg	mg/kg	PF	M2	M6	M7
DP-27718 Trial 6 red wine	bunches	<u>0.56</u>	ND	<u>0.56</u>		ND		
	grapes	0.16	ND	0.16	0.29	ND		
	stems	0.69	ND	0.69	1.2	< 0.01	ND	ND
	must	0.44	ND	0.44	0.79	ND	ND	ND
	wet pomace	0.77	ND	0.77	1.4	ND	< 0.01	ND
	lees	0.32	0.02	0.34	0.61	ND	ND	ND
	dry pomace	1.4	0.1	1.5	2.7	< 0.01	0.02	ND
	AF wine	0.3	ND	0.3	0.54	ND	ND	ND
	MF wine	0.28	< 0.01	0.29	0.52	ND	ND	ND
	bottled wine	0.27	< 0.01	0.28	0.5	ND	ND	ND
	juice	0.25	0.02	0.27	0.48	ND	< 0.01	< 0.01
	raisins	0.26	< 0.01	0.27	0.48	ND		
DP-27718 Trial 7 red wine	bunches	<u>0.21</u>	ND	<u>0.21</u>		ND		
	grapes	0.12	ND	0.12	0.57	ND		
	stems	0.48	ND	0.48	2.3	< 0.01		
	must	0.32	ND	0.32	1.5	ND	ND	ND
	wet pomace	0.8	0.02	0.82	3.9	< 0.01	ND	ND
	lees	0.38	0.02	0.4	1.9	ND	ND	ND
	dry pomace	0.73	0.05	0.78	3.7	ND	< 0.01	ND
	AF wine	0.24	ND	0.24	1.1	ND	ND	ND
	MF wine	0.23	< 0.01	0.24	1.1	ND	ND	ND
	bottled wine	0.24	< 0.01	0.25	1.2	ND	ND	ND
	juice	0.1	0.01	0.11	0.52	ND	ND	ND
	raisins	0.1	< 0.01	0.11	0.52	ND		

GRAPE Study ID	Matrix	Cyantraniliprole	IN-J9Z38	Total		Other metabolites (mg/kg)		
		mg/kg	mg/kg	mg/kg	PF	M2	M6	M7
DP-27718 Trial 8 white wine	bunches	0.07	ND	0.07		ND		
	grapes	0.11	ND	0.11	1.6	ND		
	stems	0.31	< 0.01	0.32	4.6	ND		
	must	0.1	< 0.01	0.11	1.6	ND	ND	ND
	wet pomace	0.18	< 0.01	0.19	2.7	ND	ND	ND
	lees	0.46	ND	0.46	6.6	ND	ND	ND
	dry pomace	0.17	ND	0.17	2.4	ND	ND	ND
	AF wine	0.07	ND	0.07	1.0	ND	ND	ND
	MF wine	0.07	ND	0.07	1.0	ND	ND	ND
	bottled wine	0.07	ND	0.07	1.0	ND	ND	ND
	juice	0.09	< 0.01	0.1	1.4	ND	ND	ND
	raisins	0.15	< 0.01	0.16	2.3	ND		

M2: Residues of metabolite IN-MYX98

M6: Residues of metabolite IN-N5M09

M7: Residues of metabolite IN-F6L99

For calculation purposes, where the residue in the processed commodity was reported as ND (< LOD), a value of 0.003 mg/kg was used and where residues were above the LOD but below the LOQ, a value of 0.01 mg/kg was used. In both cases, the PF was expressed as “less than” (e.g. < 0.01). Where residues of IN-J9Z38 are below the LOQ in the RAC, a value of 0.01 has been used to calculate ‘total’ residues.

Table 162 Summary of processing factors for cyantraniliprole and cyantraniliprole + IN-J9Z38

RAC	Matrix	Cyantraniliprole + IN-J9Z38 ^a	
		Calculated processing factors	PF median
Potato	tubers		
	flakes	0.1	0.1
	waste	0.1	0.1
	peeled tubers	0.1	< 0.1
	chips	0.1	0.1
	wet peel	2.3	2.3
	culls	<1.0	< 1.0
	fries	0.1	0.1
	cooking water	0.1	0.1
	unpeeled, boiled	0.1	0.1
	unpeeled mwaved	< 0.33	< 0.33
Spinach	fresh leaves		
	cooked leaves	0.81, 1.0 1.3	1.0
	water	0.06, 0.09, 0.06	0.06
Tomato	fresh		
	washed	0.15, < 0.29, 0.17	0.17
	peeled	< 0.08, 0.1, < 0.08	< 0.08
	sun-dried	3.7, 3.8, 3.0	3.7
	canned	< 0.02, < 0.05, < 0.08	< 0.05
	juice	< 0.15, 0.19, < 0.17	< 0.17
	wet pomace	1.0, 2.2, 0.75	1.0
	dry pomace	3.2, 4.0, 1.7	3.2
	paste	0.62, 0.86, 1.0	0.86
	puree	0.23, 0.43, 0.25	0.25
Orange	fruit		
	juice	0.08, < 0.03, < 0.02	< 0.03
	wet pulp	0.46, 0.22, 0.24	0.24
	dry pulp	0.92, < 0.33, 0.47	< 0.33

RAC	Matrix	Cyantraniliprole + IN-J9Z38 ^a	
		Calculated processing factors	PF median
	meal	0.85, 0.22, 0.47	0.47
	molasses	0.69, 0.33, 0.59	0.59
	marmalade	< 0.15, < 0.03, < 0.06	< 0.06
	oil	8.5, 2.9, 8.8	8.5
	canned	< 0.02, < 0.03, < 0.06	< 0.03
Apple	fruit		
	washed	0.63, 0.58, 0.46	0.58
	puree	1.0, 0.88, 1.3	1.0
	canned	0.13, 0.04, 0.15	0.13
	frozen	1.5, 0.96, 0.62	0.96
	juice	0.38, 0.19, 0.31	0.31
	wet pomace	1.0, 1.2, 0.77	1.0
	dry pomace	3.9, 2.7, 2.0	2.7
	sauce	2.4, 2.2, 2.7	2.2
Plum	plum flesh		
	dried prunes	2.0, 1.6, 1.3	1.6
Cottonseed	seed		
	raw oil (solvent extr)	0.06, 0.04, 0.08	0.06
	refined oil (solvent extr)	0.04, 0.03, 0.05	0.04
	meal (solvent extr)	0.09, < 0.03, 0.05	0.05
	hulls	0.34, 0.37, < 0.27	0.34
	raw oil (cold press)	0.3, < 0.21	0.25
	refined oil (cold press)	0.04, 0.04	0.04
	meal (cold press)	0.11, 0.07	0.09
Olive	whole fruit		
	canned fruit	0.62, 0.58, 0.2	0.58
	olive flesh	1.7, 1.8, 1.5	1.7
	canned flesh	0.95, 0.96, 0.7	0.95
	raw oil	1.7, 1.2, 0.6	1.2
	refined oil	1.3, 0.81, 0.4	0.81
Grape	bunches		
	grapes	0.29, 0.57, 1.6	0.57
	stems	1.2, 2.3, 4.6	2.3
	must	0.79, 1.5, 1.6	1.5
	wet pomace	1.4, 3.9, 2.7	2.7
	lees	0.61, 1.9, 6.6	1.9
	dry pomace	2.7, 3.7, 2.4	2.7
	AF wine	0.54, 1.1, 1.0	1.0
	MF wine	0.52, 1.1, 1.0	1.0
	bottled wine	0.5, 1.2, 1.0	1.0
	juice	0.48, 0.52, 1.4	0.52
	raisins	0.48, 0.52, 2.3	0.52

^a Each value represents a separate study where residues were above the LOQ in the RAC. The factor is the ratio of the combined cyantraniliprole plus IN-J9Z38 metabolite residues in the processed item divided by the residue of cyantraniliprole in the RAC.

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

Dairy cow

In a dairy cow feeding study reported by Ward & Vance, 2011 [Ref: 27180], cyantraniliprole was administered orally in gelatine capsules to four groups of lactating Holstein cows (three cows/group) twice daily for 28 consecutive days. Dosing was made at target treatment levels of 3, 10, 30, and 100 ppm feed. Based on the average dietary intake and average dosing levels of 0.088, 0.276, 0.82 and 3.15 mg/kg body weight, the actual average dose levels were equivalent to 3.53, 11.7, 35.0, and 112 ppm feed. An additional three cows were dosed at 112 ppm feed to obtain depuration data. Body weights ranged from 457–730 kg and remained relatively constant throughout the study period.

Milk was collected twice daily and samples from afternoon sampling were combined with samples from the next morning. Milk samples from the depuration group were collected during the dosing period and up until sacrifice during the depuration phase. Except for the depuration group, cows were sacrificed within 24 hours after the last dose. One of the animals from the depuration group was sacrificed on Days 4, 10, and 15 after the last dose. Samples of liver, kidney, muscle, and fat were collected from all animals at sacrifice.

Samples were stored at about -80 °C for a maximum of 42 days. Samples were stored at about -80 °C for a maximum of 42 days before analysis, with the liver and kidney samples being extracted on the day of collection. Analysis for cyantraniliprole and seven metabolites was by HPLC/MS/MS method 18844, with an LOQ of 0.01 mg/kg for all analytes in all matrices. Average concurrent recovery rates were 75–103% (cyantraniliprole) and 71–112% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Residues reached a plateau in milk after about 5 days and were concentrated in the cream fraction by a factor of approximately 1.7. Residues in skim milk were approximately 60% of those in raw milk.

Residues in milk were dose-dependant and were predominantly cyantraniliprole and IN-N7B69. In the 3 ppm dose group, the maximum average residue of cyantraniliprole was 0.03 mg/kg and for IN-N7B69, 0.028 mg/kg. In the 10 ppm dose group, residues of cyantraniliprole and IN-N7B69 were 0.11 and 0.074 mg/kg, respectively. In the 30 ppm group, residues of cyantraniliprole, IN-N7B69, IN-J9Z38, and IN-MYX98 were 0.25, 0.17, 0.01, and 0.025 mg/kg, respectively. In the 100 ppm dose group, residues of cyantraniliprole, IN-N7B69, IN-J9Z38, and IN-MYX98 were 0.71, 0.28, 0.034, and 0.085 mg/kg, respectively. Residues of all other metabolites were < LOQ.

Residues in cream were comparable on Days 14 and 21. The predominant residues in cream were cyantraniliprole, IN-N7B69, and IN-J9Z38. In the 3 ppm dose group, analytes present above the LOQ were cyantraniliprole (0.066 mg/kg), IN-N7B69 (0.021 mg/kg) and IN-J9Z38 (0.013 mg/kg).

In the 10 ppm dose group the average residues in cream were: cyantraniliprole, 0.18 mg/kg; IN-N7B69, 0.051 mg/kg; and IN-J9Z38, 0.03 mg/kg. In the 30 ppm dose group the average residues of analytes were: cyantraniliprole, 0.55 mg/kg; IN-N7B69, 0.13 mg/kg; IN-J9Z38, 0.078 mg/kg; IN-MLA84, 0.024 mg/kg; and IN-MYX98, 0.022 mg/kg. In the 100 ppm dose group the average residues were: cyantraniliprole, 1.8 mg/kg; IN-N7B69, 0.22 mg/kg; IN-J9Z38, 0.31 mg/kg; IN-MYX98, 0.073 mg/kg; and IN-MLA84, 0.04 mg/kg. All other residues were < LOQ.

Residues in skim milk were comparable on Days 14 and 21. The predominant residues in cream were cyantraniliprole and IN-N7B69. In the 3 ppm dose group the average residues of analytes present above the LOQ were: cyantraniliprole, 0.017 mg/kg and IN-N7B69, 0.02 mg/kg.

In the 10 ppm dose group the average residues in skim milk were: cyantraniliprole, 0.044 mg/kg and IN-N7B69, 0.052 mg/kg. All other residues were < LOQ. In the 30 ppm dose group the average residues were: cyantraniliprole, 0.14 mg/kg; IN-N7B69, 0.13 mg/kg; and IN-MYX98,

0.021 mg/kg. In the 100 ppm dose group the average residues were: cyantraniliprole, 0.47 mg/kg; IN-N7B69, 0.20 mg/kg; and IN-YX98, 0.059 mg/kg. All other residues were < LOQ.

In tissues, the highest residues were found in liver, followed by kidney, fat, and muscle, with cyantraniliprole being the predominant residue in all tissues and was dose dependent.

In the 3 ppm dose group, average residues of analytes present above the LOQ in liver were cyantraniliprole, 0.054 mg/kg and IN-MLA84, 0.032 mg/kg. In the 10 ppm dose group, the average residues were: cyantraniliprole, 0.15 mg/kg and IN-MLA84, 0.075 mg/kg. In the 30 ppm dose group, the average residues were: cyantraniliprole, 0.46 mg/kg; IN-MLA84, 0.22 mg/kg; and IN-N7B69, 0.042 mg/kg. In the 100 ppm dose group, average residues were: cyantraniliprole, 1.7 mg/kg; IN-MLA84, 0.41 mg/kg; IN-N7B69, 0.075 mg/kg; IN-MYX98, 0.025 mg/kg; IN-J9Z38, 0.015 mg/kg; and IN-HGW87, 0.010 mg/kg. All other residues were < LOQ.

In the 3 ppm dose group, average residues of analytes present above the LOQ in kidney were cyantraniliprole, 0.023 mg/kg and IN-N7B69, 0.012 mg/kg. In the 10 ppm dose group, the average residues were: cyantraniliprole, 0.084 mg/kg; IN-N7B69, 0.031 mg/kg; and IN-MLA84, 0.013 mg/kg. In the 30 ppm dose group, the average residues were: cyantraniliprole, 0.20 mg/kg; IN-N7B69, 0.071 mg/kg; IN-MLA84, 0.041 mg/kg; and IN-MYX98, 0.034 mg/kg. In the 100 ppm dose group, average residues were: cyantraniliprole, 0.73 mg/kg; IN-MYX98, 0.14 mg/kg; IN-N7B69, 0.12 mg/kg; IN-MLA84, 0.099 mg/kg; IN-J9Z38, 0.024 mg/kg; and IN-HGW87, 0.011 mg/kg. All other residues were < LOQ.

In the 3 ppm dose group, average residues of analytes present above the LOQ in fat were: cyantraniliprole, 0.014 mg/kg and IN-J9Z38, 0.010 mg/kg. In the 10 ppm dose group, the average residues were: cyantraniliprole, 0.042 mg/kg and IN-J9Z38, 0.023 mg/kg. In the 30 ppm dose group, the average residues were: cyantraniliprole, 0.12 mg/kg; IN-J9Z38, 0.082 mg/kg; and IN-N7B69, 0.01 mg/kg. In the 100 ppm dose group, the average residues were: cyantraniliprole, 0.51 mg/kg; IN-J9Z38, 0.38 mg/kg; and IN-N7B69, 0.02 mg/kg. All other residues were < LOQ.

In the 3 ppm dose group, there were no residues present in muscle above the LOQ. In the 10 ppm dose group, only cyantraniliprole was present above the LOQ (0.026 mg/kg). In the 30 ppm dose group, the average residues were: cyantraniliprole, 0.071 mg/kg and IN-J9Z38, 0.01 mg/kg. In the 100 ppm dose group, the average residues were: cyantraniliprole, 0.28 mg/kg and IN-J9Z38, 0.027 mg/kg. All other residues were < LOQ.

Following cessation of dosing residues declined rapidly. All residues were < LOQ in milk, liver and kidney within 10 days after the last dose, in muscle within 4 days, and in fat within 15 days of the last dose.

Table 163 Average residues of cyantraniliprole and metabolites in milk from cows dosed with cyantraniliprole for 28 days

Matrix	Analyte	Average residues of cyantraniliprole and metabolites (values in milk represent the highest single day value)							
		3 ppm ^a		10 ppm ^a		30 ppm ^a		100 ppm ^a	
		Mean residue (mg/kg)							
Milk	Cyantraniliprole	0.03		0.11		0.25		0.71	
	IN-HGW87	0.0001		0.001		0.004		0.007	
	IN-J9Z38	0.003		0.004		0.010		0.034	
	IN-JCZ38	0.0004		0.0004		0.0008		0.001	
	IN-K7H19	ND		ND		ND		0.001	
	IN-MLA84	0.004		0.005		0.006		0.007	
	IN-MYX98	0.003		0.009		0.025		0.085	
	IN-N7B69	0.028		0.074		0.17		0.28	
Study day		14	21	14	21	14	21	14	21
Cream	Cyantraniliprole	0.072	0.059	0.2	0.15	0.63	0.46	1.9	1.7
	IN-HGW87	0.0002	0.0002	0.0007	0.0007	0.002	0.002	0.008	0.009
	IN-J9Z38	0.014	0.011	0.032	0.027	0.085	0.066	0.37	0.31

Matrix	Analyte	Average residues of cyantraniliprole and metabolites (values in milk represent the highest single day value)							
		3 ppm ^a		10 ppm ^a		30 ppm ^a		100 ppm ^a	
		Mean residue (mg/kg)							
	IN-JCZ38	ND	ND	ND	ND	ND	0.00001	ND	0.00009
	IN-K7H19	ND	ND	ND	ND	ND	ND	ND	0.00001
	IN-MLA84	0.004	0.004	0.009	0.009	0.026	0.021	0.039	0.041
	IN-MYX98	0.002	0.002	0.007	0.006	0.020	0.023	0.066	0.079
	IN-N7B69	0.019	0.022	0.048	0.053	0.12	0.14	0.19	0.25
	Skim milk	Cyantraniliprole	0.019	0.014	0.049	0.039	0.15	0.13	0.47
	IN-HGW87	0.00009	0.00005	0.0004	0.0004	0.001	0.001	0.004	0.003
	IN-J9Z38	ND	0.0002	0.0001	0.0004	0.001	0.002	0.005	0.008
	IN-JCZ38	0.000007	ND	0.00002	ND	0.00003	0.00002	0.030	0.00009
	IN-K7H19	ND	ND	ND	ND	ND	ND	ND	ND
	IN-MLA84	0.0003	0.0002	0.0007	0.0004	0.002	0.001	0.003	0.002
	IN-MYX98	0.002	0.002	0.007	0.006	0.022	0.020	0.066	0.051
	IN-N7B69	0.019	0.020	0.047	0.057	0.12	0.13	0.22	0.18

^a Actual dose rates were 3.5 ppm, 11.7 ppm, 35 ppm and 112 ppm diet

Table 164 Residues of cyantraniliprole and metabolites in tissues from lactating cows dosed with cyantraniliprole for 28 days

Matrix	Analyte	Residues of cyantraniliprole and metabolites (mg/kg feed) in tissues							
		3 ppm ^a		10 ppm ^a		30 ppm ^a		100 ppm ^a	
		mean	max	mean	max	mean	max	mean	max
Muscle	Cyantraniliprole	0.008	0.011	0.026	0.037	0.071	0.092	0.28	0.33
	IN-HGW87	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	0.0015	0.0017
	IN-J9Z38	0.001	0.0013	0.002	0.0026	0.010	0.018	0.027	0.043
	IN-JCZ38	ND	ND	ND	ND	< 0.0005	0.0008	0.0008	0.0009
	IN-K7H19	ND	ND	ND	ND	ND	ND	ND	ND
	IN-MLA84	0.0007	0.0009	0.001	0.0014	0.002	0.0029	0.004	0.0045
	IN-MYX98	0.001	0.0012	0.002	0.002	0.003	0.0035	0.01	0.011
	IN-N7B69	0.001	0.0015	0.003	0.0037	0.005	0.0056	0.009	0.0095
Liver	Cyantraniliprole	0.054	0.066	0.15	0.16	0.46	0.6	1.7	2.1
	IN-HGW87	< 0.0005	< 0.0005	0.0006	0.0008	0.002	0.0027	0.01	0.01
	IN-J9Z38	< 0.0005	0.0013	0.002	0.0025	0.006	0.0093	0.015	0.026
	IN-JCZ38	< 0.0005	< 0.005	< 0.0005	0.005	0.001	0.0018	0.008	0.011
	IN-K7H19	ND	ND	ND	ND	< 0.0005	< 0.0005	< 0.0005	< 0.0005
	IN-MLA84	0.032	0.043	0.075	0.099	0.22	0.29	0.41	0.57
	IN-MYX98	0.0008	0.001	0.003	0.0034	0.007	0.0082	0.025	0.026
	IN-N7B69	0.008	0.01	0.021	0.024	0.042	0.046	0.076	0.079
Kidney	Cyantraniliprole	0.023	0.031	0.084	0.14	0.20	0.25	0.73	0.89
	IN-HGW87	< 0.0005	< 0.005	0.0005	0.0006	0.002	0.0028	0.011	0.012
	IN-J9Z38	0.0009	0.0013	0.002	0.003	0.009	0.013	0.024	0.031
	IN-JCZ38	ND	ND	ND	ND	< 0.0005	< 0.005	0.0005	0.0007
	IN-K7H19	ND	ND	ND	ND	ND	ND	ND	ND
	IN-MLA84	0.007	0.011	0.013	0.017	0.041	0.044	0.099	0.13
	IN-MYX98	0.003	0.0037	0.009	0.0094	0.034	0.039	0.14	0.15
	IN-N7B69	0.012	0.015	0.031	0.031	0.071	0.081	0.12	0.15
Fat	Cyantraniliprole	0.014	0.015	0.042	0.066	0.12	0.15	0.51	0.58
	IN-HGW87	ND	ND	< 0.0005	< 0.005	< 0.0005	< 0.005	0.001	0.0014
	IN-J9Z38	0.01	0.012	0.023	0.031	0.082	0.12	0.38	0.45
	IN-JCZ38	ND	ND	ND	ND	< 0.0005	0.0007	ND	ND
	IN-K7H19	ND	ND	ND	ND	ND	ND	ND	ND

Matrix	Analyte	Residues of cyantraniliprole and metabolites (mg/kg feed) in tissues							
		3 ppm ^a		10 ppm ^a		30 ppm ^a		100 ppm ^a	
		mean	max	mean	max	mean	max	mean	max
	IN-MLA84	0.001	0.0012	0.002	0.0022	0.004	0.0051	0.008	0.0087
	IN-MYX98	0.001	0.0012	0.002	0.0021	0.002	0.0024	0.005	0.007
	IN-N7B69	0.002	0.0027	0.006	0.0088	0.01	0.012	0.02	0.024

^a Actual dose rates were 3.5 ppm, 11.7 ppm, 35 ppm and 112 ppm diet

Table 165 Residue depuration of cyantraniliprole and metabolites in tissues and milk from lactating cows dosed with 100 ppm cyantraniliprole in feed for 28 days

Days after last dose	Analyte	Mean residues of cyantraniliprole and metabolites following withdrawal of dose				
		Milk	Muscle	Liver	Kidney	Fat
4	cyantraniliprole	0.025	0.009	0.063	0.022	0.013
	IN-HGW87	0.0002	0.00007	ND	0.0004	0.00003
	IN-J9Z38	0.002	0.004	0.003	0.011	0.14
	IN-JCZ38	0.0004	ND	0.0002	ND	ND
	IN-K7H19	ND	ND	ND	ND	ND
	IN-MLA84	0.008	0.001	0.17	0.043	0.002
	IN-MYX98	0.004	0.001	0.001	0.004	0.001
	IN-N7B69	0.028	0.001	0.007	0.012	0.002
10	cyantraniliprole	0.002	0.0007	0.005	ND	ND
	IN-HGW87	ND	ND	ND	ND	ND
	IN-J9Z38	ND	0.0006	0.0006	0.001	0.02
	IN-JCZ38	ND	ND	ND	ND	ND
	IN-K7H19	ND	ND	ND	ND	ND
	IN-MLA84	0.00009	ND	0.006	0.0008	0.0005
	IN-MYX98	ND	ND	ND	ND	ND
	IN-N7B69	0.0009	ND	ND	ND	ND
15	cyantraniliprole	0.003	0.0007	0.007	0.004	ND
	IN-HGW87	ND	ND	ND	ND	ND
	IN-J9Z38	ND	ND	0.0005	0.0003	0.004
	IN-JCZ38	ND	ND	ND	ND	ND
	IN-K7H19	ND	ND	ND	ND	ND
	IN-MLA84	0.00009	ND	0.0003	0.0003	ND
	IN-MYX98	ND	ND	0.003	ND	ND
	IN-N7B69	0.002	ND	ND	0.00006	ND

Poultry

In a poultry feeding study reported by Roberts & Ward, 2011 [Ref: DP-27181], cyantraniliprole was administered orally in gelatine capsules to three groups of hens (3 or 4 hens/sub-group with three groups/treatment) daily for 28 consecutive days. Dosing was made at treatment levels of 3, 10, and 30 ppm feed based on the animal diet on a dry weight basis, equivalent to 0.24, 0.86, and 2.34 mg/kg body weight. An additional group (three sub-groups) was dosed at 30 ppm feed (2.37 mg/kg body weight) to obtain depuration data. Body weights ranged from 1.3–1.96 kg and remained relatively constant throughout the study period.

Eggs were collected twice daily and samples from afternoon sampling were combined with samples from the next morning. Eggs from the depuration group were collected during the dosing period and up until sacrifice during the depuration phase. Except for the depuration group, hens were sacrificed within 6 hours after the last dose. Animals from the relevant sub-group from the depuration group were sacrificed on Days 5, 9, and 14 after the last dose. Samples of liver, muscle, and skin with

fat were collected from all animals at sacrifice and were pooled in approximately equal quantities according to sub-group.

Samples were stored at about -80 °C for a maximum of 97 days before analysis, with the liver samples being extracted on the day of collection. Analysis for cyantraniliprole and seven metabolites was by HPLC/MS/MS method 18844, with an LOQ of 0.01 mg/kg for all analytes in all matrices. Average concurrent recovery rates were 95–125% (cyantraniliprole) and 67–126% (metabolites) in samples spiked with 0.01 and 0.1 mg/kg.

Residues in eggs were dose dependant and were predominantly cyantraniliprole and IN-J9Z38. In the 3 ppm dose group, the maximum average residue of cyantraniliprole was 0.08 mg/kg and for IN-J9Z38, 0.04 mg/kg. Residues of IN-MLA84 and IN-MYX98 were also found at 0.016 and 0.014 mg/kg, respectively. In the 10 mg/kg dose group, residues of cyantraniliprole and IN-N7B69 were 0.17 and 0.077 mg/kg, respectively. Residues of IN-MLA84 and IN-MYX98 also exceeded the LOQ (0.038 and 0.035 mg/kg, respectively). In the 30 mg/kg group, residues of cyantraniliprole, IN-J9Z38, IN-MLA84, IN-MYX98, and IN-HGW87 were 0.80, 0.41, 0.12, 0.10, and 0.016 mg/kg, respectively. Residues of all other metabolites were < LOQ.

The predominant residues in egg whites were cyantraniliprole (0.08 mg/kg, 0.17 mg/kg and 0.64 mg/kg) and IN-J9Z38 (0.04 mg/kg, 0.07 mg/kg and 0.27 mg/kg) in the 3 ppm, 10 ppm and 30 ppm dose groups respectively. Other metabolites present were IN-MYX98 and IN-MLA84, at levels less than 0.02 mg/kg (3 ppm dose group), less than 0.04 mg/kg (10 ppm dose group) and less than 0.1 mg/kg in the 10 ppm dose group. All other residues were < LOQ.

The predominant residues in yolks were also cyantraniliprole and IN-J9Z38. In the 3 mg/kg dose group only cyantraniliprole was present above the LOQ (0.015 mg/kg). In the 10 mg/kg dose group the average cyantraniliprole residues were 0.03 mg/kg and were 0.1 mg/kg in the 30 ppm dose group. Residues of IN-J9Z38, IN-MYX98 and IN-MLA84 were less than 0.02 mg/kg in the 10 ppm dose group and less than 0.06 mg/kg in the 30 ppm dose group. All other residues were < LOQ.

In tissues, the highest residues were found in liver with cyantraniliprole, IN-MYX98 and IN-MLA84 being the predominant residues in all tissues. Residues of cyantraniliprole were dose dependant.

In liver, the predominant residue was IN-MYX98, present at average levels of 0.03 mg/kg (3 ppm dose group), 0.07 mg/kg (10 ppm dose group) and 0.19 mg/kg (30 ppm dose group). Average cyantraniliprole residues in these dose groups were 0.017, 0.04 and 0.13 mg/kg respectively and IN-MLA84 was also found at similar levels (0.015, 0.04 and 0.1 mg/kg) in the respective dose groups. Other metabolites found in the 10 ppm and 30 ppm dose groups were IN-HGW87 (0.03 and 0.06 mg/kg respectively) and IN-N7B69 (0.013 and 0.05 mg/kg respectively). All other residues were < LOQ.

In skin with fat, no residues were found above the LOQ, with cyantraniliprole (0.033 mg/kg) and IN-MYX98 (0.015 mg/kg) reported in the 10 mg/kg dose group. In the 30 mg/kg dose group, the average cyantraniliprole residues were 0.08 mg/kg with IN-MYX98, IN-J9Z38 and IN-HGW87 found at levels less than 0.03 mg/kg. All other residues were < LOQ.

In muscle, the only residues found above the LOQ were IN-MYX98, found at 0.012 mg/kg in the 10 ppm dose group and cyantraniliprole (0.025 mg/kg), IN-MYX98 (0.014 mg/kg and IN-HGW87 (0.011 mg/kg) in the 30 ppm dose group. All other residues were < LOQ.

Following cessation of dosing residues rapidly declined, with residues in eggs, muscle and skin with fat all being below the LOQ within 5 days after the last dose. Residues in liver were also below the LOQ after 9 days depuration (first sample taken).

Table 166 Average residues of cyantraniliprole and metabolites in eggs from hens dosed with cyantraniliprole for 28 days

Matrix	Analyte	Average residues of cyantraniliprole and metabolites (mg/kg) (values in eggs represent the highest single day value)					
		3 ppm dose group		10 ppm dose group		30 ppm dose group	
		Mean residue (mg/kg)					
Eggs	cyantraniliprole	0.082		0.17		0.80	
	IN-HGW87	0.0053		0.0069		0.016	
	IN-J9Z38	0.039		0.077		0.41	
	IN-JCZ38	< 0.002		< 0.002		< 0.002	
	IN-K7H19	< 0.002		ND		ND	
	IN-MLA84	0.016		0.038		0.12	
	IN-MYX98	0.014		0.035		0.10	
	IN-N7B69	< 0.002		< 0.002		0.0029	
Study day		14	21	14	21	14	21
Egg whites	cyantraniliprole	0.098	0.059	0.20	0.14	0.68	0.60
	IN-HGW87	< 0.002	0.0020	0.0037	0.0038	0.010	0.0097
	IN-J9Z38	0.045	0.026	0.078	0.066	0.27	0.27
	IN-JCZ38	ND	ND	ND	ND	ND	ND
	IN-K7H19	ND	ND	ND	ND	ND	ND
	IN-MLA84	0.015	0.015	0.034	0.033	0.092	0.093
	IN-MYX98	0.017	0.014	0.037	0.030	0.10	0.089
	IN-N7B69	< 0.002	0.0023	< 0.002	< 0.002	0.0038	0.0036
Egg yolks	cyantraniliprole	0.017	0.012	0.034	0.023	0.090	0.11
	IN-HGW87	< 0.002	< 0.002	0.0040	0.0034	0.0099	0.0081
	IN-J9Z38	0.0081	0.0056	0.018	0.014	0.053	0.062
	IN-JCZ38	ND	ND	ND	ND	ND	ND
	IN-K7H19	ND	ND	ND	ND	ND	ND
	IN-MLA84	0.0064	0.0077	0.017	0.016	0.039	0.046
	IN-MYX98	0.0086	0.0059	0.017	0.012	0.041	0.039
	IN-N7B69	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002

Table 167 Residues of cyantraniliprole and metabolites in poultry tissues

Matrix	Analyte	Residues of cyantraniliprole and metabolites (mg/kg)					
		3 ppm dose group		10 ppm dose group		30 ppm dose group	
		mean	max	mean	max	mean	max
Muscle	cyantraniliprole	0.0034	0.0055	0.0093	0.015	0.025	0.05
	IN-HGW87	< 0.002	< 0.002	0.0052	0.0064	0.011	0.015
	IN-J9Z38	ND	ND	ND	ND	ND	ND
	IN-JCZ38	ND	ND	ND	ND	ND	ND
	IN-K7H19	ND	ND	ND	ND	ND	ND
	IN-MLA84	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.002
	IN-MYX98	0.0041	0.0045	0.012	0.013	0.014	0.022
	IN-N7B69	< 0.002	< 0.002	< 0.002	< 0.002	0.0026	0.0037
Liver	cyantraniliprole	0.017	0.03	0.041	0.064	0.13	0.24
	IN-HGW87	0.0076	0.009	0.028	0.036	0.059	0.083
	IN-J9Z38	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.0034
	IN-JCZ38	0.0030	0.0043	0.0094	0.011	0.0060	0.0074
	IN-K7H19	ND	ND	ND	ND	ND	ND
	IN-MLA84	0.015	0.022	0.043	0.048	0.096	0.099
	IN-MYX98	0.023	0.034	0.068	0.096	0.19	0.32
	IN-N7B69	0.0067	0.012	0.013	0.017	0.045	0.072

Matrix	Analyte	Residues of cyantraniliprole and metabolites (mg/kg)					
		3 ppm dose group		10 ppm dose group		30 ppm dose group	
		mean	max	mean	max	mean	max
Skin with fat	cyantraniliprole	0.0093	0.014	0.033	0.058	0.080	0.16
	IN-HGW87	< 0.002	0.002	0.0078	0.01	0.015	0.021
	IN-J9Z38	0.0029	0.0033	0.0064	0.0079	0.018	0.023
	IN-JCZ38	ND	ND	ND	ND	ND	ND
	IN-K7H19	ND	ND	ND	ND	ND	ND
	IN-MLA84	< 0.002	< 0.002	0.0034	0.0037	0.0080	0.009
	IN-MYX98	0.0037	0.0046	0.015	0.026	0.027	0.049
	IN-N7B69	< 0.002	< 0.002	< 0.002	0.002	0.0030	0.005

Table 168 Residue depuration of cyantraniliprole and metabolites in eggs from hens dosed with 30 ppm cyantraniliprole for 28 days

Analyte	Residues of cyantraniliprole and metabolites in eggs following withdrawal of dose					
	Mean residue (mg/kg)					
	Study day (days post last dose)					
	29 (1)	31 (3)	33 (5)	35 (7)	38 (10)	40 (12)
cyantraniliprole	0.22	0.010	0.0040	< 0.002	< 0.002	< 0.002
IN-HGW87	0.00086	0.0030	< 0.002	< 0.002	ND	ND
IN-J9Z38	0.12	0.0065	0.0024	< 0.002	ND	ND
IN-JCZ38	ND	ND	ND	ND	ND	ND
IN-K7H19	ND	ND	ND	ND	ND	ND
IN-MLA84	0.050	0.0068	< 0.002	ND	ND	ND
IN-MYX98	0.041	0.0079	0.0033	< 0.002	< 0.002	< 0.002
IN-N7B69	< 0.002	< 0.002	ND	ND	ND	ND

Table 169 Residue depuration of cyantraniliprole and metabolites in tissues from hens dosed with 30 ppm cyantraniliprole for 28 days

Study day (days post last dose)	Analyte	Residues of cyantraniliprole and metabolites following withdrawal of dose		
		Mean residue (mg/kg)		
		Muscle	Liver	Skin with fat
33 (5)	cyantraniliprole	< 0.002	-	0.0030
	IN-HGW87	ND	-	ND
	IN-J9Z38	ND	-	ND
	IN-JCZ38	ND	-	ND
	IN-K7H19	ND	-	ND
	IN-MLA84	ND	-	< 0.002
	IN-MYX98	ND	-	< 0.002
	IN-N7B69	ND	-	ND
37 (9)	cyantraniliprole	< 0.002	< 0.002	0.0057
	IN-HGW87	ND	ND	< 0.002
	IN-J9Z38	ND	ND	< 0.002
	IN-JCZ38	ND	ND	ND
	IN-K7H19	ND	ND	ND
	IN-MLA84	ND	< 0.002	< 0.002
	IN-MYX98	ND	ND	< 0.002
	IN-N7B69	ND	ND	ND
42 (14)	cyantraniliprole	< 0.002	< 0.002	0.0044
	IN-HGW87	ND	ND	ND
	IN-J9Z38	ND	ND	< 0.002
	IN-JCZ38	ND	ND	ND

Study day (days post last dose)	Analyte	Residues of cyantraniliprole and metabolites following withdrawal of dose		
		Mean residue (mg/kg)		
		Muscle	Liver	Skin with fat
	IN-K7H19	ND	ND	ND
	IN-MLA84	ND	< 0.002	ND
	IN-MYX98	ND	ND	ND
	IN-N7B69	ND	ND	ND

NATIONAL RESIDUE DEFINITIONS

Table 170 Cyantraniliprole: National residue definitions for MRL-compliance and dietary intake estimation

Country	MRL-compliance	Dietary intake estimation		
	All commodities	Plant commodities (unprocessed)	Plant commodities (processed)	Animal commodities
Canada	cyantraniliprole	cyantraniliprole	cyantraniliprole + IN-J9Z38	
New Zealand	cyantraniliprole	cyantraniliprole	cyantraniliprole	Not established ^a
Global Joint Review (proposed)	cyantraniliprole	cyantraniliprole	cyantraniliprole + IN-J9Z38	cyantraniliprole + IN-J9Z38 + IN-MLA84 + IN-MYX98 + IN-N7B69

^a A residue definition has not yet been established as the current authorized GAPs are not expected to result in detectable residues in animal products.

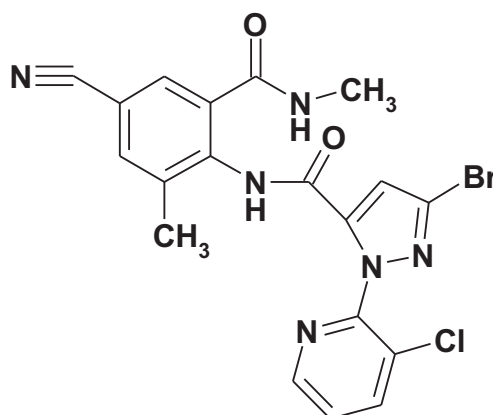
APPRAISAL

Cyantraniliprole is a diamide insecticide with a mode of action (ryanodine receptor activation) similar to that of chlorantraniliprole and flubendiamide with root systemic and translaminar activity against the larval stages of lepidopteran insects; and also on thrips, aphids, and some other chewing and sucking insects.

It was scheduled by the Forty-fourth Session of the CCPR (REP12/PR) as a new compound for consideration by the 2013 JMPR. The manufacturer submitted studies on metabolism, analytical methods, supervised field trials, processing, freezer storage stability, environmental fate in soil and rotational crop residues.

Authorisations exist for the use of cyantraniliprole in Canada, Columbia, Malaysia, New Zealand, Vietnam and in a regional grouping of countries in West Africa (CLISS).

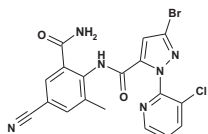
Cyantraniliprole is 3-bromo-1-(3-chloro-2-pyridyl)-4'-cyano-2'-methyl-6'-(methylcarbamoyl) pyrazole -5-carboxanilide. It is relatively insoluble in water (12 mg/L at pH 7, 6 mg/L at pH 9) and hydrolyses under alkaline conditions and at higher temperatures (above 25 °C), the major hydrolysis product being IN-J9Z38. It is not volatile (1.2×10^{-15} Pa at 20 °C), has a log P_{ow} of 1.9, its solubility in organic solvents ranges from < 1 g/L (octanol, xylene) to 5–7 g/L (methanol, dichloromethane, acetone) and is rapidly degraded by photolysis.



Cyantraniliprole (DPX-HGW86)
(MW 473.7)

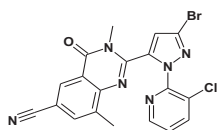
The following abbreviations are used for the metabolites discussed below:

IN-HGW87



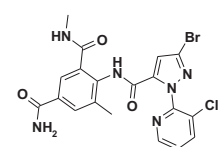
N-[2-(Aminocarbonyl)-4-cyano-6-methylphenyl]-3-bromo-1-(3-chloro-2-pyridinyl)-1*H*-pyrazole-5-carboxamide

IN-J9Z38



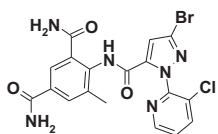
2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1*H*-pyrazol-5-yl]-3,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarbonitrile MW 455.7

IN-JCZ38



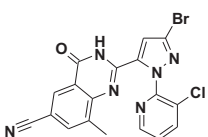
4-[[[3-Bromo-1-(3-chloro-2-pyridinyl)-1*H*-pyrazol-5-yl]carbonyl]amino]-N',5-dimethyl-1,3-benzenedicarboxamide MW 491.7

IN-K7H19



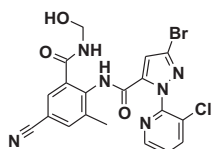
4-[[[3-Bromo-1-(3-chloro-2-pyridinyl)-1*H*-pyrazol-5-yl]carbonyl]amino]-5-methyl-1,3-benzenedicarboxamide MW 477.7

IN-MLA84



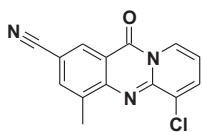
2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1*H*-pyrazol-5-yl]-1,4-dihydro-8-methyl-4-oxo-6-quinazolinecarbonitrile MW 441.7

IN-MYX98



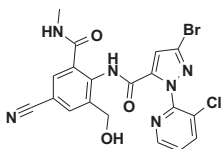
3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-[(hydroxymethyl)amino]carbonyl]-6-methylphenyl]-1*H*-pyrazole-5-carboxamide MW 489.7

IN-N5M09



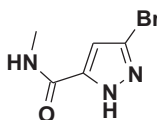
6-Chloro-4-methyl-11-oxo-11H-pyrido[2,1-b]quinazoline-2-carbonitrile MW 441.6

IN-N7B69



3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-(hydroxymethyl)-6-[(methylamino)carbonyl]phenyl]-1H-pyrazole-5-carboxamide MW 489.7

IN-F6L99



3-Bromo-N-methyl-1H-pyrazole-5-carboxamide MW 204

Animal metabolism

The Meeting received information on the metabolism of radiolabelled cyantraniliprole, separately ^{14}C -labelled at the 4-cyano (CN) and the pyrazole carbonyl (PC) groups, in rats, lactating goats and laying hens.

The WHO panel of the 2013 JMPR concluded that in rats, the majority of the dose was excreted within 24 to 48 hours, with about 1–5.5% TRR being recovered in tissues and that tissue elimination half-lives ranged from 2.6 days (fat) to about 6 days in whole blood.

The metabolic pathway was primarily through hydroxylation (to form IN-N7B69 and IN-MYX98), with IN-N7B69 being further metabolized to a glucuronide conjugate. Cyantraniliprole undergoes ring closure to generate IN-J9Z38 which is then in turn hydroxylated to form IN-NBC94, its carboxylic acid, and its glucuronide conjugate. IN-MYX98 is also metabolized to the closed-ring metabolite IN-MLA84, which, like IN-NBC94, is further oxidized to a hydroxylated metabolite, a carboxylic acid, and the glucuronide of the hydroxyl metabolite. Further, the hydroxylated metabolite IN-MYX98 can be N-dealkylated to form IN-HGW87 as well as being hydroxylated a second time to form bis-hydroxy-cyantraniliprole. Cyantraniliprole can also be hydroxylated on the pyridine ring, followed by a ring closure analogous to the conversion of cyantraniliprole to IN-J9Z38.

Lactating goats were orally dosed with $[\text{CN-}^{14}\text{C}]$ - or $[\text{PC-}^{14}\text{C}]$ -cyantraniliprole at doses equivalent to approximately 13 ppm in the feed for 7 consecutive days and sacrificed 23 hours after the last dose.

The majority of the administered dose was recovered in excreta (84–88% in faeces, 7% in urine). About 1–2% (0.08–0.15 mg/kg) of the applied radioactivity was retained in milk, with 0.5 mg/kg (0.3% AR) found in liver and < 0.01% AR in other tissues. Solvent extraction was able to retrieve 99% TRR from milk, 90–98% TRR from fat, 61–81% TRR from muscle and 63–79% TRR from kidney. Solvent extractable TRR in the liver were lower (54–60% TRR) but an additional 21–27% TRR were recovered following digestion of the post extracted solids (PES) with protease.

In milk, TRR reached a plateau of 0.09 and 0.18 mg/kg after 2–3 days in the CN and PC label studies respectively. Cyantraniliprole was the major residue component, making up 40–50% (0.03–0.07 mg/kg) of the radiochemical label. Metabolite IN-MYX98 was also present at 15–18% TRR (0.01–0.03 mg/kg). Other metabolites (except IN-N7B69 at 11% TRR in the CN-label study) were found each < 0.01 mg/kg and less than 10% TRR.

In liver, TRR were 0.43–0.5 mg/kg. Cyantraniliprole (0.07–0.14 mg/kg) made up about 17–23% of the TRR and in kidney (TRR 0.14–0.21 mg/kg) with the major residue was also cyantraniliprole, accounting for 13–19% TRR (0.02–0.04 mg/kg).

In muscle, TRR were 0.03–0.04 mg/kg with the significant residue being cyantraniliprole, found at about 30% TRR and 0.01 mg/kg in the CN-label study and 15% TRR, 0.006 mg/kg in the PC-label study. The IN-MYX98 metabolite also accounted for 33% TRR (0.01 mg/kg) in the PC-label study.

TRR in fat were 0.05 and 0.12 mg/kg in the CN-label and PC-label studies respectively, with consistent results in omental, subcutaneous and renal fat. Cyantraniliprole was the major residue, averaging 31–42% TRR (0.01–0.025 mg/kg) with the IN-J9Z38 metabolite also accounted for 24–27% TRR (0.01–0.03 mg/kg).

Laying hens were orally dosed with [CN-¹⁴C]- or [PC-¹⁴C]-cyantraniliprole at doses equivalent to approximately 11 ppm in the feed for 14 consecutive days and sacrificed 23 hours after the last dose.

The majority of the administered dose was excreted, with 0.4–0.5% (0.20–0.26 mg/kg) remaining in egg whites, 0.07% (0.09 mg/kg) in yolks. Radioactivity in liver (0.14–0.2 mg/kg) accounted for 0.3–0.4% of the applied dose with muscle, abdominal fat and skin with fat each containing $\leq 0.1\%$ AR (< 0.01 mg/kg).

In eggs, %TRR reached a plateau of about 0.1 mg/kg in yolks after 5–7 days. The %TRRs in egg white increased to 0.26–0.56 mg/kg over the first 2 days and decreased to a steady state of about 0.2–0.24 mg/kg after 7 days.

Solvent extraction was able to retrieve 79–99% TRR from eggs, 63–120% TRR from fat, 100% TRR from muscle and 53–72% TRR from skin with fat. Solvent extractable TRR in the liver were lower (17–23% TRR) but an additional 38% TRR were recovered following digestion of the post extracted solids (PES) with protease.

In eggs, cyantraniliprole was the major residue component, making up 33–42% TRR (0.09 mg/kg) in egg whites and 9–10% TRR (< 0.01 mg/kg) in yolks. Metabolite IN-J9Z38 made up about 17–29% TRR (0.03–0.08 mg/kg) in egg whites and 7–13% TRR (0.006–0.011 mg/kg) in yolks. IN-MLA84 was also present in egg whites at about 18–19% TRR (0.04–0.05 mg/kg) and in yolks at about 12–17% TRR (0.01–0.015 mg/kg).

In liver, TRR were 0.14–0.17 mg/kg. Cyantraniliprole was not found in any samples and while metabolites IN-JCZ38, IN-K5A78, IN-K5A79, IN-K7H19, IN-MLA84, IN-MYX98 and IN-N7B69 were identified, these were each present at $< 4\%$ TRR (< 0.01 mg/kg).

In muscle, abdominal fat and skin with fat, no further analysis was conducted because of the low TRR (< 0.004 mg/kg) present.

In summary, the metabolism of cyantraniliprole in lactating goats (ruminant) and laying hen was consistent with that in the rat. Cyantraniliprole residues were rapidly eliminated in the excreta (94–100% of the dose) in goats and laying hens, with less than 1% of the total administered dose remaining in tissues and eggs and 1–2% found in milk). Cyantraniliprole was the predominant residue, with IN-N7B69 (milk), IN-MYX98 (muscle and milk), IN-J9Z38 (fat and eggs) and IN-MLA84 (eggs) being the principal metabolites present at more than 10% TRR or > 0.01 mg/kg.

Plant metabolism

The Meeting received plant metabolism studies on cotton, lettuce, tomato and rice seedlings following foliar and soil treatments with [¹⁴C]-cyantraniliprole. A 1:1 ($\mu\text{Ci}/\mu\text{Ci}$ ratio) mixture of [CN-¹⁴C]-cyantraniliprole and [PC-¹⁴C]-cyantraniliprole was used in the foliar treatments and separate treatments of the two radiolabels were applied as soil treatments.

Cotton

In cotton plants, treated three times with the equivalent of 0.15 kg ai/ha per application as foliar sprays, 7 days apart from 3 weeks after emergence, TRR in leaves immediately after the first treatment were 2.7 and 7.9 mg/kg immediately after the last application and after 13 days had

decreased to 0.43 mg/kg. At harvest (124 days after the last application), TRRs in cotton gin by-products, lint and undelinted seed were 0.13, 0.01, and < 0.01 mg/kg, respectively.

Surface washing removed 56–70% TRR from immature leaves with a further 27–33% extracted into acidified aqueous acetone.

Cyantraniliprole was the major residue in leaves, decreasing from 70% TRR immediately after the first application to 20% TRR seven days later and accounted for 37% TRR (0.19 mg/kg) and 27% TRR (0.12 mg/kg), respectively, 7 and 13 days after the final application.

IN-NXX70, a photodegradate of IN-J9Z38, found predominately in the surface wash, accounted for 22% TRR seven days after the first application but decreased to 1% TRR in leaves sampled 7 days after the third application.

Surface washing of cotton gin by-products removed about 19% TRR (0.03 mg/kg) with a further 65% TRR (0.07 mg/kg) being extracted into acetone or with more aggressive extraction methods. Cyantraniliprole was the predominant residue, accounting for 34% TRR (0.04 mg/kg).

In plants from soil treatments where three applications of 0.15 kg ai/ha cyantraniliprole (SC formulation) were made to wetted soil at 7 day intervals from 7 weeks after emergence, TRRs in leaves from immature plants sampled up to 14 days after the last application were all ≤ 0.005 mg/kg. At maturity, 125 days after the last application, residues in lint and undelinted seed were < 0.001 mg/kg and TRR values in cotton gin by-products were 0.1 mg/kg (CN-label) and 0.02 mg/kg (PC-label).

Cyantraniliprole was the only significant residue in gin by-products, making up 26–47% TRR (0.01–0.03 mg/kg).

Lettuce

In lettuce plants, treated three times with the equivalent of 0.15 kg ai/ha per application as foliar sprays, 7 days apart from 3 weeks after emergence, TRR in leaves immediately after the first treatment was 11 mg/kg, 10 mg/kg immediately after the second application and about 8 mg/kg just after the last application. Seven days after the last application, TRRs had decreased to about 2 mg/kg and were 0.43 mg/kg at maturity, 32 days after the last application. Surface residues decreased from about 91% TRR immediately after the first application and 32 days after the last application surface residues were 13% TRR.

Cyantraniliprole was the major residue in leaves, decreasing from about 98% TRR immediately after the first application to 50% TRR in mature leaves, 32 days after the last application. The IN-J9Z38 metabolite, present in mature leaves at about 23% TRR (0.01 mg/kg) was only metabolite accounting for more than 5% TRR.

In plants from soil treatment where three applications of 0.15 kg ai/ha cyantraniliprole (SC formulation) were made to wetted soil at 7 day intervals from 7 weeks after emergence, TRRs (CN-label) in leaves from immature plants declined from 0.14 mg/kg immediately after the first application to about 0.05 mg/kg (7 days after the 2nd and 3rd applications) and were about 0.01 mg/kg at maturity. TRRs following the PC-label soil treatment were ≤ 0.06 mg/kg in immature leaves and at crop maturity.

Cyantraniliprole was the major radioactive component present in leaves, up to 77–84% TRR in young leaves and 37% TRR (0.004 mg/kg) and 69% TRR (0.04 mg/kg) in mature leaves for the CN-label and PC-labels respectively.

Tomatoes

In tomato plants, treated three times with the equivalent of 0.15 kg ai/ha per application as foliar sprays, 7 days apart from 3 weeks after emergence, TRR in leaves immediately after the first treatment were 2.5 mg/kg, 8.5 mg/kg immediately after the second application and 7.6 mg/kg just after the last application. Seven days after the last application, TRRs had decreased to about

2.2 mg/kg and were 1.3 mg/kg 14 days after the last application. Residues in fruit and leaves at harvest (132 days after the last treatment) were < 0.01 mg/kg. The majority of the TRR (66–85%) were found in the surface wash with 15–34% TRR present in the extract.

Cyantraniliprole was the major residue in leaves, decreasing from about 95% TRR immediately after the first application to 61% TRR seven days later and accounted for 64 and 43% TRR respectively, 7 and 14 days after the last application. In leaves taken at maturity, residues in the surface wash were < 0.01 mg/kg and 0.01 mg/kg in the tissue extracts.

Concentrations of the unresolved radioactivity corresponding to both IN-MLA84 and IN-NXX70, (mostly in the surface wash) reached 11.5% TRR 7 days after the first application, decreasing to 4.4% TRR thereafter.

In plants from soil treatments where three applications of 0.15 kg ai/ha cyantraniliprole (SC formulation) were made to wetted soil in pots at 7 day intervals from 7 weeks after emergence, TRRs reached a maximum of 0.03 mg/kg in immature leaves 7 days after the last application and were < 0.01 mg/kg in leaves and 0.001 mg/kg in fruit at harvest (125 days after the last application).

Cyantraniliprole was the major radioactive component in leaves 7–14 days after the last application, ranging from 22–26% TRR (< 0.01 mg/kg).

Rice

Rice seedlings were treated with three foliar applications of 0.15 kg ai/ha at the 3–4 leaf stage and 7 and 14 days later and grown under flooded conditions (pots immersed in about 3 cm water) from 2 days after the initial treatment until 2–3 days before harvest.

TRRs in foliage were 2.1 mg/kg immediately after the first application, decreasing to 0.38 mg/kg after 7 days. Seven and 14 days after the last application, TRRs in leaves were 1.6 mg/kg and 1.2 mg/kg respectively. At harvest, 140 days after the last application, TRRs in straw were 0.45 mg/kg and 0.02 mg/kg in grain. In roots, TRRs increased from 0.24 mg/kg seven days after the first application to 0.68 mg/kg seven days after the last application and were 0.45 mg/kg at harvest. In immature leaves, 7 days after the last application, the surface wash contained about 75% TRR, reducing to 47% TRR in leaves sampled 14 days after the last treatment.

Cyantraniliprole was the major residue in immature leaves, making up 76–81% TRR (about 1.0 mg/kg) in samples taken 7 and 14 days after the last application. IN-J9Z38 was the predominant metabolite found at 0.6% TRR immediately after the first application and increasing to 11% TRR 14 days after the last application.

In straw, cyantraniliprole was the major component, accounting for 24.4% TRR (0.11 mg/kg) and cyantraniliprole was also the predominant residue in grain, accounting for 21% TRR (0.005 mg/kg).

Rice seedlings were also treated with a single soil application of 0.3 kg ai/ha (as surface-applied granules) at the 3–4 leaf stage and the plants were grown under flooded conditions (pots immersed in about 3 cm water) from 2 days after the initial treatment until 2–3 days before harvest, 175 days after treatment.

TRRs in foliage increased from 0.08 mg/kg (7 days after treatment) to 0.15 mg/kg (14 days after treatment) and reached 0.4 mg/kg after 56 days. Residues in roots were about 0.3 mg/kg after 56 days and at harvest (175 days after treatment). At harvest, TRRs were 0.28–0.3 mg/kg in straw and 0.01–0.03 mg/kg in grain.

Cyantraniliprole was the major residue in leaves sampled 56 days after treatment (49–57% TRR and about 0.2 mg/kg). The IN-J9Z38 metabolite was found in these samples at 16–22% TRR (about 0.08 mg/kg).

The major residue in straw was also cyantraniliprole (42–45% TRR, 0.13 mg/kg), with IN-J9Z38 (14–18% TRR) being the only significant metabolite, found at 14–18% TRR and in grain, cyantraniliprole accounted for 46–63% TRR (0.007–0.014 mg/kg).

In summary, cyantraniliprole was the predominant residue in most crop fractions at various sampling points up to crop maturity. Metabolites identified in foliar treated samples (with the exception of the photodegrade IN-NXX70) were also found in samples from plants treated with a soil drench application, indicating that the main metabolic pathways were similar. Overall, total radioactive residues were greater following foliar treatment than following soil application. A similar profile was observed in all studies.

The metabolite IN-J9Z38 was present at levels above 10% TRR only in rice foliage and lettuce (after foliar applications) and also in rice foliage and straw after soil treatment. Where present, residues were significantly lower (10–50%) than the levels of cyantraniliprole.

The metabolism of cyantraniliprole in plants was generally consistent with those in animals, except for the minor plant photodegradation pathway leading to the formation of IN-NXX70 and IN-QKV54).

Environmental fate

The Meeting received information on the environmental fate and behaviour of cyantraniliprole, including aerobic degradation in soil, photolysis on the soil surface, field soil dissipation, hydrolytic stability, soil and water/sediment degradation and confined and field rotational crop studies. Separate treatments of [CN-¹⁴C]-cyantraniliprole and [PC-¹⁴C]-cyantraniliprole were used in the confined studies.

Hydrolysis

Hydrolysis of cyantraniliprole was pH and temperature dependant. The rate of hydrolysis was significantly higher at high pH and temperature. The half lives at 15 °C decreased from 362 days (pH 4) to 126 days (pH 7) and was about 3 days at pH 9. A similar pattern was observed at the higher temperature of 35 °C, with the respective half-lives being 55 days, 7.5 days and < 1 day at pH 9. Under environmental conditions (pH 7, 25 °C) the half-life for cyantraniliprole was 212 days.

At all pH's, the predominant hydrolysis product was the cyclisation product IN-J9Z38 which accounted for about 28% AR (pH 4), 89% AR (pH 7) and 98% AR in the pH 9 samples.

Photolysis

In aqueous solutions, cyantraniliprole is rapidly degraded by photolysis. Half-lives in natural water and pH 4 sterile buffer exposed to continuous artificial sunlight for 15 days at 25 °C were 4–5 hours, with the formation of IN-NXX69, IN-NXX70, IN-QKV54 and IN-QKV55 as photodegradates. DT_{90s} were less than 16 hours.

In moist (non-sterile) soil (75% field capacity), treated with [¹⁴C]-cyantraniliprole at the equivalent of 1 kg ai/ha parent residues decreased to about 1% AR after 30 days in the irradiated samples and to 33% AR in the non-irradiated samples. The IN-J9Z38 metabolite was the predominant residue (up to about 50% AR) with IN-RNU71 and IN-QKV54 also found at about 13–14% AR. Estimated photolysis DT₅₀ and DT₉₀ values for cyantraniliprole (derived from the difference in the degradation constants (k) for the irradiated and non-irradiated samples) were 12 and 41 days respectively. Kinetic modeling suggested that nearly 34% of the cyantraniliprole in soil is degraded by photolysis and about 64% through soil degradation pathway.

Aerobic soil metabolism

Two studies were conducted in five soils (one loam soil, two silty clay loams, one silt loam and a sandy loam) with the equivalent of 0.4 kg ai/ha [CN-¹⁴C]-cyantraniliprole or [PC-¹⁴C]-cyantraniliprole. In these studies, the moist soils were incubated in the dark for up to a year at 20 °C or 22 °C.

Half-lives for cyantraniliprole were 9 days in the loam soil, 21–39 days in the silty clay loams, 44 days in the silty loam and 92 days in the sandy loam.

DT₅₀ values for the seven major transformation products (average DT₅₀ values in brackets) were: IN-JCZ38 (8 days), IN-K5A79 (64 days), IN-K5A77 (132 days), IN-J9Z38 (139 days), IN-JSE76 (410 days), IN-K5A78 (423 days) and IN-PLT97 (1032 days).

Soil dissipation

Ten field studies were conducted to investigate the degradation and mobility of cyantraniliprole under field conditions. In all of the trials a single application of 0.3 kg ai/ha or 0.45 kg ai/ha was made to bare soil in late spring or early summer and cropped soils were also treated in three of these studies. Soil samples were collected to a maximum depth of 90 cm, immediately prior to application and at pre-determined intervals over an 18 month period.

Cyantraniliprole was rapidly degraded in field soils with half-lives ranging from 17 to 51 days. While laboratory studies suggested that pH had some effect on degradation rates, degradation rate under field conditions does not appear to be pH-dependent. Downward mobility of the parent compound as well as its metabolites was limited, with residues rarely found below 15 cm. Soil metabolites formed in the bare soil treatments at levels greater than 10% of the initial soil concentration were IN-J9Z38 (max 42%), IN-K5A78 (max 17%), IN-JSE76 (max 14%), IN-JCZ38 (max 13%) and IN-K5A77 (max 11%). Lower metabolite levels were observed in soil from the cropped soil treatments, predominantly IN-J9Z38 (max 27%) and IN-JCZ38 (max 13%).

The mean temperature-normalized field DT₅₀ value from all studies was 32 days, consistent with the mean laboratory derived value.

Water/sediment dissipation

Under anaerobic conditions, cyantraniliprole degraded in the water phase and also partitioned to the sediment where it was further degraded and incorporated into the sediment organic fraction. The major degradate was IN-J9Z38, present in the total system at up to 23–40% AR (0.09–0.16 ppm) during the first 28 days after treatment and declining to 5–7% AR (0.02–0.03 ppm) at the end of the study period (Day 100).

The aerobic degradation of [¹⁴C]-cyantraniliprole was studied in a water/silt-loam system and a water/sand system treated with [PC-¹⁴C]-cyantraniliprole at a rate of 0.5 µg ai/g and incubated outdoors for 14 days under natural sunlight at 23 ± 2 °C.

In the water phase, cyantraniliprole residues were 1–2% AR at the end of the 14-day study period and in the sediment phase, after reaching maximum levels of 15–22% AR after 2–3 days, residues declined to 6–9% AR on Day 14.

One significant degradate, IN-J9Z38, was found in the surface water at a maximum of about 15–27% AR after 3–5 days and declining to 4.5% AR (silt-loam system) and 12% AR (sand system) at the end of the 14-day study period. In the sediment extracts residues of IN-J9Z38 increased from about 2% AR at Day 1 to about 42% AR at Day 14.

The calculated half-lives in the water/sediment systems were 3.5–4.4 days for cyantraniliprole and 40 days for the IN-J9Z38 metabolite.

Residues in succeeding crops

In two rotational crop metabolism studies using [PC-¹⁴C]-cyantraniliprole or [CN-¹⁴C]-cyantraniliprole, wheat, soya bean, lettuce and red beet were planted as rotational crops 25–30 and 120 days after a single bare soil application of 0.3 kg ai/ha in one study and 0.45 kg ai/ha in the second study. In the second study, after 365 days aging, a further planting of wheat was made in the 30-day rotation plots.

In the first rotation crops, total radioactive residues in food items ranged from 0.02–0.06 mg/kg in wheat grain, 0.08–0.11 mg/kg in lettuce, 0.02–0.03 mg/kg in beet roots and 0.04 mg/kg in soya bean seeds. Higher residues were seen in animal feed items; wheat hay and straw (0.97–1.6 mg/kg), soya bean foliage (0.19 mg/kg) and beet foliage (0.11 mg/kg).

The metabolic fates of cyantraniliprole in the three rotational crops were similar. Cyantraniliprole was the predominant residue in wheat straw and hay (41–53% TRR, 0.4–0.85 mg/kg), wheat grain (10–36% TRR, < 0.01–0.02 mg/kg), soya bean foliage (36% TRR, 0.07 mg/kg), red beet roots (21–27% TRR, < 0.01 mg/kg) and lettuce (60–69% TRR, 0.05–0.08 mg/kg). No cyantraniliprole was detected in soya bean seeds and parent residues in beet foliage were 3–4% TRR.

In food commodities, IN-MYX98 was the only significant metabolite present above 10% TRR, being found in 2nd rotation (120 day) lettuce leaves at 16% TRR but < 0.01 mg/kg. In animal feed commodities, IN-J9Z38 was found in wheat hay, forage and straw at up to 13% TRR (0.18 mg/kg) and IN-K7H19 was present in wheat hay and straw at 10–11% TRR (0.04–0.06 mg/kg) in the 365 day rotation crop.

Overall, the metabolism in rotational crops was consistent with metabolism seen in primary crops and in the animal studies.

Rotational crop field studies were conducted in Europe and North America to estimate residue uptake in follow crops. In two European studies, where spinach, lettuce, spring barley, oats, soya bean and radish were planted into bare soil treated with 0.2 kg ai/ha or 0.45 kg ai/ha at plant-back intervals of 14, 30, 120, 270 and 365 days, with the exception of soya bean (seeds and forage) and radish tops, residues of cyantraniliprole and metabolites were not found in succeeding crops. In soya bean forage, residues of cyantraniliprole were 0.02–0.03 mg/kg and in soya bean seed, residues of the IN-N7B69 metabolite were < 0.01 mg/kg.

In five North American studies, bare soil was treated with three applications of cyantraniliprole at about 5 day intervals to achieve a total seasonal application rate of 0.45 kg ai/ha. In three of these studies, four rotational crops (lettuce/spinach, oats, radish and soya bean) were planted 14, 30, 120, and 365 days after the last application. In the other two studies, strawberries, turnip, sugar beet, garden beet, radish, carrot, bean, pea, soya bean, alfalfa, clover, field corn, sweet corn, sorghum, rice, wheat, Bermuda grass, brome grass, clover, bluegrass and peanut were planted 30 days after the last application.

Residues of cyantraniliprole and metabolites in the first rotation crops (30 day plant-back interval) were below 0.05 mg/kg in commodities for human consumption (cereal grains, root crops, legumes and pulses, leafy vegetables). Higher residues were reported in animal feed commodities, up to 0.2 mg/kg in forage crops and 0.3 mg/kg in most hays and straws. Highest residues were found in soya bean hay, up to 0.63 mg/kg in one sample.

In the first rotation crops (30 day plant-back interval (PBI)), highest residues of cyantraniliprole were above 0.01 mg/kg in radish roots (0.02 mg/kg), radish and turnip tops (0.02–0.04 mg/kg), legume forages (0.02–0.14 mg/kg), legume hays (0.05–0.63 mg/kg), leafy vegetables (0.03 mg/kg), cereal forages (0.01–0.11 mg/kg), cereal hays and straws (0.07–0.21 mg/kg), forage grasses (0.01–0.09 mg/kg) and grass hays (0.02–0.23 mg/kg).

Metabolites present at more than 0.01 mg/kg were IN-J9Z38 (up to 0.03 mg/kg in cereal and legume hays and straws), IN-JZ38 (in cereal and legumes, up to 0.06 mg/kg hays and 0.03 mg/kg in forages) and IN-MLA84 (in legumes, up to 0.02 mg/kg in forage and 0.07 mg/kg in hays).

Methods of analysis

Several analytical methods have been reported for the analysis of cyantraniliprole and up to eight metabolites in plant and animal commodities. The basic approach employs extraction with acetonitrile/water and analysis by high pressure liquid chromatography with tandem mass spectrometry.

For plant and processed plant commodities, the HPLC-MS/MS method used in most of the supervised residue field trials, was validated for the analysis of cyantraniliprole and its metabolites (IN-N7B69, IN-JCZ38, IN-K7H19, IN-MYX98, IN-MLA84 and IN-J9Z38) in a range of representative matrices. The LOQ is 0.01 mg/kg for each analyte. Adequate extraction efficiencies

were demonstrated in plant matrices using radiolabelled samples from metabolism and confined rotational crop studies.

For animal commodities, the HPLC-MS/MS method was validated for the analysis of cyantraniliprole, IN-HGW87, IN-N7B69, IN-K7H19, IN-JCZ38, IN-MYX98, IN-J9Z38 and IN-MLA84 in livestock tissues, milk and eggs. After extraction with acetonitrile, extracts are partitioned against hexane before SPE clean-up and analysis. The LOQ is 0.01 mg/kg for each analyte. The method was validated by an independent laboratory using kidney, muscle, and milk. The extraction efficiency was successfully demonstrated with samples of liver, muscle, milk, egg white, and egg yolk from livestock metabolism studies.

The DFG S19 multi-residue method with LC-MS/MS analysis was validated for the analysis of cyantraniliprole residues in tomato (representing high water content), orange (high acid content), wheat grain (high starch content) and almond (high oil content), and is suitable as an enforcement method for cyantraniliprole in plant commodities. It was also validated in milk, eggs, meat and liver as being a suitable enforcement method for cyantraniliprole residues in animal commodities.

The US-FDA PAM multi-residue methods were shown to be unsuitable for the detection and enforcement of cyantraniliprole and metabolites (Protocols A through F).

Stability of pesticide residues in stored analytical samples

Freezer storage stability of cyantraniliprole and metabolites IN-F6L99, IN-J9Z38, IN-JCZ38, IN-K7H19, IN-MLA84, IN-MYX98, IN-N5M09 and IN-N7B69 was investigated in five representative commodities: apples (high-water content), grapes (high-acid content), potatoes (high-starch content), dry bean seeds (high-protein content), and peanuts (high-oil content).

Residues were shown to be stable in these representative substrates for at least 24 months in frozen storage, with residues in the stored samples being greater than 80% of the spiked levels except in peanuts (high oil content), where reduced recoveries were observed at all storage intervals for the metabolites IN-JCZ38, IN-K7H19 and IN-N7B69.

Definition of the residue

In animal commodities, the predominant residues identified in the metabolism studies were cyantraniliprole, IN-J9Z38, IN-MLA84, IN-N7B69 and IN-MYX98. Where residues were found in animal tissues in the metabolism studies or the feeding studies, cyantraniliprole was the major or a significant component. Noting that a multi-residue method was available to measure cyantraniliprole in animal commodities, the Meeting agreed that for MRL-compliance, the residue definition for animal commodities should be cyantraniliprole.

The compound cyantraniliprole has a log K_{ow} of 1.9, suggesting that it is not fat soluble, and this is supported by the residue distribution in muscle and fat reported in a cow feeding study, where the residues in fat were generally only about 2-fold higher than in muscle. The Meeting therefore concluded that cyantraniliprole is not fat soluble.

For dietary intake estimation, in addition to the parent compound, metabolites found at significant levels in the animal metabolism studies were IN-N7B69 (milk), IN-MYX98 (muscle and milk), IN-J9Z38 (fat and eggs) and IN-MLA84 (eggs). In the feeding studies, at doses that reflect the expected animal burden, these individual metabolites were also found at levels ranging from about 20% to 100% of the parent concentrations in different matrices but when combined, were generally found at levels close to those of the parent.

IN-N7B69 was found in milk at a level equivalent to parent and at about half the parent concentration in kidney. IN-J9Z38 was present in eggs at about 50% parent concentration. IN-MLA84 was found in cattle liver at about 60% of the parent concentration and in eggs at about 50% parent concentration. IN-MYX98, found in eggs at about 20% parent and in poultry liver at about 135% of parent.

These metabolites also occur in rats, are not considered more toxic than the parent compound, are adequately covered in the derived toxicological reference dose and a validated HPLC-MS/MS method is available to analyse for them.

The Meeting agreed that while not all of these metabolites would occur in all tissues; these four metabolites (IN-N7B69, IN-J9Z38, IN-MLA84 and IN-MYX98) should be included in the residue definition for dietary intake estimation for animal commodities. The Meeting considered that if animal commodities were analysed only for cyantraniliprole, a conservative correction factor of 2 could be applied for the purpose of dietary intake estimation to account for these metabolites.

In plant commodities from treated crops, the metabolism studies indicated that cyantraniliprole was the major residue in rice, lettuce, cotton and tomato. In rotational crops, where residues are present, cyantraniliprole is also the main residue in food commodities. The Meeting noted that a multi-residue method exists to measure parent residues and agreed that for MRL-compliance, the residue definition for plant commodities should be cyantraniliprole.

The only metabolite identified in the plant metabolism studies at more than 10% TRR or greater than 0.01 mg/kg in commodities at harvest was IN-J9Z38, reported in leaves from foliar-treated rice (11% TRR and 0.13 mg/kg), rice straw from rice grown in treated soil (up to 18% TRR and 0.05 mg/kg) and in foliar-treated lettuce where residues of 23% TRR (0.01 mg/kg) were measured in mature leaves from seedling plants treated up to 32 days before sampling. The Meeting noted that in the supervised field trials, residues of IN-J9Z38 were also reported in some trials, but mostly < 0.01 mg/kg and rarely found at levels more than 10% of the cyantraniliprole residue.

In rotational crops, metabolite residues in food commodities did not exceed 0.01 mg/kg, with IN-J9Z38, IN-JZ38 and IN-MLA84 only present in animal feeds (cereal and legume forage, hays and straws) at up to 0.07 mg/kg.

In processed food commodities, metabolites IN-J9Z38 and to a lesser extent IN-N5M09 and IN-F6L99 were formed under conditions of heat and/or hydrolysis. In addition to cyantraniliprole, only IN-J9Z38 was observed at significant levels, being the predominant residue in cooked spinach, cottonseed oil and present at more than 50% of the parent levels in tomato paste, apple sauce and canned olives. IN-N5M09 and IN-F6L99 were only quantifiable in a few processed food commodities (e.g., cooked spinach, apple sauce) and were much lower than the levels of the parent compound and IN-J9Z38.

The main metabolite in some processed commodities (IN-J9Z38) was also observed in the animal metabolism studies and the toxicology of IN-J9Z38 is addressed in the rat studies and covered by the derived reference dose. Sufficient toxicological information is available to confirm that the IN-J9Z38 metabolite is no more toxic than cyantraniliprole and analytical methods are available to measure this metabolite.

The Meeting concluded that for dietary intake risk assessment, the residue definition for plant commodities should be cyantraniliprole but that for processed commodities, the IN-J9Z38 should also be included.

Proposed definition of the residue (for compliance with the MRL, animal and plant commodities): *cyantraniliprole*.

Proposed definition of the residue (for estimation of dietary intake for unprocessed plant commodities): *cyantraniliprole*.

Proposed definition of the residue (for estimation of dietary intake for processed plant commodities): *sum of cyantraniliprole and IN-J9Z38, expressed as cyantraniliprole*.

Proposed definition of the residue (for estimation of dietary intake for animal commodities: *sum of cyantraniliprole, 2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl]-3,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarbonitrile [IN-J9Z38], 2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl]-1,4-dihydro-8-methyl-4-oxo-6-quinazolinecarbonitrile [IN-MLA84], 3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-(hydroxymethyl)-6-[(methylamino)carbonyl]phenyl]-1H-pyrazole-*

5-carboxamide [IN- N7B69] and 3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2[[hydroxymethyl]amino]carbonyl]-6-methylphenyl]-1H-pyrazole-5-carboxamide [IN- MYX98], expressed a cyantraniliprole.

The residue is not fat soluble.

Results of supervised residue trials on crops

The Meeting received supervised trial data for foliar and soil applications of cyantraniliprole on a range of fruit and vegetable crops, rice, tree nuts, oilseeds and coffee and for seed treatments (potatoes, oil-seed rape). These trials were conducted mainly in Europe and/or North America.

Where residues have been reported as ND (< LOD) the values have been considered as < LOQ (< 0.01 mg/kg) for the purposes of MRL setting. If a higher residue level was observed at a longer PHI than the GAP, the higher value has been used in MRL setting.

The Meeting noted that GAP has been authorised for the use of cyantraniliprole and that product labels were available from Canada, Columbia, New Zealand Malaysia, Vietnam and from a regional group of countries in West Africa. Supervised trial data were provided for citrus, grapes, olives, pomegranate, beans and sunflower, but no GAP information was available to support maximum residue level estimations for these commodities.

Pome fruits

The critical GAP for cyantraniliprole on pome fruit is in Canada, up to four foliar applications of 0.05–0.15 kg ai/ha applied at least 7 days apart with a PHI of 3 days and with a total of 0.45 kg ai/ha/season.

In trials on apples in North America matching the Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.06, 0.07, 0.1, 0.12, 0.13, 0.13, 0.15, 0.15, 0.16, 0.17, 0.18, 0.21, 0.26, 0.26, 0.29 and 0.31 mg/kg (n=16).

In trials on pears in North America matching the Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.08, 0.1, 0.12, 0.14, 0.16, 0.23, 0.42, 0.44, 0.56 and 0.58 mg/kg (n=10).

The Meeting noted that the GAP in Canada was for pome fruit and that the medians of the two data sets differed by less than 5-fold and agreed to consider a group maximum residue level. As the Mann-Whitney U-test indicated that the residue populations for apples and pears were not different it was agreed to combine the results to give a data set of: 0.06, 0.07, 0.08, 0.1, 0.1, 0.12, 0.12, 0.13, 0.13, 0.14, 0.15, 0.15, 0.16, 0.16, 0.17, 0.18, 0.21, 0.23, 0.26, 0.26, 0.29, 0.31, 0.42, 0.44, 0.56 and 0.58 mg/kg (n=26) for the pome fruit crop group.

The Meeting estimated an STMR of 0.16 mg/kg and a group maximum residue level of 0.8 mg/kg for cyantraniliprole on pome fruit.

Stone fruits

The critical GAP for cyantraniliprole on stone fruit is in Canada, up to four foliar applications of 0.05–0.15 kg ai/ha with a total of 0.45 kg ai/ha/season, applied at least 7 days apart with a PHI of 3 days.

In trials on cherries in North America matching the Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues in whole fruit were: 0.3, 0.32, 0.7, 0.8, 0.89, 0.9 and 3.4 mg/kg (n=7). In flesh residues were: 0.33, 0.36, 0.89, 0.93, 0.96, 0.98 and 3.8 mg/kg (n=7).

In trials on peaches in North America matching the Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.16, 0.18, 0.19, 0.19, 0.23, 0.24, 0.28, 0.34, 0.39, 0.45, 0.51, 0.79 and 0.81 mg/kg. In flesh, residues were: 0.19, 0.19, 0.2, 0.23, 0.25, 0.27, 0.34, 0.35, 0.42, 0.49, 0.56, 0.89 and 0.94 mg/kg (n=13).

In trials on plums in North America matching the Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.03, 0.05, 0.06, 0.06, 0.06, 0.07, 0.12, 0.19 and 0.28 mg/kg. In flesh, residues were: 0.03, 0.05, 0.06, 0.06, 0.07, 0.07, 0.13, 0.2 and 0.29 mg/kg (n=9).

The Meeting noted that the GAP in Canada was for stone fruit and that the medians of the data sets for cherries, peaches and plums differed more than 5-fold and agreed not to consider a group maximum residue level for stone fruit.

The Meeting estimated an STMR of 0.93 mg/kg (based on residues in flesh), and based on residues in the whole fruit, estimated a subgroup maximum residue level of 6 mg/kg for cyantraniliprole on cherries.

The Meeting estimated an STMR of 0.34 mg/kg (based on residues in flesh, and based on residues in the whole fruit, estimated a subgroup maximum residue level of 1.5 mg/kg for cyantraniliprole on peaches.

The Meeting estimated an STMR of 0.07 mg/kg (based on residues in flesh) and based on residues in the whole fruit, estimated a subgroup maximum residue level of 0.5 mg/kg for cyantraniliprole on plums.

Bush berries

The critical GAP for cyantraniliprole on bush berries is in Canada, up to four foliar applications of 0.05–0.15 kg ai/ha with a total of 0.45 kg ai/ha/season, applied at least 7 days apart with a PHI of 3 days.

In trials on blueberries in North America matching the Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.42, 0.51, 0.52, 0.52, 0.75, 0.8, 1.5, 1.5 and 2.0 mg/kg (n=9).

The Meeting noted that blueberry can be used as a representative crop for bush berries and estimated an STMR of 0.75 mg/kg and a subgroup maximum residue level of 4.0 mg/kg for cyantraniliprole on bush berries.

Bulb vegetables

The critical GAP for cyantraniliprole on bulb vegetables is in Canada, up to four foliar applications of 0.1–0.15 kg ai/ha with a total of 0.45 kg ai/ha/season, applied at least 5 days apart with a PHI of 1 day.

In trials on bulb onions in North America matching the Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: < 0.01, < 0.01, < 0.01, < 0.01, 0.01, 0.02, 0.02, 0.02, 0.02 and 0.03 mg/kg (n=10).

The Meeting noted that the GAP in Canada also includes use on garlic and shallot and agreed to extrapolate the data for bulb onions to these commodities.

The Meeting estimated an STMR of 0.02 mg/kg and a maximum residue level of 0.05 mg/kg for cyantraniliprole on onion, bulb, garlic and shallot.

In trials on spring onions (green onions) in North America matching the Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.38, 0.63, 1.3, 1.6 and 4.1 mg/kg (n=5).

The Meeting noted that the GAP in Canada also includes use Welsh onion and agreed to extrapolate the data for spring onions to onion, Welsh.

The Meeting estimated an STMR of 1.3 mg/kg and a maximum residue level of 8.0 mg/kg for cyantraniliprole on spring onion and onion, Welsh.

Brassica (cole or cabbage) vegetables

The critical GAP for cyantraniliprole on brassica vegetables is in Canada, up to four foliar applications of 0.025–0.15 kg ai/ha with a total of 0.45 kg ai/ha/season, applied at least 5–7 days apart with a PHI of 1 day.

In trials on broccoli in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.22, 0.28, 0.51, 0.59, 0.61, 0.69, 0.82 and 1.1 mg/kg (n=8).

In trials on cauliflowers in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues in the flower heads were: 0.01 and 0.08 mg/kg (n=2).

In trials on head cabbage in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues in cabbages (with wrapper leaves) were: 0.29, 0.32, 0.32, 0.42, 0.47, 0.56, 0.57, 0.65, 0.71, 0.86 and 0.95 mg/kg (n=11).

The Meeting noted that the GAP in Canada was for brassica vegetables and that the medians of the data sets for broccoli and cabbage differed by less than 5-fold (insufficient data on cauliflower) and agreed to consider a group maximum residue level. In deciding on the data set to use for estimating a group maximum residue level, since a Mann-Whitney U-test indicated that the residue populations for broccoli and cabbage were not different, it was agreed to combine the results to give a data set of: 0.01, 0.08, 0.22, 0.28, 0.29, 0.32, 0.32, 0.42, 0.47, 0.51, 0.56, 0.57, 0.59, 0.61, 0.65, 0.69, 0.71, 0.82, 0.86, 0.95 and 1.1 mg/kg (n=21) for brassica vegetables.

The Meeting estimated an STMR of 0.56 mg/kg and a group maximum residue level of 2.0 mg/kg for cyantraniliprole on brassica (cole or cabbage) vegetables. The Meeting also estimated a highest residue of 1.1 mg/kg for calculating animal dietary burdens.

Fruiting vegetables, Cucurbits

The critical GAP for cyantraniliprole on cucurbit vegetables is in Canada, up to four foliar applications of 0.025–0.15 kg ai/ha with a total of 0.45 kg ai/ha/season, applied at least 5–7 days apart with a PHI of 1 day.

In trials on cucumber in North America matching the GAP of Canada (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.02, 0.02, 0.02, 0.03, 0.04, 0.05, 0.05, 0.07, 0.12 and 0.16 mg/kg (n=10).

In trials on summer squash in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.01, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.11 mg/kg (n=9).

In trials on melons in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.04, 0.05, 0.08, 0.09, 0.09, 0.1, 0.11, 0.15 and 0.17 mg/kg (n=9). In these trials, cyantraniliprole residues in the melon edible portion were all < 0.01 (n=9).

The Meeting noted that the GAP in Canada was for cucurbit vegetables and that the medians of the data sets for cucumber, summer squash and melons differed by less than 5-fold and agreed to consider a group maximum residue level. In deciding on the data set to use for estimating a group maximum residue level, since a Kruskal-Wallis H-test indicated that the residue populations for cucumber, summer squash and melons were not different, it was agreed to combine the results to give a data set of: 0.01, 0.02, 0.02, 0.02, 0.03, 0.03, 0.04, 0.04, 0.04, 0.05, 0.05, 0.05, 0.05, 0.06, 0.07, 0.07, 0.08, 0.08, 0.09, 0.09, 0.09, 0.1, 0.11, 0.11, 0.12, 0.15, 0.16 and 0.17 mg/kg (n=28) for cucurbit vegetables.

The Meeting estimated an STMR of 0.01 mg/kg for cucurbits with an inedible peel (based on the melon data on residues in flesh), an STMR of 0.065 mg/kg (based on the summer squash data) for

cucurbits with an edible peel and a group maximum residue level of 0.3 mg/kg for cyantraniliprole on fruiting vegetables, Cucurbits.

Fruiting vegetables, other than Cucurbits

The critical GAP for cyantraniliprole on fruiting vegetables (except cucurbits) is in Canada, up to four foliar applications of 0.025–0.15 kg ai/ha with a total of 0.45 kg ai/ha/season, applied at least 5–7 days apart with a PHI of 1 day.

In trials on tomatoes in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.04, 0.05, 0.06, 0.06, 0.07, 0.07, 0.07, 0.07, 0.08, 0.08, 0.08, 0.09, 0.09, 0.1, 0.12, 0.14, 0.14, 0.16, 0.17 and 0.26 mg/kg (n=20).

In trials on sweet peppers in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.03, 0.04, 0.06, 0.07, 0.07, 0.08, 0.08, 0.15, 0.21, 0.24 and 0.28 mg/kg (n=11).

In trials on chilli peppers (non-bell peppers) in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.07, 0.07, 0.08, 0.09, 0.1, 0.2, 0.25, 0.31 and 0.42 mg/kg (n=9).

The Meeting noted that the GAP in Canada was for fruiting vegetables (except cucurbits) and that the medians of the data sets for sweet peppers, tomatoes and chilli peppers differed by less than 5-fold and agreed to consider a group maximum residue level. In deciding on the data set to use for estimating a group maximum residue level, since a Kruskal-Wallis H-test indicated that the residue populations for sweet peppers, tomatoes and chili peppers were not different, it was agreed to combine the results to give a data set of: 0.03, 0.04, 0.04, 0.05, 0.06, 0.06, 0.06, 0.07, 0.07, 0.07, 0.07, 0.07, 0.07, 0.07, 0.08, 0.08, 0.08, 0.08, 0.08, 0.08, 0.09, 0.09, 0.09, 0.1, 0.1, 0.12, 0.14, 0.14, 0.15, 0.16, 0.17, 0.2, 0.21, 0.24, 0.25, 0.26, 0.28, 0.31 and 0.42 mg/kg (n=40) for the non-cucurbit fruiting vegetables group.

The Meeting estimated an STMR of 0.08 mg/kg and a group maximum residue level of 0.5 mg/kg for cyantraniliprole on fruiting vegetables, other than Cucurbits (excluding sweet corn and mushrooms).

For dried chilli peppers, applying the default processing factor of 7 to the data set for fresh chilli peppers, the Meeting estimated an STMR-P of 0.7 mg/kg and a maximum residue level of 5 mg/kg for cyantraniliprole on dried chilli peppers.

Leafy vegetables (including Brassica leafy vegetables)

The critical GAP for cyantraniliprole on leafy vegetables is in Canada, up to four foliar applications of 0.025–0.15 kg ai/ha with a total of 0.45 kg ai/ha/season, applied at least 5–7 days apart with a PHI of 1 day.

In trials on head lettuce in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 0.02, 0.08, 0.16, 0.18, 0.64, 0.75, 0.83, 1.3, 1.6, 1.8, 2.1 and 2.7 mg/kg (n=12).

In trials on leaf lettuce in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 1.1, 1.2, 2.1, 2.4, 2.4, 2.5, 3.2, 3.3, 4.0, 5.3, 6.8 and 6.8 mg/kg (n=12).

In trials on spinach in North America matching the critical Canadian GAP (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 3.8, 4.1, 4.2, 4.6, 4.7, 4.9, 5.8, 8.2, 10 and 13 mg/kg (n=10).

In trials on mustard greens in North America matching the critical Canadian GAP for vegetable brassicas (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: 2.4, 3.4, 3.9, 5.5, 5.8, 6.0, 7.1, 7.2, 8.0, 13 and 19 mg/kg (n=11).

The Meeting noted that the GAP in Canada was for leafy vegetables and that the medians of the data sets for leaf lettuce, spinach and mustard greens (but not head lettuce) differed by less than 5-fold and agreed to consider a group maximum residue level for leafy vegetables except head lettuce. In deciding on the data set to use for estimating a group maximum residue level, since a Kruskal-Wallis H-test indicated that the residue populations for leaf lettuce, spinach and mustard greens were not different it was agreed to combine the results to give a data set of: 1.1, 1.2, 2.1, 2.4, 2.4, 2.4, 2.5, 3.2, 3.3, 3.4, 3.8, 3.9, 4.0, 4.1, 4.2, 4.6, 4.7, 4.9, 5.3, 5.5, 5.8, 5.8, 6.0, 6.8, 6.8, 7.1, 7.2, 8.0, 8.2, 10, 13, 13 and 19 mg/kg for leafy vegetables (n=33) except head lettuce and to use the head lettuce data to estimate a maximum residue level for head lettuce.

The Meeting estimated an STMR of 4.7 mg/kg and a group maximum residue level of 20 mg/kg for cyantraniliprole on leafy vegetables (except head lettuce).

The Meeting estimated an STMR of 0.79 mg/kg and a maximum residue level of 5 mg/kg for cyantraniliprole on head lettuce.

Root and tuber vegetables

The critical GAP for cyantraniliprole on root and tuber vegetables is in Canada, up to four foliar applications of 0.05–0.15 kg ai/ha with a total of 0.45 kg ai/ha/season, applied at least 5–14 days apart with a PHI of 7 days.

In trials on potatoes in North America matching the critical Canadian GAP for foliar applications to root and tuber vegetables (with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season), cyantraniliprole residues were: < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, 0.01, 0.02, 0.02 and 0.03 mg/kg (n=20).

The Meeting also noted that residues of cyantraniliprole may also arise in potatoes planted as rotational crops, and agreed to consider maximum residue level recommendations for potatoes when discussing rotational crop residues.

Stalk and stem vegetables

The critical GAP for cyantraniliprole on celery is in Canada, up to four foliar applications of 0.025–0.15 kg ai/ha with a total of 0.45 kg ai/ha/season, applied at least 5–7 days apart with a PHI of 1 day.

In trials on celery in North America matching the critical Canadian GAP for leafy vegetables (including celery), with three applications of 0.15 kg ai/ha, 0.45 kg ai/ha/season, cyantraniliprole residues were: 0.28, 0.73, 1.0, 1.1, 1.2, 2.0, 2.3, 2.5, 4.7, 5.7 and 9.1 mg/kg (n=11).

The Meeting estimated an STMR of 2.0 mg/kg and a maximum residue level of 15 mg/kg for cyantraniliprole on celery.

Rice

The critical GAP for cyantraniliprole on rice is in Vietnam, for foliar applications of 0.05–0.1 kg ai/ha with a PHI of 5 days.

Results were available from six trials on rice in China where three foliar applications of cyantraniliprole were applied up to 7 days before harvest.

The Meeting agreed that these data did not match the GAP in Vietnam in that the PHI deviated from GAP by more than 25%.

Tree nuts

The critical GAP for cyantraniliprole on tree nuts is in Canada, up to four foliar applications of 0.05–0.1 kg ai/ha with a total of 0.45 kg ai/ha/season, applied at least 7 days apart with a PHI of 5 days.

In six trials on almonds in the USA, 3 foliar sprays of 0.15 kg ai/ha (0.45 kg ai/ha/season) were applied at 6–8 day intervals up to 5 days before harvest.

In six trials on pecans in the USA, 3 foliar sprays of 0.15 kg ai/ha (0.45 kg ai/ha/season) were applied at 6–8 day intervals up to 5 days before harvest.

The Meeting noted that since both the number of applications and the treatment rates in the trials for almonds and pecans did not match the Canadian GAP, the use of the proportionality approach to estimate maximum residue levels was not appropriate.

Oilseeds

The critical GAP for cyantraniliprole on cotton is in the region of West Africa, up to three foliar applications of 0.05 kg ai/ha with a total of 0.15 kg ai/ha/season, applied at least 14 days apart with a PHI of 7 days.

Results were available from trials conducted in the USA on cotton, where three foliar applications of 0.15 kg ai/ha cyantraniliprole were applied at 6–8 day intervals up to 7–9 days before harvest.

The Meeting noted that the application rates used in the USA trials were higher and the retreatment intervals were shorter than the GAP in West Africa and the Meeting agreed that the concept of proportionality could not be used to recommend a maximum residue level for cyantraniliprole on cotton seed.

The critical GAP for cyantraniliprole on oil seed crops (excluding cotton and peanut) is in Canada, up to 4 foliar applications of 0.025–0.1 kg ai/ha with a total of 0.11 kg ai/ha/season, applied at least 7 days apart with a PHI of 7 days.

Results were available from trials on oilseed rape and on sunflower in North America, where three foliar sprays of 0.15 kg ai/ha (0.45 kg ai/ha/season) were applied at 5–9 day intervals up to 7 days before harvest.

The Meeting noted that for both oilseed rape and sunflower, in addition to the application rate in the field trials differing from the Canadian GAP, the lower seasonal application rate associated with the Canadian GAP supports only a single application of the maximum recommended application rate of 0.1 kg ai/ha, compared to the three applications used in the field trials.

The Meeting concluded that these trials did not match the Canadian GAP.

Seed for beverages and sweets

The critical GAP for cyantraniliprole on coffee is in Columbia, one foliar application of 2.5–3.5 g ai/5 L/100 trees, equivalent to 0.125–0.175 kg ai/ha with a total of 0.3 kg ai/ha/season, with a PHI of 28 days.

In two Brazilian trials matching the Columbian GAP, cyantraniliprole residues were < 0.01 and 0.02 mg/kg.

The Meeting noted that in a further six trials in Brazil involving foliar applications that matched the Columbian GAP but where two soil drenches (0.01–0.06 g ai/100 mL/plant to achieve the equivalent of 0.2 kg ai/ha/treatment) were also applied approximately 90 and approximately 120 days before harvest, cyantraniliprole residues were < 0.01 (5) and 0.01 mg/kg.

The Meeting agreed that since the early season soil drench treatments did not appear to contribute to the final residue in coffee beans, the data from these two sets of results could be combined, giving a data set of: < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, 0.01 and 0.02 mg/kg, to recommend a maximum residue level for cyantraniliprole on coffee beans.

The Meeting estimated an STMR of 0.01 mg/kg and a maximum residue level of 0.03 mg/kg for cyantraniliprole on coffee bean.

Estimation of residues in plant commodities grown as potential succeeding crops

Residues of cyantraniliprole, while not persistent, can be taken up by following crops. In Canada, the GAP includes a maximum seasonal foliar application rate of 0.45 kg ai/ha for most crops except oil seeds where the maximum seasonal rate is 0.11 kg ai/ha. In Columbia, the maximum seasonal rate for onions and Welsh onions is 0.3 kg ai/ha and in West Africa, the total seasonal rate on cotton is 0.15 kg ai/ha.

In Canada, recommended plant-back intervals (PBIs) have been established for crops likely to be grown in rotation with treated crops. In general, for annual crops for human consumption and where MRLs have been established, there is no plant-back interval specified, but for crops likely to be used as animal feed (cereals, grasses, legumes etc) the label recommends a 30-day plant-back interval.

Field rotational crop studies conducted in the USA on a range of representative crops, involving treatment rates equivalent a 0.45 kg ai/ha maximum seasonal rate to bare soil, reported cyantraniliprole residues of less than 0.05 mg/kg in representative food commodities and higher residues in animal feed commodities.

The Meeting agreed that the results of the USA field rotational crop studies, in particular the cyantraniliprole residues reported from the 30 day PBI crops, could be used to estimate residues in follow crops.

Leafy vegetables (including Brassica leafy vegetables)

Highest cyantraniliprole residues in rotational leafy vegetables were < 0.01 mg/kg in spinach and beet tops, 0.02 mg/kg in lettuce and turnip tops and 0.04 mg/kg in radish tops. These levels are adequately covered by the recommendations for leafy vegetables.

Root and tuber vegetables

Cyantraniliprole residues in rotational root and tuber vegetables ranged from < 0.01 to 0.014 mg/kg (n=29, median < 0.01 mg/kg) in beet roots, turnip roots, carrot roots and radish roots.

The Meeting agreed to use the data from 20 field trials on potatoes in North America, treated according to the Canadian GAP for root and tuber vegetables (residues in tubers ranging from < 0.01 to 0.03 mg/kg, STMR 0.01 mg/kg, n=20) and the results of the rotational crop studies on root and tuber vegetables to recommend a group maximum residue level for potatoes (to accommodate residues in follow-crop potatoes that may also be treated with cyantraniliprole).

The Meeting established a maximum residue level of 0.05 mg/kg, a highest residue of 0.044 mg/kg (for estimating animal dietary burdens) and a median residue of 0.02 mg/kg for cyantraniliprole on potato.

The Meeting also agreed to use the rotational crop studies on root and tuber vegetables to recommend a group maximum residue level for the remaining root and tuber vegetables to accommodate residues in these crops grown as follow-crops.

The Meeting established a maximum residue level of 0.05 mg/kg, a highest residue of 0.014 mg/kg and a median residue of 0.01 mg/kg for cyantraniliprole on root and tuber vegetables except potato.

Miscellaneous fodder root crops

The Meeting also agreed to use the results of the rotational crop studies on root and tuber vegetables (residues ranging from < 0.01 to 0.014 mg/kg, median < 0.01 mg/kg, n=29) to recommend maximum residue levels for turnips and fodder beet to accommodate residues in these crops grown as follow-crops.

The Meeting established a maximum residue level of 0.02 mg/kg, a highest residue of 0.014 mg/kg and a median residue of 0.01 mg/kg for cyantraniliprole on fodder beet and turnip fodder.

Legume animal feeds

Cyantraniliprole residues in legume animal feeds (forage) ranged from < 0.01 to 0.14 mg/kg (n=24, median < 0.01 mg/kg) in clover forage, bean forage, pea forage, alfalfa forage and soya bean forage. For the purpose of estimating livestock dietary burdens, the Meeting agreed to combine the data on rotational crop residues in legume animal feeds to estimate residues in legume feed crops grown as follow-crops.

Meeting estimated a median residue of 0.01 mg/kg and a highest residue of 0.14 mg/kg for cyantraniliprole in legume forages (fresh weight).

Cyantraniliprole residues in legume animal feeds (fodders) ranged from < 0.01 to 0.58 mg/kg (n=24, median 0.017 mg/kg) in peanut hay, clover hay, pea hay, bean, alfalfa hay and soya bean hay. The Meeting agreed to combine the data on rotational crop residues in legume fodder crops to recommend a group maximum residue level to accommodate residues in these crops grown as follow-crops.

The Meeting established a median residue of 0.017 mg/kg and a highest residue of 0.58 mg/kg (0.67 mg/kg DM after correction for an average dry matter content of 87%) and recommended a maximum residue level of 0.8 mg/kg (dry weight) for cyantraniliprole in legume animal feeds.

Cereal and grass forages, straws and hays

Cyantraniliprole residues in cereal and grass forage ranged from < 0.01 to 0.053 mg/kg (n=23, median < 0.01 mg/kg) in corn forage, sorghum, Bermuda grass and brome grass forages, oat forage, bluegrass forage and wheat forage. For the purpose of estimating livestock dietary burdens, the Meeting agreed to combine the data on rotational crop residues in cereal and grass forages to estimate residues in cereal and grasses grown as follow-crops.

Meeting established an STMR of 0.01 mg/kg and a highest residue of 0.053 mg/kg for cyantraniliprole in cereal and grass forages (fresh weight).

Cyantraniliprole residues in cereal and grass straws and hays ranged from < 0.01 to 0.14 mg/kg (median < 0.01 mg/kg) in sorghum stover, rice straw, corn stover, brome grass hay, Bermuda grass hay, oat straw, wheat straw, oat hay, wheat hay bluegrass hay. The Meeting agreed to combine the data on rotational crop residues in cereal and grass straws and hays to recommend a group maximum residue level to accommodate residues in these crops grown as follow-crops.

The Meeting established a median residue of 0.01 mg/kg and a highest residue of 0.14 mg/kg (0.16 mg/kg DM after correction for an average dry matter content of 89%) and recommended a maximum residue level of 0.2 mg/kg (dry weight) for cyantraniliprole in straw, fodder (dry) and hay of cereal grains and other grass-like plants.

Miscellaneous fodder leaf crops

The Meeting agreed to use the results of the rotational crop studies on beet, turnip and radish tops (residues ranging from < 0.01 to 0.021 mg/kg (n=22, median < 0.01 mg/kg)) to estimate residues in fodder beet tops and the miscellaneous fodder leaf crops listed in the OECD Feedstuffs Table to accommodate residues in these commodities grown as follow-crops.

The Meeting established median residue of 0.01 mg/kg and a highest residue of 0.021 mg/kg for cyantraniliprole on sugar beet tops, fodder beet tops or leaves, kale forage, rape greens and turnip tops (fresh weight).

Fate of residues during processing

The effect of processing on the nature of residues was investigated in buffer solutions under conditions simulating pasteurisation, boiling and sterilisation. Cyantraniliprole was stable under most processing conditions. Hydrolysis to IN-J9Z38 was a significant pathway under sterilisation

conditions (20 minutes at 120 °C and pH 6) making up 12–14% AR. Other degradates present were IN-F6L99 and IN-N5M09 making up a further 5–8% AR.

The fate of cyantraniliprole residues has been examined in a number of studies simulating household and commercial processing of potatoes, spinach, tomatoes, oranges, apples, plums, cottonseed, olives and grapes. Estimated processing factors and STMR-Ps for the commodities considered at this Meeting are summarized below.

Summary of selected processing factors and STMR-P values for cyantraniliprole

RAC	Commodity (RAC: STMR mg/kg ^b)	Cyantraniliprole+IN-J9Z38 ^a			
		Processing factors	PF best estimate	RAC STMR (mg/kg)	STMR-P (mg/kg)
Potato	RAC: tubers			0.02	
	flakes	0.1	0.1		0.002
	waste	0.1	0.1		0.002
	peeled tubers	0.1	0.1		0.002
	chips	0.1	0.1		0.002
	wet peel	2.3	2.3		0.046 hi-res 0.1 ^c
	culls	1.0	1.0		0.02
	fries	0.1	0.1		0.002
	unpeeled, boiled	0.1	0.1		0.002
	unpeeled microwaved	< 0.33	< 0.33		0.006
Spinach	RAC: leaves			4.7	
	cooked leaves	0.81, 1.0, 1.2	1.0		4.7
Tomato	RAC: fruit (0.08 mg/kg)				
	washed	0.15, 0.17, < 0.29	0.17		0.014
	peeled	< 0.08, < 0.08, 0.1	< 0.08		0.006
	sun-dried	3.0, 3.7, 3.8	3.7		0.3
	canned	< 0.02, < 0.05, < 0.08	< 0.05		0.004
	juice	< 0.15, < 0.17, 0.19	< 0.17		0.014
	wet pomace	0.75, 1.0, 2.2	1.0		0.08
	dry pomace	1.7, 3.2, 4.0	3.2		0.26
	paste	0.62, 0.86, 1.0	0.86		0.07
	puree	0.23, 0.25, 0.43	0.25		0.02
Apple	RAC: fruit			0.16	
	washed	0.46, 0.58, 0.63	0.58		0.09
	puree	0.88, 1.0, 1.3	1.0		0.16
	canned	0.04, 0.13, 0.15	0.13		0.02
	frozen	0.62, 0.96, 1.5	0.96		0.15
	juice	0.19, 0.31, 0.38	0.31		0.05
	wet pomace	0.77, 1.0, 1.2	1.0		0.16
	dry pomace	2.0, 2.7, 3.9	2.7		0.43
	sauce	2.2, 2.4, 2.7	2.2		0.35
Plum	RAC: flesh			0.34	
	dried prunes	1.3, 1.6, 2.0	1.6		0.54

^a Each PF value represents a separate study where residues were above the LOQ in the RAC and is the ratio of the combined cyantraniliprole+IN-J9Z38 metabolite residues in the processed item divided by the combined residues of cyantraniliprole+IN-J9Z38 in the RAC.

^b Residues in the RAC are the sum of cyantraniliprole and IN-J9Z38

^c Based on the highest residue in the RAC (0.044 mg/kg)

The Meeting noted that in the studies available, cyantraniliprole residues did not concentrate in food commodities during processing except in apple sauce and in dehydrated commodities such as dried prunes and sun-dried tomatoes. Residues also concentrated in dry pomace (apple and tomato).

In three plum processing studies conducted in the USA, cyantraniliprole residues increased (median processing factor of 1.5) when fresh prunes (flesh) were dried to a moisture content of 15–18% (from about 85% in fresh fruit).

The Meeting estimated a maximum residue level for prunes of 0.8 mg/kg based on the maximum residue level estimated for plums of 0.5 mg/kg and a median processing factor of 1.6.

Residues in animal commodities

Farm animal dietary burden

The Meeting estimated the dietary burden of cyantraniliprole in farm animals on the basis of the diets listed in Annex 6 of the 2009 JMPR Report (OECD Feedstuffs Derived from Field Crops). Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are presented in Annex 6 and are summarized below.

Estimated maximum and mean dietary burdens of farm animals

	Animal dietary burden, cyantraniliprole, ppm of dry matter diet							
	US-Canada		EU		Australia		Japan	
	max	mean	max	mean	max	mean	max	mean
Beef cattle	0.41	0.19	1.9 ^a	0.98 ^c	0.68	0.13	0.13	0.004
Dairy cattle	0.44	0.1	1.9 ^b	0.95 ^d	0.67	0.11	0.29	0.02
Poultry-broiler	0.0	0.0	0.05 ^e	0.02 ^f	0.0	0.0	0.0	0.0
Poultry-layer	0.0	0.0	0.37 ^g	0.19 ^h	0.0	0.0	0.0	0.0

^a Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian tissues

^b Highest maximum dairy cattle dietary burden suitable for MRL estimates for mammalian milk

^c Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian tissues.

^d Highest mean dairy cattle dietary burden suitable for STMR estimates for milk.

^e Highest maximum poultry dietary burden suitable for MRL estimates for poultry tissues.

^f Highest mean poultry dietary burden suitable for STMR estimates for poultry tissues.

^g Highest maximum poultry dietary burden suitable for MRL estimates for poultry eggs.

^h Highest mean poultry dietary burden suitable for STMR estimates for poultry eggs.

For beef and dairy cattle, the calculated maximum dietary burden suitable for estimating maximum residue levels in mammalian tissues and milk is 1.9 ppm dry weight of feed and the calculated mean dietary burdens, suitable for estimating STMRs in mammalian tissues and in milk are 0.98 ppm and 0.95 ppm dry weight of feed respectively.

For poultry, noting that in some countries, laying hens may also be consumed, the calculated maximum dietary burden suitable for estimating maximum residue levels in poultry tissues and eggs is 0.37 ppm dry weight of feed and the calculated mean dietary burden, suitable for estimating STMRs in poultry tissues and in eggs is 0.19 ppm dry weight of feed.

Farm animal feeding studies

The Meeting received information on the residue levels arising in animal tissues and milk when dairy cows were dosed with cyantraniliprole for 28 days at the equivalent of 3.5, 12, 35 and 112 ppm in the diet. A separate dose group (112 ppm) was used to estimate residue depuration of cyantraniliprole and its major metabolites.

In milk, residues reached a plateau after about 5 days. Average residues of cyantraniliprole were 0.03 mg/kg in the 3.5 ppm dose group and increased to 0.7 mg/kg in the highest dose group (112 ppm). In skim milk, cyantraniliprole residues were about 60% of the whole milk levels (0.016 mg/kg up to 0.47 mg/kg) and 0.066 mg/kg up to 1.8 mg/kg in cream. Residues of IN-N7B69, the predominant metabolite in milk, increased from 0.03 mg/kg to 0.28 mg/kg over the four dose groups while residues of the other metabolites (IN-MLA84, IN-J9Z38 and IN-MYX98) were present at levels at least ten-fold lower than parent.

In muscle, maximum residues of cyantraniliprole increased from 0.01 mg/kg to 0.33 mg/kg in the four dose groups, with IN-J9Z38 being the predominant metabolite, found at more than

0.01 mg/kg only in the two highest dose groups (up to 0.04 mg/kg). Other metabolites were $\leq$ 0.01 mg/kg at all dose levels.

In fat, maximum residues of cyantraniliprole increased from 0.015 mg/kg to 0.58 mg/kg in the four dose groups, with IN-J9Z38 being the predominant metabolite, found at 0.012 mg/kg (low dose) up to 0.45 mg/kg (highest dose). Other metabolites were found at lower levels, more than 5-fold lower than parent and only IN-N7B69 was present at more than 0.01 mg/kg, found at 0.02 mg/kg in the highest dose group.

In kidney, maximum residues of cyantraniliprole increased from 0.03 mg/kg to 0.89 mg/kg in the four dose groups, with IN-N7B69 being the predominant metabolite, found at 0.012 mg/kg (low dose) up to 0.15 mg/kg (highest dose). Other metabolites were found at levels more than 5-fold lower than parent, with residues of IN-J9Z38 and IN-MYX98 present above 0.01 mg/kg only in the two higher dose groups.

In liver, maximum residues of cyantraniliprole increased from 0.066 mg/kg to 2.1 mg/kg in the four dose groups, with IN-MLA84 being the predominant metabolite, present at 0.04 mg/kg in the lowest dose group and up to 0.57 mg/kg in the highest dose group. Metabolite IN-N7B69 residues were up to 0.01 mg/kg in the lowest dose group, increasing to 0.08 mg/kg in the highest dose group and other metabolites were all $<$ 0.01 mg/kg except in the highest dose group where levels of $<$ 0.03 mg/kg were found.

Residue depletion was studied in cows dosed orally for 28 days with the equivalent of 112 ppm cyantraniliprole. Parent residues depleted to $<$ 0.01 mg/kg in muscle within 4 days after the last dose, were $<$ 0.01 mg/kg in milk, liver and kidney within 10 days and $<$ 0.01 mg/kg in fat within 15 days. Metabolites were all $<$ 0.01 mg/kg in all matrices after 4 days except IN-J9Z38 ($<$ 0.01 within 10 days in kidney and 15 days in fat), IN-MLA84 ($<$ 0.01 mg/kg within 10 days in liver) and IN-N7B69 ($<$ 0.01 mg/kg within 10 days in kidney).

The Meeting also received information on the residues in tissues and eggs when laying hens were dosed with cyantraniliprole for 28 days at levels equivalent to 3, 10 and 30 ppm in the diet. A separate dose group (30 ppm) was used to estimate residue depuration of cyantraniliprole and its major metabolites.

In eggs, residues reached a plateau after about 3 days. Average residues of cyantraniliprole were 0.08 mg/kg in the 3 ppm dose group and increased to 0.8 mg/kg in the highest dose group (30 ppm). In egg whites, cyantraniliprole was the predominant residue, averaging 0.08 mg/kg in the low dose group up to 0.64 mg/kg in the high dose group. Lower levels of parent were found in egg yolks, averaging 0.015 mg/kg (low dose) up to 0.1 mg/kg (high dose). Residues of IN-J9Z38, the predominant metabolite in eggs, present at levels of about 50% of parent, increased from 0.04 mg/kg to 0.4 mg/kg over the three dose groups while residues of IN-MLA84 and IN-MYX98 were present at levels of 0.015 mg/kg in the low dose group up to 0.12 in the high dose group. In general, residues of these metabolites were about 2-fold higher in egg whites than in the yolks.

In muscle, maximum residues of cyantraniliprole increased from 0.003 mg/kg to 0.05 mg/kg in the three dose groups, with the only metabolites found at more than 0.01 mg/kg being IN-MYX98 and IN-HGW87 (up to 0.02 mg/kg in the highest dose group. Other metabolites were all $\leq$ 0.01 mg/kg at all dose levels.

In skin + fat, maximum residues of cyantraniliprole increased from 0.014 mg/kg to 0.16 mg/kg in the three dose groups, with IN-MYX98 being the predominant metabolite, found at 0.005 mg/kg (low dose) up to 0.05 mg/kg (highest dose). Other metabolites were found at lower levels, with IN-J9Z38 and IN-HGW87 present at more than 0.01 mg/kg only in the highest dose group (0.021 mg/kg and 0.023 mg/kg respectively).

In liver, maximum residues of cyantraniliprole increased from 0.03 mg/kg to 0.24 mg/kg in the three dose groups. Metabolite IN-MLA84 was present at levels similar to the parent (0.034 mg/kg in the lowest dose group and up to 0.32 mg/kg in the highest dose group). Maximum IN-MLA84, IN-

HGW87 and IN-N7B69 residues were 0.01–0.02 mg/kg in the lowest dose group and 0.07–0.1 mg/kg in the highest dose group. Other metabolites were all < 0.01 mg/kg in all dose groups.

In the residue depuration dose group (30 ppm), residues depleted to < 0.01 mg/kg in all matrices within 5 days of the last dose (within 9 days in liver, when the first sample was taken).

Animal commodity maximum residue levels

The maximum dietary burden for beef and dairy cattle is 1.9 ppm. The mean dietary burdens are 0.98 ppm (beef cattle) and 0.95 ppm (dairy cattle). Residue levels of cyantraniliprole and the metabolites included in the residue definition in milk and tissues were obtained by extrapolation below the 3.5 ppm feeding level in the dairy cow feeding study.

Cyantraniliprole feeding study	Feed level (ppm) for milk residues	Residues (mg/kg) in milk	Feed level (ppm) for tissue residues	Residues ^a (mg/kg) in			
				Muscle	Liver	Kidney	Fat
MRL beef or dairy cattle							
Feeding study ^b	3.5	0.03	3.5	0.011	0.066	0.031	0.015
Dietary burden and high residue	1.9	0.016	1.9	0.006	0.036	0.017	0.008
STMR beef or dairy cattle							
Feeding study ^c	3.5	0.03	3.5	0.008	0.094	0.042	0.024
Dietary burden and residue estimate	0.95	0.016	0.98	0.002	0.026	0.012	0.007

^a Residue values used in estimating STMRs are the sum of cyantraniliprole and metabolites IN-N7B69, IN-J9Z38, IN-MLA84 and IN-MYX98, expressed as cyantraniliprole

^b highest residues for tissues and mean residues for milk

^c mean residues for tissues and mean residues for milk

Residues of cyantraniliprole expected in cattle milk and tissues for use in estimating maximum residue levels are: 0.008 mg/kg (fat), 0.006 mg/kg (muscle), 0.036 mg/kg (liver) and 0.017 mg/kg (kidney) and the mean residue for milk is 0.016 mg/kg.

The Meeting estimated maximum residue levels of 0.01 mg/kg for cyantraniliprole in meat (from mammals other than marine mammals), 0.05 mg/kg for edible offal (mammalian), 0.01 mg/kg for mammalian fat and 0.02 mg/kg for milks. Estimated STMRs (parent plus metabolites) for dietary intake estimation are 0.002 mg/kg for meat, 0.026 mg/kg for edible offal, 0.007 mg/kg for fat and 0.016 mg/kg for milk.

For poultry, the maximum dietary burden is 0.37 ppm and the mean dietary burden is 0.19 ppm (based on the diet for laying hens). Residue levels of cyantraniliprole and the metabolites included in the residue definition in eggs and tissues were obtained by extrapolation below the 3.0 ppm feeding level in the dairy cow feeding study.

Cyantraniliprole feeding study	Feed level (ppm) for egg residues	Residues (mg/kg) in egg	Feed level (ppm) for tissue residues	Residues ^a (mg/kg) in			
				Muscle	Liver	Skin	Fat
MRL broiler or laying hen							
Feeding study ^b	3.0	0.082	3.0	0.0055	0.03	0.014	
Dietary burden and high residue	0.37	0.01	0.37	0.0007	0.004	0.002	
STMR broiler or laying hen							
Feeding study ^c	3.0	0.082	3.0	0.007	0.062	0.016	
Dietary burden and residue estimate	0.19	0.01	0.19	0.0004	0.004	0.001	

^a Residue values used in estimating STMRs are the sum of cyantraniliprole and metabolites IN-N7B69, IN-J9Z38, IN-MLA84 and IN-MYX98, expressed as cyantraniliprole

^b highest residues for tissues and mean residues for egg

^c mean residues for tissues and mean residues for egg

Residues of cyantraniliprole expected in eggs and poultry tissues for use in estimating maximum residue levels are: 0.002 mg/kg (skin plus fat), 0.0007 mg/kg (muscle), 0.004 mg/kg (liver) and the mean residue for eggs is 0.01 mg/kg.

The Meeting estimated maximum residue levels of 0.01 mg/kg for cyantraniliprole in poultry meat, 0.01 mg/kg for poultry offal, 0.01 mg/kg for poultry fat and 0.015 mg/kg for eggs. Estimated STMRS for dietary intake estimation are 0 mg/kg for poultry fat, 0 mg/kg for poultry meat, 0.004 mg/kg for poultry offal and 0.01 mg/kg for eggs.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

Definition of the residue (for compliance with the MRL, animal and plant commodities): *cyantraniliprole*.

Definition of the residue (for estimation of dietary intake for unprocessed plant commodities): *cyantraniliprole*.

Definition of the residue (for estimation of dietary intake for processed plant commodities): *sum of cyantraniliprole and 2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl]-3,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarbonitrile*.

Proposed definition of the residue (for estimation of dietary intake for animal commodities): *sum of: cyantraniliprole, 2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl]-3,4-dihydro-3,8-dimethyl-4-oxo-6-quinazolinecarbonitrile, 2-[3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl]-1,4-dihydro-8-methyl-4-oxo-6-quinazolinecarbonitrile, 3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-(hydroxymethyl)-6-[(methylamino)carbonyl]phenyl]-1H-pyrazole-5-carboxamide and 3-Bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-[(hydroxymethyl)amino]carbonyl]-6-methylphenyl]-1H-pyrazole-5-carboxamide*.

The residue is not fat soluble.

CCN	Commodity Name	MRL New	STMR or STMR-P	Highest residue ^c
VB 0040	Brassica (cole or cabbage) vegetables	2.0	0.56	1.1
FB 2006	Bush berries	4.0	0.75	
VS 0624	Celery	15	2.0	
FS 0013	Cherries	6.0	0.93	
SB 0716	Coffee beans	0.03	0.01	
DV 0444	Dried chilli peppers	5	0.7	
MO 0105	Edible offal (Mammalian)	0.05	0.026	
PE 0112	Eggs	0.015	0.01	
AM 1050	Fodder beet (follow-crop)	0.02	0.01	0.014
VC 0045	Fruiting vegetables, Cucurbits	0.3	0.065 ^a 0.01 ^b	

CCN	Commodity Name	MRL New	STMR or STMR-P	Highest residue ^c
VO 0050	Fruiting vegetables, other than Cucurbits (except mushrooms & sweetcorn)	0.5	0.08	
VA 0381	Garlic	0.05	0.02	
VL 0053	Leafy vegetables (except lettuce, Head)	20	4.7	
AL 0157	Legume animal feeds (follow-crop)	0.8 (dw)	0.017	0.58
VL 0482	Lettuce, Head	5	0.79	
MM 0069	Mammalian fat	0.01	0.007	
MM 0095	Meat (from mammals other than marine mammals)	0.01	0.002	
ML 0106	Milks	0.02	0.016	
VA 0385	Onion, bulb	0.05	0.02	
VA 0387	Onion, Welsh	8.0	1.3	
FS 2001	Peaches	1.5	0.34	
FS 0014	Plums	0.5	0.07	
FP 0009	Pome fruit	0.8	0.16	
VR 0589	Potato (follow-crop+foliar)	0.05	0.02	0.044
PO 0111	Poultry, Edible offal of	0.01	0.004	
PF 0111	Poultry fat	0.01	0	
PM 0110	Poultry meat	0.01	0	
DF 0014	Prunes	0.8	0.54	
VR 0075	Root and tuber vegetables except potato (follow-crop)	0.05	0.01	0.014
VA 0388	Shallot	0.05	0.02	
VA 0389	Spring onion	8.0	1.3	
AS 0161	Straw, fodder (dry) & hay of cereal grains and other grass-like plants (follow crop)	0.2 (dw)	0.01	0.14
AM 0506	Turnip fodder (fodder-crop)	0.02	0.01	0.014

^a STMR is for cucurbits with edible peel

^b STMR is for cucurbits with an inedible peel

^c Highest residue values for calculating animal dietary burdens

CCN	Commodity Name		STMR or STMR-P	Highest residue ^a
JF 0226	Apple juice		0.05	

CCN	Commodity Name		STMR or STMR-P	Highest residue ^a
	Apple pomace (wet)		0.16	
	Cereal and grass forages (follow crop)		0.01	0.053
AV 1051	Fodder beet leaves or tops		0.01	0.021
	Legume forages (follow-crop)		0.01	0.14
AV 0480	Kale forage		0.01	0.021
	Potato waste (wet)		0.046	0.1
VL 0495	Rape greens		0.01	0.021
	Spinach (cooked)		4.7	
AV 0596	Sugar beet leaves or tops		0.01	0.021
	Tomato (canned)		0.004	
JF 0048	Tomato juice		0.014	
	Tomato paste		0.07	
	Tomato pomace (wet)		0.08	
AV 0506	Turnip leaves or tops		0.01	0.021

^a Highest residue values for calculating animal dietary burdens

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intake (IEDI) for cyantraniliprole was calculated for the food commodities for which STMRs or HRs were estimated and for which consumption data were available. The results are shown in Annex 3 of the 2013 JMPR Report.

The International Estimated Daily Intakes of cyantraniliprole for the 13 GEMS/Food regional diets, based on estimated STMRs were 1–10% of the maximum ADI of 0.03 mg/kg bw (Annex 3). The Meeting concluded that the long-term intake of residues of cyantraniliprole from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The 2013 JMPR decided that an ARfD was unnecessary. The Meeting therefore concluded that the short-term intake of cyantraniliprole residues is unlikely to present a public health concern.

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DP-21415	Livingstone, K., Haigh, I., Cairns, S., Woodmansey, L.	2010	Magnitude and decline of DPX-HGW86 and metabolite residues in protected lettuce (leaf vegetables) following foliar application of DPX-HGW86 100 g/L OD or drip irrigation application of DPX-HGW86 200 g/L SC- Europe, 2008. Charles River Laboratories. DuPont Report No. DuPont-21415, Revision No. 1. Unpublished

Reference	Author(s)	Year	Title
DP-21446	Thiel, A.	2010	Magnitude of DPX-HGW86 and metabolite and/or degradation product residues in field rotational crops following application of DPX-HGW86 100 g/L OD insecticide - Ontario, Canada location 2008/2009. ABC Laboratories, Inc. DuPont Report No. DuPont-21446. Unpublished
DP-21477	Haigh, I., Woodmansey, L.	2010	Magnitude and decline of DPX-HGW86 and metabolite and/or degradation product residues in field rotational crops following foliar application of DPX-HGW86 100 g/L OD – northern Europe, 2008 and 2009. Charles River Laboratories. DuPont Report No. DuPont-21477. Unpublished
DP-23885	Haigh, I., Cairns, S.	2010	Magnitude and decline of DPX-HGW86 and metabolite residues in protected peppers (fruiting vegetables, solanacea) following foliar application of DPX-HGW86 100 g/L OD or drip irrigation application of DPX-HGW86 200 g/L SC - Europe 2008. Charles River Laboratories. DuPont Report No. DuPont-23885. Unpublished
DP-24754	Lowrie, C., MacKinnon, I.	2009	Extraction efficiency of [14C]DPX-HGW86 from crops. Charles River Laboratories. DuPont Report No. DuPont-24754. Unpublished
DP-24798	Wardrope, L., Sharma, A.K.	2010	Outdoor water sediment study (aerobic aquatic metabolism) of [14C]-DPX-HGW86. Charles River Laboratories. DuPont Report No. DuPont-24798, Revision No. 1. Unpublished
DP-25543	Ward, C.	2010	Validation of an analytical method for the determination of DPX-HGW86, IN-HGW87, IN-N7B69, IN-K7H19, IN-JCZ38, IN-MYX98, IN-J9Z38 and IN-MLA84 in bovine tissues, milk and eggs. Charles River Laboratories. DuPont Report No. DuPont-25543. Unpublished
DP-25544	Bacher, R.	2010	Method assessment and validation for the determination of residues of DPX-HGW86 and metabolites in animal tissues using multi-residue method DFG S19 (LC/MS/MS module). PTRL Europe. DuPont Report No. DuPont-25544. Unpublished
DP-25641	Carringer, S.J., Schierhoff, R.	2010	Magnitude and decline of DPX-HGW86 and metabolite residues in brassica vegetables (broccoli/cauliflower, cabbage, mustard greens) following foliar applications of DPX-HGW86 100 g/L OD, DPX-HGW86 100 g/L SE, and soil applications of DPX-HGW86 200 g/L SC -. The Carringers, Inc.; ABC Laboratories, Inc. DuPont Report No. DuPont-25641. Unpublished
DP-25642	Carringer, S.J., Schierhoff, R.	2010	Magnitude and decline of DPX-HGW86 and metabolite residues in cucurbits (cucumber, cantaloupe/muskmelon, summer squash) following foliar applications of DPX-HGW86 100 g/L OD and soil applications of DPX-HGW86 200 g/L SC - U.S. The Carringers, Inc.; ABC Laboratories, Inc. DuPont Report No. DuPont-25642. Unpublished
DP-25643	Carringer, S.J., Vogl, E.	2010	Magnitude and decline of DPX-HGW86 and metabolite residues in fruiting vegetables (tomato, bell pepper, non-bell pepper) following foliar application of DPX-HGW86 100 g/L OD and soil applications of DPX-HGW86 200 g/L SC - U.S. The Carringers, Inc.; ABC Laboratories, Inc. DuPont Report No. DuPont-25643. Unpublished
DP-25644	Carringer, S.J., Vogl, E.	2010	Combined processing and magnitude and decline of DPX-HGW86 and metabolite residues in leafy vegetables (head/leaf lettuce, celery, spinach) following foliar applications of DPX-HGW86 100 g/L, DPX-HGW86 100 g/L SE, soil applications of DPX-HGW86 200 g/L SC. The Carringers, Inc.; ABC Laboratories, Inc. DuPont Report No. DuPont-25644. Unpublished
DP-25645	Carringer, S.J., Vogl, E.	2009	Magnitude of DPX-HGW86 and metabolite residues in processed fractions of tomatoes following foliar applications of DPX-HGW86 100 g/L OD - U.S., The Carringers, Inc.; ABC Laboratories, Inc. DuPont Report No. DuPont-25645. Unpublished
DP-26000	Seal, S.	2010	Independent laboratory validation of "Analytical method for the determination of DPX-HGW86 and metabolites in crops and processed fractions using LC/MS/MS". Pyxant Labs, Inc. DuPont Report No. DuPont-26000, Revision No. 1. Unpublished
DP-26458	Schwarz, T.	2010	Independent laboratory validation of DuPont-18844 method for the determination of residues of DPX-HGW86 and metabolites in milk and bovine tissues using LC/MS/MS. Charles River Laboratories. DuPont Report No. DuPont-26458. Unpublished
DP-27180	Ward, C., Vance, C.	2011	DPX-HGW86: Magnitude of residues of cyantraniliprole (DPX-HGW86) and metabolites in edible tissues and milk of lactating dairy cows following dosing with cyantraniliprole. Charles River Laboratories. DuPont Report No. DuPont-27180, Revision No. 1. Unpublished

Reference	Author(s)	Year	Title
DP-27181	Roberts, S., Ward, C.	2010	Magnitude of residues of cyantraniliprole (DPX-HGW86) and metabolites in edible tissues and eggs of poultry following dosing with cyantraniliprole. Charles River Laboratories. DuPont Report No. DuPont-27181. Unpublished
DP-27356	Kinney, J., Melville, S.	2010	Extraction efficiency of [¹⁴ C]DPX-HGW86 from muscle, liver and milk from goats and eggs from hens. Charles River Laboratories. DuPont Report No. DuPont-27356. Unpublished
DP-27436	Rice, F.	2010	HGW86: Magnitude of the residue on dry bulb and green onion. ABC Laboratories, Inc. DuPont Report No. DuPont-27436. Unpublished
DP-27437	Thiel, A.	2010	Combined processing and magnitude and decline of cyantraniliprole and metabolite residues in stone fruit (peach, plum, and cherry) following foliar applications of DPX-HGW86 100 g/L SE - NAFTA, 2009. ABC Laboratories, Inc. DuPont Report No. DuPont-27437. Unpublished
DP-27438	Thiel, A.	2010	Combined processing and magnitude and decline of cyantraniliprole and metabolite residues in pome fruit (apple and pear) following foliar applications of DPX-HGW86 100 g/L SE - NAFTA, 2009. ABC Laboratories, Inc. DuPont Report No. DuPont-27438. Unpublished
DP-27440	Radhakrishnan, D.	2009	DPX-HGW86: Laboratory study of physical and chemical properties of appearance (physical state, colour, odor), relative density, bulk density melting point and boiling point. International Institute of Biotechnology and Toxicology (IIBAT). DuPont Report No. DuPont-27440. Unpublished
DP-27446	Thiel, A.	2010	Magnitude of cyantraniliprole and metabolite residues in tree nuts (almonds and pecans) following foliar applications (DPX-HGW86 100 g/L OD and DPX-HGW86 100 g/L SE) and soil applications (DPX-HGW86-200 g/L SC) - NAFTA, 2009. Inc.; ABC Laboratories, Inc. DuPont Report No. DuPont-27446. Unpublished
DP-27447	Krishnan, V.N.	2009	DPX-HGW86: Laboratory study of solubility in organic solvents. International Institute of Biotechnology and Toxicology (IIBAT). DuPont Report No. DuPont-27447. Unpublished
DP-27554	Rice, F.	2010	Combined processing and magnitude of DPX-HGW86 and metabolite residues in citrus fruit (orange, lemon, and grapefruit) following foliar applications of DPX-HGW86 100 g/L SE and systemic delivery applications of DPX-HGW86 200 g/L SC - USA, 2009. ABC Laboratories, Inc. DuPont Report No. DuPont-27554. Unpublished
DP-27565	Thiel, A.	2010	Combined processing and magnitude of cyantraniliprole and metabolite residues in cotton following foliar applications of DPX-HGW86 100 g/L OD and soil applications of DPX-HGW86 200 g/L SC - USA, 2009. Inc.; ABC Laboratories, Inc. DuPont Report No. DuPont-27565. Unpublished
DP-27582	Thiel, A.	2010	Combined processing and magnitude of cyantraniliprole and metabolite residues in oil seeds (canola and sunflowers) following foliar applications of DPX-HGW86 100 g/L OD and seed treatment with 625 g/L FS - NAFTA, 2009. Inc.; ABC Laboratories, Inc. DuPont Report No. DuPont-27582. Unpublished
DP-27583	Thiel, A.	2010	Combined processing and magnitude of cyantraniliprole and metabolite residues in tuberous and corm vegetables (potatoes) following foliar applications (DPX-HGW86 100 g/L OD and DPX-HGW86 100 g/L SE), soil applications (DPX-HGW86 200 g/L SC), and seed treatment. ABC Laboratories, Inc. DuPont Report No. DuPont-27583. Unpublished
DP-27709	Haigh, I., Cairns, S.	2011	Combined processing and magnitude and decline of cyantraniliprole and metabolite residues in olives following foliar application of DPX-HGW86 100 g/L SE - southern Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-27709. Unpublished
DP-27710	Haigh, I., Cairns, S., Ferguson, L.	2010	Magnitude and decline of cyantraniliprole and metabolite residues in field-grown green beans (fresh legume vegetables) following foliar application of DPX-HGW86 100 g/L OD - France and Southern Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-27710. Unpublished
DP-27711	Aitken, A., Cairns, S., Ferguson, L.	2011	Magnitude and decline of cyantraniliprole and metabolite residues in field-grown melons, courgettes and cucumbers (fruiting vegetables, inedible-peel cucurbits) following foliar application of DPX-HGW86 100 g/L OD and soil application of DPX-HGW86 200 g/L. Charles River Laboratories. DuPont Report No. DuPont-27711. Unpublished

Reference	Author(s)	Year	Title
DP-27712	Haigh, I., Cairns, S.	2011	Magnitude and decline of cyantraniliprole and metabolite residues in field-grown tomatoes, peppers, and hot peppers (fruiting vegetables, solanacea) following foliar application of DPX-HGW86 100 g/L OD - Southern Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-27712. Unpublished
DP-27713	Haigh, I., Cairns, S.	2010	Magnitude and decline of cyantraniliprole and metabolite residues in field-grown lettuce and scarole following foliar application of DPX-HGW86 100 g/L OD and soil application of DPX-HGW86 200 g/L SC - France and Southern Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-27713. Unpublished
DP-27714	Haigh, I., Cairns, S.	2011	Magnitude and decline of cyantraniliprole and metabolite residues in apples and pears (pome fruit) following foliar application of DPX-HGW86 100 g/L SE - Northern and Southern Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-27714. Unpublished
DP-27716	Haigh, I., Cairns, S., Just, G.	2011	Magnitude and decline of cyantraniliprole and metabolite residues in oranges and mandarins (citrus fruit) following foliar application of DPX-HGW86 100 g/L SE - southern Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-27716. Unpublished
DP-27717	Aitken, A., Cairns, S.	2011	Magnitude and decline of cyantraniliprole and metabolite residues in peaches and apricots (stone fruit) following foliar application of DPX-HGW86 100 g/L SE - Southern Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-27717. Unpublished
DP-27718	Aitken, A.	2011	Combined processing and magnitude and decline of cyantraniliprole and metabolite residues in wine and table grapes (berries and small fruit) following foliar application of DPX-HGW86 100 g/L SE - northern and southern Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-27718. Unpublished
DP-27971	Thiel, A.	2010	Magnitude of cyantraniliprole and metabolite residues in blueberries following foliar applications of DPX-HGW86 100 g/L SE - USA, 2009. ABC Laboratories, Inc. DuPont Report No. DuPont-27971. Unpublished
DP-27972	Thiel, A.	2010	Magnitude of cyantraniliprole and metabolite residues in field rotational crops following bare ground applications of DPX-100 g/L SE - USA, 2009. The Carringers, Inc.; ABC Laboratories, Inc. DuPont Report No. DuPont-27972. Unpublished
DP-28186	Aitken, A., Cairns, S.	2010	Magnitude and decline of cyantraniliprole and metabolite residues in protected melons (fruiting vegetables, inedible-peel cucurbits) following foliar application of DPX-HGW86 100 g/L OD and soil application of DPX-HGW86 200 g/L SC - Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-28186. Unpublished
DP-28187	Aitken, A., Cairns, S.	2010	Magnitude and decline of cyantraniliprole and metabolite residues in protected tomatoes and cherry tomatoes (fruiting vegetables, solanacea) following foliar application of DPX-HGW86 100 g/L OD and soil application of DPX-HGW86 200 g/L SC - Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-28187. Unpublished
DP-28188	Haigh, I., Cairns, S., Hoskins, M.	2010	Magnitude and decline of cyantraniliprole and metabolite residues in protected peppers and hot peppers (fruiting vegetables, solanacea) following foliar application of DPX-HGW86 100 g/L OD and soil application of DPX-HGW86 200 g/L SC - Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-28188. Unpublished
DP-28200	Aitken, A., Cairns, S., Hoskins, M.	2010	Magnitude and decline of cyantraniliprole and metabolite residues in protected lettuce, lamb's lettuce, and scarole (leaf vegetables) following foliar application of DPX-HGW86 100 g/L OD and soil application of DPX-HGW86 200 g/L SC - Europe, 2009 initiation. Charles River Laboratories. DuPont Report No. DuPont-28200. Unpublished
DP-28201	Aitken, A., Cairns, S.	2010	Magnitude and decline of cyantraniliprole and metabolite residues in protected cucumbers and courgettes (fruiting vegetables, edible-peel cucurbits) following foliar application of DPX-HGW86 100 g/L OD and soil application of DPX-HGW86 200 g/L SC - Europe. Charles River Laboratories y. DuPont Report No. DuPont-28201. Unpublished
DP-28730	Wardrope, L.	2010	Photodegradation of [¹⁴ C]-DPX-HGW86 on moist soil. Charles River Laboratories. DuPont Report No. DuPont-28730. Unpublished

Reference	Author(s)	Year	Title
DP-29456	Thiel, A.	2011	Magnitude of cyantraniliprole and metabolite residues in field rotational crops following bare ground applications of DPX-100 g/L SE - USA and Canada, 2010. ABC Laboratories Inc. DuPont Report No. DuPont-29456. Unpublished
DP-29555	Wardrope, L.	2010	Rate of degradation [¹⁴ C]-IN-QKV54 in five aerobic soils. Charles River Laboratories. DuPont Report No. DuPont-29555. Unpublished
DP-29556	Vogl, E., Sharma, A.K.	2010	Analysis of photolysis products of DPX-HGW86 in field soil dissipation samples - North America. ABC Laboratories, Inc. DuPont Report No. DuPont-29556, Revision No. 1. Unpublished
DP-29557	Vogl, E., Sharma, A.K.	2010	Analysis of photolysis products of DPX-HGW86 in field soil dissipation samples - EU studies. ABC Laboratories, Inc. DuPont Report No. DuPont-29557, Revision No. 2. Unpublished
DP-29747	Vogl, E.	2010	Analytical method for the determination of DPX-HGW86 and photoproducts in soil using LC/MS/MS. ABC Laboratories, Inc. DuPont Report No. DuPont-29747. Unpublished
DP-29809	McCorquodale, G.	2010	Rate of degradation [¹⁴ C]-IN-RNU71 in five aerobic soils. Charles River Laboratories. DuPont Report No. DuPont-29809, Revision No. 1. Unpublished
DP-31410	Keats, A.	2010	To determine Cyazypyr residues in cotton following two applications of DPX-HGW86 100 SE Applied at a 7 day Interval. AgriSolutions Australia Pty Ltd. DuPont Report No. DuPont-31410. Unpublished
DP-31412	Keats, A.	2010	Determination of Cyazypyr residues in canola seed, oil and trash (fodder). AgriSolutions Australia Pty Ltd. DuPont Report No. DuPont-31412. Unpublished
DP-31413	Keats, A.	2010	Determination of Cyazypyr residues in cucurbit fruit. AgriSolutions Australia Pty Ltd. DuPont Report No. DuPont-31413. Unpublished
DP-31454	Snyder, N.J., White, M.	2010	Field dissipation of cyantraniliprole (DPX-HGW86) in North America and Europe - summary of normalized kinetic calculations. Waterborne Environmental, Inc. (WEI). DuPont Report No. DuPont-31454. Unpublished
DP-31520	Keats, A.	2010	Determination of Cyazypyr residues in tomato and capsicum fruit. AgriSolutions Australia Pty Ltd. DuPont Report No. DuPont-31520. Unpublished
S09-01571	Gemrot, F.	2010	SYN545377 - Residue study on apple in northern France and Germany in 2009. Eurofins/ADME Bioanalyses. Syngenta Report No. S09-01571-Reg. Unpublished
S09-01572	Gemrot, F.	2010	SYN545377 - Residue study on apple in southern France and Spain in 2009. Eurofins/ADME Bioanalyses. Syngenta Report No. S09-01572-Reg. Unpublished
S09-01573	Oppillart, S.	2010	SYN545377 - Residue study on pears in northern France and Germany in 2009. Eurofins/ADME Bioanalyses. Syngenta Report No. S09-01573-Reg. Unpublished
S09-01574	Oppillart, S.	2010	SYN545377 - Residue study on pears in southern France and Spain in 2009. Eurofins/ADME Bioanalyses. Syngenta Report No. S09-01574-Reg. Unpublished
S09-01576	Gemrot, F.	2010	SYN545377 - Residue study on peaches in southern France, Spain, and Italy in 2009. Eurofins/ADME Bioanalyses. Syngenta Report No. S09-01576-Reg. Unpublished
S09-01577	Oppillart, S.	2010	SYN545377 - Residue study on peaches in northern France, and Germany in 2009. Eurofins/ADME Bioanalyses. Syngenta Report No. S09-01577-Reg. Unpublished
S09-01578	Oppillart, S.	2010	SYN545377 - Residue study on plums in southern France, and Spain in 2009. Eurofins/ADME Bioanalyses. Syngenta Report No. S09-01578-Reg. Unpublished
S10-01051	Gemrot, F.	2011	Cyantraniliprole - Residue study on apples in northern France, and Germany in 2010. Eurofins/ADME Bioanalyses. Syngenta Report No. S10-01051. Unpublished
S10-01052	Gemrot, F.	2011	Cyantraniliprole - Residue study on apples in southern France, in 2010. Eurofins/ADME Bioanalyses. Syngenta Report No. S10-01052-Reg. Unpublished
S10-01053	Tessier, V.	2011	Cyantraniliprole - Residue study on pears in northern France and Germany in 2010. Eurofins/ADME Bioanalyses. Syngenta Report No. S10-01053. Unpublished
S10-01054	Tessier, V.	2011	Cyantraniliprole - Residue study on pears in southern France and Italy in 2010. Eurofins/ADME Bioanalyses. Syngenta Report No. S10-01054-Reg. Unpublished

Reference	Author(s)	Year	Title
S10-01055	Gemrot, F.	2011	Cyantraniliprole - Residue study on peaches in southern France, Italy, and Spain, in 2010. Eurofins/ADME Bioanalyses. Syngenta Report No. S10-01055-Reg. Unpublished
S10-01056	Amic. S.	2011	Cyantraniliprole - Residue study on plums in northern France, and Germany in 2010. Eurofins/ADME Bioanalyses. Syngenta Report No. S10-01056. Unpublished
S10-01057	Amic. S.	2011	Cyantraniliprole - Residue study on plums in southern France, and Spain in 2010. Eurofins/ADME Bioanalyses. Syngenta Report No. S10-01057. Unpublished

CYPROCONAZOLE (239)

The first draft was prepared by Professor Eloisa Dutra Caldas

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APPRAISAL

Cyproconazole was first evaluated by the 2010 JMPR (T, R), when an ADI of 0–0.02 mg/kg bw and an ARfD of 0.06 mg/kg bw were set, and maximum residue levels were recommended for a variety of crops. Cyproconazole was scheduled at the Forty-fourth Session of the CCPR (2012) for the evaluation of residues in coffee by the 2013 JMPR. The residue definition for cyproconazole in commodities of plant and animal origin is the parent compound.

Methods of analysis

Two methods for the analysis of cyproconazole in coffee beans or roasted coffee were submitted. Residues can be extracted with acetone:water (95:5), the extract cleaned by gel permeation chromatography and the analyte analysed by LC/MS/MS (m/z 292.2 and 70.1), or extracted with methanol and analysed by LC/MS/MS after centrifugation. In both cases, satisfactory recoveries were obtained at 0.01 mg/kg (LOQ). No study was submitted to evaluate the stability of the residues in coffee samples. Studies evaluated by the 2010 JMPR on various fruits, peanuts and wheat had shown that cyproconazole residues are stable for at least 39 months under frozen conditions. The Meeting agreed that this conclusion could be extended to coffee.

Results from supervised residue trials on crops

Cyproconazole is registered in various central and South American countries. The critical GAP is found in Colombia, 3×0.06 kg ai/ha and 15 days PHI. A total of nine supervised residue trials were conducted on coffee from 2010 to 2012 in the region.

In two trials conducted in Brazil according to Colombian GAP, residues were 0.02 and 0.03 mg/kg. In two trials conducted in Colombia and one in Guatemala according to Colombian GAP, residues were 0.03 (2) and 0.04 mg/kg. Two declining studies conducted in Colombia according to GAP showed that residues at 10 and 14 days DAT are the same, and can be considered at GAP. Residues are 0.02 and 0.03 mg/kg.

In two other Brazilian trials, a soil drench application was applied in addition to a foliar application at 0.5 kg ai/ha, giving residues of 0.03 and 0.04 mg/kg at 23–37 DAT. Although these trials are not conducted according to GAP, they can be used as supporting information.

The Meeting agreed to combined the residues from trials conducted according to Colombian GAP (n=7) as 0.02 (2), 0.03 (4) and 0.04 mg/kg.

The Meeting estimates a maximum residue level of 0.07 mg/kg, and a STMR of 0.03 mg/kg for cyproconazole in coffee beans.

Fate of residues in processing

In one study conducted in Guatemala, green coffee beans containing 0.094 mg/kg cyproconazole were processed to roasted beans and instant coffee. Residues were 0.119 mg/kg in roasted beans and 0.151 mg/kg in instant coffee, resulting in processing factors of 1.3 and 1.6, respectively.

Based on these processing factors, the Meeting recommends a maximum residue level of 0.1 mg/kg and a STMR of 0.039 mg/kg for cyproconazole in roasted coffee beans, and a STMR of 0.048 mg/kg for cyproconazole in instant coffee.

RECOMMENDATIONS

Definition of the residue for compliance with maximum residue levels and estimation of dietary intake in plant commodities: *cyproconazole*.

CCN	Commodity name	Maximum residue level (mg/kg)		STMR (P) mg/kg
		New	Previous	
SB 0716	Coffee beans	0.07		0.03
SM 0716	Coffee beans, roasted	0.1		0.039
	Instant coffee			0.048

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDIs) of cyproconazole calculated for the 13 GEMS/Food Consumption Cluster Diets using STMRs and STMR-Ps estimated by the 2010 Meeting ranged from 0.5 to 2% of the maximum ADI. The impact of coffee on the IEDI is unlikely to affect the previous conclusion that the long-term intake of residues of cyproconazole resulting from the uses considered by the current JMPR is unlikely to present a public health concern.

Short-term intake

The International Estimated Short-Term Intakes (IESTI) of cyproconazole was calculated for coffee using STMR-P estimated by the current Meeting (Annex 4). The ARfD is 0.06 mg/kg and the calculated IESTI was 0% of the ARfD. The Meeting concluded that the short-term intake of residues of cyproconazole, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

CYPRODINIL (207)

First draft prepared by Dr Samuel Margerison, Australian Pesticides and Veterinary Medicines Authority, Canberra, Australia

EXPLANATION

Cyprodinil is a fungicide belonging to the anilinopyrimidine group of chemicals. It is a systemic fungicide with uptake through the leaves and translocation throughout the plant. It is used as a foliar fungicide for control of a range of fungal diseases in cereals, grapes, pome fruit, stone fruit, strawberries, vegetables, field crops and ornamentals, and as a seed dressing for barley.

Cyprodinil was evaluated by JMPR for the first time in 2003, when an ADI of 0–0.03 mg/kg bw/day was established. An ARfD was deemed to be unnecessary. A residue definition of cyprodinil was recommended for plant and animal commodities, for both compliance with MRLs and estimation of dietary intake. The residue is fat soluble.

At the Forty-fourth Session of the CCPR (2012), cyprodinil was scheduled for evaluation of additional use patterns by the 2013 JMPR.

The Meeting received residue data for avocados, dry beans, lima beans, common beans (snap beans), blueberries, Brassica vegetables (broccoli and cabbage), cane berries, cucurbit fruiting vegetables (cantaloupe, cucumber and squash), other fruiting vegetables (sweet and chilli pepper, and tomatoes), herbs (parsley, basil and chives), kiwifruit, leafy vegetables (mustard greens, lettuce and spinach), lemons (including processing data), lychees, pome fruit, root vegetables (carrot and radish), strawberry and watercress.

SPECIFICATIONS

Specifications for cyprodinil technical active constituent, emulsifiable concentrates and suspension concentrates were published by FAO in 2009.

Formulations

Two formulations were used in the residue trials submitted for evaluation by JMPR; both water-dispersible granular (WG) formulations, one containing 750 g/kg cyprodinil as the only active constituent, and the second containing 375 g/kg cyprodinil and 250 g/kg fludioxonil.

RESIDUE ANALYSIS***Plant matrices******Method number AG-631A/AG-631B***

This method was used for determination of residues in pome fruit, dry beans, avocado, blueberry, broccoli, cabbage, mustard greens, raspberry, chilli and sweet pepper, tomato, basil, chives, kiwifruit, lettuce, spinach, lemon (including processed lemon commodities), lychee, parsley, carrot, radish, strawberry and watercress. Samples were extracted with methanol/water (80:20 v/v), then an aliquot of the extract was centrifuged, filtered and acidified with 1M hydrochloric acid. The extract was cleaned up using a strong cation exchange solid phase extraction cartridge. The cyprodinil residues were eluted with methanol/25% ammonia solution (95:5 v/v), before evaporation and reconstitution in a suitable solvent (e.g. 1:1 v/v methanol/water, 1:1 v/v acetonitrile/water). Samples were analysed by HPLC-UV (detection wavelength = 255 or 270 nm), or LC-MS/MS (quantification transition: 226.1 → 93.1). The calculated method LOQ was 0.01 mg/kg, although depending on the residue trial, the method was validated at various fortification levels, giving lowest limits of method validation (LLMV) of 0.01–0.1 mg/kg.

Method number 2213-01

This method was used for determination of cyprodinil residues in cucurbit fruiting vegetables. Samples were extracted with methanol/water (80:20 v/v), then the extract was filtered and diluted to volume, before evaporation of the solvent from an aliquot of the sample and reconstitution in 0.1% aqueous ammonium acetate, and analysis by LC-MS ($m/z=226$). The method LOQ was 0.01 mg/kg.

The methods were validated for each matrix in conjunction with the analyses of the residue trial samples. Recovery data are tabulated below. The mean recoveries were acceptable, being within 70–120%, at fortification levels ranging from 0.01 to 115 mg/kg.

Table 1 Cyprodinil recovery data for method number AG-631B and 2213-01

Matrix	Fortification level (mg/kg)	n	Mean recovery (%)	RSD (%)	Reference (Author, Year)
Avocado	0.02	8	84	3.5	Barney, 2005
	0.2	4	79	3.3	
	2	3	80	2.2	
Beans (dry)	0.02	7	93	5.9	Chen, 2003
	0.1	9	90	4.1	
	1	5	87	3.3	
Blueberry	0.02	3	103	3.4	Thompson, 2001
	0.2	4	80	2.7	
	2	8	95	16	
Broccoli	0.025	7	98	10	Arsenovic, 2002
	0.25	1	114	–	
	0.5	1	104	–	
	0.6	3	101	5.0	
	10	5	109	5.3	
Cabbage	0.02	6	99	16	Arsenovic, 2002
	0.4	7	85	15	
	10	1	82	–	
	20	3	86	6.8	
Mustard greens	0.05	7	85	12	Arsenovic, 2002
	0.5	8	87	8.4	
	1	2	97	–	
	10	2	82	–	
	20	3	88	4.0	
Raspberry	0.02	3	98	7.7	Starnier, 2001
	0.2	3	77	4.6	
	2	9	92	11	
	10	3	83	10	
Cantaloupe	0.01	9	81	10	Oakes, 2007
	0.02	1	84	–	
	0.05	2	85	–	
	0.1	2	86	–	
	0.5	3	111	3.6	
Cucumber	0.01	9	80	5.8	
	0.02	1	79	–	
	0.05	5	86	12	
	0.1	3	100	15	
	0.5	1	101	–	
Squash	0.01	8	87	–7	
	0.02	1	83	–	
	0.05	2	82	–	
	0.1	2	98	–	
	0.5	2	97	–	
	1	1	106	–	
Chilli and	0.01	9	89	12	Lennon, 2011

Matrix	Fortification level (mg/kg)	n	Mean recovery (%)	RSD (%)	Reference (Author, Year)
sweet					
	0.1	2	78	–	
	0.2	3	81	7.7	
	0.5	8	83	9.5	
	1	3	81	6.3	
	2	3	81	4.0	
Tomato (fruit)	0.01	22	94	9.0	Thompson, 2005
	0.1	1	82	–	
	0.2	20	90	8.9	
	1	1	83	–	
	2	4	87	6.9	
Tomato (puree)	0.01	6	96	18	
	0.2	4	92	2.8	
	1	1	85	–	
	2	3	90	4.0	
Tomato (paste)	0.01	6	86	11	
	0.2	4	88	6.1	
	1	1	101	–	
	2	3	85	7.7	
Basil (fresh)	0.05	3	83	3.6	Chen, 2002
	0.1	1	90	–	
	0.5	3	81	3.1	
	1	3	86	3.1	
	10	2	80	–	
Basil (dried)	0.1	3	82	7.5	
	0.5	3	73	5.2	
	1	3	96	2.6	
	10	3	82	6.5	
Chives (fresh)	0.05	9	94	9.5	Chen, 2002
	0.2	3	87	0	
	1	7	82	4.1	
Chives (dried)	0.05	3	75	2.0	
	0.2	3	81	2.8	
	5	3	81	2.5	
Kiwifruit	0.01	6	91	16	Thompson, 2007
	0.5	7	79	8.4	
	1	1	90	–	
	5	3	83	6.0	
Lettuce	0.02	6	108	3.5	Chen, 2003
	1	16	87	4.7	
	10	4	91	3.3	
	30	3	86	4.1	
Spinach	0.02	7	93	13	Thompson, 2011
	0.2	3	79	7.6	
	1	4	88	13	
	2	4	92	17	
	10	4	85	11	
	15	2	78	–	
	25	1	86	–	
	50	4	88	11	
Lemon	0.02	7	99	13	Thompson, 2007
	0.2	5	87	6.6	
	0.5	3	82	4.2	
	1	1	90	–	
	2	3	91	2.3	

Matrix	Fortification level (mg/kg)	n	Mean recovery (%)	RSD (%)	Reference (Author, Year)
Lemon	0.02	1	82	–	Barney, 2010
	0.2	1	73	–	
Lemon dried pulp	0.01	5	80	10	
	0.02	3	107	1.9	
	0.2	3	84	6.6	
	2	3	79	0.7	
Lemon juice	0.01	5	96	3.0	
	0.02	1	84	–	
	0.2	4	77	6.6	
	2	3	75	7.4	
Lemon oil	0.02	6	99	11	
	0.2	3	105	1.6	
	2	4	96	9.8	
	50	3	88	15	
Lychee (whole)	0.02	3	92	13	Chen, 2002
	0.5	3	93	8.8	
	1	4	77	10	
	5	3	88	8.8	
Lychee (peeled fruit)	1	1	75	–	
Lychee (peel)	1	1	71	–	
Parsley (fresh)	0.05	7	103	13	Barney, 2006
	1	4	82	6.5	
	30	6	89	8.4	
Parsley (dried)	0.1	7	83	6.9	
	1	5	86	6.9	
	30	6	85	13	
	115	4	81	2.5	
Carrot	0.02	4	91	16	Chen, 2002
	0.1	4	85	6.3	
	0.4	6	80	9.0	
	1	5	99	11	
	0.02	7	87	14	Barney, 2006
	0.8	5	78	10	
Radish tops	0.01	10	90	15	Barney, 2007
	0.5	7	85	12	
	1	1	93	–	
	2	3	89	7.4	
Radish roots	0.01	7	94	12	
	0.025	3	81	10	
	0.5	9	80	7.7	
	1	1	85	–	
	2	3	76	3.5	
Strawberry	0.02	9	92	8.8	Chen, 2004
	0.2	3	82	5.3	
	2	8	82	6.3	
Watercress	0.05	3	109	7.1	Starner, 2001
	0.5	4	80	9.7	
	2	1	73	–	
	5	3	76	2.6	
	20	3	93	11	
Apple	0.01	9	100	15	Mazlo, 2010
	0.1	6	95	7.6	
	1	3	70	6.8	
	2	2	76	–	

Matrix	Fortification level (mg/kg)	n	Mean recovery (%)	RSD (%)	Reference (Author, Year)
Pear	0.01	3	102	3.4	Mazlo, 2010
	0.1	3	98	7.4	
	1	3	87	21	

Stability of pesticide residues in stored analytical samples

Plant matrices

Storage stability data was determined concurrently with sample storage as part of the analytical phase of the residue trials submitted to the Meeting. The storage intervals for the plant matrices in the residue trials are tabulated below, together with storage stability data.

Table 2 Storage stability data for cyprodinil residues in frozen plant matrices

Matrix	Sample storage interval (days)	Test storage interval (days)	Fortification level (mg/kg)	Stored recoveries (%)	Procedural recoveries (%)	Reference (Author, Year)
Avocado	103	229	1	64, 64, 64	90	Barney, 2005
Beans (dry)	164	164	1	89, 90, 94	90	Chen, 2003
Blueberry	329	335	2	95, 98, 110	95 (mean)	Thompson, 2001
Broccoli	180	183	10	84, 95, 90	105	Arsenovic, 2002
Cabbage	219	360	10	96, 102, 103	82	Arsenovic, 2002
Mustard greens	581	601	10	77, 84, 85	82 (mean)	Arsenovic, 2002
Raspberry	234	234	2	87, 94, 95	96	Starner, 2001
Cantaloupe	613	–	–	–	–	Oakes, 2007
Cucumber	596	–	–	–	–	
Squash	598	–	–	–	–	
Peppers	258	–	–	–	–	Lennon, 2011
Tomato (fruit)	221	292	1	89, 107, 108	83	Thompson, 2005
Tomato (puree)	90	123	1	78, 80, 86	85	
Tomato (paste)	65	126	1	89, 92, 93	101	
Basil (fresh)	416	428	1	83, 87, 97	75	Chen, 2002
Chives (fresh)	493	489	1	87, 88, 90	85	Chen, 2002
Kiwifruit	118	123	1	80, 83, 89	90	Thompson, 2007
Lettuce	182	207	1	87, 89, 89	89	Chen, 2003
Spinach	670	–	–	–	–	Thompson, 2011
Lemon	118	125	1	80, 86, 99	90	Thompson, 2007
Lemon	97	–	–	–	–	Barney, 2010
Lemon dried pulp	146	–	–	–	–	
Lemon juice	169	–	–	–	–	
Lemon oil	313	–	–	–	–	
Lychee	107	125	1	67, 71, 74	73	Chen, 2002
Parsley (fresh)	113	181	30	71, 79, 81	78	Barney, 2006
Parsley (dried)	101	180	30	80, 94, 95	83	
Carrot	256	439	1	73, 75, 80	85, 89	Chen, 2002
	80	–	–	–	–	Barney, 2006
Radish top	153	178	1	86, 95, 97	93	Barney, 2007
Radish roots	190	181	1	82, 91, 94	85, 93	
Strawberry	149	–	–	–	–	Chen, 2004
Watercress	303	308	2	63, 65, 73	73	Starner, 2001

Matrix	Sample storage interval (days)	Test storage interval (days)	Fortification level (mg/kg)	Stored recoveries (%)	Procedural recoveries (%)	Reference (Author, Year)
Apple	357	—	—	—	—	Mazlo, 2010
Pear	356	—	—	—	—	Mazlo, 2010

Further storage stability data was evaluated by JMPR for the 2003 evaluation of cyprodinil. A study by Kissling (1995) evaluated the stability (at -18°C) of incurred cyprodinil residues in grapes, apples, wheat ears, and wheat stalks, and of fortified residues in strawberries, potatoes and wine. Acceptable stability was observed in all of these matrices over 24 months.

The maximum interval for which samples were stored in the residue trials considered by this Meeting was 670 days (spinach). Stability of cyprodinil residues has been verified in a study conducted for a range of plant matrices over 24 months. Mean concurrent storage stability data was generally within the range 70–120%, with the exception of avocado and watercress. For the latter, it is noted that the analytical recovery was also low (73%).

USE PATTERNS

Cyprodinil is registered in the USA for use on lemons and limes, pome fruit, bush berries, cane berries, strawberries, tropical fruits—inedible peel, Brassica vegetables, cucurbits, non-cucurbit fruiting vegetables, leafy vegetables (including Brassica leafy vegetables), beans (succulent and dry), root and tuber vegetables and herbs.

Table 3 Registered uses of cyprodinil in the USA relevant to the evaluation

Crop	Application			PHI (days), or latest growth stage at application
	Method	Rate (g ai/ha, max)	No. (max)	
Lemon Lime	Foliar	289–368	1	0
Pome fruits ^a	Foliar	158–263	6 (at the maximum rate, max. seasonal rate 1578 g ai/ha)	0
	Foliar (aerial)	158–263	2	0
Berries and other small fruits ^b	Foliar	289–368	4 (at the maximum rate, max. season rate 1471 g ai/ha)	0
	Foliar (aerial)	289–368	1	0
Strawberries	Foliar	289–368	4 (at the maximum rate, max. season rate 1471 g ai/ha)	0
	Foliar (aerial)	289–368	1	0
Assorted tropical and subtropical fruits—inedible peel ^c	Foliar	289–368	4 (at the maximum rate, max. season rate 1471 g ai/ha)	0
	Foliar (aerial)	289–368	1	0
Kiwifruit (75 WG)	Foliar	525	2	0
	Foliar (aerial)	525	2	0
Brassica vegetables (includes some Brassica leafy vegetables) ^d	Foliar	263–368	4 (at the maximum rate, max. season rate 1471 g ai/ha)	7
Fruiting vegetables, Cucurbits ^e	Foliar	289–368	4 (at the maximum rate, max. season rate 1471 g ai/ha)	1
Fruiting vegetables, other than Cucurbits ^f	Foliar	289–369	4 (at the maximum rate, max. season rate 1471 g ai/ha)	0
Leafy vegetables ^g	Foliar	289–369	4 (at the maximum rate, max. season rate 1471 g ai/ha)	0
Watercress	Foliar	289–369	4 (at the maximum rate, max. season rate 1471 g ai/ha)	0
Legume vegetables ^h	Foliar	289–369	4 (at the maximum rate, max. season rate 1471 g ai/ha)	7
Pulses ⁱ	Foliar	289–369	4 (at the maximum rate, max. season rate 1471 g ai/ha)	7

Crop	Application			PHI (days), or latest growth stage at application
	Method	Rate (g ai/ha, max)	No. (max)	
Root and tuber vegetables ^j	Foliar	289–369	4 (at the maximum rate, max. season rate 1471 g ai/ha)	7
Radish	Foliar	289–369	2	7
Herbs ^k	Foliar	289–369	4 (at the maximum rate, max. season rate 1471 g ai/ha)	7

^a Apple, Pear, Crab-apple, Quince, Loquat, Mayhaw.

^b Bush berry subgroup (Aronia berry, black currant, blueberry, high and low bush, Buffalo currant, Chilean guava, Edible honeysuckle, elderberry, European barberry, gooseberry, highbush cranberry, huckleberry, jostaberry, junberry, lingonberry, native currant, redcurrant, salal, sea buckthorn) Cane berry subgroup (blackberry, loganberry, red and black raspberry, wild raspberry).

^c Tropical fruits (avocado, black sapote, canistel, dragon fruit, longan, lychee, mamey sapote, mango, papaya, pulasan, rambutan, sapodilla, Spanish lime, star apple).

^d Brassica (cole) leafy vegetables (broccoli, Chinese broccoli, broccoli raab, Brussels sprouts, cabbage, Chinese cabbage, cauliflower, cavalo broccolo, collards, kale, kohlrabi, mizuna, mustard greens, mustard spinach, rape greens, turnip greens).

^e Cucurbits (cantaloupe, chayote, Chinese waxgourd, cucumber, gourds, honeydew, bitter melon, balsam apple, muskmelon, watermelon, pumpkin, squash, zucchini).

^f Fruiting vegetable crop group (African eggplant, bush tomato, bell pepper, cocona, currant tomato, eggplant, garden huckleberry, goji berry, groundcherry, martynia, naranjilla, okra, pea eggplant, pepino, non-bell pepper, roselle, scarlet eggplant, sunberry, tomatillos, tomato, tree tomato).

^g Leafy greens subgroup 4A (except Brassica and leaf petioles subgroup 4B) (amaranth, arugula, cardoon, celery, Chinese celery, celtuce, chervil, edible chrysanthemum, corn salad, cress, dandelion, dock, endive, Florence fennel, head and leaf lettuce, New Zealand spinach, orach, parsley, purslane, radicchio, rhubarb, spinach, vine spinach, Swiss chard).

^h Beans, succulent, except cowpea (chickpea, bean (*Lupinus* spp.), bean (*Phaseolus* spp.), broad bean, bean (*Vigna* spp.).

ⁱ Beans, dry, except cowpea (chickpea, bean (*Lupinus* spp.), bean (*Phaseolus* spp.), broad bean, bean (*Vigna* spp.).

^j Root vegetables (edible burdock, carrot, celeriac, chicory, garden beet, ginseng, horseradish, parsnip, oriental radish, rutabaga, salsify, skirret, turnip, turnip-root parsley, turnip rooted chervil).

^k Herbs (dried and fresh) (angelica, balm, basil, borage, burnet, camomile, catnip, chervil (dried leaves), chives, clary, coriander leaves, costmary, culantro, curry leaves, dillweed, horehound, hyssop, lavender, lemongrass, lovage, marigold, marjoram, nasturtium, parsley (dried), pennyroyal, rosemary, rue, sage, savory (summer and winter), sweet bay, tansy, tarragon, thyme, wintergreen, woodruff, wormwood).

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on cyprodinil supervised field residue trials for the following commodities:

Crop group	Commodity	Table
Citrus fruits	Lemon	4
Pome fruits	Apples	5
	Pears	6
Berries and other small fruits	Blueberries	7
	Raspberries	8
	Strawberry	9
Assorted tropical and sub-tropical fruits—inedible peel	Avocado	10
	Kiwifruit	11
	Litchi	12
Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead Brassicas	Cabbage	13

Crop group	Commodity	Table
Fruiting vegetables, Cucurbits	Broccoli	14
	Melons	15
	Cucumber	16
	Squash	17
Fruiting vegetables, other than Cucurbits	Peppers (sweet), field grown	18
	Peppers (sweet), greenhouse grown	19
	Peppers (chilli), field grown	20
	Peppers (chilli), greenhouse grown	21
	Tomato, greenhouse grown	22
	Tomato, field grown	23
	Lettuce, Head	24
	Lettuce, Leaf	25
Leafy vegetables (including Brassica leafy vegetables)	Watercress	26
	Spinach	27
	Mustard greens	28
	Common bean	29
Legume vegetables	Lima bean	30
	Beans, dry	31
Pulses	Carrot	32
Root and tuber vegetables	Radish	33
	Basil	34
Herbs	Chives	35
	Parsley	36

Citrus fruits

Lemon

Five residue trials were conducted in lemons in California, USA during 2004/05 (Thompson, 2007-a). Cyprodinil was applied as a water-dispersible granular (WG) co-formulation with fludioxonil. A single foliar application was made to the treated plot at each trial site at a target application rate of 368 g ai/ha. No spray adjuvants were included in the tank mix. Fruit was sampled on the day of application, after the spray had dried. Residues of cyprodinil were analysed using an LC/MS/MS method (method number AG-631B). Analyses were completed within 4 months of harvest.

Table 4 Residues of cyprodinil in lemons

Location, Trial no., Year (Variety)	Application				Sample	DAT	Residue (mg/kg)		
	No. (RTI, days)	Growth stage	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mean
Orange Cove, CA, USA, 04-CA122 (Lisbon)	1	mature fruit	0.39	1800	Fruit	0	0.17	0.17	0.17
Orange Cove, CA, USA,	1	mature	0.38	1100	Fruit	0	0.16	0.22	0.19

Location, Trial no., Year (Variety)	Application				Sample	DAT	Residue (mg/kg)		
	No. (RTI, days)	Growth stage	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mean
04-CA123 (Lisbon)		fruit							
Riverside, CA, USA, 04- CA124 (Lisbon)	1	mature fruit	0.37	1100	Fruit	0	0.21	0.36	0.28
Riverside, CA, USA, 04- CA125 (Lisbon)	1	mature fruit	0.37	1100	Fruit	0	0.36	0.32	<u>0.34</u>
Porterville, CA, USA, 04- CA126 (Pryor)	1	mature fruit	0.37	1900	Fruit	0	0.35	0.27	<u>0.31</u>

Pome fruit

Apples

A series of twelve trials in apples was conducted in the USA during the 2008 and 2009 growing seasons (Mazlo, 2010). Five applications of cyprodinil as a 750 g/kg WG formulation were made at each site, at target intervals of 7 days, with application rates of 278–296 g ai/ha (1× the GAP of the USA). A spray adjuvant (non-ionic surfactant or crop oil concentrate) was included in the tank mix for all applications. Residues of cyprodinil in apples were determined using an LC/MS/MS method (method number AG-631B). Samples were stored frozen until analysis, which took place up to 12 months later.

Pears

A series of six trials in pears was conducted in the USA during the 2008 growing season (Mazlo, 2010). Five applications of cyprodinil as a 750 g/kg WG formulation were made at each site, at target intervals of 7 days, with application rates of 256–286 g ai/ha (1× the GAP of the USA). Residues of cyprodinil in pears were determined using an LC/MS/MS method (method number AG-631B). Samples stored frozen until analysis, which took place up to 12 months later.

Table 5 Results of residue trials conducted with cyprodinil (375 g/kg WG) in apples in the USA in 2008 and 2009 (study number T003061-07)^a

Location, Trial no., Year (Variety)	Application				DAT	Residue (mg/kg)		
	No. (RTI, days)	Growth stage	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Hereford, PA, E04PA081221, 2008 (Stark Crimson)	5 (6, 8, 7, 8)	77, 78, 78, 85, 87	0.28, 0.28, 0.28, 0.28, 0.28	2300, 2300, 2300, 2300, 2200	0	0.54	0.49	<u>0.52</u>
					13	0.38	0.32	0.35
North Rose, NY, E03NY081222, 2008 (Cortland)	5 (7, 7, 7, 7)	77, 81, 81, 85, 87	0.28, 0.28, 0.28, 0.28, 0.28	610, 620, 610, 620, 610	0	0.20	0.17	0.19
North Rose, NY, E03NY081223, 2008 (Ida Red)	5 (6, 7, 7, 8)	81, 81, 85, 85, 87	0.28, 0.28, 0.28, 0.28, 0.28	2100, 2100, 2100, 2100, 2100	0	0.18	0.22	<u>0.20</u>
Hart, MI, C01MI081225, 2008 (Golden Delicious)	5 (8, 6, 7, 7)	81, 77–78, 88, 85, 89	0.28, 0.28, 0.28, 0.28, 0.28	750, 760, 750, 760, 760	0	0.41	0.38	<u>0.40</u>
					14	0.36	0.35	0.36
Shelby, MI, C01MI081226, 2008 (Ida Red)	5 (7, 7, 9, 7)	81, 85, 88, 89, 89	0.29, 0.29, 0.28, 0.28, 0.28	1200, 1200, 1200, 1200, 1200	0	0.40	0.60	<u>0.50</u>
					14	0.30	0.38	0.34
Cedardge, CO, W12CO081227, 2008 (Gala)	5 (7, 7, 7, 7)		0.30, 0.29, 0.28, 0.28, 0.29	1700, 1600, 1600, 1600, 1600	0	0.61	0.63	0.62
					14	0.82	0.58	<u>0.70</u>
Hickman, CA, W26CA081228, 2008 (Gala)	5 (7, 6, 8, 7)	75, 77, 77, 79, 89	0.28, 0.28, 0.28, 0.28, 0.28	1500, 1500, 1400, 1400, 1500	0	0.54	0.47	<u>0.51</u>
					14	0.23	0.31	0.27
Ephrata, WA, W18WA081229, 2008 (Braeburn)	5 (7, 7, 7, 7)	75, 78, 82, 85, 85	0.28, 0.29, 0.29, 0.28, 0.28	93, 96, 96, 95, 95	0	1.1	0.77	<u>0.94</u>

Location, Trial no., Year (Variety)	Application				DA T	Residue (mg/kg)		
	No. (RTI, days)	Growth stage	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
					13	0.84	0.97	0.91
Ephrata, WA, W18WA081229, 2008 (Red Delicious)	5 (7, 7, 7, 7)	75, 78, 78, 85, 85	0.28, 0.28, 0.28, 0.28, 0.28	1900, 1900, 1900, 1900, 1900	0	0.33	0.45	0.39
					5	0.40		
					10	0.23		
					14	0.36	0.40	0.38
					19	0.28		
Hood River, OR, W20OR081231, 2008 (Ginger Gold)	5 (7, 7, 7, 7)		0.29, 0.28, 0.29, 0.28, 0.29	580, 590, 540, 680, 690	0	0.30	0.26	0.28
Hood River, OR, W20OR081232, 2008 (Jona Gold)	5 (7, 7, 7, 7)		0.29, 0.28, 0.28, 0.28, 0.28	1700, 1500, 1700, 1600, 1700	0	0.18	0.34	0.26
Alto, GA, E12GA091239, 2009 (Arkansas Black)	5 (7, 7, 7, 6)	77–79, 78–79, 80, 84–85, 85	0.28, 0.28, 0.28, 0.28, 0.28	580, 590, 580, 580, 590	0	1.1	1.4	1.3
					14	0.28	0.48	0.38

^a Apple fruit were sampled.

Table 6 Results of residue trials conducted with cyprodinil (375 g/kg WG) in pears in the USA in 2008 (study number T003061-07) ^a

Location, Trial no., Year (Variety)	Application				Residue (mg/kg)		
	No. (RTI, days)	Growth stage	Rate (kg ai/ha)	Volume (L/ha)	rep 1	rep 2	mean
Orefield, PA, E04PA081233, 2008 (Bartlett)	5 (7, 7, 7, 7)	75, 76, 77, 78, 81	0.28, 0.28, 0.28, 0.28, 0.28	520, 510, 520, 510, 510	0.49	0.42	0.46
Poplar, CA, W32CA081234, 2008 (Olympia)	5 (7, 7, 7, 7)	77, 79, 80–81, 81, 89	0.28, 0.26, 0.28, 0.29, 0.28	710, 720, 670, 720, 730	0.73	0.57	0.65
Lindsay, CA, W32CA081235, 2008 (Olympic)	5 (7, 7, 7, 7)	78, 79–80, 81, 88, 89	0.28, 0.28, 0.28, 0.29, 0.28	1900, 1900, 1900, 2000, 1900	0.48	0.22	0.35
Ephrata, WA, W18WA081236, 2008 (Bartlett)	5 (7, 7, 7, 7)	75, 77, 79, 81, 85	0.28, 0.28, 0.28, 0.28, 0.28	96, 96, 98, 95, 97	0.32	0.40	0.36
Ephrata, WA, W18WA081237, 2008 (Concord)	5 (7, 7, 7, 7)	69, 77, 78, 84, 87	0.28, 0.28, 0.28, 0.28, 0.28	1900, 1900, 1900, 1900, 1900	0.31	0.28	0.30
Hood River, OR, W20OR081238, 2008 (Starkrimson)	5 (7, 7, 7, 7)		0.28, 0.28, 0.28, 0.29, 0.28	440, 460, 630, 530, 520	0.11	0.22	0.17

^a Fruit samples were taken at day 0.

Berries and other small fruits

Blueberries

Residue trials in blueberries were conducted at eight sites across the USA during the 1998 and 1999 growing seasons (Thompson, 2001). Cyprodinil was applied as a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil.

Samples were analysed for cyprodinil using an HPLC-UV method (method number AG-631B, with minor modifications). Recoveries ranged from 75–118% at fortification levels of 0.02, 0.2 and 2 mg/kg. The samples were stored frozen for up to 11 months between harvest and analysis.

Raspberries

Five residue trials in raspberries were conducted in the USA during the 1998 growing season (Starner, 2001-a). A series of four applications of a water dispersible granular formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil was made. The first two applications were made during flowering, approximately 7 days apart, followed by a gap of around 2–5 weeks before the third and fourth applications, which were made around 7 days apart around the time of commercial harvest. Fruit was sampled on the day of the last application, after the spray had dried.

Residues of cyprodinil were determined using an HPLC-UV method (method number AG-631B, with minor modifications).

Strawberries

Eight trials using a water dispersible granule fungicide containing 375 and 250 g/kg respectively of cyprodinil and fludioxonil were conducted in strawberries in the USA during 2002 (Chen, 2004). Cyprodinil was applied as a foliar-directed spray at a target rate of 368 g ai/ha using a pressurised backpack sprayer with a hand-held boom; spray adjuvants were not included. Four applications were made, at target intervals of 7 days. Fruit was sampled on the day of the last application, after the spray had dried.

Residues of cyprodinil were determined using an HPLC-UV method (method number AG-631B, with minor modifications).

Table 7 Residues of cyprodinil in blueberries ^a

Location, Trial no., Year (Variety)	Application			Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)	rep 1	rep 2	mean
Castle Hayne, NC, USA, NC06, 1998 (Harrison)	4 (9, 37, 7)	0.36, 0.36, 0.36, 0.36	320, 320, 320, 320	1.7	1.2	1.4
Castle Hayne, NC, USA, NC07, 1998 (Harrison)	4 (9, 37, 7)	0.36, 0.37, 0.36, 0.37	320, 330, 320, 330	1.6	1.2	1.4
Jonesboro, ME, USA, ME04, 1999 (wild)	4 (6, 71, 7)	0.37, 0.37, 0.36, 0.37	280, 280, 280, 280	1.1	0.99	1.0
Chatsworth, NJ, USA, NJ29, 1999 (Bluecrop)	4 (7, 48, 5)	0.36, 0.36, 0.37, 0.37	330, 320, 330, 330	0.56	0.45	0.50
Fennville, MI, USA, MI23, 1999 (Rubel)	4 (7, 72, 7)	0.38, 0.37, 0.37, 0.37	480, 460, 470, 470	0.92	0.96	0.94
Fennville, MI, USA, MI24, 1999 (Rubel)	4 (8, 64, 7)	0.37, 0.37, 0.37, 0.37	470, 460, 470, 470	1.9	1.9	1.9
Fennville, MI, USA, MI25, 1999 (Rubel)	4 (7, 63, 6)	0.37, 0.37, 0.37, 0.37	460, 470, 470, 470	1.5	1.8	1.7
Aurora, OR, USA, OR29, 1999 (Bluecrop)	4 (9, 77, 7)	0.38, 0.38, 0.38, 0.38	480, 480, 480, 480	0.55	0.68	0.62

^a Fruit samples were taken at day 0.

Table 8 Residues of cyprodinil in raspberries ^a

Location, Trial no., Year (Variety)	Application			Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)	rep 1	rep 2	mean
Jackson Springs, NC, USA, NC05, 1998 (Southland)	4 (9, 16, 3)	0.36, 0.37, 0.36, 0.37	460, 470, 460, 460	6.2	5.6	5.9
Durham, NH, USA, NH02, 1998 (Heritage)	4 (7, 36, 8)	0.37, 0.36, 0.36, 0.36	510, 490, 500, 490	2.8	2.2	2.5
Mt Vernon, WA, USA, WA56, 1998 (Meeker red)	4 (9, 21, 8)	0.38, 0.37, 0.38, 0.37	760, 580, 630, 590	1.3	1.6	1.5
Burlington, WA, USA, WA57, 1998 (Meeker red)	4 (9, 21, 8)	0.38, 0.37, 0.37, 0.37	750, 580, 620, 600	1.7	1.4	1.6
Walla Walla, WA, USA, WA58, 1998	4 (9, 27, 7)	0.37, 0.36, 0.38,	580, 580, 590,	2.4	1.9	2.1

Location, Trial no., Year (Variety)	Application			Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)	rep 1	rep 2	mean
(Canby)		0.37	610			

^a Fruit samples were taken at day 0.

Table 9 Residues of cyprodinil in strawberries ^a

Location, Trial no., Year (Variety)	Application			Residue (mg/kg)		
	No. (RTI, days)	Rate (g ai/ha)	Volume (L/ha)	rep 1	rep 2	mean
Madera, CA, USA, CA19, 2002 (Hecker)	4 (7, 7, 7)	0.38, 0.38, 0.37, 0.37	480, 480, 470, 470	2.0	1.3	1.6
Salinas, CA, USA, CA20, 2002 (Diamonte)	4 (7, 6, 8)	0.35, 0.37 0.36, 0.36	360, 380, 560, 400	0.53	0.83	0.68
Fresno, CA, USA CA21, 2002 (Hecker)	4 (7, 7, 7)	0.38, 0.37, 0.37, 0.38	480, 470, 470, 480	1.7	2.2	2.0
Suwannee, FL, USA, FL04, 2002 (Sweet Charlie)	4 (6, 6, 7)	0.36, 0.37, 0.37, 0.37	270, 280, 280, 280	1.1	1.9	1.5
Clinton, NC, USA, NC05, 2002 (Camarosa)	4 (8, 6, 6)	0.37, 0.36, 0.37, 0.37	320, 320, 330, 330	1.3	0.87	1.1
Ithaca, NY, USA, NY07, 2002 (Jewel)	4 (6, 6, 7)	0.39, 0.37, 0.37, 0.38	490, 470, 470, 490	0.11 _b	0.08 _b	0.10 _b
Aurora, OR, USA, OR05, 2002 (Totem)	4 (6, 8, 7)	0.40, 0.38, 0.39, 0.39	500, 480, 500, 500	0.29	0.32	0.30
Greenwood, WI, USA, WI02, 2002 (Honeye)	4 (7, 7, 8)	0.37, 0.37, 0.37, 0.37	400, 400, 410, 430	0.89	0.92	0.91

^a Fruit samples were taken at day 0.

^b Results may be rain affected, rain fell within < 2 hours of the final application.

Assorted tropical and sub-tropical fruits—inedible peel

Avocado

Six trials in avocados were conducted across the USA during 2003 (Barney, 2005). Four applications of a water dispersible granular formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil, was made to each treated plot. Fruit was harvested from the treated plot on the day of the last application. The fruit were quartered in the field, and the stones discarded. It appears that the results were determined on the fruit minus stone, not on the whole fruit, as weights of the stones were not recorded.

Residues of cyprodinil were determined using an HPLC-UV method (method number AG-631B), with minor modifications.

Kiwifruit

Three residue trials for cyprodinil in kiwifruit were conducted in California in 2004 (Thompson, 2007-b). Cyprodinil was applied to kiwifruit vines with near-mature fruit as a 750 g/kg water dispersible granule formulation twice at 7–10 day intervals at a target application rate of 526 g ai/ha. Treated and control fruit were sampled on the day of the final application, after the spray had dried.

Samples were analysed for cyprodinil using HPLC/UV method number AG-631B, with minor modifications.

Lychees

Three residue trials in lychees were conducted in Florida during 2000 (Chen, 2002-a). Cyprodinil was applied as a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg

fludioxonil. Between five and seven applications were made at a target rate of 368 g ai cyprodinil/ha, commencing at fruit setting and continuing at approximately 7 day intervals until commercial maturity. Fruit was sampled on the day of the last application, after the spray had dried.

Lychees were analysed for cyprodinil using an HPLC-UV method (method number AG-631B, with minor modifications). Fruit from one site was separated into peel and peeled fruit for analysis to determine the partitioning of the residue between peel and pulp. Good recoveries were achieved in whole and peeled lychees, and peel, ranging from 71–105%. The samples were stored frozen for up to 3.5 months between harvest and analysis; recoveries after storage of cyprodinil from stability samples fortified at 1 mg/kg and stored for 125 days ranged from 67–74% (it is noted that the concurrent recovery at analysis after storage was 73%). It is unlikely that samples were adversely affected by storage.

Table 10 Residues of cyprodinil in avocados^a

Location, Trial no., Year (Variety)	Application			Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)	rep 1	rep 2	mean
Homestead, FL, USA, FL22, 2003 (Miguel)	4 (7, 20, 7)	0.37, 0.38, 0.38, 0.38	850, 860, 860, 870	0.34	0.26	0.30
Monte Alto, TX, USA, TX14, 2003 (Lula)	4 (7, 22, 8)	0.37, 0.36, 0.37, 0.37	1800, 1800, 1900, 1900	0.07	0.09	0.08
Porterville, CA, USA, CA35, 2003 (Zutano)	4 (7, 21, 7)	0.38, 0.37, 0.37, 0.37	880, 870, 880, 890	0.22	0.13	0.18
Nipomo, CA, USA, CA36, 2003 (Gwen and Bacon)	4 (7, 19, 8)	0.38, 0.37, 0.37, 0.38	1600, 1600, 1600, 1600	0.45	0.26	0.35
Irvine, CA, USA, CA37, 2003 (Haas)	4 (7, 21, 8)	0.37, 0.38, 0.37, 0.38	750, 760, 750, 760	0.56	0.63	0.60
Orosi, CA, USA, CA38, 2003 (Haas)	4 (7, 19, 8)	0.37, 0.37, 0.37, 0.37	1600, 1600, 1600, 1600	0.21	0.25	0.23

^a Fruit samples were taken at day 0.

Table 11 Residues of cyprodinil in kiwifruit^a

Location, Trial no., Year (Variety)	Application			Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)	rep 1	rep 2	mean
Davis, CA, USA, CA70, 2004 (unspecified)	2 (10)	0.53, 0.53	670, 680	1.1	0.86	<u>0.99</u>
Porterville, CA, USA, CA71, 2004 (Hayward)	2 (7)	0.52, 0.52	790, 790	0.69	0.52	<u>0.61</u>
Parlier, CA, USA, CA72, 2004 (Hayward)	2 (7)	0.53, 0.55	880, 940	1.1	1.1	<u>1.1</u>

^a Fruit samples were taken at day 0.

Table 12 Residues of cyprodinil in lychees^a

Location, Trial no., Year (Variety)	Application			Sample	Residue (mg/kg)		
	No. (RTI, days)	Rate (g ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Homestead, FL, FL23, 2000 (Mauritius)	5 (7, 8, 6, 7)	0.37, 0.37, 0.37, 0.37, 0.37	700, 700, 700, 700, 700	Whole fruit	1.4	0.94	1.2
Homestead, FL, FL24, 2000 (Mauritius)	5 (7, 7, 7, 7)	0.38, 0.37, 0.37, 0.37, 0.37	1200, 1200, 1200, 1200, 1200	Whole fruit	0.94	1.4	1.1
Homestead, FL, FL25, 2000 (Mauritius)	7 (7, 7, 8, 8, 7, 7)	0.37, 0.37, 0.37, 0.37, 0.38, 0.38, 0.38	1200, 1200, 1200, 1200, 1200, 1200, 1200	Whole fruit	1.5	1.1	1.3
				Peeled fruit	< 0.02		
				Peel	3.1		

^a Fruit samples were taken at day 0.

*Brassica (cole or cabbage) vegetables, Head Cabbage, Flowerhead Brassicas**Cabbage*

Residue trials were conducted at six sites in the USA for cabbage during 2000 (Arsenovic, 2002-a). Between four and six applications were made by foliar broadcast or foliar directed application at a target rate of 368 g ai/ha cyprodinil, with applications 1 and 2 being made at a target interval of 7 days, application 3 being made around 3 weeks after application 2, and all subsequent applications being made at a target interval of 7 days.

Cabbages, both with and without wrapper leaves, were analysed for cyprodinil residues using an HPLC-UV method (method number AG-631B, with minor modifications).

Broccoli

Seven residue trials was conducted in the USA and Canada for a 375 g/kg cyprodinil and 250 g/kg fludioxonil water dispersible granule formulation in broccoli (Arsenovic, 2002-b). Between four and six applications were made at a target rate of 368 g ai/ha cyprodinil, with the first two applications being made early in the season roughly 7 days apart, while the third application was made at a target interval of 3 weeks after the second depending on how quickly the crop was maturing. The remaining applications were made at target intervals of 7 days.

Residues of cyprodinil in broccoli were determined using an HPLC-UV method (method number AG-631B, with minor modifications)

With the exception of the sample from the Quebec site (where a low level of residue, 0.029 mg/kg, was found), no residues of cyprodinil were found in the untreated control samples at levels above the limit of quantitation.

Table 13 Residues of cyprodinil in cabbage ^a

Location, Trial no., Year (Variety)	Application			Sample	DAT	Residue (mg/kg)
	No. (RTI, days)	Rate (g ai/ha)	Volume (L/ha)			
Stillwater, ME, USA, ME04, 2000 (Danish Ballhead)	4 (7, 20, 8)	0.35, 0.36, 0.38, 0.35	310, 320, 330, 310	Cabbage ^a	7	0.02
				Cabbage ^a	7	< 0.02
Weslaco, TX, USA, TX33, 2000 (Cheers)	4 (6, 19, 6)	0.37, 0.37, 0.37, 0.37	400, 390, 420, 400	Cabbage ^a	7	< 0.02
				Cabbage ^a	7	< 0.02
Gainesville, FL, USA, FL48, 2000 (Asgrow Blue Dynasty)	6 (7, 26, 8, 8, 7)	0.37, 0.38, 0.38, 0.37, 0.37, 0.38	380, 380, 380, 370, 370, 380	Cabbage ^a	8	0.36
				Cabbage ^a	8	0.08
Weslaco, TX, USA, TX34, 2000 (Cheers)	4 (8, 20, 8)	0.37, 0.37, 0.37, 0.37	450, 460, 450, 460	Cabbage ^a	7	0.19
				Cabbage ^a	7	< 0.02
Salinas, CA, USA, CA15, 2000 (Red Rookie)	4 (6, 23, 6)	0.39, 0.38, 0.36, 0.38	500, 510, 670, 720	Cabbage ^a	7	0.04
				Cabbage ^a	7	< 0.02
Arlington, WI, USA, WI03, 2000 (Blue Thunder)	4 (6, 22, 7)	0.62, 0.60, 0.61, 0.62 ^b	310, 300, 310, 310	Cabbage ^a	6	0.04
				Cabbage ^a	6	< 0.02

^a Heads without wrapper leaves.

^b Product was over-applied by approximately 62–68% per application. The results were scaled for MRL determination; actual results are tabulated.

Table 14 Residues of cyprodinil in broccoli ^a

Location, Trial no., Year (Variety)	Application			DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Weslaco, TX, USA, TX06, 2000 (Baccus hybrid)	4 (7, 14, 8)	0.37, 0.37, 0.37, 0.37	450, 450, 450, 460	6	0.02	< 0.02	<u>0.02</u>
Salinas, CA, USA, CA05, 2000 (Patriot)	4 (6, 23, 6)	0.37, 0.38, 0.37, 0.38	480, 520, 680, 710	7	0.15	0.12	0.14
Salinas, CA, USA, CA06, 2000 (Marathon)	4 (6, 23, 6)	0.37, 0.38, 0.38, 0.38	480, 520, 700, 720	8	0.19	0.11	<u>0.15</u>
El Centro, CA, USA, CA78, 2000 (Greenbelt)	4 (7, 21, 8)	0.37, 0.38, 0.37, 0.37	510, 520, 510, 520	6	0.24	0.16	<u>0.20</u>
Madera, CA, USA, CA126, 2000 (Green sprouting)	4 (7, 24, 8)	0.37, 0.37, 0.38, 0.37	370, 380, 380, 370	8	0.31	0.38	<u>0.34</u>
Abbotsford, BC, Canada, BC04, 2000 (Greenbelt)	4 (6, 40, 6)	0.37, 0.37, 0.37, 0.38	350, 350, 350, 360	7	0.40	0.46	<u>0.43</u>
Saint-Lin, QC, Canada, QC05, 2000 (Marathon)	6 (8, 6, 7, 22, 7)	0.38, 0.38, 0.38, 0.38, 0.38, 0.38	360, 360, 360, 360, 360, 360	7	1.2	0.91	<u>1.1</u> c0.03

^a Broccoli heads were sampled.

Fruiting vegetables, Cucurbits

Melons

Six trials in melons (cantaloupe variety) were conducted for a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil in the USA during 2004 and 2005 (Oakes, 2007). Four applications were made by foliar broadcast at a target application rate of 368 g ai/ha cyprodinil, at target intervals of 7 days, with the final application occurring around one week prior to scheduled harvest. Melons were sampled at all sites at target PHIs of 1 and 7 days after the last application. Additional samples were collected at the decline trial sites on days 0 (after the spray had dried), 3, 5 and 9 days after the last application.

Cyprodinil residues were determined using an LC/MS method (method number 2213-01, with modifications omitting the solid phase extraction clean-up stage).

Cucumber

Seven trials in cucumber were conducted using a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil in the USA during 2004 and 2005 (Oakes, 2007). Four applications were made by foliar broadcast using a backpack sprayer or tractor-mounted boom sprayer at a target application rate of 368 g ai/ha cyprodinil, at target intervals of 7 days, with the final application occurring around one week prior to scheduled harvest. Cucumbers were sampled at all sites at target PHIs of 1 and 7 days after the last application. Additional samples were collected at the decline trial sites on days 0 (after the spray had dried), 3, 5 and 9 days after the last application.

Cyprodinil residues were determined using an LC/MS method (method number 2213-01, with modifications omitting the solid phase extraction clean-up stage).

Summer squash

Six trials in summer squash were conducted using a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil in the USA during 2004 and 2005 (Oakes, 2007). Four applications were made by foliar broadcast at a target application rate of 368 g ai/ha cyprodinil, at target intervals of 7 days, with the final application occurring around one week prior to scheduled harvest. Squash were sampled at all sites at target PHIs of 1 and 7 days after the last application.

Additional samples were collected at the decline trial sites on days 0 (after the spray had dried), 3, 5 and 9 days after the last application.

Cyprodinil residues were determined using an LC/MS method (method number 2213-01, with modifications omitting the solid phase extraction clean-up stage). Recoveries of cyprodinil from squash fortified at concentrations between 0.01–1.0 mg/kg ranged from 73–116%. Samples were stored frozen for up to 20 months between collection and analysis.

Table 15 Residues of cyprodinil in melons (cantaloupe type) ^a

Location, Trial no., Year (Variety)	Application				DAT	Residue (mg/kg)		
	No. (RTI, days)	Growth stage	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Champaign, IL, USA, 4A- FR-04-5178, 2004 (Superstar)	4 (7, 9, 5)	71, 71, 73, 75	0.38, 0.38, 0.36, 0.37	28, 23, 32, 30	1	0.05	0.04	0.05
					8	0.03	0.04	0.04
Wharton, TX, USA, SA- FR-05-5188, 2005 (Earligold)	4 (7, 7, 7)	51–71, 71–74, 75–79, 64–81	0.39, 0.37, 0.36, 0.36	190, 200, 170, 190	1	0.05	0.06	0.06
					8	0.02	0.03	0.03
Chula, GA, USA, SI-FR- 04-5177, 2004 (Edisto 47)	4 (7, 7, 7)	71, 75, 79, 85	0.37, 0.37, 0.36, 0.37	120, 120, 120, 150	1	0.09	0.10	0.10
					7	0.06	0.07	0.07
Madera, CA, USA, WC- FR-04-5180, 2004 (Top Net SR)	4 (7, 7, 7)		0.37, 0.36, 0.37, 0.37	280, 280, 280, 280	0	0.24	0.14	0.19
					1	0.17	0.17	0.17
					3	0.06	0.06	0.06
					5	0.06	0.28	0.17
					7	0.10	0.11	0.11
					9	0.14	0.05	0.10
Live Oak, CA, USA, WD- FR-04-5181, 2004 (Durango)	4 (6, 7, 7)		0.37, 0.37, 0.37, 0.37	140, 140, 140, 140	1	0.08	0.10	0.09
					7	0.10	0.07	0.09
Live Oak, CA, USA, WD- FR-04-5182, 2004 (Top Mark)	4 (7, 7, 7)		0.37, 0.37, 0.37, 0.37	140, 140, 140, 140	1	0.47	0.18	0.33
					7	0.18	0.11	0.15

^a Fruit samples were taken

Table 16 Residues of cyprodinil in cucumbers ^a

Location, Trial no., Year (Variety)	Application				DAT	Residue (mg/kg)		
	No. (RTI, days)	Growth stage	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Delavan, WI, USA, NI-FR- 04-5174, 2004 (Marketmore 86)	4 (7, 7, 7)		0.37, 0.38, 375, 0.37	190, 170, 170, 190	1	0.03	0.06	0.05
					7	0.02	0.02	0.02
Conklin, MI, USA, NI-FR- 04-5173, 2004 (Marketmore 86)	4 (8, 6, 8)		0.37, 0.37, 0.37, 0.36	19, 19, 19, 18	1	0.04	0.04	0.04
					7	0.02	0.01	0.02
Wharton, TX, USA, SA- FR-04-5175, 2004 (Slice master select)	4 (7, 8, 6)	61–71, 61–73, 81–84, 81–87	0.37, 0.37, 0.37, 0.38	160, 180, 180, 190	1	0.13	0.09	0.11
					8	0.04	0.10	0.07

Location, Trial no., Year (Variety)	Application				DAT	Residue (mg/kg)		
	No. (RTI, days)	Growth stage	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Chula, GA, USA, SI-FR-04-5170, 2004 (Lightning)	4 (7, 7, 7)		0.37, 0.37, 0.37, 0.38	260, 260, 260, 260	1	0.08	0.10	0.09
					7	0.02	0.03	0.03
Rose Hill, NC, USA, SJ-FR-04-5171, 2004 (Poinsett 79)	4 (6, 7, 8)		0.37, 0.37, 0.37, 0.37	150, 140, 250, 160	1	0.15	0.14	0.15
					7	0.01	< 0.01	0.01
Vero Beach, FL, USA, VF-FR-04-5172, 2004 (Straight Eight)	4 (8, 9, 7)	51–59, 61–65, 69–71, 71–77	0.36, 0.36, 0.36, 0.37	280, 280, 280, 280	1	0.21	0.26	0.24
					7	0.05	0.10	0.08
Hickman, CA, USA, WC-FR-04-5176, 2004 (Poinsett 76)	4 (6, 7, 7)	65, 65, 71, 75	0.37, 0.37, 0.37, 0.37	230, 230, 230, 230	0	0.06	0.05	0.06
					1	0.05	0.12	0.09
					3	0.03	0.03	0.03
					5	0.02	0.02	0.02
					7	0.01	0.01	0.01
					9	0.02	0.02	0.02

^a Fruit samples were taken

Table 17 Residues of cyprodinil in summer squash ^a

Location, Trial no., Year (Variety)	Application				DAT	Residue (mg/kg)		
	No. (RTI, days)	Growth stage	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Champaign, IL, USA, 4A-FR-04-5186 (Lemondrop)	4 (7, 7, 8)	71, 73, 73, 75	0.40, 0.36, 0.39, 0.40	32, 28, 28, 29	1	0.02	0.02	0.02
					6	0.01	0.01	0.01
Hudson, NY, USA, 5E-FR-04-5183 (Yellow straight)	4 (7, 7, 7)	41, 45, 47, 49	0.38, 0.35, 0.37, 0.37	400, 370, 390, 380	1	0.07	0.06	0.07
					7	0.02	0.02	0.02
Elko, SC, USA, SJ-FR-04-5184, 2004 (Lemondrop L)	4 (6, 5, 5)		0.37, 0.37, 0.37, 0.37	310, 310, 310, 300	1	0.12	0.05	0.09
					6	0.01	0.01	0.01
Vero Beach, FL, USA, VF-FR-04-5185, 2004 (Burpee hybrid zucchini)	4 (7, 8, 8)	69–71, 71– 77, 77–85, 85–89	0.37, 0.38, 0.38, 0.37	280, 280, 280, 280	1	0.06	0.08	0.07
					7	0.01	0.01	0.01
Visalia, CA, USA, WC-FR-04-5187, 2004 (Black Beauty)	4 (7, 7, 7)	62, 64, 72, 75	0.37, 0.37, 0.37, 0.37	140, 140, 140, 140	0	0.02	0.03	0.03
					1	0.03	0.02	0.03
					3	< 0.01	< 0.01	< 0.01
					5	< 0.01	< 0.01	< 0.01
					7	< 0.01	< 0.01	< 0.01
					9	< 0.01	< 0.01	< 0.01

^a Fruit samples were taken

Fruiting vegetables, other than Cucurbits

Peppers (sweet) and peppers chili

Fourteen trials were conducted in field-grown peppers (sweet peppers and chilli peppers) in the USA and Canada in 2006 (Lennon, 2011-a). At each site, a plot was treated with a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil. Four applications at a target rate of 368 g ai/ha cyprodinil were made by foliar application, with target intervals of 7 days between

applications 1 and 2, and 3 and 4, and 21 days between applications 2 and 3. Applications 1 and 2 generally took place during flowering or early fruiting, while applications 3 and 4 were to plants with near-mature fruit. Spray adjuvants were not included in the tank mix. Mature green peppers were harvested on the day of the last application, after the spray had dried.

Samples were analysed for residues of cyprodinil using an HPLC-UV method (method number AG-631B, with minor modifications).

A series of trials in greenhouse grown peppers (four trials in sweet peppers and one trial in chilli peppers) was conducted in the USA and Canada during 2005 and 2006 (Lennon, 2011-b). Plots were treated with a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil. Four applications were made at a target rate of 368 g ai/ha, with an interval of approximately 7 days between applications 1 and 2, and between 3 and 4, while the interval between applications 2 and 3 was generally around 21 days. Samples were collected at each site on the day of the final application, after the spray had dried. At one site, a decline trial was conducted, and additional samples were collected at later intervals.

Samples were analysed for cyprodinil using an HPLC/UV method (method number AG-631B, with minor modifications).

Tomato

A series of eighteen trials (fourteen in field-grown tomatoes, and four in greenhouse tomatoes) was conducted in tomatoes in the USA during the 2002 growing season (Thompson, 2005). At each site, plots were treated with four applications of a water dispersible granule containing 375 g/kg cyprodinil and 250 g/kg fludioxonil. Applications were made at target intervals of 7 days for applications 1 and 2, and applications 3 and 4, with a target interval of 21 days for applications 2 and 3. This resulted in the first two applications being conducted at late flowering/early fruiting, and the second two when fruit was maturing.

Residues of cyprodinil were determined using an HPLC-UV method (method number AG-631B).

With one exception, residues were not found above the limit of quantitation in any of the untreated control samples.

Table 18 Residues of cyprodinil in field-grown sweet peppers ^a

Location, Trial no., Year (Variety)	Application			DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Holtville, CA, USA, CA45, 2006 (Maccabi)	4 (6, 21, 6)	0.37, 0.37, 0.37, 0.37	580, 550, 560, 550	0	0.23	0.24	<u>0.23</u>
Five Points, CA, USA, CA46, 2006 (Baron)	4 (7, 20, 7)	0.37, 0.37, 0.37, 0.36	380, 370, 380, 370	0	0.09	0.11	<u>0.10</u>
Citra, FL, USA, FL19, 2006 (Camelot 3XR)	4 (7, 21, 7)	0.37, 0.38, 0.38, 0.37	330, 340, 340, 330	0	0.25	0.24	<u>0.25</u>
Clinton, NC, USA, NC07, 2006 (Revolution)	4 (6, 23, 7)	0.36, 0.36, 0.37, 0.36	290, 290, 300, 290	0	0.19	0.11	<u>0.15</u>
Dresden, ON, Canada, ON02, 2006 (Revolution)	4 (5, 22, 8)	0.38, 0.40, 0.38, 0.39	310, 320, 310, 320	0	0.05	0.02	<u>0.04</u>
Dresden, ON, Canada, ON03, 2006 (Aristotle)	4 (5, 21, 7)	0.41, 0.43, 0.38, 0.37	330, 350, 310, 310	0	0.04	0.03	0.04
				1	0.03	0.03	0.03
				3	0.02	0.02	0.02
				6	0.01	0.01	0.01
				13	< 0.01	< 0.01	< 0.01
Delhi, ON, Canada, ON04, 2006 (Crusader)	4 (6, 21, 8)	0.37, 0.37, 0.36, 0.37	610, 610, 590, 610	0	0.13	0.13	<u>0.13</u>
St Jean sur Richelieu, QC, USA, QC01, 2006 (Redstart)	4 (7, 22, 6)	0.38, 0.37, 0.37, 0.38	410, 400, 410, 410	0	0.67	0.70	<u>0.68</u>

Location, Trial no., Year (Variety)	Application			DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Weslaco, TX, USA, TX17, 2006 (Capistrano)	4 (7, 22, 6)	0.37, 0.37, 0.37, 0.37	320, 320, 310, 310	0	0.21	0.16	<u>0.19</u>

^a Fruit samples were taken.

Table 19 Residues of cyprodinil in greenhouse grown sweet peppers ^a

Location, Trial no., Year (Variety)	Application			DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Bridgeton, NJ, USA, NJ01, 2005 (King Arthur)	4 (7, 21, 6)	0.36, 0.38, 0.35, 0.37	690, 730, 670, 710	0	0.16	0.30	0.23
Kingsville, ON, Canada, ON01, 2006 (Striker)	4 (7, 18, 7)	0.37, 0.37, 0.37, 0.37	800, 800, 1000, 1000	0	0.20	0.21	0.21
				3	0.14	0.10	0.12
				7	0.04	0.09	0.07
				12	0.02	0.03	0.03
Kingsville, ON, Canada, ON06, 2005 (Zamboni)	4 (7, 21, 7)	0.37, 0.37, 0.37, 0.37	2000, 2000, 2000, 2000	0	0.11	0.04	0.08
Crossville, TN, USA, TN01, 2005 (Spartacus F1)	4 (7, 21, 7)	0.38, 0.37, 0.36, 0.36	870, 830, 820, 830	0	0.22	0.32	0.27

^a Fruit samples were taken.

Table 20 Residues of cyprodinil in field-grown chilli peppers ^a

Location, Trial no., Year (Variety)	Application			Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)	rep 1	rep 2	mean
Las Cruces, NM, USA, NM03, 2006 (Joe E. Parker)	4 (7, 19, 8)	0.37, 0.37, 0.37, 0.37	230, 230, 230, 230	0.22	0.12	0.17
Las Cruces, NM, USA, NM04, 2006 (Joe E. Parker)	4 (6, 21, 6)	0.37, 0.37, 0.37, 0.37	840, 840, 850, 840	0.36	0.19	0.27
Wooster, OH, USA, OH06, 2006 (San Ardo)	4 (7, 21, 7)	0.37, 0.37, 0.37, 0.37	630, 650, 670, 640	0.23	0.18	0.20
Weslaco, TX, USA, TX16, 2006 (Sonora Anaheim)	4 (6, 20, 8)	0.37, 0.37, 0.37, 0.37	360, 370, 370, 370	0.33	0.22	0.28
Citra, FL, USA, FL20, 2006 (Mesilla 242)	4 (7, 21, 7)	0.37, 0.38, 0.37, 0.39	330, 340, 330, 350	0.82	0.52	0.67

^a Fruit samples were taken at day 0.

Table 21 Residues of cyprodinil in greenhouse grown chilli peppers ^a

Location, Trial no., Year (Variety)	Application			Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)	rep 1	rep 2	mean
Weslaco, TX, USA, TX01, 2005 (TAM Veracruz)	4 (6, 18, 6)	0.37, 0.37, 0.37, 0.37	330, 330, 330, 330	0.58	0.60	0.59

^a Fruit samples were taken at day 0.

Table 22 Residues of cyprodinil in greenhouse tomatoes ^a

Location, Trial no., Year (Variety)	Application			DAT		Residue (mg/kg)	
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean

Location, Trial no., Year (Variety)	Application			DAT		Residue (mg/kg)	
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Bridgeton, NJ, USA, NJ14, 2002 (FL47)	4 (7, 21, 7)	0.38, 0.39, 0.38, 0.38	710, 720, 710, 700	0	0.13	0.21	0.17
Weslaco, TX, USA, TX12, 2002 (Mariachi RZ)	4 (7, 7, 7)	0.39, 0.37, 0.37, 0.37	510, 490, 490, 490	0	0.17	0.28	0.22
Crossville, TN, USA, TN02, 2002 (Celebrity)	4 (8, 21, 7)	0.37, 0.37, 0.37, 0.37	940, 940, 930, 940	0	0.18	0.21	0.20
				3	0.30	0.35	0.32
				7	0.26	0.08	0.17
				14	0.07	0.14	0.10
Fort Collins, CO, USA, CO05, 2002 (Trust)	4 (7, 22, 7)	0.37, 0.37, 0.37, 0.36	280, 280, 280, 270	0	0.02	0.04	0.03

^a Fruit samples were taken

Table 23 Residues of cyprodinil in field-grown tomatoes ^a

Location, Trial no., Year (Variety)	Application			Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)	rep 1	rep 2	mean
Salisbury, MD, USA, MD01, 2002 (Mountain Pride)	4 (10, 22, 7)	0.37, 0.37, 0.37, 0.37	490, 490, 490, 480	0.10	0.08	0.09
Freeville, NY, USA, NY10, 2002 (Celebrity)	4 (7, 22, 7)	0.37, 0.38, 0.39, 0.38	370, 380, 390, 390	0.13	0.19	0.16
Citra, FL, USA, FL20, 2002 (Sun Pride)	4 (7, 21, 7)	0.37, 0.38, 0.37, 0.38	380, 380, 380, 390	0.20	0.19	0.20
Citra, FL, USA, FL21, 2002 (Sun Pride)	4 (8, 20, 7)	0.37, 0.37, 0.37, 0.37	370, 370, 380, 380	0.24	0.24	0.24
Clinton, NC, USA, NC10, 2002 (Mountain Spring)	4 (7, 21, 8)	0.37, 0.37, 0.37, 0.36	260, 260, 260, 250	0.15	0.13	0.14
Visalia, CA, USA, CA43, 2002 (Ace)	4 (6, 21, 7)	0.37, 0.37, 0.37, 0.37	440, 430, 430, 440	0.06	0.10	0.08
Five Points, CA, USA, CA44, 2002 (Heinz 8892)	4 (6, 20, 7)	0.38, 0.38, 0.39, 0.38	320, 320, 330, 330	0.24	0.28	0.26
Parlier, CA, USA, CA45, 2002 (Shady Lady)	4 (7, 21, 7)	0.38, 0.37, 0.37, 0.36	320, 320, 330, 320	0.22	0.17	0.20
Visalia, CA, USA, CA46, 2002 (Rio Grande)	4 (6, 21, 7)	0.37, 0.37, 0.37, 0.37	440, 430, 430, 440	0.13	0.09	0.11
Porterville, CA, USA, CA47, 2002 (APT 410)	4 (7, 21, 7)	0.37, 0.37, 0.38, 0.37	290, 280, 290, 290	0.24	0.36	0.30
Mesilla, NM, USA, NM05, 2002 (Rio Grande)	4 (7, 7, 7)	0.36, 0.37, 0.36, 0.37	200, 220, 220, 210	0.05	0.07	0.06
				0.05	0.03	0.04
				0.03	0.02	0.03
				0.02	0.02	0.02
Rincon, NM, USA, NM06, 2002 (Rio Grande)	4 (7, 21, 7)	0.37, 0.38, 0.38, 0.38	210, 210, 210, 210	0.15	0.14	0.14
Prosser, WA, USA, WA13, 2002 (Big Boy)	4 (7, 20, 8)	0.37, 0.37, 0.38, 0.36	440, 440, 460, 440	0.01	0.02	0.02
Arlington, WI, USA, WI20, 2002 (Puebla)	4 (6, 22, 7)	0.38, 0.37, 0.37, 0.38	320, 310, 310, 320	0.14	0.12	0.13

^a Fruit samples were taken at day 0

*Leafy vegetables (including Brassica leafy vegetables)**Lettuce*

A series of fourteen residue trials for cyprodinil in lettuce (both head and leafy varieties) was conducted in the USA during the 2001 growing season (Chen, 2003-a). At each site, a plot was treated with a water dispersible granule containing 375 g/kg cyprodinil and 250 g/kg fludioxonil. Four foliar applications at a target rate of 368 g ai/ha cyprodinil were made at target intervals of 7 days. Samples were collected on the day of the last application, after the spray had dried. At the head lettuce trial sites, samples both with and without wrapper leaves were collected. Additional samples were collected at 7 and 14 days after the last application at two of the leaf lettuce sites to generate decline data.

Residues of cyprodinil in lettuce were determined using an HPLC-UV method (method number AG-631B, with minor modifications).

Spinach

Eleven residue trials in spinach were conducted in the USA and Canada during 2008 and 2009 (Thompson, 2011). At each site, a plot was treated with a water dispersible granule containing 375 g/kg cyprodinil and 250 g/kg fludioxonil. Four applications at a target rate of 368 g ai/ha cyprodinil were made by foliar application, with target intervals of 7 days between applications 1 and 2 and 3 and 4, and 14 days between applications 2 and 3. Spray adjuvants were included in the tank mix at most of the sites. Samples were collected on the day of the last application, after the spray had dried. At one site, additional samples were collected at intervals of 2-14 days after the last application in order to generate decline data.

Residues of cyprodinil in spinach were determined using HPLC-UV (method number AG-631B, with minor modifications).

Residues were found in control samples at levels at or very slightly above the LOQ at two sites.

Watercress

Two field trials were conducted in watercress in Florida during 1999 (Starter, 2001-b). A water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil was applied four times at a target rate of 368 g ai/ha cyprodinil, with target intervals of 7 days. Samples were collected at on the day of the last application, after the spray had dried.

Residues of cyprodinil in watercress were determined using HPLC-UV (method number AG-631A, with minor modifications). Samples were stored frozen for up to 10 months before analysis. Untreated control samples of watercress fortified at 2 mg/kg and stored frozen for up to 10 months showed recoveries of 63–73% (mean recovery = 67%). It is noted that the recoveries are slightly below the generally accepted range of 70–120%; the samples may have been adversely affected by storage to a small extent.

Mustard greens

Seven field trials in mustard greens was conducted in the USA during 2000 (Arsenovic, 2001-c). Four applications of a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil at a target rate of 368 g ai/ha cyprodinil were made at target intervals of 7 days between applications 1 and 2 and 3 and 4, and 14 days between applications 2 and 3. Samples were collected at a target interval of 7 days after the last application.

Residues of cyprodinil in mustard greens were determined using HPLC-UV (method number AG-631B, with minor modifications).

Table 24 Residues of cyprodinil in head lettuce^a

Location, Trial no., Year (Variety)	Application			Sample	Residue (mg/kg)
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		
Freeville, NY, USA, NY11, 2001 (Ithaca)	4 (6, 6, 6)	0.36, 0.37, 0.39, 0.35	450, 460, 490, 450	Heads with wrapper leaves	2.7
				Heads without wrapper leaves	0.07
Gainesville, FL, USA, FL15, 2001 (Crispino MTO)	4 (7, 8, 6)	0.37, 0.37, 0.37, 0.37	370, 380, 370, 370	Heads with wrapper leaves	21
				Heads without wrapper leaves	1.6
Mesilla, NM, USA, NM04, 2001 (Merit)	4 (7, 7, 7)	0.36, 0.37, 0.37, 0.35	340, 360, 340, 320	Heads with wrapper leaves	2.9
				Heads without wrapper leaves	0.15
Aurora, OR, USA, OR06, 2001 (Summer Time)	5 (8, 7, 8, 8)	0.37, 0.37, 0.37, 0.37, 0.37	380, 380, 380, 380, 380	Heads with wrapper leaves	5.1
				Heads without wrapper leaves	3.2
Willard, OH, USA, OH06, 2001 (Ithaca)	4 (6, 8, 8)	0.38, 0.38, 0.38, 0.36	560, 570, 360, 550	Heads with wrapper leaves	2.3
				Heads without wrapper leaves	0.69
Salinas, CA, USA, CA27, 2001 (Sharp Shooter)	4 (7, 7, 7)	0.37, 0.38, 0.37, 0.38	480, 500, 490, 510	Heads with wrapper leaves	1.6
				Heads without wrapper leaves	0.63
Holtville, CA, USA, CA29, 2001 (Red Coach 74)	4 (6, 7, 7)	0.40, 0.37, 0.36, 0.36	370, 380, 360, 370	Heads with wrapper leaves	2.0
				Heads without wrapper leaves	0.32
Parlier, CA, USA, CA31, 2001 (Bayview)	4 (8, 6, 8)	0.38, 0.38, 0.38, 0.38	360, 350, 350, 350	Heads with wrapper leaves	2.2
				Heads without wrapper leaves	0.31

^a Samples were taken at day 0.

Table 25 Residues of cyprodinil in leaf lettuce

Location, Trial no., Year (Variety)	Application			Sample	DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mean
Salisbury, MD, USA, MD08, 2001 (Salad Bowl)	5 (6, 6, 14, 9)	0.37, 0.37, 0.37, 0.37, 0.37	310, 310, 310, 310, 310	Leaves	0	12	15	14
Live Oak, FL, USA, FL16, 2001 (Waldmanns Dark Green MTO)	4 (6, 7, 8)	0.37, 0.38, 0.37, 0.37	370, 380, 370, 380	Leaves	0	25	24	24
				Leaves	7	13	15	14
				Leaves	14	11	7.8	9.5
Mesilla, NM, USA, NM05, 2001 (Salad Bowl)	4 (7, 7, 7)	0.38, 0.38, 0.38, 0.40	340, 350, 370, 360	Leaves	0	9.3	11	10
Salinas, CA, USA, CA28, 2001 (Green Gene's #1)	4 (7, 7, 7)	0.38, 0.54, 0.38, 0.38	420, 740, 500, 500	Leaves	0	10	9.9	10
				Leaves	7	1.3	1.4	1.3
				Leaves	14	0.31	0.27	0.29
Holtville, CA, USA, CA30, 2001 (Royal Groon)	4 (7, 7, 6)	0.37, 0.37, 0.37, 0.37	370, 380, 380, 380	Leaves	0	8.8	8.3	8.5

Location, Trial no., Year (Variety)	Application			Sample	DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mean
Parlier, CA, USA, CA32, 2001 (Green Vision)	4 (7, 7, 7)	0.39, 0.40, 0.39, 0.37	350, 360, 350, 340	Leaves	0	11	11	11

Table 26 Residues of cyprodinil in watercress ^a

Location, Trial no., Year (Variety)	Application			Sample	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Fellsmere, FL, USA, FL28, 1999 (B & W New and Improved Variety No. 3)	4 (6, 7, 7)	0.39, 0.37, 0.38, 0.37	477, 457, 481, 476	Leaves	12	12	12
Fellsmere, FL, USA, FL29, 1999 (B & W Standard Variety No. 1)	4 (6, 7, 7)	0.37, 0.37, 0.36, 0.38	703, 705, 700, 720	Leaves	9.2	12	10

^a Samples were taken at day 0

Table 27 Residues of cyprodinil in spinach leaves

Location, Trial no., Year (Variety)	Application				DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)	Adjuvant		rep 1	rep 2	mean
Salisbury, MD, USA, MD22, 2008 (Melody)	4 (7, 13, 6)	0.37, 0.37, 0.37, 0.37	290, 290, 290, 290	Silwet L77 (0.25% v/v)	0	6.4	5.7	6.1
Freeville, NY, USA, NY30, 2008 (Tyee)	4 (6, 14, 6)	0.37, 0.37, 0.37, 0.37	320, 320, 320, 320	Induce (1% v/v)	0	16	11	13
Weslaco, TX, USA, TX02, 2008 (Samish)	4 (7, 15, 7)	0.37, 0.37, 0.37, 0.37	40, 240, 360, 360	ROC (0.5% v/v, 3 and 4 only)	0	15	13	14
Charleston, SC, USA, SC07, 2008 (Skookum hybrid)	4 (7, 14, 7)	0.37, 0.37, 0.36, 0.37	310, 320, 320, 310	Activator 90 (0.25% v/v)	0	6.7	4.6	5.6
Weslaco, TX, USA, TX03, 2008 (Space F1)	4 (6, 15, 6)	0.37, 0.37, 0.37, 0.37	200, 200, 200, 210	None	0	9.8	9.5	9.6
Brighton, CO, USA, CO13, 2008 (Spinner)	4 (6, 12, 8)	0.39, 0.39, 0.39, 0.37	340, 340, 350, 330	Activator 90 (0.058% v/v)	0	11	12	11 c0.02
Holtville, CA, USA, CA18, 2008 (1B12A)	4 (8, 13, 7)	0.38, 0.38, 0.36, 0.38	230, 240, 220, 230	Induce (1% v/v)	0	10	11	11 c0.02
Salinas, CA, USA, CA17, 2008 (Whale)	4 (7, 14, 6)	0.38, 0.37, 0.38, 0.38	250, 320, 420, 420	R-11 (0.125% v/v)	0	6.8	6.4	6.6
Harrow, ON, Canada, ON13, 2009 (Unipack 151)	4 (8, 16, 6)	0.37, 0.38, 0.38, 0.38	300, 310, 310, 310	Merge (1% v/v, app 1 only)	0	11	13	12
					2	0.49	0.64	0.56
					6	0.07	0.05	0.06
					12	0.03	0.02	0.02
					14	< 0.02	< 0.02	< 0.02
Agassiz, BC, Canada, BC02, 2008 (Unipack)	4 (8, 13, 8)	0.38, 0.38, 0.38, 0.38	330, 330, 330, 330	Assist (1% v/v)	0	37	27	32
Ste-Clotilde, QC, Canada, QC04,	4 (6, 14, 7)	0.39, 0.36, 0.37, 0.36	370, 340, 350, 340	Merge (1% v/v)	0	8.8	7.7	8.3

Location, Trial no., Year (Variety)	Application				DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)	Adjuvant		rep 1	rep 2	mean
2008 (Unipack 151)								

Table 28 Residues of cyprodinil in mustard green leaves

Location, Trial no., Year (Variety)	Application			DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Bridgeton, NJ, USA, NJ26, 2000 (Southern Giant Curled)	4 (6, 22, 6)	0.37, 0.36, 0.36, 0.36	390, 380, 380, 370	8	5.0	5.9	5.4
Crossville, TN, USA, TN15, 2000 (Southern Giant Curled)	4 (6, 21, 7)	0.36, 0.37, 0.37, 0.37	330, 330, 340, 340	7	0.38	0.36	0.37
Gainesville, FL, USA, FL49, 2000 (Florida Broadleaf)	4 (7, 13, 8)	0.37, 0.38, 0.37, 0.37	350, 390, 370, 370	7	7.3	8.7	8.0
Clinton, NC, USA, NC17, 2000 (Southern Giant Curled)	4 (6, 22, 7)	0.38, 0.38, 0.38, 0.38	310, 310, 310, 310	7	0.22	0.24	0.23
Weslaco, TX, USA, TX35, 2000 (India)	4 (13, 14, 7)	0.37, 0.37, 0.38, 0.38	450, 450, 450, 460	6	0.29	0.44	0.36
Salinas, CA, USA, CA16, 2000 (Southern Giant Curled)	4 (7, 23, 6)	0.37, 0.37, 0.36, 0.37	490, 540, 680, 700	7	0.75	0.66	0.71
Lansing, MI, USA, MI05, 2000 (Southern Giant Curled)	4 (7, 22, 6)	0.61, 0.61, 0.60, 0.58 ^a	380, 380, 380, 370	7	0.71	0.48	0.59

^a Product was over-applied by approximately 62–68% per application. The results were scaled for MRL determination; actual results are tabulated.

Legume vegetables

Beans (edible pods and succulent seeds)

Eight residue trials were conducted in the USA for cyprodinil in common beans (snap beans, succulent pods and seeds) during 2001 (Chen, 2003-b). Four late season applications of a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil were made at target intervals of 7 days and a target application rate of 368 g ai/ha cyprodinil. Samples of succulent beans with pods were collected at a target PHI of 7 days after the last application. Additional duplicate samples at target intervals of 0 and 14 days were collected at two sites.

Bean samples were analysed for cyprodinil residues using an HPLC-UV method (method number AG-631B, with minor modifications).

Beans (succulent shelled)

Eight residue trials were conducted in the USA in succulent shelled lima beans during 2001 (Chen, 2003-c). A series of 4–6 late season applications of a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil was made to the treated plot at target intervals of 7 days and a target application rate of 368 g ai/ha cyprodinil. Samples of succulent beans with and without pods were collected at a target PHI of 7 days after the last application.

Bean samples were analysed for cyprodinil residues using an HPLC-UV method (method number AG-631B, with minor modifications).

Table 29 Residues of cyprodinil in common beans (snap beans), pods and succulent seeds

Location, Trial no., Year (Variety)	Application	Sample	DAT	Residue (mg/kg)

	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mean
Ithaca, NY, USA, NY09, 2001 (Labrador)	4 (7, 7, 7)	0.38, 0.36, 0.37, 0.36	290, 270, 270, 270	Pods and seeds	8	0.15	0.16	0.16
Salisbury, MD, USA, MD05, 2001 (Slenderette)	4 (6, 7, 8)	0.37, 0.37, 0.38, 0.37	380, 380, 380, 380	Pods and seeds	7	0.18	0.19	0.18
Gainesville, FL, USA, FL18, 2001 (Blue lake)	4 (7, 7, 7)	0.37, 0.38, 0.39, 0.38	280, 290, 290, 290	Pods and seeds	7	0.24	0.22	0.23
East Lansing, MI, USA, MI09, 2001 (Strike)	4 (7, 7, 7)	0.37, 0.37, 0.37, 0.37	190, 190, 180, 190	Pods and seeds	0	0.42	0.41	0.41
				Pods and seeds	7	0.18	0.17	0.17
				Pods and seeds	14	0.07	0.07	0.07
Madison, WI, USA, WI08, 2001 (Hystyle)	4 (7, 7, 6)	0.39, 0.37, 0.38, 0.38	200, 190, 190, 190	Pods and seeds	7	0.11 ^a	0.09 ^a	0.10 ^a
Holtville, CA, USA, CA34, 2001 (Derby)	4 (7, 7, 8)	0.37, 0.37, 0.37, 0.38	390, 400, 380, 380	Pods and seeds	0	1.09	0.92	1.0
				Pods and seeds	6	0.52	0.46	0.49
				Pods and seeds	15	0.31	0.24	0.27
Twin Falls, ID, USA, ID05, 2001 (Idelite Garden Bean)	4 (8, 7, 8)	0.38, 0.38, 0.38, 0.39	340, 340, 330, 350	Pods and seeds	8	0.14	0.13	0.13
Madison, OH, USA, OH09, 2001 (Bronco)	4 (8, 8, 6)	0.37, 0.37, 0.37, 0.38	370, 370, 360, 380	Pods and seeds	6	0.13	0.11	0.12

^a Results may be rain affected; rain fell within < 4 hours of the final application.

Table 30 Residues of cyprodinil in succulent shelled lima beans seeds

Location, Trial no., Year (Variety)	Application			DA T	Residue (mg/kg)			
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	rep 3	mean
Salisbury, MD, USA, MD03, 2001 (Eastland)	4 (7, 7, 7)	0.38, 0.39, 0.39, 0.39	370, 380, 380, 380	8	< 0.02	< 0.02		< 0.02
Salisbury, MD, USA, MD04, 2001 (Green Baby)	4 (7, 7, 7)	0.38, 0.39, 0.39, 0.39	370, 390, 380, 380	8	< 0.02	< 0.02		< 0.02
Clinton, NC, USA, NC08, 2001 (Thorogreen)	6 (6, 7, 8, 6, 8)	0.37, 0.37, 0.37, 0.37, 0.38, 0.37	280, 280, 280, 280, 290, 280	7	< 0.02	< 0.02		< 0.02
Kimberly, ID, USA, ID07, 2001 (Henderson)	5 (6, 8, 8, 8)	0.39, 0.38, 0.36, 0.39, 0.36	230, 230, 230, 230, 230	7	0.04	0.04	0.03	0.04
Salinas, CA, USA, CA26, 2001 (not specified)	4 (7, 7, 7)	0.38, 0.37, 0.38, 0.36	590, 620, 860, 820	6	0.02	0.02	< 0.02	0.02
Salinas, CA, USA, CA81, 2001 (not specified)	5 (7, 7, 7, 7)	0.38, 0.38, 0.38, 0.38, 0.37	750, 720, 800, 750, 810	8	< 0.02	< 0.02		< 0.02
Fremont, OH, USA, OH11, 2001 (Fordhook)	5 (6, 8, 8, 6)	0.37, 0.38, 0.39, 0.37, 0.38	360, 380, 390, 380, 380	8	< 0.02	< 0.02		< 0.02
Tifton, GA, USA, GA08, 2001 (Cangreen)	5 (7, 7, 7, 8)	0.37, 0.37, 0.38, 0.38, 0.37	470, 470, 470, 470, 470	8	0.04	0.04	0.02	0.03

Where three replicates are reported, replicates 1 and 2 are replicate analyses of the same sample, while replicate 3 is an analysis of a second sample. Where two replicates are reported, replicates 1 and 2 are replicate samples.

*Pulses**Beans, dry*

Nine residue trials for cyprodinil in dry beans were conducted in the USA during 2001 (Chen, 2003-d). Four late season applications of a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil were made to the treated plot at target intervals of 7 days and a target application rate of 368 g ai/ha cyprodinil. Samples of dry beans were collected at a target PHI of 7 days after the last application.

Dry bean samples were analysed for cyprodinil residues using an HPLC-UV method (method number AG-631B, with minor modifications).

With the exception of the samples from the Salinas, California site (trial number CA25), where it appears that the control and treated samples were inadvertently switched, residues were not found in the untreated control samples at levels above the limit of quantitation.

Table 31 Residues of cyprodinil in beans (dry) seeds

Location, Trial no., Year (Variety)	Application			DAT		Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean	
Velva, ND, USA, ND07, 2001 (Othello)	4 (7, 7, 7)	0.37, 0.36, 0.37, 0.37	190, 180, 190, 190	7	0.03	0.03	0.03	
Brookings, SD, USA, SD04, 2001 (Vista)	4 (7, 8, 7)	0.37, 0.38, 0.38, 0.37	200, 200, 210, 200	7	0.19	0.10	0.15	
Aurora, SD, USA, SD05, 2001 (Vista)	6 (7, 8, 7, 7, 6)	0.37, 0.39, 0.38, 0.38, 0.38, 0.38	200, 210, 210, 210, 210, 210	7	0.04	0.05	0.04	
Holt, MI, USA, MI10, 2001 (Strike)	4 (6, 8, 7)	0.37, 0.37, 0.37, 0.37	190, 190, 180, 190	6	0.04	0.03	0.04	
Fort Collins, CO, USA, CO08, 2001 (Bill Z)	4 (7, 7, 7)	0.44, 0.38, 0.37, 0.38	220, 190, 180, 190	7	0.02	0.03	0.02	
Wellington, CO, USA, CO09, 2001 (UI 126)	4 (7, 7, 7)	0.41, 0.37, 0.37, 0.37	210, 190, 180, 190	6	0.02	0.02	0.02	
Kimberly, ID, USA, ID06, 2001 (Chase Pinto)	4 (6, 8, 8)	0.38, 0.36, 0.37, 0.37	190, 180, 190, 190	6	0.02	0.05	0.04	
Fremont, OH, USA, OH10, 2001 (not reported)	4 (6, 8, 8)	0.35, 0.39, 0.39, 0.37	350, 390, 390, 380	8	0.03	0.02	0.02	
Salinas, CA, USA, CA25, 2001 (not reported)	4 (7, 7, 7)	0.37, 0.38, 0.38, 0.38	580, 620, 630, 860	5	< 0.02	< 0.02	< 0.02	

*Root and tuber vegetables**Carrot*

Ten trials were conducted in the USA and Canada for cyprodinil in carrots during 2000 and 2004 (Chen, 2002-b and Barney, 2006-a). Four applications of a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil were made at a target interval of 7 days (between applications 1 and 2 and between applications 3 and 4) and 21 days between applications 2 and 3 at a target application rate of 368 g ai/ha cyprodinil. Duplicate samples of treated carrot roots were collected at a target PHI of 7 days after the last application, and frozen within 3 hours of collection. Decline samples were collected at one site at intervals between 0 and 21 days after the last application.

Carrot root samples were analysed for cyprodinil residues using an HPLC-UV method (method number AG-631B, with minor modifications).

Table 32 Residues of cyprodinil in carrot roots

Location, Trial no., Year (Variety)	Application	DAT	Residue (mg/kg)

	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)		rep 1	rep 2	mean
Weslaco, TX, USA, TX05, 2000 (Nantes coreless, a baby carrot variety)	4 (7, 21, 6)	0.38, 0.38, 0.37, 0.38	370, 380, 390, 410	7	0.16	0.09	0.12
Salinas, CA, USA, CA04, 2000 (Minicor, a baby variety)	4 (6, 23, 6)	0.37, 0.37, 0.38, 0.37	480, 500, 700, 680	8	0.18	0.18	0.18
Laingsburg, MI, USA, MI01, 2000 (Premium)	4 (7, 21, 7)	0.61, 0.58, 0.61, 0.58 ^a	390, 370, 380, 370	7	0.09	0.11	0.10
Prosser, WA, USA, WA43, 2000 (Bolero)	4 (8, 24, 7)	0.38, 0.37, 0.38, 0.37	390, 370, 380, 370	7	0.09	0.12	0.10
El Centro, CA, USA, CA86, 2000 (Caropak)	4 (6, 21, 6)	0.38, 0.38, 0.36, 0.37	520, 530, 500, 510	8	< 0.02	0.03	0.02
Madera, CA, USA, CA104, 2000 (Nantes)	4 (7, 21, 7)	0.37, 0.37, 0.37, 0.38	380, 380, 380, 380	7	0.05	0.05	0.05
Chowchilla, CA, USA, CA105, 2000 (Imperator)	4 (7, 21, 7)	0.38, 0.37, 0.37, 0.37	380, 380, 380, 380	7	0.07	0.04	0.05
Abbotsford, BC, Canada, BC06, 2000 (Bolero)	4 (6, 19, 8)	0.37, 0.37, 0.37, 0.37	350, 350, 350, 350	6	0.38	0.42	0.40
Live Oak, FL, USA, FL75, 2000 (Navajo F1)	4 (8, 22, 6)	0.19, 0.19, 0.19, 0.19 ^b	290, 290, 280, 290	8	0.03	0.05	0.04
Citra, FL, USA, FL16, 2004 (Indiana F1)	4 (7, 21, 7)	0.38, 0.38, 0.39, 0.39	280, 280, 290, 290	0	0.36	0.37	0.37
				3	0.36	0.32	0.34
				7	0.34	0.31	0.33
				14	0.35	0.44	0.39
				21	0.35	0.35	0.35

^a Product was over-applied by 56–65% per application. The results were scaled for MRL determination; actual results are tabulated.

^b Product was under-applied at an average of 52% of the target rate per application. The results were scaled for MRL determination; actual results are tabulated.

Radish

Six trials were conducted in the USA for cyprodinil in radish during 2004 (Barney, 2007). Two late season applications of a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil were made to the treated plot at a target interval of 7 days and a target application rate of 368 g ai/ha cyprodinil. Samples of radish roots and tops were collected at a target PHI of 7 days after the last application.

Radish root and top samples were analysed for cyprodinil residues using an HPLC-UV method (method number AG-631B, with minor modifications).

Table 33 Residues of cyprodinil in radish roots and tops

Location, Trial no., Year (Variety)	Application			Sample	DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mean
Freeville, NY, USA, NY06, 2004 (Cheriette F1)	2 (6)	0.39, 0.41	300, 310	Roots	7	< 0.01	< 0.01	< 0.01
				Tops	7	0.44	0.46	0.45
Citra, FL, USA, FL14, 2004 (Fireball)	2 (8)	0.38, 0.38	290, 280	Roots	7	0.03	0.03	0.03
				Tops	7	0.57	0.50	0.53
Citra, FL, USA, FL15, 2004 (Fireball)	2 (7)	0.38, 0.37	290, 280	Roots	7	0.03	0.02	0.03
				Tops	7	1.3	1.2	1.3
Salinas, CA, USA, CA08, 2004 (Cheriette)	2 (6)	0.38, 0.39	430, 400	Roots	7	0.19	0.10	0.14
				Tops	7	0.13	0.20	0.17

Location, Trial no., Year (Variety)	Application			Sample	DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mean
Willard, OH, USA, OH01, 2004 (Cabernet)	2 (7)	0.38, 0.39	280, 280	Roots	7	< 0.01	< 0.01	< 0.01
				Tops	7	0.48	0.32	0.40
Moxee, WA, USA, WA02, 2004 (Crunchy Royale)	2 (7)	0.36, 0.36	390, 390	Roots	8	< 0.01	< 0.01	< 0.01
				Tops	8	0.12	0.14	0.13

Herbs

Basil

Three residue trials were conducted in the USA during 2000 (Chen, 2002-c). Four applications of a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil were made at a target rate of 368 g ai/ha cyprodinil. Applications 1 and 2 were timed for earlier in the growing season, and applications 3 and 4 closer to harvest. Samples were collected at a target PHI of 7 days after the final application. Additional samples were harvested at one site and dried, initially by lying out in the field, then indoors using an electric fan for 48 hours before frozen storage, to determine the effect of drying on residue levels.

Basil leaf samples were analysed for cyprodinil residues using an HPLC-UV method (method number AG-631B, with minor modifications).

Chives

Three residue trials were conducted in the USA during 2000 (Chen, 2002-d). Four applications of a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil were made at a target rate of 368 g ai/ha cyprodinil. Applications 1 and 2 were timed for earlier in the growing season, and applications 3 and 4 closer to harvest. Samples were collected at a target PHI of 7 days after the final application. Additional samples were harvested at one site and air dried in a greenhouse before frozen storage, to determine the effect of drying on residue levels.

Chives samples were analysed for cyprodinil residues using an HPLC-UV method (method number AG-631B, with minor modifications).

Parsley

Four residue trials were conducted in the USA during 2003 (Barney, 2006-b). Four applications of a water dispersible granule formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil were made at a target rate of 368 g ai/ha cyprodinil. Applications 1 and 2 were timed for earlier in the growing season, and applications 3 and 4 closer to harvest. Samples of fresh parsley were collected at a target PHI of 7 days after the final application. Additional samples were collected at each site and dried for 1–7 days, either using an air dryer or in a greenhouse.

Parsley leaf samples were analysed for cyprodinil residues using an HPLC-UV method (method number AG-631B, with minor modifications).

Residues were not found in any of the untreated control samples of fresh parsley leaves at levels above the limit of quantitation. Low levels of residue just above the limit of quantitation were found in control samples of dried parsley leaves from one trial site.

Table 34 Residues of cyprodinil in basil

Location, Trial no., Year (Variety)	Application			Sample	DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mea n

Location, Trial no., Year (Variety)	Application			Sample	DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mean
Freeville, NY, USA, NY29, 2000 (Genovese)	4 (7, 15, 7)	0.60, 0.62, 0.57, 0.56	330, 340, 316, 311	Fresh leaves	8	2.1	2.2	2.1
Gainesville, FL, USA, FL58, 2000 (HBA 105)	4 (6, 22, 7)	0.38, 0.37, 0.37, 0.38	280, 280, 280, 290	Fresh leaves	7	2.0	1.5	1.7
Visalia, CA, USA, CA113, 2000 (Italian Large Leaf)	4 (7, 21, 7)	0.37, 0.37, 0.37, 0.37	390, 380, 380, 370	Fresh leaves	7	1.5	1.5	1.5
				Dried leaves	7 (3)	8.8		

Table 35 Residues of cyprodinil in chives

Location, Trial no., Year (Variety)	Application			Sample	DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mean
Salisbury, MD, USA, MD11, 2000 (Fancy)	4 (8, 18, 8)	0.59, 0.60, 0.60, 0.60	390, 400, 400, 400	Fresh leaves	6	1.1	1.0	1.0
Aurora, OR, USA, OR04, 2000 (Standard open)	4 (7, 21, 7)	0.38, 0.38, 0.38, 0.38	520, 530, 530, 530	Fresh leaves	7	1.1	1.0	1.1
Porterville, CA, USA, CA114, 2000 (Common)	4 (7, 21, 7)	0.39, 0.38, 0.37, 0.39	160, 150, 150, 150	Fresh leaves	7	0.69	0.56	0.62
				Dried leaves	7	2.9	3.0	2.9

Table 36 Residues of cyprodinil in parsley

Location, Trial no., Year (Variety)	Application			Sample	DAT	Residue (mg/kg)		
	No. (RTI, days)	Rate (kg ai/ha)	Volume (L/ha)			rep 1	rep 2	mean
Willard, OH, USA, OH04, 2003 (Dark Green Italian Flat Leaf)	4 (6, 22, 8)	0.37, 0.37, 0.37, 0.37	480, 510, 340, 470	Fresh leaves	6	3.1	2.8	3.0
				Dried leaves	6 (7)	20	21	20
Salinas, CA, USA, CA34, 2003 (Italian Dark Green)	4 (8, 21, 6)	0.37, 0.38, 0.36, 0.37	430, 320, 520, 540	Fresh leaves	7	3.2	2.7	2.9
				Dried leaves	8 (2)	23	18	20
Citra, FL, USA, FL21, 2003 (Italian Dark Green)	4 (7, 14, 6)	0.37, 0.37, 0.36, 0.38	370, 370, 370, 380	Fresh leaves	7	14	19	16
				Dried leaves	7 (5)	109	115	112 c0.11, 0.10
Aurora, OR, USA, OR05, 2003 (Italian Plain Leaf)	4 (7, 21, 8)	0.37, 0.37, 0.37, 0.38	420, 420, 420, 430	Fresh leaves	6	8.4	5.8	7.1
				Dried leaves	6 (2)	31	28	30

FATE OF RESIDUES IN PROCESSING

Lemons

A processing study in lemons was conducted in the USA (Barney, 2010). Cyprodinil was applied as a water-dispersible granular formulation containing 375 g/kg cyprodinil and 250 g/kg fludioxonil using an airblast sprayer. A petroleum oil spray adjuvant was included in the tank mix. A single application

was made at 375 g ai/ha cyprodinil and fruit was sampled on the day of application after the spray had dried.

The lemons were transported fresh to the processing laboratory, and processing was completed within nine days of harvest. The fruit was washed in a tank, and undesirable fruit was removed. Washed fruit was then scarified using a modified Hobart abrasive peeler, and the collected emulsion was screened to remove flavedo fragments and passed through a cream separator and an IEC centrifuge to separate the oil from water. The first run free oil was removed, and the remaining emulsion frozen and stored overnight, thawed, centrifuged again, and the separated oil added to the first run oil. Scarified fruit was then transferred to a juice extractor and halved and juiced using a reaming auger. The extracted juice was then pulped and screened to remove solid material such as peel fragments, seeds, and vesicular and segment membranes. Finally, the peel was shredded, and flavedo fragments, rag and seeds from earlier stages added. The resulting wet pulp was then treated with lime, pressed and dried to < 10% moisture to give dried citrus pulp, before finally being milled using a hammer mill and the moisture content checked. Samples of fresh fruit, oil, juice and dried pulp were collected and frozen for transport to the analytical laboratory.

Residues of cyprodinil in lemon and processed fractions were determined using method number AG-631B, with analysis by HPLC with UV detection. The extraction procedure was modified for analysis of the oil samples by inclusion of an additional clean-up of the aqueous acidic extract by partition with hexane, prior to the solid phase extraction clean up using a strong cation exchange (SCX) cartridge. Samples were stored frozen until analysis, and all samples were analysed within 10 months of collection.

Table 37 Residues of cyprodinil in lemon fresh fruit and processed fractions

Location, Year (variety)	Application			Sample	PHI, days	Residues (mg/kg)				PF
	No.	Rate (kg ai/ha)	Volume (L/ha)			Rep 1	Rep 2	Rep 3	Mean	
Nipomo, CA, USA, 2009 (Lisbon)	1	0.38	980	Fruit	0	0.19	0.21		0.20	NA
				Juice	0	< 0.01	< 0.01		< 0.01	< 0.05
				Dried pulp	0	0.58	0.64		0.61	3.1
				Oil	0	35	35	33	34	171

Tomatoes

A processing study in tomatoes was conducted as part of the package of residue trials in field and greenhouse tomatoes (Thompson, 2005).

The effect of washing tomatoes in the field was studied, with samples of tomatoes being washed and dried before dispatch to the laboratory. Samples were washed for approximately 10 seconds, patted dry, and then frozen for transport to the laboratory.

Additionally, large samples of tomatoes (both untreated control and treated) from a single site were shipped to a processing laboratory. Processing was completed within two days of harvest, and samples were frozen within an hour of collection.

Tomato samples were first washed by passing through a flume, and a spray washer, then a second flume, and finally a second spray washer. Washed tomatoes were crushed in a grinder, and then pumped into a hot break system where they were heated to approximately 96 °C using a heat exchanger, followed by pumping into a finisher where the resulting hog crush was screened to remove pomace (seeds and peel fragments). Pomace was weighed and discarded, and the filtered juice was passed to a vacuum evaporator, where the volume was reduced to a range of 8–16% solids content to give tomato purée. A weighed portion of the purée was transferred to a steam jacketed kettle, heated with stirring to 89–91 °C, and filled into cans, which were sealed, inverted and water cooled, then

dried, labelled and frozen. The remaining purée was transferred to a vacuum kettle evaporator, and the volume reduced by heating to a solids content of 24–35%. The resulting paste was transferred to a steam-jacketed kettle, heated to 89–91 °C, then filled into cans, which were sealed, inverted and water cooled, then dried, labelled and frozen.

Samples of unwashed and washed tomatoes, tomato purée and tomato paste were analysed by HPLC-UV (method number AG-631B, with minor modifications). Recoveries in tomatoes are summarised in the tomato residue data section above. Recoveries of cyprodinil from tomato puree ranged from 88–102% at fortification levels ranging from 0.02–2.0 mg/kg. Recoveries of cyprodinil from tomato paste ranged from 72–101% at fortification levels of 0.01–2.0 mg/kg.

Table 38 Residues of cyprodinil in raw tomatoes and processed products

Location, Trial No, Year (variety)	Application			Sample	PHI (days)	Residue (mg/kg)			PF
	No. (RTI, days)	Rate (kg ai/ha)	Spray volume (L/ha)			Rep 1	Rep 2	Mean	
Five Points, CA, USA, CA44, 2002 (Heinz 8892)	4 (6, 20, 7)	0.38, 0.38, 0.39, 0.38	320, 320, 330, 330	Fruit	0	0.25	0.24	0.25	—
				Puree	0	0.12	0.13	0.13	0.52
				Paste	0	0.56	0.55	0.56	2.3
Clinton, NC, USA, NC10, 2002 (Mountain Spring)	4 (7, 21, 8)	0.37, 0.37, 0.37, 0.36	260, 260, 260, 250	Unwashed fruit	0	0.15	0.14	0.14	—
				Washed fruit	0	0.05	0.05	0.05	0.37
Weslaco, TX, USA, TX12, 2002 (Mariachi RZ)	4 (7, 7, 7)	0.39, 0.37, 0.37, 0.37	510, 490, 490, 490	Unwashed fruit	0	0.17	0.28	0.22	—
				Washed fruit	0	0.10	0.10	0.10	0.43

RESIDUES IN ANIMAL COMMODITIES

No new animal feeding studies were supplied to the Meeting.

APRAISAL

Cyprodinil was first evaluated for residues and toxicological aspects by the 2003 JMPR. The 2003 Meeting established an ADI of 0–0.03 mg/kg bw for cyprodinil and concluded that an ARfD was not necessary. The 2003 Meeting recommended a number of maximum residue levels for cyprodinil. The residue definition was established as cyprodinil for both compliance with MRLs and dietary risk assessment, for both plant and animal commodities. The residue is fat soluble.

Cyprodinil was scheduled by the Forty-fourth CCPR meeting in 2012 for evaluation of residue data for additional crops by the 2013 JMPR.

Methods of analysis

The Meeting received two analytical methods for determination of cyprodinil residues in plant matrices which were relevant to this evaluation. The LOQ for the HPLC-UV and HPLC-MS/MS methods was 0.01 mg/kg.

Stability of residues in stored analytical samples

The Meeting received information on the storage stability of cyprodinil residues in plant matrices from trials conducted in conjunction with the residue studies submitted to the Meeting. These data and stability data from JMPR 2003 cover the maximum storage period for samples in the residue studies submitted to the Meeting.

Results of supervised residue trials on crops

The Meeting received supervised trial data for application of cyprodinil to dry beans, lima beans, common beans (snap beans), berry fruit (blueberries, caneberries and strawberries), brassica vegetables (broccoli and cabbage), cucurbit fruiting vegetables (cantaloupe, cucumber and squash), other fruiting vegetables (sweet pepper, chili pepper, and tomato), herbs (parsley, basil and chives), leafy vegetables (mustard greens, lettuce, spinach and watercress), lemons (including processing data), pome fruit (apples and pears), root vegetables (carrot and radish), and tropical fruits-inedible peel (avocado, kiwifruit and litchi).

Citrus fruits

Cyprodinil is registered in the USA for use on lemons and limes at a GAP of 1×0.37 kg ai/ha, and a 0-day PHI.

Three residue trials were conducted in lemons at GAP in the USA. Residues in lemons at the 0-day PHI were 0.19, 0.31 and 0.34 mg/kg.

The Meeting determined that there were insufficient data for the estimation of a maximum residue level in lemons.

Pome fruits

The 2003 JMPR estimated a maximum residue level of 0.05 mg/kg in apple based on a previous GAP in the USA of 4×0.26 kg ai/ha, with applications only until the end of flowering. The 2003 JMPR estimated a maximum residue level of 1 mg/kg in pear based on the European GAP of 3×0.38 kg ai/ha, with a 14-day PHI.

The Meeting received new residue data from the USA for both apples and pears at a different GAP from those previously considered. Cyprodinil is registered in the USA for use in apples and pears at a GAP of 6×0.26 kg ai/ha, and a 0-day PHI.

Nine residue trials were conducted in apples at GAP in the USA. Residues in apples at the 0-day PHI were 0.20, 0.28, 0.40, 0.50, 0.51, 0.52, 0.70, 0.94, and 1.3 mg/kg.

Five residue trials were conducted in pears at GAP in the USA. Residues in pears at the 0-day PHI were 0.17, 0.35, 0.36, 0.46, and 0.65 mg/kg.

The Meeting noted that the USA GAP is for the pome fruits group, and considered a group maximum residue level. To consider a group maximum residue level, residues in individual crops should be similar (e.g., medians should not differ by more than 5×). The Meeting agreed to estimate a maximum residue level for the crop group Pome fruits. In deciding whether to combine the datasets for apple and pear for use in the statistical calculator or to only utilize the data from the commodity with the highest residues, the Meeting recognized the similarity of the datasets (confirmed by the Mann-Whitney U test), and decided to combine the datasets for apples and pears for the purposes of determining a group maximum residue level for pome fruit. Residues found were: 0.17, 0.20, 0.28, 0.35, 0.36, 0.40, 0.46, 0.50, 0.51, 0.52, 0.65, 0.70, 0.94 and 1.3 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg for pome fruit, and a STMR of 0.48 mg/kg. The Meeting withdrew its previous maximum residue level recommendations of 0.05 mg/kg for apple and 1 mg/kg for pear.

Berries and other small fruits

Cyprodinil is registered in the USA for use in bushberries at a GAP of 4×0.37 kg ai/ha with a 0-day PHI.

Five residue trials were conducted at GAP in blueberries in the USA. Residues in blueberries at the 0-day PHI were 0.50, 0.62, 1.0, 1.4 and 1.9 mg/kg.

The 2003 JMPR estimated a maximum residue level of 0.5 mg/kg in raspberries, red, black based on the Swiss GAP of 2×0.45 kg ai/ha, with a 14-day PHI.

The Meeting received residue data from the USA for raspberries. Cyprodinil is registered in the USA for use in caneberries at a GAP of 4×0.37 kg ai/ha, with a 0-day PHI.

Five residue trials were conducted in raspberries in the USA. Residues in raspberries at the 0-day PHI were 1.5, 1.6, 2.2, 2.5, and 5.9 mg/kg.

The 2003 JMPR estimated a maximum residue level of 2 mg/kg in strawberries, based on various GAPs in Europe.

The Meeting received residue data from the USA in strawberries. Cyprodinil is registered in the USA for use in strawberries at a GAP of 4×0.37 kg ai/ha, with a 0-day PHI.

Eight residue trials were conducted in strawberries in the USA. Residues in strawberries at the 0-day PHI were 0.10, 0.30, 0.68, 0.91, 1.1, 1.5, 1.6, and 2.0 mg/kg.

The Meeting noted that the USA GAP is the same for all berry fruit (except grapes) and considered a group maximum residue level. To consider a group maximum residue level, residues in individual crops should be similar (e.g., medians should not differ by more than 5×). The Meeting agreed to estimate a maximum residue level for the group Berry fruit (except grapes). In deciding whether to combine the datasets for blueberries, raspberries and strawberries for use in the statistical calculator or to only utilize the data from the commodity with the highest residues, the Meeting agreed not to combine the data sets (Kruskal-Wallis test). Therefore, recommendations on berry fruit will be based on raspberries, as the commodity with the highest residues. Based on the data set for raspberries, the Meeting estimated a maximum residue level of 10 mg/kg for Berries and other small fruits, except grapes, together with an STMR of 2.2 mg/kg. The Meeting withdrew its previous maximum residue level recommendations of 0.5 mg/kg for raspberries, red, black and 2 mg/kg for strawberry.

*Assorted tropical and sub-tropical fruits - inedible peel**Avocado*

Cyprodinil is registered in the USA for use in avocado at a GAP of 4×0.37 kg ai/ha, with a 0-day PHI.

Six trials were conducted in avocados in the USA. Residues in avocados at the 0-day PHI were 0.08, 0.18, 0.23, 0.30, 0.35, and 0.60 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg for avocados, along with an STMR of 0.265 mg/kg.

Kiwifruit

Cyprodinil is registered in the USA for use in kiwifruit at a GAP of 2×0.53 kg ai/ha, with a 0-day PHI.

Three residue trials were conducted in kiwifruit in the USA. Residues in kiwifruit at the 0-day PHI were 0.61, 0.99, and 1.1 mg/kg.

The Meeting determined that there were insufficient data for the estimation of a maximum residue level in kiwifruit.

Litchi (lychee)

Cyprodinil is registered in the USA for use in litchi at a GAP of 4×0.37 kg ai/ha, with a 0-day PHI.

One residue trial was conducted in litchi in the USA. Residues in litchi at the 0-day PHI were 1.3 mg/kg.

The Meeting determined that there were insufficient data for estimation of a maximum residue level in litchi.

*Brassica vegetables**Cabbages, Head*

Cyprodinil is registered in the USA for use in brassica vegetables at a GAP of 4×0.37 kg ai/ha, with a 7-day PHI.

Six trials were conducted in cabbage in the USA. Residues in cabbages (with wrapper leaves) at a PHI of 6–8 days were < 0.02, 0.02 (s), 0.02, 0.04, 0.19, and 0.36 mg/kg, where (s) indicates a result scaled to account for application rates outside $\pm 25\%$ of GAP. Residues in cabbages (without wrapper leaves) were < 0.02 (5), and 0.08 mg/kg.

The Meeting estimated a maximum residue level of 0.7 mg/kg for head cabbages, along with an STMR of 0.03 mg/kg.

Flowerhead Brassicas

Six trials were conducted in broccoli in the USA and Canada. Residues in broccoli at a PHI of 6–8 days were 0.02, 0.15, 0.20, 0.34, 0.43 and 1.1 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg for broccoli, along with an STMR of 0.27 mg/kg and agreed to extend the MRL and STMR to the subgroup Flowerhead brassicas.

Fruiting vegetables, Cucurbits

The 2003 JMPR estimated maximum residue levels of 0.2 mg/kg for both cucumber and summer squash, based on data matching Spanish and Italian GAPs of 4×0.038 kg ai/hL with a 7-day PHI, and 3×0.30 kg ai/ha with a 7-day PHI respectively.

The Meeting received residue data from the USA in melon, cucumber and summer squash.

Cyprodinil is registered in the USA for use in fruiting vegetables, other than cucurbits at a GAP of 4×0.37 kg ai/ha, with a 1-day PHI.

Five residue trials were conducted in melons in the USA. Residues in melons at the 1-day PHI were 0.05, 0.06, 0.10, 0.17 and 0.33 mg/kg.

Seven residue trials were conducted in cucumber in the USA. Residues in cucumber at the 1-day PHI were 0.04, 0.05, 0.09 (2), 0.11, 0.15, and 0.24 mg/kg.

Five residue trials were conducted summer squash in the USA. Residues in summer squash at the 1-day PHI were 0.02, 0.03, 0.07 (2), and 0.09 mg/kg.

The Meeting noted that the USA GAP is for all cucurbit fruiting vegetables, and considered a group maximum residue level. To consider a group maximum residue level, residues in individual crops should be similar (e.g., medians should not differ by more than 5 $\times$). The Meeting agreed to estimate a maximum residue level for the group Fruiting vegetables, Cucurbits. In deciding whether to combine the datasets for melons, cucumbers and summer squash for use in the statistical calculator or to only utilize the data from the commodity with the highest residues, the Meeting recognized the similarity of the datasets (confirmed by the Kruskal-Wallis test), and decided to combine the datasets.

Combines residues were: 0.02, 0.03, 0.04, 0.05 (2), 0.06, 0.07 (2), 0.09 (3), 0.10, 0.11, 0.15, 0.17, 0.24, and 0.33 mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg for Fruiting vegetables, Cucurbits, together with an STMR of 0.09 mg/kg. The Meeting withdrew the previous maximum residue level recommendations of 0.2 mg/kg for cucumber and summer squash.

Fruiting vegetables, other than Cucurbits

The 2003 JMPR estimated a maximum residue level of 0.2 mg/kg for eggplant, based on data matching the Italian GAP of 3×0.30 kg ai/ha, with a 7-day PHI, and the Spanish GAP of 3×0.038 kg ai/hL, with a 7-day PHI. Based on a combined data set from three European GAPs (Italy: 3×0.30 kg ai/ha, with a 7-day PHI, Spain: 3×0.038 kg ai/hL, with a 7-day PHI, and Switzerland: 0.30 kg ai/ha, with a 3-day PHI), the 2003 JMPR estimated a maximum residue level of 0.5 mg/kg for tomatoes. The 2003 JMPR estimated a maximum residue level of 0.5 mg/kg for peppers, sweet, based on data matching the Italian GAP of 3×300 g ai/ha, with a 7-day PHI, and the Spanish GAP of 3×38 g ai/hL, with a 7-day PHI.

The Meeting received residue data from the USA and Canada in tomatoes, sweet peppers and chili peppers. Both field and greenhouse trial data were supplied for all three crops.

Cyprodinil is registered in the USA for use in fruiting vegetables, other than cucurbits, at a GAP of 4×0.37 kg ai/ha, with a 0-day PHI.

Eleven residue trials were conducted in sweet pepper in the USA and Canada. Residues in sweet pepper at the 0-day PHI were 0.04, 0.10, 0.13, 0.15, 0.19, 0.21 (GH), 0.23, 0.23 (G), 0.25, 0.27 (GH), and 0.68 mg/kg. 'GH' indicates a trial conducted in a greenhouse, all other trials were conducted in the field.

Five trials were conducted in chili pepper in the USA. Residues in chili pepper at the 0-day PHI were 0.20, 0.27, 0.28, 0.59 (GH), and 0.67 mg/kg.

Sixteen trials were conducted in tomatoes in the USA. Residues in tomatoes at the 0-day PHI were 0.02, 0.03 (GH), 0.06, 0.09, 0.11, 0.13, 0.14 (2), 0.16, 0.17 (GH), 0.20, 0.22 (GH), 0.24, 0.26, 0.30, and 0.32 (GH) mg/kg.

A series of residue trials in fruiting vegetables (eggplant, sweet pepper and tomato), was considered by the 2003 JMPR. Most of the trials were conducted in greenhouse crops, and in accordance with a GAP of 3×0.38 kg ai/ha applications, with a 7-day PHI. The majority were conducted as decline trials and have data for the USA PHI of 0 days. The application rates from the 2003 trials are within $\pm 25\%$ of the USA GAP (4×0.37 kg ai/ha).

At a PHI of 0 days, residues of cyprodinil in greenhouse grown eggplant from trials from Italy and Spain relevant to USA GAP were 0.07, 0.14, and 0.23 (2) mg/kg.

At a PHI of 0 days, residues of cyprodinil in greenhouse grown tomato from trials from Greece, Italy, Spain, Switzerland and the UK, relevant to USA GAP were 0.08, 0.12, 0.13, 0.20, 0.21 (2), 0.22 (3), 0.23, 0.25 (3), 0.36, 0.41 mg/kg.

At a PHI of 0 days, residues of cyprodinil in field and greenhouse grown sweet pepper from Spanish and Italian trials relevant to USA GAP were 0.02, 0.26 (G), 0.27, 0.41 (GH), 0.73 (GH), 1.0 (GH), and 1.2 (GH) mg/kg. (GH) indicates a result from a greenhouse trial.

The Meeting agreed to combine the datasets for the USA (field and greenhouse) and European (greenhouse) to give a larger dataset for the purposes of estimation of dietary parameters and a maximum residue level for fruiting vegetables, other than cucurbits.

Residues in field and greenhouse grown tomatoes from trials carried out in the USA, Greece, Italy, Spain, Switzerland and the UK relevant to USA GAP were 0.02, 0.03 (G), 0.06, 0.08 (G), 0.09, 0.11, 0.12 (GH), 0.13, 0.13 (GH), 0.14 (2), 0.16, 0.17 (G), 0.20, 0.20 (GH), 0.21 (GH) (2), 0.22 (GH) (4), 0.23 (GH), 0.24, 0.25 (GH) (3), 0.26, 0.30, 0.32 (GH), 0.36 (GH), 0.41 (GH) mg/kg.

Residues in field and greenhouse grown sweet pepper from trials carried out in the USA, Spain and Italy relevant to USA GAP were 0.02, 0.04, 0.10, 0.13, 0.15, 0.19, 0.21 (GH), 0.23, 0.23 (GH), 0.25, 0.26 (GH), 0.27, 0.27 (GH), 0.41 (GH), 0.68, 0.73 (GH), 1.0 (GH), and 1.2 (GH) mg/kg.

The Meeting considered that the USA GAP is for all fruiting vegetables, other than cucurbits, except mushroom and sweet corn, and considered a group maximum residue level. To consider a group MRL, residues in individual crops should be similar (e.g. medians should not differ by more than 5×). The Meeting agreed to estimate a maximum residue level for the group fruiting vegetables, other than cucurbits, except mushroom and sweet corn. In deciding whether to combine the datasets for sweet peppers, chili peppers, tomatoes and eggplants for use in the statistical calculator or to only utilize the data from the commodity with the highest residues, the Meeting agreed not to combine the data sets (Kruskal-Wallis test). Therefore, recommendations on fruiting vegetables, other than cucurbits, except mushroom and sweet corn will be based on the 2003 data set for sweet peppers, as the commodity with the highest residues.

Based on the combined data set for sweet pepper, the Meeting estimated a maximum residue level of 2 mg/kg for fruiting vegetables, other than cucurbits, except sweet corn and mushrooms, together with an STMR of 0.24 mg/kg. The Meeting agreed to withdraw the previous maximum residue level recommendations of 0.2 mg/kg for eggplant, 0.5 mg/kg for tomatoes, and 0.5 mg/kg for peppers, sweet.

The Meeting noted that the residues in chili pepper and other commodities within the group of fruiting vegetables differed significantly. Using the default dehydration factor of 7 for peppers, the following data set was obtained for dried chili peppers: 1.4, 1.9, 2.0, 4.1, and 4.7 mg/kg. The Meeting estimated a maximum residue level of 9 mg/kg for dried chili peppers, together with an STMR-P of 2.0 mg/kg.

Brassica leafy vegetables

Cyprodinil is registered in the USA for use in brassica leafy vegetables (including mustard greens), at a GAP of 4×0.37 kg ai/ha, with a 7-day PHI.

Seven trials were conducted in mustard greens in the USA in accordance with GAP. Residues in mustard green leaves at the 7-day PHI were 0.23, 0.36, 0.36 (s), 0.37, 0.71, 5.4, and 8.0 mg/kg, where (s) indicates a result scaled to account for application rates outside $\pm 25\%$ of GAP.

The Meeting estimated a maximum residue level of 15 mg/kg for mustard greens, together with an STMR of 0.37 mg/kg. The Meeting agreed to extrapolate to estimate a maximum residue level of 15 mg/kg for brassica leafy vegetables.

Leafy vegetables, except brassica leafy vegetables

The 2003 JMPR estimated maximum residue levels of 10 mg/kg for lettuce, head and lettuce, leaf, based on data matching GAP for France (2×0.19 kg ai/ha, with a 14-day PHI) and Italy (3×0.26 kg ai/ha, with a 14-day PHI).

The Meeting received residue data from the USA and Canada in head lettuce, leaf lettuce, spinach, and watercress.

Cyprodinil is registered in the USA for use in leafy vegetables, other than brassica leafy vegetables, at a GAP of 4×0.37 kg ai/ha, with a 0-day PHI.

Eight trials were conducted in lettuce, head in accordance with the USA GAP. Residues in lettuce heads, with wrapper leaves at the 0-day PHI were 1.6, 2.0, 2.2, 2.3, 2.7, 2.9, 5.1, and 21 mg/kg. Residues in lettuce head with wrapper leaves removed were 0.07, 0.15, 0.31, 0.32, 0.63, 0.69, 1.6, and 3.2 mg/kg.

Six trials were conducted in leaf lettuce, in accordance with the USA GAP. Residues in lettuce leaves at the 0-day PHI were: 8.5, 10 (2), 11, 14, and 24 mg/kg.

Ten trials were conducted in spinach in accordance with the USA GAP. Residues in spinach at the 0-day PHI were 5.6, 6.1, 6.6, 8.3, 11 (2), 12, 13, 14, and 32 mg/kg.

One trial was conducted in watercress in accordance with the USA GAP. Residues in watercress at the 0-day PHI were 12 mg/kg.

The Meeting noted that the USA GAP is the same for all leafy vegetables other than brassica leafy vegetables and considered a group maximum residue level. To consider a group maximum residue level, residues in individual crops should be similar (e.g., medians should not differ by more than 5×). However, the Meeting agreed not to combine the data sets (Kruskal-Wallis test). TAs a result recommendations on leafy vegetables other than brassica leafy vegetables were based on the spinach dataset, as the commodity with the highest residues. Based on the dataset for spinach, the Meeting estimated a maximum residue level of 50 mg/kg for leafy vegetables, except brassica leafy vegetables, together with an STMR of 11 mg/kg. The Meeting agreed to withdraw the previous maximum residue level recommendations of 10 mg/kg for lettuce, head and lettuce, leaf.

Legume vegetables

The 2003 JMPR estimated a maximum residue level of 0.5 mg/kg for beans (in pods), except broad bean and soya bean, based on data matching the GAPs of Spain (3×0.038 kg ai/hL, with a 14-day PHI) and (2×0.38 kg ai/ha, with a 14-day PHI).

The Meeting received residue data from the USA in common beans (snap beans, pods and succulent seed) and lima beans (succulent shelled seeds).

Cyprodinil is registered in the USA for use in beans (succulent), including chickpea, lupin, kidney, lima, mung, navy, pinto, snap, wax, and broad bean, asparagus bean and blackeyed pea, with a GAP of 4×0.37 kg ai/ha, with a 7-day PHI.

Eight trials were conducted in common beans (pods and succulent seeds) in accordance with the USA GAP. Residues in pod and seed samples at the 7-day PHI were 0.10, 0.12, 0.13, 0.16, 0.17, 0.18, 0.23, and 0.49 mg/kg.

The Meeting estimated a maximum residue level of 0.7 mg/kg in beans, except broad bean and soya bean (green pods and immature seeds), together with an STMR of 0.165 mg/kg. The Meeting agreed to withdraw the previous maximum residue level recommendation of 0.5 mg/kg for beans, except broad bean and soya bean (green pods and immature seeds).

Six trials were conducted in lima beans (seeds without pods) in accordance with the USA GAP. Residues in succulent seeds at the 7-day PHI were < 0.02 (3), 0.02, 0.03 and 0.04 mg/kg.

The Meeting estimated a maximum residue level of 0.06 mg/kg for beans, shelled, together with an STMR of 0.02 mg/kg.

Beans (dry)

Cyprodinil is registered in the USA for use in beans (dry) at a GAP of 4×0.37 kg ai/ha, with a 7-day PHI.

Nine trials in beans (dry) were conducted in accordance with the USA GAP. Residues in beans at the 7-day PHI were < 0.02 , 0.02 (3), 0.03, 0.04 (3), and 0.15 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg for beans, dry, together with an STMR of 0.03 mg/kg.

Carrots

Cyprodinil is registered in the USA for use in carrots at a GAP of 4×0.37 kg ai/ha, with a 7-day PHI.

Ten trials in carrots were conducted in the USA and Canada in accordance with the USA GAP. Residues in carrots at the 7-day PHI were: 0.02, 0.05 (2), 0.06 (s), 0.08 (s) 0.10, 0.12, 0.18,

0.39, and 0.40 mg/kg, where (s) indicates a result scaled to account for application rates outside $\pm 25\%$ of GAP.

The Meeting estimated a maximum residue level of 0.7 mg/kg for carrots, together with an STMR of 0.09 mg/kg.

The Meeting noted that the US GAP for parsnips is the same as that for carrots, and agreed to extrapolate the residue data for carrots and estimated a maximum residue level of 0.7 mg/kg for parsnips, together with an STMR of 0.09 mg/kg.

Radish

Cyprodinil is registered in the USA for use in radish at a GAP of 2×0.37 kg ai/ha, with a 7-day PHI.

Five trials in radish were conducted in accordance with the USA GAP. Residues in radish roots at the 7-day PHI were < 0.01 (3), 0.03, and 0.14 mg/kg.

Residues in radish tops at the 7-day PHI were 0.13, 0.17, 0.40, 0.45, and 1.3 mg/kg.

The Meeting estimated a maximum residue level of 0.3 mg/kg for radish, together with an STMR of 0.01 mg/kg.

The Meeting agreed that residues of cyprodinil arising in radish tops would be covered by the proposed maximum residue level of 15 mg/kg for brassica leafy vegetables.

Herbs

Cyprodinil is registered in the USA for use in herbs at a GAP of 4×0.37 kg ai/ha, with a 7-day PHI.

Three trials in basil were conducted in accordance with the USA GAP. Residues in fresh basil leaves at the 7-day PHI were 1.5, 1.7 and 2.1 mg/kg. Residues in dried basil leaves at the 7-day PHI were 8.8 mg/kg.

Three trials in chives were conducted in accordance with the USA GAP. Residues in fresh chives at the 7-day PHI were 0.62, 1.0, and 1.1 mg/kg. Residues in dried chives at the 7-day PHI were 2.9 mg/kg.

Four trials in parsley were conducted in accordance with the USA GAP. Residues in fresh parsley at the 7-day PHI were 2.9, 3.0, 7.1, and 16 mg/kg. Residues in dried parsley at the 7-day PHI were 20 (2), 30, and 112 mg/kg.

The Meeting noted that the USA GAP is for all herbs and considered a group maximum residue level. To consider a group maximum residue level, residues in individual crops should be similar (e.g., medians should not differ by more than $5\times$). The Meeting agreed to estimate a maximum residue level for the group herbs. In deciding whether to combine the datasets for basil, chives and parsley for use in the statistical calculator, or to only utilize the data from the commodity with the highest residues, the Meeting agreed not to combine the data sets (Kruskal-Wallis test). Therefore, recommendations on herbs were based on parsley, as the commodity with the highest residues. Based on the data set for fresh parsley, the Meeting estimated a maximum residue level of 40 mg/kg for herbs, together with an STMR of 5.05 mg/kg.

The Meeting estimated a maximum residue level of 300 mg/kg for dried herbs except hops, dry, based on the data set for dried parsley, together with an STMR of 25 mg/kg.

Processing studies

A processing study for lemons was evaluated by the current Meeting; however as the residue data set for lemons was insufficient for the estimation of a maximum residue level or STMR, STMR-P values for citrus processed products were not estimated.

Some processing data for tomatoes was generated as part of the residue trial in tomatoes provided to the Meeting. Processing studies for apples, barley, grapes, plums, tomatoes and wheat

were considered by the 2003 JMPR. The studies in apples and tomatoes are relevant to the crops being considered by the current Meeting. Processing factors are tabulated below.

RAC	Processed product	PF
Apples	Wet pomace	3.5
	Juice	0.03
Tomatoes	Juice	0.17
	Purée	0.52
	Paste	0.86, 2.3

The processing factors were applied to the STMRs for the raw commodities to produce the following STMR-P values: wet apple pomace 1.8 mg/kg; apple juice 0.015 mg/kg; tomato juice 0.036 mg/kg; tomato purée 0.11 mg/kg; and tomato paste 0.48 mg/kg.

Residues in animal commodities

Farm animal dietary burden

Dietary burden calculations incorporating all commodities considered by the current and 2003 Meetings for beef cattle, dairy cattle, broilers and laying poultry are presented in Annex 6. The calculations are made according to the livestock diets of the USA/Canada, the European Union, Australia and Japan as laid out in the OECD table.

	US/CAN		EU		AU		Japan	
	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean
Beef cattle	0.91	0.37	13.9	1.8	5.8	1.4	0.46	0.46
Dairy cattle	1.7	0.87	13.5	1.4	23.3^a	1.8^b	0.26	0.26
Poultry – broiler	0.49	0.49	0.80	0.54	0.12	0.12	0.066	0.066
Poultry – layer	0.49	0.49	4.1^c	0.76^d	0.12	0.12	-	-

^a Highest maximum dairy cattle dietary burden suitable for HR and MRL estimates for mammalian milk

^b Highest mean dairy cattle dietary burden suitable for STMR estimates for mammalian milk

^c Highest maximum poultry dietary burden suitable for HR and MRL estimates for poultry meat and eggs

^d Highest mean poultry dietary burden suitable for STMR estimates for poultry meat and eggs

Animal commodity maximum residue levels

Mammals

A feeding study on lactating dairy cattle was considered by the 2003 JMPR.

Lactating Holstein dairy cows were dosed daily by gelatin capsule with cyprodinil at the equivalent of 5, 15 and 50 ppm in the dry-weight diet for 28 consecutive days. Milk was collected throughout and on days 28, 29, and 30, a cow from each dosing group was slaughtered for tissue collection. Cyprodinil residues were not detected (LOQ 0.01 mg/kg) in the milk (days 0, 1, 3, 7, 14, and 21), kidney, or fat of cows from the highest dose group (50 ppm), nor in milk (day 26) or muscle from any dose groups. Cyprodinil was present in liver (highest residue 0.013 mg/kg) from the highest dose group but not from the other groups.

The 2003 JMPR estimated a maximum residue level of 0.0004* mg/kg (F) for milk, together with an STMR of 0 mg/kg, based on a maximum dietary burden for dairy cattle of 8.2 ppm, and a mean dietary burden of 0.53 ppm.

The highest dietary burden for dairy cattle is for Australia (max. dietary burden of 23.3 ppm and mean dietary burden of 1.8 ppm). The Meeting noted that no residues of cyprodinil were quantified in milk above the LOQ (0.01 mg/kg) at feeding levels up to 50 ppm in cattle. The Meeting concluded that the existing maximum residue level and STMR for milk remain appropriate.

The 2003 JMPR estimated maximum residue levels of 0.01* mg/kg (fat) and STMRs of 0 mg/kg for meat (from mammals other than marine mammals), and edible offal (mammalian). These limits were based on a maximum dietary burden of 8.2 ppm, and a mean dietary burden of 0.53 ppm.

As for dairy cattle, the highest dietary burdens for calculation of meat MRLs are 23.3 ppm (max.) and 1.8 ppm (mean), considering all the use patterns evaluated by the 2003 JMPR and the present Meeting. Given that no residues of cyprodinil were found above the LOQ in muscle or fat of cattle at a feeding level of 50 ppm, the Meeting considers that the existing maximum residue level for meat (from mammals other than marine mammals), and the STMR values remain appropriate. No residues were found above the LOQ in kidney even at the highest dose of 50 ppm. In liver, no residues were found above the LOQ in liver at feeding levels of 5 and 15 ppm, while at 50 ppm, low residues up to 0.013 mg/kg were found. The Meeting estimated a maximum residue level of 0.01 mg/kg for edible offal (mammalian), together with an STMR of 0 mg/kg. The Meeting agreed to withdraw the previous recommendation of 0.01* mg/kg for edible offal (mammalian).

Poultry

A feeding study in poultry was not presented to the 2003 JMPR or to the present Meeting.

The 2003 JMPR estimated maximum residue levels of 0.01* mg/kg for eggs and poultry, edible offal of, and 0.01* mg/kg (fat) for poultry meat and STMRs of 0 mg/kg. These limits were based on a maximum dietary burden of 2.6 ppm and a mean dietary burden of 0.50 ppm, and consideration of the laying hen metabolism study.

Based on the use patterns considered by the 2003 JMPR and the present Meeting, the Meeting noted that the highest dietary burden for poultry (both for meat and egg producing birds) was the EU diet, with a maximum dietary burden of 4.1 ppm and a mean dietary burden of 0.76 ppm.

As noted by the 2003 JMPR, cyprodinil parent compound was not detected in poultry tissues in the laying hen metabolism study (except in kidney at 0.001 mg/kg), even at feeding levels of 215 and 226 ppm. Cyprodinil was detected in eggs at 0.002-0.011 mg/kg from birds dosed at 215 and 226 ppm. Given that these feeding levels are around 50 times the maximum dietary burden of 4.1 ppm estimated for poultry, the Meeting considers that the existing maximum residue levels, and STMR values for poultry commodities remain appropriate.

RECOMMENDATIONS

CCN	Commodity name	Recommended maximum residue level, mg/kg		STMR (P), mg/kg
		New	Previous	
FP 0226	Apple	W	0.05	
FI 0326	Avocado	1		0.265
VD 0071	Beans (dry)	0.2		0.03
VP 0061	Beans, except broad bean and soya bean (green pods and immature seeds)	0.7	0.5	0.165
VP 0062	Beans, shelled	0.06		0.02
FB 0018	Berries and other small fruits, except grapes	10		2.2
VL 0054	Brassica leafy vegetables	15		0.37
VB 0041	Cabbages, head	0.7		0.03
VR 0577	Carrot	0.7		0.09
VC 0424	Cucumber	W	0.2	

CCN	Commodity name	Recommended maximum residue level, mg/kg		STMR (P), mg/kg
		New	Previous	
DH 0170	Dried herbs, except hops, dry	300		25
MO 0105	Edible offal (mammalian)	0.01	0.01*	0
VO 0440	Egg plant	W	0.2	
VB 0042	Flowerhead Brassicas	2		0.27
VC 0045	Fruiting vegetables, Cucurbits	0.5		0.09
VO 0050	Fruiting vegetables, other than Cucurbits, except sweet corn and mushroom	2		0.24
HH 0092	Herbs	40		5.05
VL 0053	Leafy vegetables, except brassica leafy vegetables	50		11
VL 0482	Lettuce, Head	W	10	
VL 0483	Lettuce, Leaf	W	10	
VR 0588	Parsnip	0.7		0.09
FP 0230	Pear	W	1	
HS 0444	Peppers Chili, dried	9		2.0
VO 0445	Peppers, Sweet	W	0.5	
FP 0009	Pome fruit	2		0.48
VR 0494	Radish	0.3		0.01
FB 0272	Raspberries, Red, Black	W	0.5	
VC 0431	Squash, Summer	W	0.2	
FB 0275	Strawberry	W	2	
VO 0448	Tomato	W	0.5	

CCN	Commodity name	STMR (P), mg/kg
JF 0226	Apple juice	0.015
	Apple pomace, wet	1.8
JF 0448	Tomato juice	0.036
	Tomato purée	0.11
	Tomato paste	0.48

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Dietary Intakes (IEDIs) of cyprodinil were calculated for the 13 GEMS/food cluster diets using STMRs/STMR-Ps estimated by the current Meeting and by the 2003 JMPR. The ADI is 0–0.03 mg/kg bw and the calculated IEDIs were 5–40% of the maximum ADI (0.03 mg/kg bw). The Meeting concluded that the long-term intakes of residues of cyprodinil,

resulting from the uses considered by the current Meeting and by the 2003 JMPR, are unlikely to present a public health concern.

Short-term intake

The 2003 JMPR decided that an ARfD was unnecessary and concluded that the short-term intake of cyprodinil is unlikely to present a public health concern.

REFERENCES

Code	Author	Year	Title, Institute, Report reference
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Arsenovic, 2002-a	Arsenovic, M	2002	Cyprodinil + Fludioxonil: Magnitude of the Residue on Cabbage, IR-4, Study number 07121, GLP, Unpublished, 12 July 2002
Arsenovic, 2002-b	Arsenovic, M	2002	Cyprodinil + Fludioxonil: Magnitude of the Residue on Broccoli, IR-4, Study number 07122, GLP, Unpublished, 18 July 2002
Barney, 2005	Barney, WP	2005	Cyprodinil + Fludioxonil: Magnitude of the Residue in or on Avocado, IR-4, Project number 07338, GLP, Unpublished, 13 December 2005
Barney, 2006-a	Barney, WP	2006	Cyprodinil + Fludioxonil: Magnitude of the Residue on Carrot (additional data), IR-4, Study number A7090, GLP, Unpublished, 13 June 2006
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Barney, 2007	Barney, WP	2007	Cyprodinil + Fludioxonil: Magnitude of the Residue on Radish, IR-4, Study number 09019, GLP, Unpublished, 14 June 2007
Barney, 2010	Barney, WP	2010	Cyprodinil + Fludioxonil: Magnitude of the Residue on Lemon (Processing), IR-4, Report number A8297, GLP, Unpublished, 24 February 2010
Chen, 2002-a	Chen, H	2002	Cyprodinil + Fludioxonil: Magnitude of the Residue on Lychee, IR-4, Study number 07760, GLP, Unpublished, 15 April 2002
Chen, 2002-b	Chen, H	2002	Cyprodinil + Fludioxonil: Magnitude of the Residue on Carrot, IR-4, Study number 07090, GLP, Unpublished, 20 May 2002
Chen, 2002-c	Chen, H	2002	Cyprodinil + Fludioxonil: Magnitude of the Residue on Basil, IR-4, Study number 07123, GLP, Unpublished, 25 October 2002
Chen, 2002-d	Chen, H	2002	Cyprodinil + Fludioxonil: Magnitude of the Residue on Chives, IR-4, Study number 07126, GLP, Unpublished, 25 October 2002
Chen, 2003-a	Chen, H	2003	Cyprodinil + Fludioxonil: Magnitude of the Residue on Lettuce (Head and Leaf), IR-4, Study number 07131, GLP, Unpublished, 22 May 2003
Chen, 2003-b	Chen, H	2003	Cyprodinil + Fludioxonil: Magnitude of the Residue on Bean (Snap), IR-4, Study number 07614, GLP, Unpublished, 9 June 2003
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Chen, 2003-d	Chen, H	2003	Cyprodinil + Fludioxonil: Magnitude of the Residue on Bean (Dry), IR-4, Study number 07782, GLP, Unpublished, 9 June 2003
Chen, 2004	Chen, H	2004	Cyprodinil + Fludioxonil: Magnitude of the Residue on Strawberry, IR-4, Study number A6790, GLP, Unpublished, 9 March 2004

Code	Author	Year	Title, Institute, Report reference
Lennon, 2011-a	Lennon, GA	2011	Cyprodinil + Fludioxonil: Magnitude of the Residue on Pepper (Bell and Non-bell), IR-4, Project number 09567, GLP, Unpublished, 14 March 2011
Lennon, 2011-b	Lennon, GA	2011	Cyprodinil + Fludioxonil: Magnitude of the Residue on Greenhouse Pepper, IR-4, Project number 09140, GLP, Unpublished, 14 March 2011
Mazlo, 2010	Mazlo, J	2010	Cyprodinil—Magnitude of the Residues in or on Apple and Pear as Representative Commodities of Fruit, Pome, Group 11 (Final Report), Syngenta Crop Protection Inc., Report number T003061-07, GLP, Unpublished, 9 February 2010
Oakes, 2007	Oakes, TL	2007	Switch—Magnitude of the Residues of Cyprodinil and Fludioxonil in or on Cantaloupe, Cucumber and Squash as Representative Commodities of Vegetables, Cucurbit, Group 9, Syngenta Crop Protection, Study number T002039-03, GLP, Unpublished, 13 February 2007
Starner, 2001-a	Starner, VR	2001	Switch (Cyprodinil + Fludioxonil): Magnitude of the Residue on Cane berry (Raspberry), IR-4, Study number 06838, GLP, Unpublished, 13 April 2001
Starner, 2001-b	Starner, VR	2001	Cyprodinil + Fludioxonil: Magnitude of the Residue on Watercress, IR-4, Study number 06759, GLP, Unpublished, 25 October 2001
Thompson, 2001	Thompson, DC	2001	Switch (Cyprodinil + Fludioxonil): Magnitude of the Residue on Blueberry, Study number 06724, GLP, Unpublished, 18 September 2001
Thompson, 2005	Thompson, DC	2005	Cyprodinil + Fludioxonil: Magnitude of the Residue on Tomato, IR-4, Study number 08124, GLP, Unpublished, 4 August 2005
Thompson, 2007-a	Thompson, DC	2007	Cyprodinil + Fludioxonil: Magnitude of the Residue on Lemon, IR-4, Report number 08297, GLP, Unpublished, 18 June 2007
Thompson, 2007-b	Thompson, DC	2007	Cyprodinil: Magnitude of the Residue on Kiwifruit, IR-4, Project number 08972, GLP, Unpublished, 18 June 2007
Thompson, 2011	Thompson, DC	2011	Cyprodinil + Fludioxonil: Magnitude of the Residue on Spinach, IR-4, Study number 10006, GLP, Unpublished, 7 January 2011

DICAMBA (240)

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EXPLANATION

Dicamba, a systemic broad-spectrum herbicide, was first evaluated by the 2010 JMPR which estimated an ADI of 0–0.3 mg/kg bw and ARfD of 0.5 mg/kg bw, and recommended the following residue definitions for plant commodities:

Definition of the residue for plant commodities (for compliance with the MRL): *Dicamba*

Definition of the residue (for estimation of dietary intake) for plant commodities: *Sum of dicamba and 5-OH dicamba expressed as dicamba*

Definition of the residue for animal commodities (for compliance with the MRL and for estimation of dietary intake): *Sum of dicamba and DCSA.*

Based on the above residue definition, the 2010 Meeting also recommended maximum residue levels for 21 commodities. These maximum residue levels were adopted as Codex MRLs at the Codex Alimentarius Commission in 2011 (REP 11/CAC, Appendix III, Part 2).

The 2010 JMPR received information on metabolism, method of analysis, storage stability, supervised residue trials and processing studies on soya beans. However, supervised trials were conducted in the USA with PHI of 7 days while the approved US label at that time indicated PHI of 14 days. Since no trials matched the GAP, the Meeting could not estimate a maximum residue level for soya bean (dry).

The label of one formulation, relevant to the trials, was since revised and approved with new PHI of 7 days matching that of the supervised trials. New US GAP allows two different applications: application of 0.56 kg ai/ha as a broadcast made to the soil surface approximately 14 days prior to planting and application of 1.12 kg ai/ha applied 7 days prior to harvest. The maximum total application rate per season is 2.24 kg ai/ha.

In the supervised trials on soya beans provided to the 2010 Meeting, pre-plant application of 0.56 kg ai/ha 14 days before planting and pre-harvest application of 2.24 kg ai/ha 7 days before harvest were made. The pre-harvest application rate was two times the GAP rate. The 2011 Meeting decided to apply the concept of proportionality to the residues from these trials to recommend a maximum residue level.

The Forty-fifth Session of the Codex Committee on Pesticide Residues in 2013 considered the Principles and Guidance for Application of the Proportionality Concept to Estimation of Maximum Residue Limits for Pesticides and agreed to forward the document to the 36th Session of the Commission for adoption and inclusion in the Procedural Manual as an Annex to the Risk Analysis Principles Applied by the Codex Committee on Pesticide Residues. It agreed that desiccants should be excluded from the application of the proportionality concept (REP 13/PR, paras 93 and 98, Annex VIII). The 36th Codex Alimentarius Commission adopted the proposed amendments to the Procedural Manual as above.

The current Meeting received information on new supervised trials on soya beans following the US GAP and analytical methods used for the determination of dicamba and related compounds in the new supervised trials on soya beans

RESIDUE ANALYSIS

Analytical Methods

The 2010 JMPR reviewed a number of analytical methods, mostly employing GC-ECD with GC-MS for confirmation, developed for the determination of dicamba, 5-OH dicamba and 3,6-dichloro-2-hydroxybenzoic acid (DCSA) in plant and animal commodities. Many of these methods developed for plant commodities were applicable to analysis of soya beans (dry).

An analytical method used to determine dicamba, 5-OH dicamba and DCSA arising in newly conducted supervised residue trials on soya beans was provided to the current Meeting. The method is summarized in Table 1 and its details are given below.

Table 1 Summary of analytical method for the determination of residues

Method No. Reference	Matrix tested	Analytes	Method	Limit of Quantitation
BASF Analytical Method No. D0902, Saha, M. (2009) *	Soya bean	Dicamba 5-OH dicamba DCSA	LC-MS/MS	0.01 mg/kg for each analyte, except for 0.05 mg/kg for each analyte in forage and hay (2010 Supervised Field Trials only)

*Validity of the method was tested on corn matrices in the cited separately performed study.

The soya bean samples were homogenized using a Retsch ultra centrifugal milling with liquid nitrogen cooling. The forage and hay samples were processed using a Stephan floor chopper with dry ice. All samples were stored frozen in plastic bags until analysis.

Residues in soya bean homogenate were extracted by hydrolysis in 1N HCl at 90 °C, cooling to room temperature, centrifugation and filtration. The filtrate was diluted with water and an aliquot of the extract was cleaned-up by liquid-liquid partitioning with hexane:ethyl acetate (1:1, v/v) and the organic phase was evaporated to dryness. Residues in dried organic phase were re-dissolved in methanol-water (1:9, v/v) and analysed by LC-MS/MS. MS/MS detection in the negative ionization mode was used to monitor ion transitions from m/z 219→175 for dicamba; m/z 235→155 for 5-OH-dicamba; and m/z 205→161 for DCSA.

For the analysis of the forage and hay samples from the 2010 growing season, a hexane partition was added prior to the hexane:ethyl acetate partition. This additional clean-up step was used due to matrix interferences. Other minor modifications were also made to the method but none of them had significant influence to analytical results.

This method was validated for dicamba, 5-OH dicamba and DCSA in soya bean matrices at the fortification concentration range between 0.01 and 10 mg/kg, in conjunction with the field sample analyses obtained in 2010 and 2012 growing seasons. The results of validation are summarized in Table 2.

The mean recoveries at all fortification levels were 73–100%, within an acceptable range for the three analytes in soya bean seeds with the relative standard deviation well below 20%. On the other hand, the mean recoveries of these three analytes in soya bean forage and hay were mostly between 70 and 109% with the relative standard deviation below 20% except that occasionally at the fortification level of 0.01 mg/kg, the recoveries were lower than 70% and the relative standard deviation around 20% were observed in 2010.

The limit of quantitation (LOQ) of this method is 0.01 mg/kg for the determination of dicamba, 5-OH dicamba and DCSA in soya bean seeds, forage and hay. However, the LOQ was 0.05 mg/kg for these analytes in soya bean forage or hay in the analyses performed in 2010.

Table 2. Recoveries of dicamba, 5-OH dicamba and DCSA in soya bean matrices by the method No.D0902

Soya bean matrix	Analyte	Fortification level (mg/kg)	N	Recoveries (%)	Mean (%)	RSD (%)
Seeds (2010 season)	Dicamba	0.01	6	78, 79, 90, 101, 110, 90	91	13
		1.0	5	74* (75,73), 71, 87* (85,79,96), 81* (80,82), 72	77	9
		10	1*	83* (82,85)	83	-
	5-OH dicamba	0.01	4	65, 63, 81, 82	73	14
		0.05	2	102, 99* (90,107)	100	-
		1.0	1*	85* (83,86)	85	-
		10	1*	94* (91,96)	94	-
	DCSA	0.01	6	90, 90, 92, 102, 76, 71	87	13
		1.0	5	79, 78, 80* (67,93), 79* (79,78), 83	80	3
		10	1*	88* (90,87)	88	-
Seeds (2012 season)	Dicamba	0.01	3	95, 77, 92	88	11
		1.0	3	86, 87, 87	87	1
	5-OH dicamba	0.01	3	82, 83, 78	81	3
		1.0	3	98, 99, 99	99	1
	DCSA	0.01	3	81, 82, 79	81	2
		1.0	3	74, 80, 83	79	6
Forage (2010 season)	Dicamba	0.01	4	67, 70, 61, 71	67	6
		0.05	2	88, 98	93	-
		0.1	1	92	-	-
	5-OH dicamba	0.01	6	72, 68, 86, 88, 94, 83	82	12
		0.05	2	102, 82	92	-
		0.1	2	90, 92	91	-
	DCSA	0.01	6	82, 87, 86, 83, 76, 67	80	10
		0.05	2	105, 69	87	-
		0.1	2	83, 91	87	-
Forage (2012 season)	Dicamba	0.01	2	92, 102	97	-
		1.0	2	101, 103	102	-
	5-OH dicamba	0.01	2	95, 99	97	-
		1.0	2	109, 108	109	-
	DCSA	0.01	2	98, 95	96	-
		1.0	2	103, 101	102	-
Hay (2010 season)	Dicamba	0.01	2	72, 100	86	-
		0.05	2	81, 81	81	-
		1.0	1	73	-	-
	5-OH dicamba	0.01	4	53, 65, 62, 86	66	21
		0.05	4	87, 87, 75, 77	82	7
		1.0	1	93	-	-
	DCSA	0.01	3	55, 57, 71	61	15
		0.05	3	67, 77, 76	73	7
		1.0	1	77	77	-
Hay (2012 season)	Dicamba	0.01	1	74, 95	84	-
		1.0	1	95, 98	97	-
	5-OH dicamba	0.01	1	73, 101	87	-
		1.0	1	96, 106	101	-
	DCSA	0.01	1	75, 89	82	-
		1.0	1	103, 92	98	-

An asterisk (*) denotes that the result is the mean of duplicate or triplicate analyses of the same fortification sample.

USE PATTERNS

The authorized use on soya beans in the USA is summarized in Table 3.

Table3 Registered uses of dicamba on soya bean (dry) in the USA

Crop	Country	Formulation (g/kg or g/L and type)	F/G/P ^a	Application			PHI (days)
				Method	No. per crop season	min. - max. kg ai/ha per applic. ^b	
Soya bean (dry)	USA	480SL	F	Spray*	1 (pre-plant)	0.14–0.56	NA
					1 (pre-harvest)**	0.28–1.12	7
					Total 2	(2.24/season)	-

^a F = outdoor or field use, G = glasshouse, P = protected

^b Information given on active ingredient referring to dicamba only

NA = not applicable

* Aerial spray is also allowed.

** After soya bean pods have reached mature brown colour and at least 75% leaf drop has occurred. Do not feed soya bean fodder and hay following a pre-harvest application.

The label permits grazing after the pre-plant application while use of soya bean plants for grazing is not a common practice unless good harvest is not expected for some reasons such as natural disasters. The label prohibits feeding the plant materials after pre-harvest application.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The information on new supervised field trials of dicamba on soya beans, conducted in the USA in 2010 and 2012, were received and summarized in Table 4.

All trials were conducted outdoor. Application rates were reported as dicamba acid equivalents expressed in kg ai/ha. Residue concentrations were reported for dicamba, 5-OH dicamba and DCSA expressed in mg dicamba equivalents/kg. Residue concentrations are recorded unadjusted for recoveries or for residue values in control samples. Where duplicate samples were taken from a single plot, individual results are reported, and the calculated average concentration (in parentheses) is used for the estimation of maximum residue level. Where trials were conducted in the same location, with the same or similar varieties, similar formulations or different salt types, and at the same or similar timing, they are not regarded as independent and the highest residues from these trials were used for estimating a maximum residue level and STMR. Although trials included control plots, no control data are recorded in the tables below unless residues in control samples significantly exceeded the LOQ.

Total residues were calculated by summing up the concentrations of dicamba and 5-OH dicamba expressed in mg dicamba equivalents/kg. Residue concentrations found to be below the limit of quantitation (LOQ) or the limit of detection (LOD) were reported as < LOQ or < LOD respectively. Where the concentration of dicamba or 5-OH dicamba was < LOQ, they were regarded to be at the LOQ and where it was < LOD, they are regarded to be 0 for calculation.

Residues from the trials conducted according to maximum GAP and used for the estimation of maximum residues and STMR/HR are underlined.

Pulses

Soya bean

The approved use of dicamba in soya bean consists of two different applications: application of up to 0.56 kg ai/ha as a broadcast made to the soil surface approximately 14 days prior to planting, and/or up to 1.12 kg ai/ha applied 7 days prior to harvest. If both pre-plant and pre-harvest applications are used in one season, the maximum seasonal use rate must not exceed 2.24 kg ai/ha. Soya bean plants are susceptible to dicamba.

2010 Season (bridging trials)

Field trial data were generated for dicamba from four bridging trials (equivalent of 12 tests) on soya bean conducted in EPA Region 5 (Iowa, Minnesota, Nebraska, and South Dakota; one trial each) during the 2010 growing season.

For each trial, one untreated control plot and three “side-by-side” treated plots comparing three different soluble concentrate (SL) formulations of dicamba were established. The formulations tested were: a diglycolamine (DGA) salt of dicamba (480 g ai/L SL); a diethylenetriamine (DETA) salt of dicamba (480 g ai/L SL); and an N,N-bis (3-aminopropyl)-methylamine (BAPMA) salt of dicamba (600 g ai/L SL).

The treated plots received one broadcast application of the designated dicamba formulation to the soil targeting 28 days before planting at 0.56 kg ai/ha and one pre-harvest application targeting 7 days before the harvest of mature soya bean seed at 1.12 kg ai/ha, for a seasonal total of 1.7 kg ai/ha. The actual total application rate was 1.63–1.73 kg ai/ha/season. The applications were made using ground equipment in approximately 181–211 l/ha of water. An adjuvant was included in the spray mixture (0.25% v/v non-ionic spreader/sticker/surfactant of a minimum 80% active ingredient) together with ammonium sulfate liquid fertilizer (2% w/v).

From each untreated plot, single forage and hay (forage dried to less than 20% moisture) samples were collected at the BBCH 16 growth stage (vegetative, 6th trifoliate leaf unfolded), and a single sample of seed was collected at maturity (BBCH89). From each treated plot, duplicate forage and hay samples were collected at the BBCH 16 growth stage, 66–78 days after treatment (37–50 days after planting), and duplicate samples of seed were collected at maturity (BBCH89), 7 days after the second (last) application.

The soya bean samples were stored frozen (<-10 °C) for maximum of 872 days (29 months) for seed, 957 days (31 months) for forage, and 962 days (32 months) for hay from sample collection to extraction for analysis.

The residues of dicamba and its metabolites 5-OH-dicamba and DCSA in/on soya bean samples were quantitated by LC-MS/MS using BASF analytical method D0902. Acceptable concurrent method validation data for soya bean matrices were obtained for each analyte. In this study, the validated LOQ for residues of dicamba, 5-OH dicamba, and DCSA was 0.01 mg/kg in/on soya bean seed (dry) samples and 0.05 mg/kg in/on soya bean forage and hay samples. Apparent residues of dicamba (each analyte) were < LOQ in/on all untreated control soya bean seed, forage and hay samples. Concurrent analysis of untreated soya bean samples (seed, forage and hay) fortified with a mixture of dicamba, 5-OH-dicamba and DCSA at 0.01, 0.05, 0.1, 1 or 10 mg/kg, resulted in acceptable range of recovery of 70–120% at the stated LOQs with some isolated exceptions.

After only preplant application of three different SL formulations of dicamba, residues of dicamba were below the limit of quantitation of 0.05 mg/kg in all soya bean forage and hay samples harvested at a growth stage targeting BBCH 16.

After one pre-plant and one pre-harvest applications using the different salt types, residues measured in the seed (dry) samples were primarily the parent herbicide and mostly relatively low (< 0.1 mg/kg). However, several samples had significant residues but not in a particular pattern. These residues in the seed suggest that the pod containing the seed may have begun to split allowing residues to contact the seed. Another possibility for the significant residues is contact of the seed with the outer surface of the pods during shelling.

2012 Season

Eight field trials on soya bean were conducted during the 2012 growing season in EPA Region 2 (one trial each in New Jersey and North Carolina), Region 4 (Louisiana, one trial) and Region 5 (Illinois and Wisconsin, one trial each; Iowa, three trials). Each trial location consisted of one untreated and one treated plot. The treated plot received one broadcast pre-plant application of dicamba (a diglycolamine (DGA) salt of dicamba, 480 g dicamba acid equivalents/L SL) at the rate targeting

0.56 kg ai/ha to the soil targeting 28 days prior to planting, followed by one late-season, broadcast foliar application targeting 1.12 kg ai/ha, 7 days prior to harvest of mature seed. The actual total application rate was 1.66–1.74 kg ai/ha/season. The applications were made using ground equipment in approximately 181–219 l/ha of water with the same adjuvant as in 2010 and 2 % w/v ammonium sulfate.

From each untreated plot, single forage and hay (forage dried to less than 20% moisture) samples were collected at the BBCH 16 growth stage, and a single sample of seed was collected at maturity (BBCH89). From each treated plot, duplicate forage and hay samples were collected at the BBCH 16 growth stage, 62–88 days after treatment (33–60 days after planting); and duplicate samples of seed were collected at maturity (BBCH 89), 6 or 7 days after the last application. In one trial (Guthrie, IA), seed samples were harvested at 0, 3, 11 and 14 days after the last application, in addition to the 7 day PHI, to examine residue decline.

The soya bean samples were stored frozen from harvest to extraction, for 88–205 days (2.9 to 6.9 months). Samples were analysed within 6 days of extraction. Adequate storage stability data are available to support the storage conditions and durations for the samples in the subject study.

Soya bean samples (seed, forage and hay) were analysed for residues of dicamba and the metabolites 5-OH-dicamba and DCSA using a modified version of BASF Analytical Method No. D0902. The LOQ for each matrix was 0.01 mg/kg for these three analytes. The limit of detection (LOD) was set at 20% of the LOQ, or 0.002 mg/kg. Apparent residues of dicamba and the metabolites were < LOQ in/on all untreated control soya bean seed, forage and hay samples.

Individual procedural recoveries of dicamba, DCSA and 5-OH-dicamba from soya bean seed, forage and hay samples were within 70–120%. Mean recoveries of each analyte across all soya bean matrices and fortification levels at 0.01 and 1.0 mg/kg ranged from 80 to 103% (4–15% RSD).

After one broadcast preplant plus one late-season pre-harvest application of dicamba 480 g ai/l SL, residues of parent dicamba in soya bean seed (dry) harvested at maturity, 6 or 7 days after the last application, ranged from < 0.01 mg/kg to 0.60 mg/kg and the metabolites 5-OH dicamba and DCSA, were < 0.01 mg/kg in/on the 16 treated soya bean seed (dry) samples in this study.

Data from the residue decline site indicate that dicamba residues in soya bean seed generally declined with increasing pre-harvest intervals.

Residues of dicamba, 5-OH dicamba and DCSA were determined and reported individually. Dicamba concentrations were used for estimating a maximum residue level of dicamba in/on soya bean (dry) and the sum of dicamba and 5-OH dicamba expressed as dicamba was calculated and used for exposure assessment. Where the concentration of 5-OH dicamba was below the LOQ, the value of LOQ was used for the calculation of total concentration. However, where the concentration of 5-OH dicamba was below the LOD, its concentration was assumed to be zero.

The dicamba concentrations used for estimating a maximum residue level of dicamba in/on soya bean (dry) are underlined and the sum of dicamba and 5-OH dicamba used for estimating STMR for exposure assessment are double-underlined in the following Table.

Table4 Residues of dicamba, 5-OH dicamba and DCSA in soya beans from supervised trials conducted in the USA

SOYA BEAN Year, Location (variety) Trial No.	Application					DALT (d)	Portion analysed	Residues (mg/kg) ^a				Author Report Year Study No. Doc ID.
	Form.	Method	Rate (kg ai/ha)	Growth stage	No			Dicamba	5-OH dicamba	Total ^b	DCSA	
<u>US GAP</u>	<u>480 SL</u>	<u>Spray</u>	<u>0.56</u> +/or <u>1.12</u> (max 2.24/ season)	<u>Pre- plant</u>	<u>1</u>	<u>NA</u>						
				<u>7dbh</u>	<u>1</u>	<u>7</u>						

SOYA BEAN Year, Location (variety) Trial No.	Application					DALT (d)	Portion analysed	Residues (mg/kg) ^a				Author Report Year Study No. Doc ID.
	Form.	Method	Rate (kg ai/ha)	Growth stage	No			Dicamba	5-OH dicamba	Total ^b	DCSA	
2010 York, NE (93Y12) Trial No. R100188	480 SL (DGA)	Pre- plant + foliar	0.56 + 1.15	pre-plant 28 dbp + 7 dbh (BBCH 89)	2	7	seed	0.10	< 0.01	0.11	< 0.01	Norris, F.A. 2013 BASF# 389561 2012/7005501
								0.11	< 0.01	0.12	< 0.01	
								(0.105)		(0.115)		
	480 SL (DETA)	Pre- plant + foliar	0.56 + 1.13	pre-plant 28 dbp + 7 dbh (BBCH 89)	2	7	seed	0.09	< 0.01	0.10	< 0.01	
								0.11	< 0.01	0.12	< 0.01	
								(0.10)		(0.11)		
	600 SL (BAPMA)	Pre- plant + foliar	0.56 + 1.12	pre-plant 28 dbp + 7 dbh (BBCH 89)	2	7	seed	0.11	< 0.01	0.12	< 0.01	
								0.13	< 0.01	0.14	< 0.01	
								(0.12)		(0.13)		
2010 Stems, MN (Asgrow AG1002) Trial No. R100189	480 SL (DGA)	Pre- plant + foliar	0.54 + 1.13	pre-plant 28 dbp + 7 dbh (BBCH 89)	2	7	seed	< 0.01	< 0.01	< 0.02	< 0.01	Norris, F.A. 2013 BASF# 389561 2012/7005501
								< 0.01	< 0.01	< 0.02	< 0.01	
								(<u>< 0.01</u>)		(<u>< 0.02</u>)		
	480 SL (DETA)	Pre- plant + foliar	0.54 + 1.12	pre-plant 28 dbp + 7 dbh (BBCH 89)	2	7	seed	< 0.01	< 0.01	< 0.02	< 0.01	
								< 0.01	< 0.01	< 0.02	< 0.01	
								(< 0.01)		(< 0.02)		
	600 SL (BAPMA)	Pre- plant + foliar	0.57 + 1.13	pre-plant 28 dbp + 7 dbh (BBCH 89)	2	7	seed	< 0.01	< 0.01	< 0.02	< 0.01	
								< 0.01	< 0.01	< 0.02	< 0.01	
								(< 0.01)		(< 0.02)		
2010 Turner, SD (Hefty 6238359) Trial No. R100190	480 SL (DGA)	Pre- plant + foliar	0.56 + 1.12	pre-plant 30 dbp + 7 dbh (BBCH 96)	2	7	seed	5.01	0.19	5.20	0.16	Norris, F.A. 2013 BASF# 389561 2012/7005501
								5.84	0.23	6.07	0.20	
								(5.42)		(5.64)		
	480 SL (DETA)	Pre- plant + foliar	0.55 + 1.13	pre-plant 30 dbp + 7 dbh (BBCH 96)	2	7	seed	0.08	< 0.01	0.09	< 0.01	
								0.02	< 0.01	0.03	0.05	
								(0.05)		(0.06)		
	600 SL (BAPMA)	Pre- plant + foliar	0.55 + 1.08	pre-plant 30 dbp + 7 dbh (BBCH 96)	2	7	seed	0.02	< 0.01	0.03	< 0.01	
								0.03	< 0.01	0.04	< 0.01	
								(0.025)		(0.035)		

SOYA BEAN Year, Location (variety) Trial No.	Application				No	DALT (d)	Portion analysed	Residues (mg/kg) ^a				Author Report Year Study No. Doc ID.
	Form.	Method	Rate (kg ai/ha)	Growth stage				Dicamba	5-OH dicamba	Total ^b	DCSA	
2010 Guthrie, IA (93Y15) Trial No. R100191	480 SL (DGA)	Pre-plant + foliar	0.55 + 1.08	pre-plant 28 dbp + 7 dbh (BBCH 95)	2	7	seed	0.04	< 0.01	0.05	< 0.01	Norris, F.A. 2013 BASF# 389561 2012/7005501
								0.04	< 0.01	0.05	< 0.01	
								(0.04)		(0.05)		
	480 SL (DETA)	Pre-plant + foliar	0.55 + 1.09	pre-plant 28 dbp + 7 dbh (BBCH 95)	2	7	seed	5.75	0.47	6.22	0.81	
								5.50	0.40	5.90	0.78	
								(5.62)		(6.06)		
	600 SL (BAPMA)	Pre-plant + foliar	0.59 + 1.14	pre-plant 28 dbp + 7 dbh (BBCH 95)	2	7	seed	0.03	< 0.01	0.04	< 0.01	
								2.63	0.10	2.73	0.04	
								(1.33)		(1.385)		
2012 Hunterdon, NJ (02RM030020 / SC27-C4) Trial No. R120088	480 SL (DGA)	Pre-plant + foliar	0.57 + 1.17	pre-plant 28 dbp + 6 dbh (BBCH 89)	2	6	seed	0.04	< 0.002	0.04	< 0.002	Norris, F.A. 2013 BASF# 430098 2013/7001282
								0.03	< 0.002	0.03	< 0.01	
								(0.035)		(0.035)		
2012 Wayne, NC (S78-G6) Trial No. R120089	480 SL (DGA)	Pre-plant + foliar	0.57 + 1.14	pre-plant 28 dbp + 6 dbh (BBCH 89)	2	6	seed	0.07	< 0.002	0.07	< 0.01	Norris, F.A. 2013 BASF# 430098 2013/7001282
								0.05	< 0.002	0.05	< 0.01	
								(0.06)		(0.06)		
2012 St. Landry Parish, LA (P95Y70) Trial No. R120090	480 SL (DGA)	Pre-plant + foliar	0.56 + 1.10	pre-plant 28 dbp + 7 dbh (BBCH 85)	2	7	seed	0.60	< 0.01	0.61	< 0.01	Norris, F.A. 2013 BASF# 430098 2013/7001282
								0.49	< 0.01	0.50	< 0.01	
								(0.545)		(0.555)		
2012 Keokuk, IA (93Y82) Trial No. R120091	480 SL (DGA)	Pre-plant + foliar	0.56 + 1.13	pre-plant 29 dbp + 7 dbh (BBCH 89)	2	7	seed	0.01	< 0.01	0.02	< 0.002	Norris, F.A. 2013 BASF# 430098 2013/7001282
								< 0.01	< 0.01	< 0.02	< 0.002	
								(0.01)		(0.02)		
2012 Clinton, IL (S39-U2) Trial No. R120092	480 SL (DGA)	Pre-plant + foliar	0.59 + 1.13	pre-plant 28 dbp + 7 dbh (BBCH 89)	2	7	seed	0.02	< 0.002	0.02	< 0.002	Norris, F.A. 2013 BASF# 430098 2013/7001282
								0.03	< 0.01	0.04	< 0.002	
								(0.025)		(0.03)		
2012 Walworth, WI (AG2031RR) Trial No. R120093	480 SL (DGA)	Pre-plant + foliar	0.56 + 1.12	pre-plant 28 dbp + 7 dbh (BBCH 89)	2	7	seed	< 0.01	< 0.002	< 0.01	< 0.01	Norris, F.A. 2013 BASF# 430098 2013/7001282
								< 0.01	< 0.002	< 0.01	< 0.01	
								(<u>< 0.01</u>)		(<u>< 0.01</u>)		
2012 Boone, IA (93Y15) Trial No. R120094	480 SL (DGA)	Pre-plant + foliar	0.57 + 1.14	pre-plant 28 dbp + 7 dbh (BBCH 89)	2	7	seed	0.03	< 0.002	0.03	< 0.01	Norris, F.A. 2013 BASF# 430098 2013/7001282
								0.02	< 0.002	0.02	< 0.01	
								(0.025)		(0.025)		

SOYA BEAN Year, Location (variety) Trial No.	Application					DALT (d)	Portion analysed	Residues (mg/kg) ^a				Author Report Year Study No. Doc ID.
	Form.	Method	Rate (kg ai/ha)	Growth stage	No			Dicamba	5-OH dicamba	Total ^b	DCSA	
2012 Guthrie, IA (93Y15) Trial No. R120095	480 SL (DGA)	Pre- plant + foliar	0.56 + 1.13	pre-plant 28 dbp + 7 dbh	2	0	seed	0.08	< 0.002	0.08	< 0.01	Norris, F.A. 2013 BASF# 430098 2013/7001282
						3		0.10	< 0.002	0.10	< 0.01	
						7		< 0.01	< 0.002	< 0.01	< 0.002	
						11		0.01	< 0.002	0.01	< 0.002	
						14		0.01	< 0.002	0.01	< 0.002	
								0.01	< 0.002	0.01	< 0.002	
								0.01	< 0.002	0.01	< 0.002	
								0.02	< 0.002	0.02	< 0.01	
								0.02	< 0.002	0.02	< 0.01	
								(0.02)		(0.02)		

^a Expressed in mg dicamba equivalents/kg. Average values in parentheses.

^b Sum of dicamba and 5-OH dicamba expressed as dicamba.

DALT= days after the last application

dbp = days before planting

dbh = days before harvest

Animal feed stuffs

Soya bean forage and hay

Soya bean forage and hay samples were collected before the second application was made. Therefore, residues in these commodities came from pre-plant application.

Table 3 Residues of dicamba, 5-OH dicamba and DCSA in soya bean forage and hay from supervised trials conducted in the USA

SOYA BEAN Year, Location (variety) Trial No.	Application					DALT (d)	Portion analysed	Residues (mg/kg) ^a				Author Report Year Study No. Doc ID.
	Form.	Method	Rate (kg ai/ha)	Growth stage	No			Dicamba	5-OH dicamba	Total ^b	DCSA	
US GAP	480 SL	Spray	0.56 +/or 1.12 (max 2.24/ season)	Pre- plant 7dbh	1	NA						
					1	7						
2010 York, NE (93Y12) Trial No. R100188	480 SL (DGA)	Pre- plant	0.56	pre- plant 28 dbp	1	66	Forage	< 0.05	< 0.05	< 0.10	< 0.05	Norris, F.A. 2013 BASF# 389561 2012/700550 1
					1	66	Forage	< 0.05	< 0.05	< 0.10	< 0.05	
					1	66	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
					1	66	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
2010 York, NE (93Y12) Trial No. R100188	480 SL (DETA)	Pre- plant	0.56	pre- plant 28 dbp	1	66	Forage	< 0.05	< 0.05	< 0.10	< 0.05	Norris, F.A. 2013 BASF# 389561 2012/700550 1
					1	66	Forage	< 0.05	< 0.05	< 0.10	< 0.05	
					1	66	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
					1	66	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
Soybean USA, 2010 York, NE (93Y12) Trial No. R100188	600 SL (BAPMA)	Pre- plant	0.56	pre- plant 28 dbp	1	66	Forage	< 0.05	< 0.05	< 0.10	< 0.05	Norris, F.A. 2013 BASF# 389561 2012/700550 1
					1	66	Forage	< 0.05	< 0.05	< 0.10	< 0.05	
					1	66	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
					1	66	Hay	< 0.05	< 0.05	< 0.10	< 0.05	

SOYA BEAN Year, Location (variety) Trial No.	Application					DA LT (d)	Portion analysed	Residues (mg/kg) ^a				Author Report Year Study No. Doc ID.
	Form.	Method	Rate (kg ai/ha)	Growt h stage	No			Dicamba	5-OH dicamba	Total ^b	DCSA	
2010 Turner, SD (Hefty 6238359) Trial No. R100190	480 SL (DGA)	Pre- plant	0.56	pre- plant 30 dbp	1	67	Forage	< 0.05	< 0.05	< 0.10	< 0.05	Norris, F.A. 2013 BASF# 389561 2012/700550 1
					1	67	Forage	< 0.05	< 0.05	< 0.10	< 0.05	
					1	67	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
					1	67	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
2010 Turner, SD (Hefty 6238359) Trial No. R100190	480 SL (DETA)	Pre- plant	0.55	pre- plant 30 dbp 7 dbh (BBCH 96)	1	67	Forage	< 0.05	< 0.05	< 0.10	< 0.05	Norris, F.A. 2013 BASF# 389561 2012/700550 1
					1	67	Forage	< 0.05	< 0.05	< 0.10	< 0.05	
					1	67	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
					1	67	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
2010 Turner, SD (Hefty 6238359) Trial No. R100190	600 SL (BAPMA)	Pre- plant	0.55	pre- plant 30 dbp	1	67	Forage	< 0.05	< 0.05	< 0.10	< 0.05	Norris, F.A. 2013 BASF# 389561 2012/700550 1
					1	67	Forage	< 0.05	< 0.05	< 0.10	< 0.05	
					1	67	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
					1	67	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
2010 Guthrie, IA (93Y15) Trial No. R100191	480 SL (DGA)	Pre- plant	0.55	pre- plant 28 dbp	1	78	Forage	< 0.05	< 0.05	< 0.10	< 0.05	Norris, F.A. 2013 BASF# 389561 2012/700550 1
					1	78	Forage	< 0.05	< 0.05	< 0.10	< 0.05	
					1	78	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
					1	78	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
2010 Guthrie, IA (93Y15) Trial No. R100191	480 SL (DETA)	Pre- plant	0.55	pre- plant 28 dbp	1	78	Forage	< 0.05	< 0.05	< 0.10	< 0.05	Norris, F.A. 2013 BASF# 389561 2012/700550 1
					1	78	Forage	< 0.05	< 0.05	< 0.10	< 0.05	
					1	78	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
					1	78	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
2010 Guthrie, IA (93Y15) Trial No. R100191	600 SL (BAPMA)	Pre- plant	0.59	pre- plant 28 dbp	1	78	Forage	< 0.05	< 0.05	< 0.10	< 0.05	Norris, F.A. 2013 BASF# 389561 2012/700550 1
					1	78	Forage	< 0.05	< 0.05	< 0.10	< 0.05	
					1	78	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
					1	78	Hay	< 0.05	< 0.05	< 0.10	< 0.05	
2012 Wayne, NC (S78-G6) Trial No. R120089	480 SL (DGA)	Pre- plant	0.57	pre- plant 28 dbp	1	88	Forage	< 0.002	< 0.002	< 0.01	< 0.002	Norris, F.A. 2013 BASF# 430098 2013/700128 2
					1	88	Forage	< 0.01	< 0.002	< 0.01	< 0.01	
					1	88	Hay	< 0.002	< 0.002	< 0.01	< 0.002	
					1	88	Hay	< 0.002	< 0.002	< 0.01	< 0.002	
2012 Keokuk, IA (93Y82) Trial No. R120091	480 SL (DGA)	Pre- plant	0.56	pre- plant 29 dbp	1	62	Forage	< 0.01	< 0.002	< 0.01	< 0.01	Norris, F.A. 2013 BASF# 430098 2013/700128 2
					1	62	Forage	0.01	0.03	0.04	0.02	
					1	62	Hay	< 0.002	< 0.002	< 0.01	< 0.002	
					1	62	Hay	< 0.002	< 0.002	< 0.01	< 0.002	
2012 Clinton, IL (S39-U2) Trial No. R120092	480 SL (DGA)	Pre- plant	0.59	pre- plant 28 dbp	1	70	Forage	< 0.01	< 0.002	< 0.01	< 0.002	Norris, F.A. 2013 BASF# 430098 2013/700128 2
					1	70	Forage	< 0.002	< 0.002	< 0.01	< 0.002	
					1	70	Hay	< 0.01	< 0.002	< 0.01	< 0.01	
					1	70	Hay	< 0.01	< 0.002	< 0.01	< 0.002	
2012 Walworth, WI (AG2031RR) Trial No. R120093	480 SL (DGA)	Pre- plant	0.56	pre- plant 28 dbp	1	67	Forage	< 0.01	< 0.01	< 0.03	0.01	Norris, F.A. 2013 BASF# 430098 2013/700128 2
					1	67	Forage	0.01	0.02	0.05	0.02	
					1	67	Hay	< 0.002	< 0.01	< 0.03	< 0.002	
					1	67	Hay	< 0.01	< 0.002	< 0.03	< 0.01	
2012 Boone, IA (93Y15) Trial No. R120094	480 SL (DGA)	Pre- plant	0.57	pre- plant 28 dbp	1	80	Forage	0.01	0.02	0.03	0.02	Norris, F.A. 2013 BASF# 430098 2013/700128 2
					1	80	Forage	0.01	< 0.002	0.01	0.01	
					1	80	Hay	< 0.01	< 0.002	< 0.01	< 0.002	
					1	80	Hay	< 0.01	< 0.002	< 0.01	< 0.002	

SOYA BEAN Year, Location (variety) Trial No.	Application					DA LT (d)	Portion analysed	Residues (mg/kg) ^a				Author Report Year Study No. Doc ID.
	Form.	Method	Rate (kg ai/ha)	Growt h stage	No			Dicamba	5-OH dicamba	Total ^b	DCSA	
2012 Guthrie, IA (93Y15) Trial No. R120095	480 SL (DGA)	Pre- plant	0.56	pre- plant 28 dbp	1	81	Forage	< 0.01	< 0.002	< 0.01	< 0.01	Norris, F.A. 2013 BASF# 430098 2013/700128 2
					1	81	Forage	< 0.01	< 0.002	< 0.01	< 0.002	
					1	81	Hay	0.01	< 0.002	0.01	< 0.01	
					1	81	Hay	0.06	< 0.002	0.06	< 0.01	

^a Expressed in mg dicamba equivalents/kg. Average values in parentheses.

^b Sum of dicamba and 5-OH dicamba expressed as dicamba.

dbp = days before planting

FATE OF RESIDUES IN STORAGE AND PROCESSING

The 2010 JMPR received and reviewed information on processing of soya bean to oil. The summary of processing studies on soya bean is transcribed below.

Table 4Summary of processing studies

Processed Product	Processing factor	
	Dicamba	Total residues
Soya bean		
Meal	0.35	0.36
Hulls	3.9	3.8
Grain dust	676	669
Refined oil	< 0.019	< 0.036

APPRAISAL

Dicamba, a systemic broad-spectrum herbicide, was first evaluated by the 2010 JMPR which estimated an ADI of 0–0.3 mg/kg bw and ARfD of 0.5 mg/kg bw, and recommended the following residue definitions for plant commodities:

Definition of the residue for plant commodities (for compliance with the MRL): *Dicamba*

Definition of the residue for plant commodities (for estimation of dietary intake): *Sum of dicamba and 5-OH dicamba expressed as dicamba*

Definition of the residue for animal commodities (for compliance with the MRL and for estimation of dietary intake): *Sum of dicamba and DCSA expressed as dicamba*

The 2010 Meeting reviewed metabolism, method of analysis, storage stability, supervised residue trials and processing studies of dicamba in soya beans. However, as no supervised trials matched US GAP, the Meeting could not estimate a maximum residue level for soya bean (dry). The 2011 Meeting decided to apply the concept of proportionality to the residues from these trials to recommend a maximum residue level.

The Forty-fifth Session of the Codex Committee on Pesticide Residues in 2013 agreed to the Principles and Guidance for Application of the Proportionality Concept to Estimation of Maximum Residue Limits for Pesticides and further agreed that desiccants should be excluded from the application of the proportionality concept.

The current Meeting received information on new supervised trials on soya beans following the US GAP and analytical methods used for the determination of dicamba and related compounds in the new supervised trials on soya beans.

Method of analysis

The current Meeting received information on the analytical method used for the determination of dicamba, 5-OH dicamba and 3,6-dichloro-2-hydroxybenzoic acid (DCSA) arising in soya bean seeds, forage and hay in newly conducted supervised residue trials. The method analysed these compounds using LC-MS/MS, monitoring ion transitions from m/z 219→175 for dicamba; m/z 235→155 for 5-OH-dicamba; and m/z 205→161 for DCSA.

The method was found suitable for the determination of the three analytes in soya bean seeds, forage and hay with mean recoveries in the acceptable range of 70–110% at the fortification levels between 0.01 and 10 mg/kg.

The limit of quantitation (LOQ) is 0.01 mg/kg for the determination of dicamba, 5-OH dicamba and DCSA in soya bean seeds, forage and hay, except that this LOQ was not achievable in forage or hay for the 2010 season analysis.

Results of supervised residue trials on crops

Soya bean (dry)

A total of twelve supervised residue trials were conducted in the USA in 2010 and 2012.

The approved use of dicamba in soya bean in the USA consists of two different applications: application of up to 0.56 kg ai/ha as a broadcast application made approximately 14 days prior to planting, and/or up to 1.12 kg ai/ha applied to soya bean plants after soya bean pods have reached mature brown color and at least 75% leaf drop has occurred with a PHI of 7 days. If both pre-plant and pre-harvest applications are used in one season, the maximum seasonal use rate must not exceed 2.24 kg ai/ha. After a pre-harvest application soya bean fodder and hay must not be fed to animals.

After one pre-plant and one pre-harvest applications using the three different salt types, residues in the seed (dry) samples were primarily the parent compound and mostly relatively low (< 0.1 mg/kg). However, residue concentrations vary hugely, due possibly to the split of pods causing seeds to come into contact with dicamba itself or dicamba residue on the outer surface of pods. Since all the trials approximated normal agricultural practices, the Meeting decided to use these trial results in estimating a maximum residue level. No significant difference or pattern was observed among the trials using these different formulations.

Residues of dicamba in soya bean (dry) from those trials matching the GAP of the USA were, in rank order (n=12): < 0.01 (2), 0.01, 0.02, 0.025 (2), 0.035, 0.06, 0.12, 0.545, 5.4 and 5.6 mg/kg.

The Meeting estimated a maximum residue level of 10 mg/kg to replace the previous recommendation of 5 mg/kg. For the purpose of calculating animal dietary burden, the Meeting estimated a median residue of 0.03 mg/kg.

Corresponding total residues (dicamba and 5-OH dicamba) of dicamba were (n=12): < 0.01, < 0.02, 0.02 (2), 0.025, 0.03, 0.035, 0.06, 0.13, 0.555, 5.635 and 6.06 mg/kg.

The Meeting estimated an STMR of 0.033 mg/kg.

Soya bean forage and hay

Soya bean forage and hay samples were collected before the second application was made to avoid abscission. Therefore, residues in these commodities came from a pre-plant application only. The US label prohibits the use of fodder or hay after a pre-harvest application.

The residues from the pre-plant application were expected to be very low as shown in the trials (mostly < 0.05 mg/kg and in one trial 0.06 mg/kg for dicamba) and, as such, residues in soya bean forage and hay from only pre-plant application would not have impacted on the livestock dietary burden. Therefore, the Meeting confirmed the decision of the 2010 and 2011 JMPR that there was no need for estimating a maximum residue level, median residue or highest residue for soya bean fodder and hay.

Fate of residues during processing

The 2010 JMPR received and reviewed information on processing of soya bean seed to oil and meal.

Processed Product	Processing factor		STMR/STMR-P
	Dicamba	Total residues	
Soya bean			0.033
Refined oil	< 0.019	< 0.036	0.001

As there is no concentration of dicamba and 5-OH dicamba observed in refined oil, the estimation of a maximum residue level is not necessary for this commodity.

On the basis of the processing factor of 0.35 for dicamba only, a median residue of 0.0105 mg/kg was calculated for soya bean meal, which may be used as a livestock feed item.

Residue concentration was observed in soya bean hulls and grain dust which may also be used as animal feeds. The processing factors of dicamba only, calculated for these commodities, were 3.9 and 676, respectively. From these factors, median residues in soya bean hulls and grain dust for the estimation of animal burden were calculated to be 0.117 and 20.3 mg/kg, respectively.

Residues in animal commodities

Soya beans and processed soya bean products may be fed to dairy cattle, beef cattle, broilers and layers. The maximum and mean dietary burdens were calculated using the highest residues and median residues of dicamba in commodities for which maximum residue levels were recommended by the 2010 JMPR and current JMPR and their processed products on a basis of the OECD Animal Feeding Table.

Residues of 5-OH dicamba was not included in the calculation of animal dietary burden as its concentrations in animal feeding items were very low and the feeding study with 5-OH dicamba resulted in very low uptake (< 0.01 mg/kg) of 5-OH dicamba into tissues, milk or blood of cattle at a dose equivalent to 59 ppm in the diet.

The resulting maximum and mean dietary burdens to be used for estimating maximum residue levels for commodities of animal origin (both mammals and poultry) were identical to those of the 2010 and 2011 JMPR.

The Meeting concluded that there was no need to re-evaluate maximum residue levels, STMRs or HRs for commodities of animal origin.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue for plant commodities (for compliance with the MRL): *Dicamba*.

Definition of the residue for plant commodities (for estimation of dietary intake): *Sum of dicamba and 5-OH dicamba expressed as dicamba*.

Definition of the residue for animal commodities (for compliance with MRLs and for estimation of dietary intake): *Dicamba and 3,6-dichlorosalicylic acid (DCSA) expressed as dicamba*.

Residue is not fat-soluble.

Commodity		Recommended MRL, mg/kg		STMR/STMR-P mg/kg	HR/HR-P mg/kg
CCN	Name	New	Previous		
VD 0541	Soya bean (dry)	10	5	0.033	-
OR 0541	Soya bean oil, edible	-		0.001	-

For calculating animal dietary burdens

Commodity		Recommended MRL, mg/kg		STMR/STMR-P mg/kg ^a	HR/HR-P mg/kg
CCN	Name	New	Previous		
	Soya bean (dry)			0.03	
	Soya bean meal			0.0105	
	Soya bean hull	-		0.117	-
	Soya bean grain dust	-		20.3	-

^a residues of dicamba only.

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Dietary Intakes (IEDIs) of dicamba were calculated for the 13 GEMS/Food cluster diets using STMRs and STMRPs estimated by the 2010 and current Meeting (see Annex 3 of the 2013 Report). The ADI is 0–0.3 mg/kg bw and the calculated IEDIs were 0–1% of the maximum ADI. The Meeting concluded that the long-term intake of residues of dicamba resulting from the uses considered by the current JMPR is unlikely to present a public health concern.

Short-term intake

The International Estimated Short-Term Intakes (IESTI) of dicamba were calculated for soya bean and its processed commodity using STMRs/STMR-Ps estimated by the current Meeting (see Annex 4 of the 2013 Report). The ARfD is 0.5 mg/kg and the calculated IESTIs were 0% of the ARfD. The Meeting concluded that the short-term intake of residues of dicamba, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

REFERENCES

Document No.	Author(s)	Year	Title, Report reference, Study number
	FAO/WHO	2010	Pesticide residues in food 2010 - Joint FAO/WHO Meeting on Pesticide Residues - Evaluations Part I-Residues
	FAO/WHO	2011	Pesticide residues in food 2011 - Joint FAO/WHO Meeting on Pesticide Residues -Report
2012/7005501	Norris, F.A	2013	Magnitude of the Residue of Dicamba in Soybean Matrices, Formulation Bridging Study (BASF Study Number 389561, American Agricultural Service Number AA100712)
2013/7001282	Norris, F.A	2013	Magnitude of the Residue of Dicamba in Soybean Matrices (BASF Study Number 430098, American Agricultural Service Number AA120705)

DIFENOCONAZOLE (224)

The first draft was prepared by Professor Mi-Gyung Lee, Andong National University Republic of Korea

EXPLANATION

Difenoconazole was first evaluated by the JMPR in 2007 for toxicology when an ADI of 0–0.01 mg/kg bw and an ARfD of 0.3 mg/kg bw were established. In 2007 and 2010, the JMPR evaluated the compound for residues and recommended numerous maximum residue levels. The compound was listed by the Forty-fourth Session of the CCPR for residue evaluation for additional maximum residue levels by the 2013 JMPR.

The residue is defined, for compliance with the MRL and for estimation of dietary intake for plant commodities, as parent *difenoconazole*. For animal commodities for compliance with the MRL and for estimation of dietary intake, it is defined as *sum of difenoconazole and 1-[2-chloro-4-(4-chloro-phenoxy)-phenyl]-2-(1,2,4-triazol)-1-yl-ethanol (CGA 205375), expressed as difenoconazole*. The residue is fat soluble.

The current Meeting received supervised residue trial data for oranges, grapefruit, lemons, mandarin, tangerines, apples, pears, grapes, bulb onion, spring onion, head cabbage, broccoli, melons, gherkin, summer squash, sweet pepper, chili pepper, tomato and potatoes. The government of Republic of Korea provided residue trial data for Japanese persimmon and ginseng. Processing studies on oranges, apples, grapes, tomato, potato and ginseng were also provided. The Forty-fourth Session of the CCPR requested the 2013 JMPR to re-evaluate the ginseng processing studies evaluated in 2010, in accordance with the new classification on the processed products, i.e., dried ginseng (including red ginseng) and ginseng extracts.

RESIDUE ANALYSIS

Analytical methods

The manufacture provided information for analytical methods (REM 147.08 and AG-575B) used for analysis of parent difenoconazole in plant matrices.

Method REM 147.08 was considered by the 2007 and 2010 JMPR. The method was used for the analysis of citrus fruits, grapes, onions, brassica vegetable, cucurbits and potatoes. LOQs of the method by LC-MS/MS determination were 0.01 mg/kg in the all matrices and the procedural recoveries by matrix were in the range of 80–106% at various fortification levels.

Method AG-575B is one of the updated versions of AG-575. AG-575 and AG-575A (another updated version of AG-575) were considered by 2007 and 2010 JMPR. The method AG-575B was used for the analysis of apples, pears, peppers and tomatoes. LOQs in all matrices by GC-NPD determination were 0.01 mg/kg. The procedural recoveries by matrix were in the range of 98–109% at various fortification levels.

Table 1 Procedural recovery results for difenoconazole in various crops

Matrix	Range of fortification, mg/kg	No.	Range of recoveries, %	Mean recovery, % ± SD	Method
Oranges	0.01-1.0	18	91-114	104 ± 6.3	REM 147.08
Orange, dried pulp	0.01-5.0	3	94-118	106 ± 12	REM 147.08
Orange oil	0.01-40	3	83-92	86 ± 4.9	REM 147.08
Orange juice	0.01-0.50	2	94-119	106	REM 147.08
Grapefruit	0.01-0.50	10	83-104	94 ± 6.1	REM 147.08
Lemons	0.01-0.50	8	91-109	102 ± 7.3	REM 147.08
Apple	0.01-2.0	30	83-115	102 ± 9.0	AG-575B
Apple wet pomace	0.01-12	3	78-116	102 ± 21	AG-575B
Apple juice	0.01-0.50	4	100-117	109 ± 8.3	AG-575B
Pear	0.01-5.0	14	64-120	98 ± 14	AG-575B
Grape	0.01-5.0	19	70-113	96 ± 12	REM 147.08

Matrix	Range of fortification, mg/kg	No.	Range of recoveries, %	Mean recovery, % ± SD	Method
Raisins	0.01-10	5	95-108	102 ± 5.7	REM 147.08
Grape juice	0.01-0.50	4	94-107	99 ± 5.6	REM 147.08
Onion, bulb	0.01-5.0	8	85-99	93 ± 5.5	REM 147.08
Spring onion	0.01-7.0	9	92-111	102 ± 7.2	REM 147.08
Cabbage, head	0.01-15	32	71-120	92 ± 12	REM 147.08
Broccoli	0.01 – 2.0	12	72-108	94 ± 10	REM 147.08
Melons	0.01-0.5	12	86-120	97 ± 10	REM 147.08
Cucumber	0.01-0.5	14	89-105	96 ± 4.1	REM 147.08
Squash, summer	0.01-0.1	10	82-99	91 ± 6.3	REM 147.08
Pepper, sweet	0.01 – 2.0	12	91-130	104 ± 13	AG-575B
Chili pepper	0.01 – 0.50	7	94-119	106 ± 7.9	AG-575B
Tomato	0.01 – 3.0	30	75-121	105 ± 11	AG-575B
Tomato paste	0.01 – 3.0	3	88-109	101 ± 11	AG-575B
Tomato puree	0.01 – 2.0	3	100-105	102 ± 2.5	AG-575B
Potato	0.01	9	88-119	100 ± 11	AG-575B
	0.1	7	91-116	99 ± 9	REM 147.08
	1.0	4	80-91	85 ± 5	REM 147.08
	10	4	78-88	82 ± 4	REM 147.08
Potato flakes	0.01	6	89-114	100 ± 11	REM 147.08
	0.1	3	85-86	86 ± 1	REM 147.08
	1.0	3	77-86	80 ± 5	REM 147.08
	10	4	74-94	80 ± 10	REM 147.08
Potato chips	0.01	6	94-103	98 ± 4	REM 147.08
	0.1	3	88-95	91 ± 4	REM 147.08
	1.0	3	84-90	87 ± 3	REM 147.08
	10	4	80-87	83 ± 4	REM 147.08
Potato wet peel	0.01	6	83-118	102 ± 13	REM 147.08
	10	1	82	NA	REM 147.08

LOQs were 0.01 mg/kg in all matrices.

For potato and the processed products, recoveries from method validation were included.

In addition, the manufacturer provided information on analytical methods, Meth-160 and Meth-160, Revision #2. After minor modifications, the methods were used for analyzing triazole metabolites 1, 2, 4-triazole (T), triazole alanine (TA), and triazole acetic acid (TAA) in the same substrates subjected to difenoconazole analysis.

The triazole metabolites were extracted from 5.0 grams of sample with 60 mL of methanol:water (80:20, v/v) [Orange oil samples were first diluted with hexane then extracted twice with methanol:water (80:20, v/v), first with 60 mL, then with 30 mL. Extracts were combined and brought to a final volume of 100 mL with methanol:water (80:20, v/v)]. Individual 1.0 mL aliquots of each extract were processed separately through solid phase extraction (SPE) cleanup and/or derivatization steps, which were specific for each analyte. The TAA aliquot was purified through a C-18 SPE cartridge, then derivatized using HCl/butanol esterification. The TA aliquot underwent two derivatizations directly (bypassing a Bond Elut Certify II SPE cartridge cleanup step in order to capture conjugated residues of TA); the first was an esterification using HCl/butanol and the second was an acylation using HFBA (heptafluorobutyric anhydride). The T aliquot did not undergo further cleanup and was directly derivatized with dansyl chloride to produce the dansyl derivative of 1,2,4-triazole. The derivative was partitioned into ethyl acetate which was evaporated to dryness, then re-dissolved in 2.5 mL of acetonitrile:water (30:70, v/v). The TA and TAA derivatized extracts were evaporated to dryness as well, then brought to a final volume of 2.5 mL in acetonitrile:water (30:70, v/v). All three derivatized extracts were submitted to HPLC for individual analysis. Determination and quantitation of derivatives of 1,2,4-triazole, triazole alanine and triazole acetic acid were conducted using HPLC employing mass spectrometric (MS/MS) detection. LOQs for all analytes were 0.01 mg/kg. The procedural recoveries for the metabolites in all substrates were in the range of 70–115% at fortification levels of 0.1–2.0 mg/kg.

The metabolite, triazole alanine in apple, pear, peppers and tomato was analysed by including a Bond Elut Certify II SPE cartridge cleanup step prior to derivatization. As the cleanup removes any conjugated triazole alanine, additional analysis was again conducted without the SPE cartridge cleanup step. The results had no discrepancies in the data of triazole alanine between with or without cleanup procedure.

Table 2 Procedural recovery results and LOQs for triazole metabolites in various crops using Meth-160

Sample	Analyte	Range of fortification, mg/kg	No.	Range of recoveries, %	Mean recovery, % ± SD
Oranges	1,2,4-Triazole	0.01-0.50	16	74-79	87±7.3
	Triazole alanine	0.01-0.50	16	72-110	95 ± 11
	Triazole acetic acid	0.01-0.50	16	89-116	102 ± 8.2
Orange, dried pulp	1,2,4-Triazole	0.01-0.50	2	84-86	85
	Triazole alanine	0.01-0.50	2	70-71	70
	Triazole acetic acid	0.01-0.50	2	90-100	95
Orange oil	1,2,4-Triazole	0.01-0.50	2	77-93	85
	Triazole alanine	0.01-0.50	2	85-92	88
	Triazole acetic acid	0.01-0.50	2	96-106	101
Orange juice	1,2,4-Triazole	0.01-0.50	2	72-93	82
	Triazole alanine	0.01-0.50	2	92-104	98
	Triazole acetic acid	0.01-0.50	2	105-112	108
Grapefruit	1,2,4-Triazole	0.01-0.50	8	70-112	86 ± 12
	Triazole alanine	0.01-0.50	8	84-107	92 ± 7.5
	Triazole acetic acid	0.01-0.50	8	81-108	97 ± 9.4
Lemons	1,2,4-Triazole	0.01-0.50	6	74-90	85 ± 6.2
	Triazole alanine	0.01-0.50	6	81-94	89 ± 5.0
	Triazole acetic acid	0.01-0.50	6	89-99	93 ± 3.7
Apple	1,2,4-Triazole	0.01-0.10	30	85-111	95 ± 5.6
	Triazole alanine	0.01-0.50	30	98-130	110 ± 8.0
	Triazole acetic acid	0.01-0.10	30	98-138	108 ± 7.4
Apple wet pomace	1,2,4-Triazole	0.01-0.10	4	84-95	90 ± 5.2
	Triazole alanine	0.01-0.50	4	84-95	88 ± 4.8
	Triazole acetic acid	0.01-0.10	4	88-95	91 ± 3.3
Apple juice	1,2,4-Triazole	0.01-0.10	4	87-92	89 ± 2.2
	Triazole alanine	0.01 – 1.0	3	94-103	98 ± 4.5
	Triazole acetic acid	0.01 – 0.10	4	96-104	101 ± 3.6
Pear	1,2,4-Triazole	0.01-0.50	14	79-101	92 ± 6.0
	Triazole alanine	0.01 – 1.0	14	86-112	102 ± 7.3
	Triazole acetic acid	0.01-0.50	14	91-97	94 ± 1.8
Grape	1,2,4-Triazole	0.01-0.50	17	78-102	89 ± 6.5
	Triazole alanine	0.01-0.50	16	91-119	99 ± 6.5
	Triazole acetic acid	0.01-0.50	16	92-116	107 ± 6.9
Raisin	1,2,4-Triazole	0.01-0.50	4	78-88	83 ± 4.6
	Triazole alanine	0.01-0.50	4	79-96	90 ± 7.6
	Triazole acetic acid	0.01-0.50	4	78-100	93 ± 10
Grape juice	1,2,4-Triazole	0.01-0.50	4	84-97	90 ± 5.4
	Triazole alanine	0.01-0.50	4	101-111	106 ± 4.4
	Triazole acetic acid	0.01-0.50	4	101-110	106 ± 3.8
Onion, bulb	1,2,4-Triazole	0.01-0.1	10	82-106	96 ± 6.6
	Triazole alanine	0.01-0.8	8	98-104	101 ± 1.8
	Triazole acetic acid	0.01-0.1	8	95-114	100 ± 6.5
Spring onion	1,2,4-Triazole	0.01-0.1	6	85-96	92 ± 3.8
	Triazole alanine	0.05-0.5	6	99-149	109 ± 20
	Triazole acetic acid	0.01-0.1	6	81-121	92 ± 15
Cabbage, head	1,2,4-Triazole	0.01-0.50	32	72-104	86 ± 7.3
	Triazole alanine	0.01 – 1.6	33	73-114	94 ± 8.9
	Triazole acetic acid	0.01-0.50	32	85-114	99 ± 7.6
Broccoli	1,2,4-Triazole	0.01-0.50	12	76-108	92 ± 8.6
	Triazole alanine	0.01-0.50	12	89-119	100 ± 8.8
	Triazole acetic acid	0.01-0.50	12	79-112	98 ± 8.6
Melons	1,2,4-Triazole	0.01-0.1	12	90-106	97 ± 4.7

Sample	Analyte	Range of fortification, mg/kg	No.	Range of recoveries, %	Mean recovery, % ± SD
	Triazole alanine	0.01-0.5	12	96-120	107 ± 7.3
	Triazole acetic acid	0.01-0.1	12	93-111	99 ± 5.2
Cucumber	1,2,4-Triazole	0.01-0.1	12	90-107	96 ± 5.3
	Triazole alanine	0.025-0.25	12	99-118	110 ± 5.6
	Triazole acetic acid	0.01-0.1	12	89-104	98 ± 4.0
Squash, summer	1,2,4-Triazole	0.01-0.1	10	74-104	95 ± 9.0
	Triazole alanine	0.025-0.25	10	90-106	100 ± 4.5
	Triazole acetic acid	0.01-0.1	10	96-104	100 ± 2.5
Pepper, sweet	1,2,4-Triazole	0.01-0.10	14	86-102	91 ± 3.8
	Triazole alanine	0.01-0.10	14	91-110	99 ± 4.7
	Triazole acetic acid	0.01-0.10	14	90-106	99 ± 3.9
Chili pepper	1,2,4-Triazole	0.01-0.20	7	85-99	90 ± 4.6
	Triazole alanine	0.01-0.20	7	91-105	98 ± 4.9
	Triazole acetic acid	0.01-0.20	7	88-107	99 ± 6.1
Tomato	1,2,4-Triazole	0.01-0.10	24	86-104	96 ± 5.5
	Triazole alanine	0.01-0.50	26	92-107	101 ± 3.3
	Triazole acetic acid	0.01-0.10	24	97-113	104 ± 3.6
Tomato paste	1,2,4-Triazole	0.01-0.10	4	72-91	84 ± 8.4
	Triazole alanine	0.01-0.50	5	76-101	92 ± 9.6
	Triazole acetic acid	0.01 – 0.10	4	95-104	97 ± 4.5
Tomato puree					
Tomato puree	1,2,4-Triazole	0.01 – 0.10	4	89-94	92 ± 2.2
	Triazole alanine	0.05 – 0.50	4	100-104	102 ± 1.7
	Triazole acetic acid	0.01 – 0.10	4	96-101	98 ± 2.1
Potato	1,2,4-Triazole	0.01	10	72-100	88 ± 14
		0.1	7	70-87	80 ± 6
		1.0	3	103	103 ± 0
	Triazole alanine	0.02	9	96-118	106 ± 8
		0.2	6	93-120	103 ± 10
		2.0	3	112-117	115 ± 3
	Triazole acetic acid	0.01	9	93-114	107 ± 7
		0.1	6	98-105	102 ± 3
		1.0	3	104-110	108 ± 3
Potato flakes	1,2,4-Triazole	0.01	6	80-100	89 ± 9
		0.1	1	81	NA
		1.0	3	95-99	97 ± 2
	Triazole alanine	0.01	6	97-106	102 ± 4
		0.1	1	91	NA
		1.0	3	97-101	99 ± 2
	Triazole acetic acid	0.01	6	87-109	98 ± 9
		0.1	1	110	NA
		1.0	3	95-100	98 ± 3
Potato chips	1,2,4-Triazole	0.01	6	80-108	93 ± 12
		0.1	1	103	NA
		1.0	3	84-89	87 ± 3
	Triazole alanine	0.01	6	98-110	104 ± 4
		0.1	1	94	NA
		1.0	3	114-118	115 ± 2
	Triazole acetic acid	0.01	6	97-114	104 ± 6
		0.1	1	104	NA
		1.0	3	109	109 ± 0
Potato wet peel	1,2,4-Triazole	0.01	6	76-87	82 ± 4
		0.1	1	80	NA
	Triazole alanine	0.01	6	102-108	105 ± 2
		0.1	1	106	NA
	Triazole acetic acid	0.01	6	104-112	109 ± 3
		0.1	1	105	NA

For potato and the processed products, recoveries from method validation were included.

LOQs were 0.01 mg/kg in all matrices, with the exception of triazole alanine (TA) in potato tubers (0.02 mg/kg).

Meth-160 and Meth-160 Revision #2 were used in pome fruits; Meth-160, in peppers and tomato; Meth-160 Revision #2, in the other crops. Both Meth-160 and Meth-160 Revision #2 were modified and then applied.

Analytical methods of difenoconazole residues for ginseng and the processed products were similar to the methods considered by the JMPR in 2010, other than a change in volume of elution solvents on the florisil column. Analytical method used for fresh ginseng was changed to the method used for dried ginseng. LOQs for difenoconazole based on GC-ECD are 0.003 mg/kg for fresh ginseng and 0.007 mg/kg for the other substrates. Concurrent recoveries were 86–113% at the fortification levels of 0.003–1.0 mg/kg.

Persimmon, Japanese was ground with a blender after removing seeds and stalk. These samples were individually packed in polyethylene bags and stored at -20 °C until analysis. Difenoconazole residues were extracted using acetone and then the extract was partitioned with dichloromethane. The residue concentration was determined with GC-ECD. LOQ of difenoconazole was 0.02 mg/kg and concurrent recoveries of the compound were 88–107% at fortification levels of 0.02–2.0 mg/kg.

Table 3 Recovery results of difenoconazole in ginseng and Japanese persimmon

Matrix	Range of fortification, mg/kg	Mean recovery, % ± SD (n=5)
Ginseng	0.003	86 ± 2 ^a , 94 ± 4 ^b
	0.03	105 ± 2, 92 ± 6
	0.2	102 ± 3, 86 ± 6
Dried ginseng	0.007	109 ± 3, 92 ± 5
	0.07	101 ± 3, 90 ± 8
	0.2	108 ± 1, 93 ± 8
Red ginseng	0.007	108 ± 1, 93 ± 3
	0.07	113 ± 2, 96 ± 4
	0.2	108 ± 1
	0.5	100 ± 5
Dried ginseng extract (ethanol)	0.007	97 ± 5, 98 ± 2
	0.07	91 ± 1, 96 ± 5
	1.0	109 ± 3, 102 ± 3
Dried ginseng extract (Water)	0.007	92 ± 5, 100 ± 5
	0.07	101 ± 1, 95 ± 5
	1.0	98 ± 1, 95 ± 2
Red ginseng extract (ethanol)	0.007	97 ± 5, 90 ± 3
	0.07	92 ± 2, 102 ± 7
	0.5	100 ± 2, 97 ± 6
Red ginseng extract (water)	0.007	86 ± 2, 93 ± 6
	0.07	105 ± 2, 94 ± 6
	0.5	102 ± 3, 100 ± 2
Persimmon, Japanese	0.02	107 ± 6, 106 ± 1
	0.2	90 ± 7, 88 ± 4
	1.0	102 ± 3
	2.0	97 ± 6, 104 ± 7

^{a, b} In each case, five replicates were run.

Stability of residues in stored analytical samples

Information provided for the 2007 JMPR indicated that difenoconazole residues were stable at approximately -20 °C for 1 year in some commodity, but for 2 years in most commodities: banana, cotton seed, cotton seed meal, cotton seed oil, lettuce, potatoes, soya beans, tomatoes, wheat forage, wheat grain and wheat straw. In animal tissues and milk, difenoconazole and metabolite CGA 205375 were also stable at or below -18 °C for approximately 10 months. Difenoconazole residues in ginseng and the processed products were stable for 135 days when stored at or below -20 °C (2010 JMPR).

Stability test data for triazole metabolites (T, TA, TAA) were not provided for the Meeting.

Samples from the trials were stored at ca. -15 or -20 °C until analysis of difenoconazole for the following periods: 5 months in citrus fruits and grape, 8 months in apple and pear, 9 months in onions,

tomato and potato, 11 months in peppers, head cabbage and broccoli, 6 months in cucurbits. For analysis of triazole metabolites, the samples were stored for maximum 12 months under the same frozen conditions.

For ginseng and Japanese persimmon, stability was tested by analysing difenoconazole residues in spiked samples in parallel run when residue in field treated sample was analysed. The untreated samples were spiked at the time of sampling of the treated crops. The spiked and trial samples were kept under the same storage condition, at or below -20 °C.

Table 4 Storage stability of difenoconazole in ginseng and Japanese persimmon

Matrix	Fortification level, mg/kg	Days of storage, stored at ca. -20°C	Remaining, % Mean $\pm$ SD, n=5
Ginseng	0.03	17	107 $\pm$ 4
	0.2	24	89 $\pm$ 5
Dried ginseng	0.07	31	104 $\pm$ 1
	0.2	21	102 $\pm$ 4
Red ginseng	0.07	30	112 $\pm$ 2
	0.2	23	99 $\pm$ 1
Dried ginseng ethanol extract	0.07	20	94 $\pm$ 2
	1.0	27	103 $\pm$ 2
Dried ginseng water extract	0.07	10	101 $\pm$ 1
	1.0	28	95 $\pm$ 2
Red ginseng ethanol extract	0.07	4	97 $\pm$ 2
	0.5	24	104 $\pm$ 5
Red ginseng water extract	0.07	28	106 $\pm$ 3
	0.5	18	100 $\pm$ 3
Persimmon, Japanese	0.2	51, 37	107 $\pm$ 8, 95 $\pm$ 5

USE PATTERN

Difenoconazole is a broad-spectrum fungicide used for disease control in various crops. The registered uses on crops which were submitted for evaluation by the 2013 JMPR are summarized in Table 5.

Table 5 Registered uses of difenoconazole on crops submitted for evaluation

Crop	Country	Form., %, w/v	Method	Application					PHI, days
				Rate, kg ai/ha	Rate, kg ai/hL	No.	Interval days	Total/season, kg ai/ha	
Citrus fruits	USA	EC 250	Foliar, G, A	0.09-0.14		(4)	7-21	0.56	0
Pome fruits	USA	EC 250	Foliar, G, A	0.078		(5)	7 – 10 ^a	0.37	14
Persimmon, Japanese	Rep. of Korea	WP 10 w/w	Foliar, G		0.0054	5	10		7
Grapes	USA	EC 250	Foliar, G, A	0.09-0.13		(4)	10-21 ^a	0.52	7
Bulb vegetables (onion bulb, garlic, shallot)	USA	EC 250	Foliar, G, A, C	0.09-0.13		(4)	7-10 ^a	0.52	7
Bulb vegetables (spring onion)	USA	EC 250	Foliar, G, A, C	0.09-0.13		(3)	7-10 ^a	0.38	7
Brassica (Cole) leafy vegetables (head cabbage, broccoli, Brussels sprouts)	USA	EC 250	Foliar, G, A, C	0.09-0.13		(4)	7-10 ^a	0.52	1
Fruiting vegetables (melons, cucumber, summer squash)	USA	EC 250	Foliar, G, A, C	0.09-0.13		(4)	7-10 ^a	0.52	0
Fruiting vegetables (tomato, peppers)	USA	EC 250	Foliar, G, A, C	0.078-0.13		(4)	7-14 ^a	0.52	0
Potato	USA	EC 250	Foliar,	0.078-		(4)	7-14 ^a	0.52	14

Crop	Country	Form., %, w/v	Method	Application					PHI, days
				Rate, kg ai/ha	Rate, kg ai/hL	No.	Interval days	Total/season, kg ai/ha	
			G, A, C	0.13					
Potato	USA	FS 360	Post-harvest: in line aq. spray	3.5 g ai/t		1			
Ginseng	Rep. of Korea	SC 11.3 w/w	Foliar, G		0.0030	4	10		7
	Rep. of Korea	SC 10 w/w	Foliar, G		0.0054	5	10		14

For only citrus fruits, there is a recommendation for use of adjuvant in label of EC 250 formulation. For grapes, bulb vegetables, brassica vegetables, fruiting vegetables and potato (for pre-harvest treatment), there is a recommendation for use of adjuvant in the label of SC formulation 11.4%, w/w. In pome fruits, there is no recommendation for adjuvant in any labels.

In the USA, EC 250 formulation is registered for grapes except Concord, Concord seedless and Thomcord.

Potatoes: flowable concentrate for seed treatment (36%, w/v) was used as a post-harvest spray for the control of certain post-harvest rots caused by Silver scurf (*Helminthosporum solani*) and *Fusarium* species; tubers should be tumbling as they are treated; use T-jet controlled droplet applicator^a (CDA) or similar application system; do not use on seed potatoes or on other seed pieces.

^a No more than 2 sequential applications before alternating to another fungicide with a different mode of action

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised field trials for difenoconazole on the following crops.

Crop group	Commodity	Table No.
Citrus fruits	Orange, mandarin, tangerine	6
	Grapefruit	7
	Lemon	8
Pome fruits	Apple	9
	Pear	10
	Persimmon, Japanese	11
Berries and other small fruits	Grapes	12
Bulb vegetables	Onion, Bulb	13
	Spring onion	14
Brassica (cole or cabbage) vegetables, Head cabbages,	Cabbages, Head	15
Flowerhead cabbages	Broccoli	16
Fruiting vegetables, Cucurbits	Melons (Cantaloupe)	17
	Gherkin	18
	Squash, Summer	19
Fruiting vegetables, other than Cucurbits	Tomato	20
	Peppers, Sweet and Chili	21
Root and tuber vegetables	Potato	22
	Ginseng	23

Most residue trials were carried out in the USA according to GLP principles. Some trials had not been performed in compliance with GLP principles.

In handling duplicate samples, if two field samples were taken or results of two replicate plots were submitted, the mean value was calculated. From two trials carried out side-by-side, the higher residue was chosen.

Residue information from the USA trials included analytical results for triazole metabolites, 1, 2, 4-triazole, triazole alanine and triazole acetic acid. Triazole alanine was detected in field treated samples of most crops, up to maximum 1.5 mg/kg in head cabbage. In control samples, magnitudes of concentration of triazole alanine were nearly equivalent or less than residue concentrations determined in field treated samples.

Citrus fruits

Residue trials on citrus fruits were conducted in California, Florida and Texas in 2007 (oranges—nine trials; mandarins—two trials; tangerines one trial; grapefruits—six trials and lemons—five trials). Difenoconazole EC 250 formulation (250 g/L) was applied to citrus fruits as foliar applications four times at a rate of 0.14–0.15 kg ai/ha with 7 day intervals. Application volumes were between 95 and 935 L/ha for the concentrate sprays and 945 and 3742 L/ha for the dilute cover sprays, including NIS + Silwet or Kinetic non-ionic surfactant (0.125%, v/v) in the spray solution.

Two replicate samples of mature fruit were collected on the last day of application. In the decline trials, samples were collected at 0, 3, 7 and 10 days after last application (DLA).

Table 6 Difenoconazole and metabolite residues in orange, mandarin and tangerine from supervised trials performed in the USA with EC 250 (Report No.: T004712-06)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA ^a	TAA
GAP, USA	0.14				0.56	0					
Orange											
De Leon Springs, FL 2007 (Valencia) E13FL078043	0.14- 0.15	4	100	89-91	0.57	0	0.12 0.16	<u>0.14</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Mt. Dora, FL 2007 (Valencia) E13FL078044	0.14	4	700	87-89	0.56	0	0.17 0.12	<u>0.15</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Ft. Pierce, FL 2007 (Hamlin) E13FL078045	0.14	4	3300	89-91	0.56	0	0.28 0.23	<u>0.26</u>	< 0.01 < 0.01	< 0.01 0.01 (0.02)	< 0.01 < 0.01
De Leon Springs, FL 2007 (Hamlin) E13FL078046	0.14	4	700	85-89	0.56	0	0.23 0.23	<u>0.23</u>	nd nd	< 0.01 < 0.01	nd < 0.01
						3	0.16		nd	< 0.01	nd
						7	0.16		nd	< 0.01 (0.03)	nd
						10	0.17		nd	< 0.01	< 0.01
Oviedo, FL 2007 (Valencia) E15FL078041	0.14	4	2300	83	0.56	0	0.13 0.17	<u>0.15</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
	0.70- 0.71	4	2300	83	2.8	0	1.3 1.0	1.2	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Eustis, FL 2007	0.14	4	1400	83	0.56	0	0.15	<u>0.13</u>	< 0.01	< 0.01	< 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA ^a	TAA
(Rhode Red) E19FL078047							0.10		< 0.01	< 0.01	< 0.01
Monte Alto, TX 2007 (Marrs) W08TX078053	0.14	4	700	78-83	0.56	0	0.07 0.12	0.095	< 0.01 < 0.01	0.01 0.01 (0.04)	< 0.01 < 0.01
	0.14	4	2300	78-83	0.56	0	0.09 0.13	<u>0.11</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Orland, CA 2007 (Navel) W23CA078055	0.14	4	1400		0.56	0	0.13 0.12	<u>0.13</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Madera, CA 2007 (Washington navels) W29CA078056	0.14	4	500	89	0.56	0	0.25 0.16	0.21	nd nd	< 0.01 < 0.01	< 0.01 nd
						3	<u>0.37</u>		nd	< 0.01	< 0.01
						7	0.34			< 0.01	< 0.01
						10	0.06		nd	< 0.01	< 0.01
Mandarin											
De Leon Springs, FL 2007 (Sunburst) E13FL078042	0.14	4	3300	85-89	0.56	0	0.16 0.17	<u>0.17</u>	< 0.01 < 0.01	0.02 0.02 (0.02)	< 0.01 < 0.01
Sanger, CA 2007 (Satsuma) W30CA078059	0.14	4	700	79	0.56	0	0.30 0.29	0.30	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
	0.14	4	1900	79	0.56	0	0.46 0.30	<u>0.38</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Tangerine											
Umatilla, FL 2007 (Sunburst) E19FL078048	0.14	4	700	83	0.56	0	0.32 0.65	<u>0.49</u>	< 0.01 < 0.01	0.01 0.01 (0.01)	< 0.01 < 0.01

^a (n): residue concentration in control sample

nd: non-detected.

Table 7 Difenoconazole and metabolite residues in grapefruit from supervised trials performed in the USA with EC 250 (Report No.: T004712-06)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA ^a	TAA
GAP, USA	0.14				0.56	0					
Vero Beach, FL 2007 (Star Ruby) E13FL078050	0.14	4	700	87	0.56	0	0.12 0.13	0.13	< 0.01 < 0.01	0.02 0.02 (0.03)	< 0.01 < 0.01
	0.14	4	3300	87	0.56	0	0.24 0.11	<u>0.18</u>	< 0.01 < 0.01	0.03 0.03 (0.03)	< 0.01 < 0.01
Vero Beach, FL 2007 (Marsh) E13FL078051	0.14	4	100	85-87	0.56	0	0.15 0.20	<u>0.18</u>	< 0.01 < 0.01	0.03 0.03 (0.05)	< 0.01 < 0.01
Eustis, FL 2007 (Flame) E19FL078049	0.14	4	1400	83	0.56	0	0.07 0.08	<u>0.075</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Alamo, TX 2007 (Ruby Red) W08TX078054	0.14	4	700	78-83	0.56	0	0.14 0.11	<u>0.13</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA ^a	TAA
	0.14- 0.15	4	2300	78-83	0.57	0	0.08 0.09	0.085	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Porterville, CA 2007 (Mellogold) W32CA078057	0.14	4	800	79-89	0.56	0	0.08 0.10	<u>0.09</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Elderwood, CA 2007 (Duncan) W30CA078060	0.14	4	1900	85	0.56	0	0.13 0.09	<u>0.11</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01

^a (n): residue concentration in control sample

Table 8 Difenoconazole and metabolite residues in lemon from supervised trials performed in the USA with EC 250 (Report No.: T004712-06)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.14				0.56	0					
Ft. Pierce, FL 2007 (Bearris) E13FL078052	0.14- 0.15	4	500	85- 89	0.57	0	0.24 0.17	0.21	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
	0.14	4	2500	85- 89	0.56	0	0.24 0.24	<u>0.24</u>	< 0.01 < 0.01	< 0.01 0.01	< 0.01 < 0.01
Sanger, CA 2007 (Lizbon) W30CA078061	0.14	4	700	79	0.56	0	0.08 0.24	<u>0.16</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Porterville, CA 2007 (Pryor) W32CA078058	0.14	4	1900	81- 89	0.56	0	0.19 0.15	<u>0.17</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Arroyo Grande, CA 2007 (Eureka) W33CA078062	0.14	4	900	88- 89	0.56	0	0.09 0.09	<u>0.09</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Arroyo Grande, CA 2007 (Lisbon) W33CA078063	0.14	4	2100	81	0.56	0	0.18 0.20	<u>0.19</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01

Pome fruits

Apples and pears

Residue trials on apples and pears were conducted in California, Colorado, Idaho, Illinois, Michigan, New York, Oregon, Pennsylvania, Virginia and Washington in 2004. Difenoconazole EC 250 formulation was applied to apples (13 trials) and pears (six trials) as a foliar application five times at a rate of 0.072–0.081 kg ai/ha with 7 day intervals. Application volumes were between 94 and 935 L/ha for the concentrate sprays and between 945 and 3742 L/ha for the dilute cover sprays, non-ionic surfactant (0.125%, v/v) was included in the spray solutions. There is no recommendation for adjuvant for pome fruits in any label of difenoconazole in the USA.

After the last application, duplicate samples of mature fruit were collected 12–16 days for apples and 13–15 days for pears. In the decline trials, samples were collected at 0, 5, 9 or 10, 14 and 19 days after last application.

Table 9 Difenoconazole and metabolite residues in apple from supervised trials performed in the USA with EC 250 (Report No.:T002884-03)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA ^a	TAA
GAP, USA	0.078				0.37	14					
Champaign, IL 2004 (Honey Crisp) 4A-FR-04-5195	0.072- 0.078	5	400	77	0.37	12	0.29 0.26	<u>0.28</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Hudson, NY 2004 (Indared) 5A-FR-04-5190	0.075- 0.077	5	1100	75-85	0.38	15	0.16 0.09	<u>0.13</u>	< 0.01 < 0.01	0.14 0.13 (0.11)	< 0.01 < 0.01
Hudson, NY 2004 (Indared) 5A-FR-04-5190	0.38- 0.39	5	1100	75-85	1.9	15	0.85 0.52	0.69	< 0.01 < 0.01	0.15 0.19 (0.11)	< 0.01 < 0.01
Hudson, NY 2004 (McIntosh) 5A-FR-04-5191	0.076- 0.078	5	100	74-88	0.38	14	0.07 0.06	<u>0.07</u>	< 0.01 < 0.01	0.09 0.08	< 0.01 < 0.01
Hereford, PA 2004 (Red Delicious) EB-FR-04-5192	0.076- 0.078	5	500	81	0.39	14	0.35 0.59	<u>0.47</u>	< 0.01 < 0.01	0.02 0.03 (0.03)	< 0.01 < 0.01
	0.076- 0.079	5	2300	81	0.39	14	0.23 0.16	0.20	< 0.01 < 0.01	0.02 0.03 (0.03)	< 0.01 < 0.01
Covesville, VA 2004 (Yellow Delicious) EB-FR-04-5193	0.078- 0.080	5	700	75-85	0.40	14	0.24 0.17	<u>0.21</u>	< 0.01 < 0.01	0.02 0.02 (0.05)	< 0.01 < 0.01
	0.076- 0.077	5	2200	75-85	0.38	14	0.09 0.11	0.10	< 0.01 < 0.01	0.02 0.02 (0.05)	< 0.01 < 0.01
Conklin, MI 2004 (Golden Delicious) NL-FR-04-5194	0.076- 0.078	5	1700		0.38	0	0.32 0.26	0.29	< 0.01 < 0.01	0.12 0.16 (0.10)	< 0.01 < 0.01
						5	0.30 0.24	0.27	< 0.01 < 0.01	0.12 0.14 (0.10)	< 0.01 < 0.01
						9	0.31 0.29	0.30	< 0.01 < 0.01	0.10 0.14 (0.08)	< 0.01 < 0.01
						14	0.30 0.38	0.34	< 0.01 < 0.01	0.08 0.12 (0.07)	< 0.01 < 0.01
						19	0.37 0.38	<u>0.38</u>	< 0.01 < 0.01	0.10 0.11 (0.06)	< 0.01 < 0.01
Orchard city, CO 2004 (Red Delicious) NM-FR-04-5196	0.077- 0.080	5	800		0.39	14	0.06 0.10	<u>0.08</u>	< 0.01 < 0.01	0.04 0.03 (0.04)	< 0.01 < 0.01
	0.076- 0.078	5	1500		0.39	14	0.08 0.08	0.08	< 0.01 < 0.01	0.05 0.07 (0.04)	< 0.01 < 0.01
Madera, CA 2004 (Fuji) WC-FR-04-5197	0.077	5	1700		0.38	0	0.46 0.38	0.42	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA ^a	TAA
						5	0.41 0.41	0.41	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						10	0.26 0.17	0.22	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						14	0.47 0.30	<u>0.39</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						19	0.19 0.27	0.23	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Lakeport, CA 2004 (Granny Smith) WD-FR-04-5198	0.076- 0.078	5	500	77-79	0.38	16	0.06 0.07	<u>0.07</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Ephrata, WA 2004 (Red Delicious) WF-FR-04-5199	0.076- 0.078	5	1900	77-79	0.38	14	0.34 0.16	<u>0.25</u>	< 0.01 < 0.01	0.02 0.02 (≤ 0.01)	< 0.01 < 0.01
	0.39	5	1900	77-79	1.9	14	1.5 1.2	1.4	< 0.01 < 0.01	0.02 0.03 (≤ 0.01)	< 0.01 < 0.01
Ephrata, WA 2004 (Braeburn) WF-FR-04-5200	0.077	5	500	75-88	0.38	14	0.39 0.35	<u>0.37</u>	< 0.01 < 0.01	0.05 0.03 (0.04)	< 0.01 < 0.01
	0.077	5	2800	75-88	0.38	14	0.29 0.27	0.28	< 0.01 < 0.01	0.03 0.03 (0.04)	< 0.01 < 0.01
Hood River, OR 2004 (Jonagold) WF-FR-04-5201	0.076- 0.078	5	600		0.38	14	0.02 0.02	<u>0.02</u>	< 0.01 < 0.01	0.03 0.02 (0.04)	< 0.01 < 0.01
Parma, ID 2004 (Rome) WG-FR-04-5202	0.076- 0.081	5	2200		0.40	14	0.16 0.15	<u>0.16</u>	< 0.01 < 0.01	0.02 0.02 (0.02)	< 0.01 < 0.01

^a (n): residue concentration in control sample

Table 10 Difenoconazole and metabolite residues in pear from supervised trials performed in the USA with EC 250 (Report No.:T002884-03)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.078				0.37	14					
Orefield, PA 2004 (Bartlett) EB-FR-04-5203	0.077- 0.078	5	100		0.39	14	0.08 0.15	<u>0.12</u>	< 0.01 < 0.01	0.03 0.02 (0.01)	< 0.01 < 0.01
	0.077- 0.079		2700		0.39	14	0.07 0.08	0.08	< 0.01 < 0.01	0.03 0.03 (0.01)	< 0.01 < 0.01
Live Oak, CA 2004 (Bartlett) WD-FR-04-5204	0.077	5	1000		0.38	0	0.43 0.45	0.44	< 0.01 < 0.01	0.02 0.01 (≤ 0.01)	< 0.01 < 0.01
						5	0.31 0.28	0.30	< 0.01 < 0.01	0.02 0.02 (≤ 0.01)	< 0.01 < 0.01
						10	0.17 0.18	0.18	< 0.01 < 0.01	0.02 0.02 (≤ 0.01)	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
						14	0.15 < 0.01	0.08	< 0.01 < 0.01	0.03 0.02 (≤ 0.01)	< 0.01 < 0.01
						19	0.16 0.12	<u>0.14</u>	< 0.01 < 0.01	0.02 0.03 (≤ 0.01)	< 0.01 < 0.01
Ukiah, CA 2004 (Bartlett) WD-FR-04-5205	0.075- 0.076	5	500	75-79	0.38	15	0.07 0.07	<u>0.07</u>	< 0.01 < 0.01	0.02 0.02 (≤ 0.01)	< 0.01 < 0.01
Buena, WA 2004 (Bartlett) WF-FR-04-5206	0.077- 0.081	5	800		0.39	14	0.23 0.30	<u>0.27</u>	< 0.01 < 0.01	0.02 0.02 (≤ 0.01)	< 0.01 < 0.01
Buena, WA 2004 (Bartlett) WF-FR-04-5207	0.077- 0.080	5	1200		0.39	14	0.19 0.19	<u>0.19</u>	< 0.01 < 0.01	0.01 < 0.01 (≤ 0.01)	< 0.01 < 0.01
Hood River, OR 2004 (Red Clapp) WF-FR-04-5208	0.075- 0.078	5	600		0.38	13	0.08 0.08	0.08	< 0.01 < 0.01	0.04 0.03 (0.04)	< 0.01 < 0.01
	0.076- 0.079		1700		0.39		0.11 0.12	<u>0.12</u>	< 0.01 < 0.01	0.03 0.03 (0.04)	< 0.01 < 0.01

Persimmon, Japanese

Six residue trials were carried out on Japanese persimmon in the Republic of Korea in 2011 (3 trials) and 2012 (3 trials). The trial plots received five foliar applications of WP 10 formulation (% w/w) at a rate of 0.0054 kg ai/hL with 10 day intervals. In all trials, persimmon was harvested 0, 1, 3, 7, 14 and 21 days following the final application. The seeds and stalk of the fruit were removed prior to grinding, the samples were packed in plastic bags and stored at -20°C. Residue analyses were performed within 51 days after sampling.

In three trials conducted in 2011, five applications were made on the same dates. Likewise, in three trials of 2012, dates of five applications were the same. All six trials were performed with the same variety on different farms located within approximately 10-20 km, using the same hand sprayer with one head nozzle. All residue analyses were made in one laboratory, with four analytical replicates by the same analytical method.

Table 11 Difenoconazole residues in Japanese persimmon treated with WP 10 formulation in the Republic of Korea

Location Year (Variety)	Application ^b			PHI, days	Residue, mg/kg	Study No.
	kg ai/hL	n.	Interval days			
GAP in Rep. of Korea	0.0054	5	10	7		
Gimhae, Gyeongnam 2011 (Fuyu) ^a	0.0054	5	10	0	0.56	S-11-04-2-PSR-999-0-H
				1	0.50	
				3	0.47	
				7	<u>0.37</u>	
				14	0.23	
				21	0.23	
Changwon, Gyeongnam 2011 (Fuyu) ^a	0.0054	5	10	0	0.53	S-11-04-2-PSR-999-0-H
				1	0.52	
				3	0.45	

Location Year (Variety)	Application ^b			PHI, days	Residue, mg/kg	Study No.
	kg ai/hL	n.	Interval days			
				7	0.36	
				14	0.31	
				21	0.28	
Changwon, Gyeongnam 2011(Fuyu) ^a	0.0054	5	10	0	0.53	S-11-04-2-PSR-999-0-H
				1	0.45	
				3	0.40	
				7	0.37	
				14	0.26	
				21	0.22	
Changwon, Gyeongnam 2012 (Fuyu) ^b	0.0054	5	10	0	0.46	S-12-2-PSR-997-0-H
				1	0.45	
				3	0.43	
				7	0.43	
				14	0.35	
				21	0.18	
Changwon, Gyeongnam 2012 (Fuyu) ^b	0.0054	5	10	0	0.45	S-12-2-PSR-997-0-H
				1	0.42	
				3	0.41	
				7	0.39	
				14	0.32	
				21	0.14	
Changwon, Gyeongnam 2012 (Fuyu) ^b	0.0054	5	10	0	0.48	S-12-2-PSR-997-0-H
				1	0.46	
				3	0.41	
				7	0.40	
				14	0.33	
				21	0.19	

WP 10 (% w/w) formulation was applied.

^{a, b} All trials were conducted with the same variety on different farms located within approximately 10-20 km. Three trials of each year were performed at the same dates of application, thus the three trials were not considered as independent.

Berries and other small fruits

Grapes

Twelve residue trials on grapes were conducted in California, New York, Oregon, Pennsylvania and Washington in 2007. Difenoconazole EC 250 formulation was applied to grapes as a foliar application four times at a rate of 0.13 kg ai/ha with 7 day intervals. Treatments were made in varying post foliar spray volumes ranging from about 93 to 930 L/ha, using NIS + Silwet or Kinetic non-ionic surfactant (0.125%, v/v).

Duplicate samples of mature grapes were collected 6–7 days after the last application. In the decline trials, samples were collected at 0, 3, 5, 7 and 14 days after last application.

Table 12 Difenoconazole and metabolite residues in grapes from supervised trials performed in the USA with EC 250 (Report No.: T004711-06)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.13				0.52	7					
Dundee, NY 2007 (Concord) ^a E03NY078021	0.13	4	900	81-89	0.52	7	1.2 1.2	1.2	< 0.01 < 0.01	0.04 0.03 (0.05)	0.02 0.01
	0.39	4	900	81-89	1.6	7	2.3 3.1	2.7	< 0.01 < 0.01	0.06 0.07	0.02 0.01
Orefield, PA 2007 (Fredonia) E04PA078022	0.13	4	600	81	0.52	7	0.37 0.43	<u>0.40</u>	< 0.01 < 0.01	0.04 0.04 (0.05)	0.02 0.02
	0.39	4	700	79-89	1.6	7	0.40 0.37	0.39	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
	0.65	4	700	79-89	2.6	7	1.2 0.57	0.86	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Granger, WA 2007 (Chardonnay) W19WA078031	0.13	4	900		0.52	6	0.45 0.83	<u>0.64</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Hillsboro, OR 2007 (Pinot Noir) W21OR078032	0.13	4	500	81-89	0.52	7	0.52 0.82	<u>0.67</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Orland, CA 2007 (Centurion) W23CA078029	0.13	4	900		0.52	7	0.29 0.08	<u>0.19</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Arbuckle, CA 2007 (Arbuckle) W23CA078030	0.13	4	900		0.52	7	0.22 0.23	<u>0.23</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Aromas, CA 2007 (Tokay) W27CA078028	0.13	4	200		0.52	0	3.12		< 0.01	< 0.01	< 0.01
						3	0.02		< 0.01	< 0.01	< 0.01
						5	1.9		< 0.01	< 0.01	< 0.01
						7	1.8 1.2	<u>1.5</u>	< 0.01 < 0.01	0.02 < 0.01 ($\leq$ 0.01)	0.02 < 0.01 ($\leq$ 0.01)
						14	1.2		< 0.01	0.02 ($\leq$ 0.01)	0.02 ($\leq$ 0.01)
Kerman, CA 2007 (Thompson Seedless) W28CA078027	0.13	4	900		0.52	7	1.7 0.92	<u>1.3</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Madera, CA 2007 (Thompson Seedless) W29CA078025 ^b	0.13	4	700	77-89	0.52	0	0.74		< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						3	0.76		< 0.01	< 0.01	< 0.01
						5	0.51		< 0.01	< 0.01	< 0.01
						7	0.65 0.65	<u>0.65</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						14	0.60		< 0.01	< 0.01	< 0.01
Madera, CA 2007	0.13	4	900	81-88	0.52	7	0.40	0.29	< 0.01	< 0.01	< 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
(Thompson Seedless) W30CA078024 ^b							0.18		< 0.01	< 0.01	< 0.01
Rolinda, CA 2007 (Thompson Seedless) W30CA078026	0.13	4	90	81-88	0.52	7	0.08 0.26	<u>0.17</u>	< 0.01 < 0.01	0.02 0.02	< 0.01 < 0.01
Poplar, CA 2007 (Thompson Seedless) W32CA078023	0.13	4	700	79-89	0.52	7	0.09 0.12	<u>0.11</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01

^a The trial was not selected as use of EC 250 formulation is not permitted for Concord variety.

^b The trials were conducted with the same variety at the same dates of application under the same weather conditions, using different soil and irrigation type (flood and drip) and different sprayer (airblast, tractor). These trials were not considered independent.

Bulb onions

Onion, Bulb

Eight residue trials on bulb onion were conducted in California, Colorado, Idaho, Illinois, New York, Texas and Washington in 2006. Difenoconazole EC 250 was applied to bulb onions as broadcast foliar spray applications four times at a rate of 0.13 kg ai/ha with 7 day intervals. Treatments were made in varying spray volumes ranging from about 60 to 300 L/ha application, using NIS + Silwet or Kinetic non-ionic surfactant (0.1%, v/v).

Duplicate samples of onion bulbs were collected 7 days after the last application. In the decline trials, samples were collected at 0, 3, 5, 7 and 9 days after last application.

Table 13 Difenoconazole and metabolite residues in bulb onion from supervised trials performed in the USA with EC 250 (Report No.: T020410-04)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.13				0.52	7					
Champaign, IL 2006 (Not provided) 4A-FR-06-7005	0.13- 0.14	4	100	45-47	0.53	7	< 0.01 < 0.01	<u>< 0.01</u>	< 0.01 < 0.01	0.09 0.09 (0.04)	< 0.01 < 0.01
Hudson, NY 2006 (Stuttgarter) 5A-FR-06-7004	0.13	4	100	45-48	0.52	0	0.03 < 0.01		< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						3	< 0.01 < 0.01		< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						5	0.03 < 0.01		< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						7	< 0.01 0.02	<u>0.02</u>	< 0.01 < 0.01	0.48 0.43 (0.56)	< 0.01 < 0.01
						9	< 0.01 < 0.01		< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Ault, CO 2006	0.13	4	200		0.52	7	< 0.01	<u>0.02</u>	< 0.01	0.02	< 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
(Sequoia) NM-FR-06-7007							0.02		< 0.01	0.02 (≤ 0.01)	< 0.01
Uvalde, TX 2006 (Cimarron type) SA-FR-06-7006	0.13	4	100		0.52	7	0.02 0.04	<u>0.03</u>	< 0.01 < 0.01	0.02 0.02 (≤ 0.01)	< 0.01 < 0.01
Terra Bella, CA 2006 (Stockton red) WC-FR-06-7008	0.13	4	300	77-79	0.52	7	0.05 0.09	<u>0.07</u>	< 0.01 < 0.01	0.04 0.04 (≤ 0.01)	< 0.01 < 0.01
Hughson, CA 2006 (White sweet Spanish) WD-FR-06-7009	0.13	4	300	73-77	0.52	8	< 0.01 < 0.01	≤ 0.01	< 0.01 < 0.01	0.03 0.04 (0.02)	< 0.01 < 0.01
Burlington, WA 2006 (Walla Sweet) WF-FR-06-7011	0.13	4	200	71-79	0.52	7	< 0.01 0.01	<u>0.01</u>	< 0.01 < 0.01	0.10 0.10 (0.07)	< 0.01 < 0.01
Parma, ID 2006 (Vaquero) WG-FR-06-7010	0.13	4	300		0.52	7	< 0.01 < 0.01	≤ 0.01	< 0.01 < 0.01	< 0.01 0.01 (≤ 0.01)	< 0.01 < 0.01

Spring onion

Three residue trials on spring onion were conducted in California, Georgia and Texas in 2006. Difenoconazole EC 250 was applied to spring onions as foliar broadcast spray applications three times at rates of 0.13 kg ai/ha with 7 day intervals. Treatments were made in varying post foliar spray volumes ranging from about 160 to 300 L/ha application, using NIS + Silwet or Kinetic non-ionic surfactant (0.1%, v/v).

Duplicate samples of onions (whole plant) were collected 6 or 7 days after the last application. In the decline trial, samples were collected at 0, 3, 5, 7 and 9 days after last application.

Table 14 Difenoconazole and metabolite residues in spring onion from supervised trials performed in the USA with EC 250 (Report No.: T020410-04)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg ^a				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.13				0.38	7					
Uvalde, TX 2006 (Cimarron type) SA-FR-06-7002	0.13	3	200		0.39	6	2.9 2.7	<u>2.8</u>	< 0.01 < 0.01	0.01 0.02 (≤ 0.01)	< 0.01 < 0.01
Sycamore, GA 2006 (Yellow Grannex "Georgia Sweet") SI-FR-06-7001	0.13	3	300	47	0.39	7	2.5 2.0	<u>2.3</u>	< 0.01 < 0.01	0.02 0.03 (0.01)	< 0.01 < 0.01
Sanger, CA 2006 (Southport White 404) WC-FR-06-7003	0.13	3	300	42-49	0.39	0	3.8 3.7		< 0.01 < 0.01	0.05 0.05	< 0.01 0.01
						3	3.5 3.3		< 0.01 < 0.01	0.05 0.06	< 0.01 0.01
						5	2.9 2.6		< 0.01 < 0.01	0.07 0.06	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg ^a				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
						7	4.9 2.7	<u>3.8</u>	< 0.01 < 0.01	0.06 0.07 (0.09)	0.01 < 0.01 (< 0.01)
						9	3.6 2.3		< 0.01 < 0.01	0.06 0.07	0.01 0.01

^a Portion analysed is whole plant.

Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead brassicas

Cabbages, Head

Six residue trials on head cabbage were conducted in California, Florida, North Carolina, New York, Texas and Wisconsin in 2006. Difenoconazole EC 250 was applied to head cabbage as foliar broadcast spray applications four times at a rate of 0.12-0.13 kg ai/ha with 7 day intervals. Treatments were made with varying spray volumes ranging from about 19 to 190 L/ha of, using NIS + Silwet or Kinetic non-ionic surfactant (0.125%, v/v).

Duplicate samples of mature cabbages were collected 1 and 7 days after the last application. In the decline trials, samples were collected at 0, 1, 3, 5, 7 and 9 days after last application.

Table 15 Difenoconazole and metabolite residues in head cabbage from supervised trials performed in the USA with EC 250 (Report No.: T020412-04)

Location Year (Variety) Trial No.	Application					PHI, days	Residue ^a , mg/kg				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.13				0.52	1					
Hudson, NY 2006 (Blue Dynasty) 5A-FR-06-7056	0.13	4	20	44-49	0.52	1	0.06 0.11	<u>0.09</u>	< 0.01 < 0.01	1.5 ^b 0.79 (0.98)	0.012 0.012 (0.011)
							< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	1.2 ^b 0.97 (0.76)	0.012 0.012 (< 0.01)
							1.0 1.2	1.1	< 0.01 < 0.01	0.71 0.49 (0.64)	0.0118 0.016 (0.020)
						7	< 0.01 0.02	0.02	< 0.01 < 0.01	0.92 0.58 (0.87)	< 0.01 < 0.01
							< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.96 0.70 (0.96)	< 0.01 < 0.01
							0.23 0.19	0.21	< 0.01 < 0.01	0.58 0.36 (0.51)	0.016 < 0.01 (0.012)
Seven Springs, NC 2006 (Almanac) SJ-FR-06-7057	0.13	4	200	41-47	0.52	1	0.90 0.97	<u>0.94</u>	< 0.01 < 0.01	0.09 0.08 (0.01)	< 0.01 < 0.01
							< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.10 0.11 (0.01)	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue ^a , mg/kg				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
							2.9 3.5	3.2	<0.01 <0.01	0.06 0.06 (≤ 0.01)	<0.01 <0.01
						7	0.08 0.34	0.21	<0.01 <0.01	0.16 0.15 (0.02)	<0.01 <0.01
							<0.01 <0.01	<0.01	<0.01 <0.01	0.13 0.17 (0.01)	<0.01 <0.01
							1.7 2.4	2.1	<0.01 <0.01	0.05 0.05 (≤ 0.01)	<0.01 <0.01
Vero Beach, FL 2006 (Bravo) VC-FR-06-7058	0.12- 0.13	4	200	43-49	0.50	0	0.82 1.5	1.7	<0.01 <0.01	0.08 0.06 (≤ 0.01)	0.05 <0.01 (≤ 0.01)
							0.01 <0.01	0.01	<0.01 <0.01	0.09 0.11 (≤ 0.01)	<0.01 <0.01
							1.5 2.6	2.1	<0.01 <0.01	0.04 0.04 (≤ 0.01)	<0.01 <0.01
						1	0.96 1.6	1.3	<0.01 <0.01	0.06 0.09 (≤ 0.01)	<0.01 <0.01
							0.06 0.11	0.09	<0.01 <0.01	0.07 0.10 (≤ 0.01)	<0.01 <0.01
							2.5 3.0	2.8	<0.01 <0.01	0.04 0.03 (≤ 0.01)	0.011 0.010 (≤ 0.01)
						3	0.80 0.56	0.68	<0.01 <0.01	0.08 0.09 (≤ 0.01)	<0.01 <0.01
							0.03 0.08	0.06	<0.01 <0.01	0.09 0.10 (≤ 0.01)	<0.01 <0.01
							2.4 3.3	2.9	<0.01 <0.01	0.03 0.02 (≤ 0.01)	<0.01 <0.01
						5	0.16 0.55	0.36	<0.01 <0.01	0.10 0.10 (≤ 0.01)	<0.01 <0.01
							0.05 <0.01	0.03	<0.01 <0.01	0.11 0.08 (0.01)	<0.01 <0.01
							1.6 1.9	1.8	<0.01 <0.01	0.04 0.05 (≤ 0.01)	<0.01 <0.01
						7	0.11 0.23	0.17	<0.01 <0.01	0.07 0.11 (≤ 0.01)	<0.01 <0.01
							<0.01 <0.01	<0.01	<0.01 <0.01	0.09 0.11 (0.01)	<0.01 <0.01
							0.92 1.01	0.97	<0.01 <0.01	0.04 0.03 (≤ 0.01)	<0.01 <0.01
						9	0.18 0.15	0.17	<0.01 <0.01	0.08 0.15	<0.01 <0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue ^a , mg/kg				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
										(< 0.01)	
							< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.11 0.19 (< 0.01)	< 0.01 < 0.01
							0.88 0.67	0.78	< 0.01 < 0.01	0.08 0.06 (< 0.01)	< 0.01 < 0.01
Delavan, WI 2006 (Vantage Point) NI-FR-06-7059	0.13	4	200		0.52	1	0.28 0.32	0.30	< 0.01 < 0.01	0.04 0.04 (0.02)	< 0.01 < 0.01
							< 0.01 0.01	0.01	< 0.01 < 0.01	0.05 0.04 (0.02)	< 0.01 < 0.01
							1.9 2.7	2.3	< 0.01 < 0.01	0.02 0.02 (< 0.01)	< 0.01 < 0.01
						7	0.12 0.21	0.17	< 0.01 < 0.01	0.04 0.04 (0.02)	< 0.01 < 0.01
							< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.05 0.05 (0.02)	< 0.01 < 0.01
							1.6 1.6	1.6	< 0.01 < 0.01	0.03 0.03 (0.02)	< 0.01 < 0.01
Raymondville, TX 2006 (Copenhagen Market) SA-FR-06-7060	0.13	4	200	46-49	0.52	1	0.25 0.22	0.24	< 0.01 < 0.01	0.02 0.04 (< 0.01)	< 0.01 < 0.01
							0.12 0.02	0.07	< 0.01 < 0.01	0.05 0.03 (< 0.01)	< 0.01 < 0.01
							5.5 4.9	5.2	< 0.01 < 0.01	0.02 0.02 (< 0.01)	0.01 0.01 (< 0.01)
						7	0.38 0.29	0.34	< 0.01 < 0.01	0.04 0.04 (< 0.01)	< 0.01 < 0.01
							0.05 0.15	0.10	< 0.01 < 0.01	0.04 0.05 (< 0.01)	< 0.01 < 0.01
							3.4 4.3	3.9	< 0.01 < 0.01	0.02 0.03 (< 0.01)	0.02 0.02 (< 0.01)
Aromas, CA 2006 (Expresso) WC-FR-06-7061	0.12- 0.13	4	200		0.51	1	0.09 0.82	0.46	< 0.01 < 0.01	0.05 0.06 (0.02)	< 0.01 < 0.01
							0.05 0.03	0.04	< 0.01 < 0.01	0.07 0.05 (0.02)	< 0.01 < 0.01
							2.9 2.7	2.8	< 0.01 < 0.01	0.02 0.03 (< 0.01)	< 0.01 < 0.01
						7	0.16 0.36	0.26	< 0.01 < 0.01	0.07 0.06 (0.01)	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue ^a , mg/kg				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
							0.02 < 0.01	0.02	< 0.01 < 0.01	0.07 0.06 (0.01)	< 0.01 < 0.01
							<i>1.7</i> <i>1.8</i>	<i>1.8</i>	<i>< 0.01</i> <i>< 0.01</i>	<i>0.03</i> <i>0.03</i> (<i>< 0.01</i>)	<i>< 0.01</i> <i>< 0.01</i>

^a Residue concentration for head cabbage with wrapper leaves is indicated with normal letter. For head cabbage without wrapper leaves and wrapper leaves, the residue concentrations are indicated with italic letter and on the dot line, respectively.

^b The LOQ for TA is 0.02 mg/kg for this sample.

Broccoli

Six residue trials on broccoli were conducted in California, Texas and Washington in 2006. Difenoconazole EC 250 was applied to broccoli as foliar broadcast spray applications four times at a rate of 0.13 kg ai/ha with 7 day intervals. Treatments were made with varying spray volumes ranging from about 190 to 380 L/ha, using NIS + Silwet or Kinetic non-ionic surfactant (0.125%, v/v).

Duplicate samples of mature broccoli were collected 1 and 7 days after the last application. In the decline trial, samples were collected at 0, 1, 3, 5, 7 and 9 days after last application.

Table 16 Difenoconazole and metabolite residues in broccoli from supervised trials performed in the USA with EC 250 (Report No.: T020412-04)

Location Year (Variety) Trial No.	Application					PHI, days	Residue ^a , mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.13				0.52	1					
Raymondville, TX 2006 (Southern Comet) SA-FR-06-7050	0.13	4	200	39- 47	0.53	1	0.44 0.26	<u>0.35</u>	< 0.01 < 0.01	0.02 0.03 (<i>< 0.01</i>)	< 0.01 < 0.01
						7	0.13 0.28	0.21	< 0.01 < 0.01	0.03 0.03 (<i>< 0.01</i>)	< 0.01 < 0.01
Sanger, CA WC-FR-06-7051	0.13	4	300	41- 49	0.52	0	0.35 0.60	0.48	< 0.01 < 0.01	0.15 0.24 (0.28)	< 0.01 < 0.01
						1	0.45 0.61	<u>0.53</u>	< 0.01 < 0.01	0.21 0.24 (0.30)	< 0.01 < 0.01
						3	0.44 0.22	0.33	< 0.01 < 0.01	0.23 0.20 (0.21)	< 0.01 < 0.01
						5	0.30 0.51	0.41	< 0.01 < 0.01	0.31 0.21 (0.25)	< 0.01 < 0.01
						7	0.17 0.21	0.19	< 0.01 < 0.01	0.16 0.22 (0.15)	< 0.01 < 0.01
						9	0.22 0.38	0.30	< 0.01 < 0.01	0.21 0.21 (0.25)	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue ^a , mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
Aromas, CA 2006 (Green Belt) WC-FR-06-7052	0.13	4	200		0.52	1	0.33 0.31	<u>0.32</u>	< 0.01 < 0.01	0.18 0.10 (0.04)	< 0.01 < 0.01
						7	0.04 0.02	0.03	< 0.01 < 0.01	0.20 0.11 (0.02)	< 0.01 < 0.01
Nipomo, CA 2006 (Heritage) WC-FR-06-7053	0.13	4	400	41- 45	0.52	1	0.18 0.12	<u>0.15</u>	< 0.01 < 0.01	0.05 0.04 ($\leq$ 0.01)	< 0.01 < 0.01
						7	0.03 0.02	0.03	< 0.01 < 0.01	0.06 0.07 ($\leq$ 0.01)	< 0.01 < 0.01
Mount Vernon, WA 2006 (Laguna F1) WF-FR-06-7055	0.12- 0.13	4	200		0.52	1	0.34 0.39	<u>0.37</u>	< 0.01 < 0.01	0.13 0.11 (0.06)	< 0.01 < 0.01
						7	0.06 0.11	0.09	< 0.01 < 0.01	0.17 0.17 (0.04)	< 0.01 < 0.01
Guadalupe, CA 2006 (Alborada) WC-FR-06-7067	0.13	4	300	43- 49	0.52	1	0.38 0.26	<u>0.32</u>	< 0.01 < 0.01	0.04 0.03 ($\leq$ 0.01)	< 0.01 < 0.01
						7	0.04 0.15	0.10	< 0.01 < 0.01	0.03 0.05 ($\leq$ 0.01)	< 0.01 < 0.01

^a Analysed portion was head and stem of broccoli.

Fruiting vegetables, Cucurbits

Melons

Six residue trials on cantaloupe were conducted in California, Georgia, Illinois and Texas in 2006. Difenoconazole EC 250 was applied to melons as post over the top broadcast spray applications four times at a rate of 0.12–0.13 kg ai/ha with 7 day intervals. Treatments were made in varying spray volumes ranging from about 27 to 290 L/ha, using NIS + Silwet or Kinetic non-ionic surfactant (0.125%, v/v).

Melon (whole fruit) samples were collected 0 and 7 days after the last application. In one trial, samples were taken at PHIs of 4 and 7 days due to excessive rain on 0 day. In the decline trial, samples were collected at 0, 1, 3, 5, 7 and 9 days after last application.

Table 17 Difenoconazole and metabolite residues in melons (cantaloupe) from supervised trials performed in the USA with EC 250 (Report No.: T020413-04)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.13				0.52	0					
Athens, GA 2006 (Edisto 47) SI-FR-06-7081	0.13	4	300	75- 89	0.52	0	0.26 0.12	<u>0.19</u>	< 0.01 < 0.01	0.11 0.10 (0.02)	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
						7	0.09 0.20	0.15	< 0.01 < 0.01	0.12 0.14 (0.02)	< 0.01 < 0.01
Champaign, IL 2006 (Honey Rock) 4A-FR-06-7082	0.12- 0.13	4	30	61- 77	0.52	4	0.04 0.18	0.11	< 0.01 < 0.01	0.06 0.11 (0.03)	< 0.01 < 0.01
						7	0.06 0.12	0.09	< 0.01 < 0.01	0.05 0.07 (0.02)	< 0.01 < 0.01
Raymondville, TX 2006 (Mainstream) SA-FR-06-7083	0.13	4	200	73- 85	0.52	0	0.09 0.05	0.07	< 0.01 < 0.01	0.06 0.05 (< 0.01)	< 0.01 < 0.01
						7	0.12 0.03	<u>0.08</u>	< 0.01 < 0.01	0.06 0.06 (< 0.01)	< 0.01 < 0.01
Hickman, CA 2006 (Hale's Best Jumbo) WD-FR-06-7084	0.13	4	300	71- 79	0.52	0	0.09 0.03	<u>0.06</u>	< 0.01 < 0.01	0.03 0.03 (0.01)	< 0.01 < 0.01
						1	0.05 0.02	0.04	< 0.01 < 0.01	0.04 0.04 (< 0.01)	< 0.01 < 0.01
						3	0.02 0.04	0.03	< 0.01 < 0.01	0.04 0.03 (< 0.01)	< 0.01 < 0.01
						5	0.01 0.03	0.02	< 0.01 < 0.01	0.04 0.04 (0.01)	< 0.01 < 0.01
						7	0.02 0.02	0.02	< 0.01 < 0.01	0.05 0.04 (< 0.01)	< 0.01 < 0.01
						9	< 0.01 0.02	0.02	< 0.01 < 0.01	0.04 0.05 (0.01)	< 0.01 < 0.01
Sanger, CA 2006 (Hale's Best Jumbo) WC-FR-06-7085	0.13	4	100	79- 89	0.52	0	0.26 0.44	<u>0.35</u>	< 0.01 < 0.01	0.08 0.09 (0.09)	< 0.01 < 0.01
						7	0.08 0.02	0.05	< 0.01 < 0.01	0.09 0.09 (0.09)	< 0.01 < 0.01
San Ardo, CA 2006 (Hale's Best Jumbo) WC-FR-06-7092	0.13	4	300	45- 49	0.52	0	0.10 0.13	0.12	< 0.01 < 0.01	0.05 0.07 (0.01)	< 0.01 < 0.01
						7	0.13 0.14	<u>0.14</u>	< 0.01 < 0.01	0.06 0.08 (< 0.01)	< 0.01 < 0.01

Gherkin

Six residue trials on gherkins were carried out in Florida, Georgia, Michigan, North Carolina, Texas and Wisconsin during 2006 and 2007. Difenoconazole EC 250 was applied to gherkins as foliar broadcast spray applications four times at a rate of 0.13 kg ai/ha with 7 day intervals. Treatments were

made in varying spray volumes ranging from about 19 to 290 L/ha application, using NIS + Silwet or Kinetic non-ionic surfactant (0.125%, v/v).

The fruit samples were collected 0 and 7 days after the last application. In the decline trial, samples were collected at 0, 1, 3, 5, 7 and 9 days after last application.

Table 18 Difenoconazole and metabolite residues in gherkin from supervised trials performed in the USA with EC 250 (Report No.: T020413-04)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.13				0.52	0					
Chula, GA 2006 (Daytona) SI-FR-06-7075	0.13	4	200		0.52	0	0.03 0.04	<u>0.04</u>	< 0.01 < 0.01	0.12 0.11 (0.04)	< 0.01 < 0.01
						7	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.14 0.15 (0.03)	< 0.01 < 0.01
Seven Springs, NC 2006 (Ashley) SJ-FR-06-7076	0.13	4	300	21-77	0.52	0	0.20 0.10	<u>0.15</u>	< 0.01 < 0.01	0.21 0.27 (0.11)	< 0.01 < 0.01
						1	0.16 0.09	0.13	< 0.01 < 0.01	0.21 0.22 (0.05)	< 0.01 < 0.01
						3	0.06 0.03	0.05	< 0.01 < 0.01	0.21 0.25 (0.07)	0.01 0.01 (< 0.01)
						5	0.05 < 0.01	0.03	< 0.01 < 0.01	0.24 0.22 (0.04)	0.02 0.02 (< 0.01)
						7	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.22 0.21 (0.04)	0.03 0.02 (< 0.01)
						9	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.22 0.25 (0.05)	0.02 0.03 (< 0.01)
Conklin, MI 2006 (Marketmore 76) NL-FR-06-7078	0.13	4	20		0.52	0	< 0.01 < 0.01	<u>< 0.01</u>	< 0.01 < 0.01	0.19 0.14 (0.02)	< 0.01 < 0.01
						7	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.13 0.17 (0.02)	< 0.01 < 0.01
Devalan, WI 2006 (Marketmore 86) NI-FR-06-7079	0.13	4	200		0.52	0	0.06 0.02	<u>0.04</u>	< 0.01 < 0.01	0.03 0.03 (0.01)	< 0.01 < 0.01
						7	0.01 < 0.01	0.01	< 0.01 < 0.01	0.04 0.05 (0.01)	< 0.01 < 0.01
Raymondville, TX 2006 (Olympian) SA-FR-06-7080	0.13	4	200	71-77	0.52	0	0.04 < 0.01	<u>0.03</u>	< 0.01 < 0.01	0.05 0.05 (0.01)	< 0.01 < 0.01
						7	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.07 0.07 (< 0.01)	< 0.01 < 0.01
Oviedo, FL 2007 (Parks Bush Whooper II) E15-FL-07-8261	0.13	4	300	63-79	0.52	0	0.01 < 0.01	<u>0.01</u>	< 0.01 < 0.01	0.07 0.07 (< 0.01)	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
						7	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.08 0.07 (< 0.01)	< 0.01 < 0.01

Squash, Summer

Five residue trials were conducted on summer squash (courgette) in California, Florida, Illinois, New York and South Carolina) during 2006 and 2007.

Difenoconazole EC 250 was applied to summer squash as post over the top broadcast spray applications four times at a rate of 0.13–0.14 kg ai/ha with 7 day intervals. The spray volumes were about 25–464 L/ha including NIS + Silwet or Kinetic non-ionic surfactant (0.125%, v/v). The fruit samples were collected 0 and 7 days after the last application. In the decline trial, samples were collected at 0, 1, 3, 5, 7 and 9 days after last application.

Table 19 Difenoconazole and metabolite residues in summer squash from supervised trials performed in the USA with EC 250 (Report No.: T020413-04)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.13				0.52	0					
Hudson, NY 2006 (Fortune) 5A-FR-06-7087	0.13	4	100	13-62	0.52	0	< 0.01 < 0.01	<u>< 0.01</u>	< 0.01 < 0.01	0.22 0.25 (0.27)	< 0.01 < 0.01
						7	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.18 0.25 (0.22)	< 0.01 < 0.01
Elko, SC 2006 (Dixie Hybrid) SJ-FR-06-7088	0.13	4	200		0.52	0	0.06 0.06	<u>0.06</u>	< 0.01 < 0.01	0.11 0.10 (0.01)	< 0.01 < 0.01
						7	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.08 0.12 (< 0.01)	< 0.01 < 0.01
Champaign, IL 2006 (unknown) 4A-FR-06-7090	0.13- 0.14	4	30	61-73	0.54	0	0.02 < 0.01	<u>0.02</u>	< 0.01 < 0.01	0.04 0.06 (0.02)	< 0.01 < 0.01
						7	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.04 0.07 (0.02)	< 0.01 < 0.01
Santa Maria, CA 2006 (Ambassador) WC-FR-06-7091	0.13	4	500	73-77	0.52	0	0.06 0.05	<u>0.06</u>	< 0.01 < 0.01	0.02 0.02 (< 0.01)	< 0.01 < 0.01
						7	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.05 0.04 (0.01)	< 0.01 < 0.01
Oviedo, FL 2007 (Park's Crookneck) E15-FL-07-8262	0.13	4	300	63-79	0.52	0	0.06 0.03	<u>0.05</u>	< 0.01 < 0.01	0.06 0.06 (< 0.01)	0.01 0.01 (< 0.01)
						1	< 0.01 0.01		< 0.01	0.11 (0.05)	0.02 (< 0.01)
						3	< 0.01 < 0.01		< 0.01	0.06 (0.01)	0.01 (< 0.01)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
						5	< 0.01 < 0.01		< 0.01	0.05 (< 0.01)	0.01 (< 0.01)
						7	< 0.01 < 0.01		< 0.01 < 0.01	0.05 0.04 (0.01)	0.01 0.01 (< 0.01)
						9	< 0.01 < 0.01		< 0.01	0.05 (< 0.01)	0.01 (< 0.01)

Fruiting vegetables, other than Cucurbits

Tomato

Eleven residue trials were carried out on tomato in California, Florida, New York, Ohio, and South Carolina in 2004.

Difenoconazole EC 250 was applied to tomatoes as foliar broadcast spray four times at a rate of 0.12–0.13 kg ai/ha. The intervals between applications were 7 days and all treatments were made at spray volumes ranging from about 19 to 334 L/ha, using non-ionic surfactant (0.125%, v/v). Fruit samples were collected on the last day of application, further, 6–8 days after the last application. In the decline trial, samples were collected at 0, 1, 4, 7 and 9 days after last application.

Table 20 Difenoconazole and metabolite residues in tomato from supervised trials performed in the USA with EC 250 (Report No.: T003262-03)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.13				0.52	0					
Hudson, NY 2004 (Mountain Crest) 5A-FR-04-5215	0.13	4	20	65-81	0.52	0	0.01 0.01	<u>0.01</u>	< 0.01 < 0.01	0.21 0.13 (0.19)	< 0.01 < 0.01
						8	< 0.01 < 0.01	< 0.01	< 0.01 < 0.01	0.21 0.16 (0.18)	< 0.01 < 0.01
Elko, SC 2004 (Celebrity) SJ-FR-04-5216	0.13	4	300		0.52	0	0.26 0.25	<u>0.26</u>	< 0.01 < 0.01	0.03 0.02 (0.01)	< 0.01 < 0.01
						8	0.16 0.20	0.18	< 0.01 < 0.01	0.02 0.02 (< 0.01)	< 0.01 < 0.01
Vero Beach, FL 2004 (Florida 47) VO-FR-04-5218	0.12- 0.13	4	300	41-47	0.50	0	0.10 0.12	<u>0.11</u>	< 0.01 < 0.01	0.02 0.02 (< 0.01)	< 0.01 < 0.01
						7	0.11 0.08	0.10	< 0.01 < 0.01	0.03 0.02 (< 0.01)	< 0.01 < 0.01
Hickman, CA 2004 (Bobcat) WC-FR-04-5219	0.13	4	200	71-81	0.52	0	0.19 0.13	<u>0.16</u>	< 0.01 < 0.01	0.05 0.02 (0.08)	< 0.01 < 0.01
						7	0.13 0.09	0.11	< 0.01 < 0.01	0.03 0.03 (0.02)	< 0.01 < 0.01
Aromas, CA	0.13	4	200	81-85	0.52	0	0.13	<u>0.14</u>	< 0.01	< 0.01	< 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
2004 (Qualiti 21) WB-FR-04-5220							0.15		< 0.01	< 0.01	< 0.01
						7	0.05 < 0.01	0.03	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
New Holland, OH 2004 (H9423) NK-FR-04-5221	0.13	4	200		0.52	0	0.24 0.41	0.33	< 0.01 < 0.01	< 0.01 0.02 (< 0.01)	< 0.01 < 0.01
						6	0.48 0.30	<u>0.39</u>	< 0.01 < 0.01	0.02 0.02 (< 0.01)	< 0.01 < 0.01
Visalia, CA 2004 (H-9557) WC-FR-04-5222	0.13	4	100	76-89	0.52	0	0.13 0.17	<u>0.15</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						7	0.09 0.11	0.10	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Visalia, CA 2004 (H-9557) WC-FR-04-5222	0.64- 0.65	4	100	76-89	2.6	0	Fruit	0.41 0.59 Mean: 0.50		0.02 0.02 (< 0.01)	
						7	Fruit	0.56 0.48 Mean: 0.52		0.03 0.03 (< 0.01)	
Madera, CA 2004 (Rio Grande) WC-FR-04-5223	0.13	4	300		0.52	0	0.26 0.20	0.23	< 0.01 < 0.01	0.04 0.02 (< 0.01)	0.01 < 0.01 (< 0.01)
						7	0.30 0.24	<u>0.27</u>	< 0.01 < 0.01	0.02 0.02 (< 0.01)	< 0.01 < 0.01
Brawley, CA 2004 (Sun 6117) WB-FR-04-5224	0.12- 0.13	4	200	77-79	0.50	0	0.09 0.10	<u>0.10</u>	< 0.01 < 0.01	< 0.01 0.01 (< 0.01)	< 0.01 < 0.01
						7	0.07 0.07	0.07	< 0.01 < 0.01	0.01 0.02 (< 0.01)	< 0.01 < 0.01
Glenn, CA 2004 (H-9557) WD-FR-04-5225	0.12- 0.13	4	200		0.50	0	0.37 0.40	<u>0.39</u>	< 0.01 < 0.01	0.01 0.01 (< 0.01)	< 0.01 < 0.01
						7	0.20 0.19	0.20	< 0.01 < 0.01	0.02 0.02 (< 0.01)	< 0.01 < 0.01
Glenn, CA 2004 (H-9557) WD-FR-04-5225	0.63- 0.65	4	200		2.6	0	1.4 1.5	1.5	< 0.01 < 0.01	0.04 0.04 (< 0.01)	< 0.01 < 0.01
						7	1.4 1.4	1.4	< 0.01 < 0.01	0.01 0.04 (< 0.01)	< 0.01 < 0.01
Maxwell, CA 2004 (Cxd179) WD-FR-04-5226	0.13	4	100		0.52	0	0.17 0.11	0.14	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						1	0.11 0.10	<u>0.11</u>	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						4	0.10 0.04	0.07	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
						7	0.06 0.10	0.08	< 0.01 < 0.01	0.01 0.01 (< 0.01)	< 0.01 < 0.01
						9	0.07	0.10	< 0.01	0.01	< 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
							0.12		< 0.01	0.01 (< 0.01)	< 0.01

Peppers (Sweet and Chili)

Residue trials were conducted on sweet peppers and chili peppers in California, Florida, Illinois, North Carolina and Texas in 2004.

Difenoconazole EC 250 was applied to sweet peppers (6 trials) and chili peppers (3 trials) as foliar broadcast spray four times at a rate of 0.12–0.14 kg ai/ha. The intervals between applications were 7 days and all treatments were made at spray volumes ranging from about 27 to 493 L/ha using non-ionic surfactant (0.125%, v/v). The fruit samples were collected on the last day of application, further, 7 days after the last application. In the decline trials, samples were collected at 0, 1, 4, 7 and 9 days after last application.

Table 21 Difenoconazole and metabolite residues in peppers (Sweet and Chili) from supervised trials performed in the USA with EC 250 (Report No.: T003262-03)

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
GAP, USA	0.13				0.52	0					
Sweet peppers											
Rose Hill, NC 2004 (King Arthur) SJ-FR-04-5227	0.13	4	200		0.52	0	0.06 0.06	<u>0.06</u>	< 0.01 < 0.01	0.05 0.04 (< 0.01)	< 0.01 < 0.01
						7	0.06 0.04	0.05	< 0.01 < 0.01	0.10 0.08 (< 0.01)	< 0.01 < 0.01
Vero Beach, FL 2004 (transplants) VO-FR-04-5228	0.12- 0.13	4	300	41- 47	0.50	0	0.11 0.14	0.13	< 0.01 < 0.01	0.02 0.03 (0.01)	< 0.01 < 0.01
						7	0.11 0.16	<u>0.14</u>	< 0.01 < 0.01	0.03 0.03 (< 0.01)	< 0.01 < 0.01
Champaign, IL 2004 (Sweet Bell) 4A-FR-04-5229	0.13- 0.14	4	30	71- 75	0.54	0	0.16 0.05	<u>0.11</u>	< 0.01 < 0.01	0.04 0.04 (0.03)	< 0.01 < 0.01
						7	0.06 0.04	0.05	< 0.01 < 0.01	0.05 0.05 (0.03)	< 0.01 < 0.01
Raymondville, TX 2004 (Capistrano) SA-FR-04-5230	0.13	4	200	71- 77	0.52	0	0.17 0.11	<u>0.14</u>	< 0.01 < 0.01	0.03 0.04 (< 0.01)	< 0.01 < 0.01
						7	0.12 0.12	0.12	< 0.01 < 0.01	0.05 0.05 (< 0.01)	< 0.01 < 0.01
Visalia, CA 2004 (Baron) WC-FR-04-5231	0.13	4	100	71- 75	0.52	0	0.07 0.08	0.08	< 0.01 < 0.01	0.01 0.02 (< 0.01)	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Residue, mg/kg.				
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha		Parent	Parent, Mean	T	TA	TAA
						1	0.06 0.08	0.07	< 0.01 < 0.01	0.02 0.02 (0.01)	< 0.01 < 0.01
						4	0.12 0.07	<u>0.10</u>	< 0.01 < 0.01	0.02 0.02 (0.01)	< 0.01 < 0.01
						7	0.06 0.09	0.08	< 0.01 < 0.01	0.02 0.02 (0.01)	< 0.01 < 0.01
						9	0.04 0.04	0.04	< 0.01 < 0.01	0.03 0.03 (0.01)	< 0.01 < 0.01
Arroyo Grande, CA 2004 (Jupiter) WB-FR-04-5232	0.13	4	500	45- 49	0.52	0	0.15 0.20	<u>0.18</u>	< 0.01 < 0.01	< 0.01 0.01 (0.01)	< 0.01 < 0.01
						7	0.11 0.08	0.10	< 0.01 < 0.01	0.01 < 0.01 (0.01)	< 0.01 < 0.01
Chili peppers											
Raymondville, TX 2004 (Tam- Mild) SA-FR-04-5233	0.13	4	200	41- 77	0.52	0	0.29 0.22	<u>0.26</u>	< 0.01 < 0.01	0.06 0.06 (0.01)	< 0.01 < 0.01
						7	0.19 0.16	0.18	< 0.01 < 0.01	0.08 0.09 (0.01)	< 0.01 0.01 (0.01)
Rincon, NM 2004 (Big Jim) SC-FR-04-5234	0.13	4	200		0.52	0	0.11 0.09	<u>0.10</u>	< 0.01 < 0.01	0.01 0.01 (0.01)	< 0.01 < 0.01
						7	0.06 0.09	0.08	< 0.01 < 0.01	0.02 0.02 (0.01)	< 0.01 < 0.01
Visalia, CA 2004 (Habanero) 2A-FR-04-5235	0.13	4	300	85- 89	0.52	0	0.20 0.12	<u>0.16</u>	< 0.01 < 0.01	< 0.01 0.01 (0.01)	< 0.01 < 0.01
						7	0.11 0.11	0.11	< 0.01 < 0.01	< 0.01 0.01 (0.01)	< 0.01 < 0.01

Root and tuber vegetables

Potato (post-harvest treatment)

Potatoes were obtained from a commercial grower received a post-harvest treatment using difenoconazole FS 360 formulation (g/L). For each trial, information on potato source (soil properties, maintenance fertilizers and pesticides, some harvest/storage) was provided. In one trial, modification after harvest (washing and air-drying the day before post-harvest treatment) was reported. Until post-harvest treatment, the potato tubers were kept in on-site storage for approximately one to four months at 6 to 14 °C.

Difenoconazole solution was applied once to potatoes (five trials, conducted in Idaho, Maine, Ontario, Washington and Wisconsin) as a post-harvest treatment at a rate of 3.4–3.8 g ai/t tubers. The applications were made with a tank mixture containing also azoxystrobin (SC 250) and fludioxonil (SC 230), each at a rate of 4.5 g ai/t tubers. The spray was directed to tubers falling from a conveyor belt or moving along a roller table. The post-harvest treated tubers (approximately 14 tubers) were

collected within 0 day after the test substance had dried. At the Ontario site (trial ON14), tubers were cut in half, retaining half as the sample.

In one trial (ID19), the following additional treatments were also included to evaluate residue levels from different application methods:

Spray directed to tubers placed on a flat surface close together, allowed to dry, turned over, and sprayed again (surface/stationary).

Spray directed to tubers placed close together inside a spray chamber, allowed to dry, turned over, and sprayed again (spray chamber).

Spray directed to tubers placed on a brush table that rolled the potatoes under the spray (brush table).

At the following three sites, additional treated samples were collected for storage study. After the post-harvest treatment and the test substance had dried, tubers were placed in typical potato storage:

Trial ID19: 30 and 231 days at 6 °C, 95% RH

Trial ON14: 14, 31 and 59 days at 3–5 °C, 95% RH

Trial WA32: 13, 32, and 61 days at 5–10 °C.

Until analysis, all samples were kept frozen at below -17 °C in site facilities and at ca. -20 °C in the analytical lab. In all control samples, difenoconazole was < 0.01 mg/kg.

Table 22 Difenoconazole and metabolite residues in potato post-harvest treated with FS 360 formulation in the USA (Report No.: TK0003297)

Location Year (Variety) Trial No.	Application				WHP, days	Residue, mg/kg.				
	Method ^a	No.	Delivery rate (L/t)	Rate, g ai/t		Parent	Parent, Mean	T	TA	TAA
GAP, USA, for post-harvest treatment	In line aqueous spray	1		3.5						
Kimberly, ID2009 (Russet Burbank) ID19	Conveyor belt	1	2	3.5-3.6	0	1.9 1.8	<u>1.9</u>	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
					30	0.54 0.74	0.64	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
					231	0.97 0.67	0.82	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
					0	0.41 (Pre- processin g)		< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
					0	< 0.01 (Flake)		< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
					0	0.03 (Chip)		< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
					0	1.3 (Wet peel)		< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
	Surface	1	2	3.5	0	0.74 0.62	0.68	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
	Spray chamber	1	2	3.5	0	2.3 2.4	2.4	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
	Brush table	1	2	3.5	0	1.1 1.2	<u>1.2</u>	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
Corinth, ME 2009 (Frio Lay 1533) ME04	Conveyor belt	1	1	3.8	0	0.62 0.60	<u>0.61</u>	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
Delhi, ON 2009 (Frio Lay 1533) ON14	Roller table	1	2	3.4	0	2.2 1.8	2.0	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application				WHP, days	Residue, mg/kg.				
	Method ^a	No.	Delivery rate (L/t)	Rate, g ai/t		Parent	Parent, Mean	T	TA	TAA
					14	2.5 1.9	2.2	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
					31	1.9 1.8	1.9	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
					59	206 2.1	2.4	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01
Prosser, WA 2009 (Russet Burbank) WA32	Conveyor belt	1	2	3.5	0	1.5 1.1	<u>1.3</u>	< 0.01 < 0.01	0.025 0.024 (0.03)	< 0.01 < 0.01
					13	1.3 0.77	1.0	< 0.01 < 0.01	0.032 0.027 (0.03)	< 0.01 < 0.01
					32	1.2 0.45	0.83	< 0.01 < 0.01	0.028 < 0.02 (0.03)	< 0.01 < 0.01
					61	0.63 0.83	0.73	< 0.01 < 0.01	0.028 0.022 (0.03)	< 0.01 < 0.01
Hancock, WI 2009 (Russet Burbank) WI19	Conveyor belt	1	2	3.6	0	0.90 0.84	<u>0.87</u>	< 0.01 < 0.01	< 0.02 < 0.02	< 0.01 < 0.01

^a As application equipment, backpack CO₂ sprayer (WA32 trial), conveyor belt with backpack CO₂ sprayer (WI19 trial), CDA applicator with diaphragm pump (ME04 trial), CO₂ sprayer in rolling table chamber (On14) and conveyor belt with backpack CO₂ sprayer (ID19 trial) were used.

Ginseng

There was a request for the re-estimation of maximum residue levels for processed ginseng products as a change in grouping for the processed products was made during the 2011 CCPR Session. The 2010 JMPR recommended maximum residue levels for fresh ginseng and the products, based on the residue levels from five trials conducted in the Republic of Korea in 2009. For the present JMPR evaluation, the country additionally provided data from two trials (Study No. 09072-944 and 09072-945). The new trials were conducted in 2010 at the sites of the two trials that were carried out in 2009 and evaluated by JMPR in 2010.

Ready to harvest ginseng, 5 years in qage, was treated four times with a difenoconazole SC 10 formulation (% w/w) at a rate of 0.0054 kg ai/hL (10 mL of a formulation with 10% ai in 20 litre of water) with 10 day intervals. Fresh ginseng was harvested 14 days after the last application.

Table 23 Difenoconazole residues in ginseng treated with SC10 formulation in the Republic of Korea

Location Year (Variety) ^a	Application			PHI, days	Sample material	Residue, mg/kg		Study No.
	kg ai/hL	n.	Interval days			Sample results	Mean	
GAP in Rep. of Korea	0.0054 ^b	5 ^b	10 ^b	14 ^b				
	0.0030 ^c	4 ^c	10 ^c	7 ^c				
Gongju, Chungnam 2009	0.0054	5	10	14	Fresh root	0.018 0.017 (2)	<u>0.017</u>	09072-945
Wonju, Gangwon 2009	0.0054	5	10	14	Fresh root	< 0.02 (3)	<u>< 0.02</u>	
Icheon, Gyeonggi 2009	0.0054	5	10	14	Fresh root	< 0.02 (3)	<u>< 0.02</u>	08072-051
Chungju, Chungbuk 2009	0.0054	5	10	14	Fresh root	0.006 (3)	<u>0.006</u>	09072-944
Goesan, Chungbuk 2009 ^d	0.0030	4	10	7	Fresh root	0.040 (3)	0.04	08082-016

Location Year (Variety) ^a	Application			PHI, days	Sample material	Residue, mg/kg		Study No.
	kg ai/hL	n.	Interval days			Sample results	Mean	
Chungju, Chungbuk 2010	0.0054	5	10	14	Fresh root	0.045 0.043 0.044	<u>0.044</u>	09072-944
Gongju, Chungnam 2010	0.0054	5	10	14	Fresh root	0.030(3)	<u>0.030</u>	09072-945

Trials conducted in 2009 were evaluated by the 2010 JMPR.

^a *Panax ginseng* C.A. Mey. (Violet-stem variant)

^b GAP for SC 10 (% w/w)

^c GAP for SC 10.7 (% w/w) as of 2009. Currently, the formulation composition is 11.3 (% w/w).

^d SC 10.7 formulation was used only in the one trial, according to the registered usage.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

The Meeting received information on the fate of difenoconazole residues during the processing of oranges, apples, grapes, tomatoes, potatoes and ginseng.

Oranges (juice, oil and dried pulp)

Orange trees were treated four times with difenoconazole EC 250 by foliar cover spray applications at rates of 0.14 kg ai/ha (total rate 0.56 kg ai/ha) and at an exaggerated rate of 5× (total rate 2.8 kg ai/ha) in one residue trial (Trial No. E15FL078041) conducted in Florida in 2007. Composite samples (~200 kg) of mature fruit were collected on day 0, after the last application, and used for processing of oranges into fresh juice, citrus oil and dried pulp simulating normal commercial processing practices.

Oranges were batch tub washed. Approximately 2.75 kg of oranges per batch were abraded to scarify the flavedo for oil recovery. The scarified fruit was weighed and retained for juice processing.

The collected oil-water emulsion was screened and the scarified flavedo was set aside for later addition to the shredded peel. The first run oil-water emulsion was processed through a cream separator and centrifuge to separate the oil. The free oil was removed and frozen. The residual emulsion was centrifuged, and recovered oil was added to the oil collected the previously. The entire volume of oil collected was placed in frozen storage.

An aliquot of the scarified oranges was transferred to the juice extractor to recover the juice from the peel. The collected juice was screened to remove vesicular membranes, seed, segment membranes and peel fragments.

The peel from a juice extractor was shredded and combined with the scarified flavedo from the scarification process and with rag (the stringy axis and white fibrous membrane) and seeds from the juice finisher extraction process to generate wet peel. Lime was added to the wet peel and mixed. The limed peel was pressed. The wet peel pulp was dried to below 10% moisture and then the dried pulp was milled.

Table 24 Difenoconazole and metabolite residues in processed orange products (Report No.: T004712-06)

Location Year (Variety) Trial No.	Application					PHI, days	Sample analysed	Residue, mg/kg			
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha			Parent	T	TA	TAA
Oviedo, FL 2007	0.14	4	2300	83	0.56	0	Whole fruit	0.10 0.13	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Sample analysed	Residue, mg/kg			
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha			Parent	T	TA	TAA
(Valencia) E15FL078041							(Pre- process)	0.09 Mean: 0.11	< 0.01	< 0.01	< 0.01
							Dried pulp	0.44 PF=4.0	< 0.01	0.01	< 0.01
							Oil	4.7 PF=42.7	< 0.01	< 0.01	< 0.01
							Juice	< 0.01 PF=< 0.09	< 0.01	< 0.01	< 0.01
Oviedo, FL 2007 (Valencia) E15FL078041	0.70- 0.71	4	2300	83	2.8	0	Whole fruit (Pre- process)	0.74 0.71 0.81 Mean: 0.75	< 0.01 < 0.01 < 0.01	0.01 0.01 0.01	< 0.01 < 0.01 < 0.01
							Dried pulp	3.0 PF=4.0	< 0.01	0.02	< 0.01
							Oil	38 PF=50.7	0.03	< 0.01	< 0.01
							Juice	< 0.01 PF=< 0.01	< 0.01	< 0.01	< 0.01

Apples (juice and wet pomace)

Apples were treated five times with difenoconazole EC 250 by foliar cover spray applications with a rate of 0.075–0.078 kg ai/ha (total rate 0.38 kg ai/ha) in two residue trials (Trial No. 5A-FR-04-5190 and WF-FR-04-5199) conducted in New York and Washington in 2004. An exaggerated rate of 5× (total rate 0.19 kg ai/ha) was also applied in the each trial. Composite samples (~ 60 kg) of mature fruit were collected 14–18 days after the last application.

Processing of apples into wet pomace and fresh juice was performed under processing conditions simulating commercial practices. Unwashed apples were washed and reduced to crushed apple pulp. The crushed apple pulp was heated with low steam and treated with enzyme. The enzyme treated pulp was pressed and wet pomace and fresh juice was collected.

Table 25 Difenoconazole and metabolite residues in processed apple products (Report No.:T002884-03)

Location Year (Variety) Trial No.	Application					PHI, days	Sample analysed	Residue, mg/kg.			
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha			Parent	T	TA	TAA
GAP, USA	0.078				0.37	14					
Hudson, NY 2004 (Indared) 5A-FR-04- 5190	0.075- 0.077	5	1100	75-85	0.38	18	Pre- process	0.18	< 0.01	0.08 (0.10)	< 0.01
							Wet pomace	1.2 PF=6.67	< 0.01	0.07 (0.07)	< 0.01
							Juice	< 0.01 PF=< 0.01	< 0.01	0.16 (0.15)	< 0.01
Hudson, NY 2004 (Indared) 5A-FR-04-	0.38- 0.39	5	1100	75-85	1.9	15	Pre- process	0.73	< 0.01	0.19 (0.10)	< 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Sample analysed	Residue, mg/kg.			
	kg ai/ha	n	Vol. (L/ha)	BBCH	Total/ season, kg ai/ha			Parent	T	TA	TAA
5190											
							Wet pomace	6.5 PF=8.90	< 0.01	0.10 (0.07)	< 0.01
							Juice	0.02 PF=0.03	< 0.01	0.23 (0.15)	< 0.01
Ephrata, WA 2004 (Red Delicious) WF-FR-04- 5199	0.076- 0.078	5	1900	77-79	0.38	14	Pre- process	0.18	< 0.01	0.01 (0.01)	< 0.01
							Wet pomace	1.8 PF=10.0	< 0.01	0.01 (< 0.01)	< 0.01
							Juice	< 0.01 PF=< 0.01	< 0.01	0.03 (0.03)	< 0.01
Ephrata, WA 2004 (Red Delicious) WF-FR-04- 5199	0.39	5	1900	77-79	1.9	14	Pre- process	0.89	< 0.01	0.02 (0.01)	< 0.01
							Wet pomace	11 PF=12.4	< 0.01	0.01 (< 0.01)	< 0.01
							Juice	< 0.01	< 0.01	0.03 (0.03)	< 0.01

Grapes (raisin and juice)

Grapes were treated four times with difenoconazole EC 250 by foliar broadcast spray applications with a rate of 0.13 kg ai/ha (total rate 0.52 kg ai/ha) in two residue trials (Trial No. E03NY078021 and W32CA078023) conducted in California in 2007. Exaggerated rates of 3 $\times$ (total rate 1.6 kg ai/ha) and 5 $\times$ (total rate 2.6 kg ai/ha) were also applied. Composite samples (~ 45 kg) of mature fruit were collected approximately 7 days after the final application. Processing of grapes into juice and raisins was performed under processing conditions that simulated commercial practice.

Table 26 Difenoconazole and metabolite residues in processed grape products (Report No.: T004711-06)

Location Year (Variety) Trial No.	Application					PHI, days	Sample analysed	Residue, mg/kg			
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha			Parent	T	TA	TAA
GAP, USA	0.13				0.52	7					
Dundee, NY 2007 (Concord) ^a E03NY078021	0.13	4	900	81- 89	0.52	7	Pre- process	0.49 0.82 0.70 Mean: 0.67	< 0.01 < 0.01 < 0.01	0.05 0.04 0.04 (0.05)	0.01 0.01 0.01 (0.01)
							Raisin	1.97	< 0.01	0.13 (0.12)	0.04 (0.03)
							Juice	0.01	< 0.01	0.03 (0.03)	< 0.01
Dundee, NY 2007 (Concord) ^a E03NY078021	0.39	4	900	81- 89	1.6	7	Pre- process	2.5 2.3 2.3 Mean: 2.4	< 0.01 < 0.01 < 0.01	0.06 0.05 0.05 (0.05)	0.02 0.01 0.01 (0.01)

Location Year (Variety) Trial No.	Application					PHI, days	Sample analysed	Residue, mg/kg			
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha			Parent	T	TA	TAA
							Raisin	9.9	< 0.01	0.19 (0.12)	0.07 (0.03)
							Juice	0.06	< 0.01	0.03 (0.03)	< 0.01
Poplar, CA 2007 (Thompson Seedless) W32CA078023	0.13	4	700	79- 89	0.52	7	Pre- process	0.11 0.11 0.18 Mean: 0.13	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01
							Raisin	0.56 PF=4.31	< 0.01	0.01 (0.01)	< 0.01
							Juice	0.06 PF=0.46	< 0.01	< 0.01	< 0.01
Poplar, CA 2007 (Thompson Seedless) W32CA078023	0.65	4	700	79- 89	2.6	7	Pre- process	0.49 0.82 0.70 Mean: 0.67	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01
							Raisin	1.9 PF=2.84	< 0.01	0.01 (0.01)	< 0.01
							Juice	0.31 PF=0.46	< 0.01	< 0.01	< 0.01

^a Processing factors were not derived due to use of Concord variety.

Tomato (paste and puree)

Tomatoes were treated four times with difenoconazole EC 250 by post foliar broadcast spray applications with a rate of 0.12–0.13 kg ai/ha (total rate 0.50–0.52 kg ai/ha) in two residue trials (Trial No. WC-FR-04-5222 and WD-FR-04-5225) conducted in California in 2007. Exaggerated rates of 5× (total rate 0.63–0.65 kg ai/ha) were also applied. Composite samples (~ 135 kg) of mature fruit were collected either on day 0, after the spray was completely dry (WD-FR-04-5225) or at 7 days after the final application (WC-FR-04-5222). Processing of tomatoes into paste and puree was performed according to commercial processing practices.

As a first step, tomatoes were washed by the washing system consisted of two sets of washing flumes/spray washers. The washed tomatoes were crushed by a grinder and pumped into the hot break system to be heated to 91–92 °C. Peel and seeds (wet pomace) were removed from the crush, producing tomato juice. Concentration of juice to puree was done using a vacuum evaporator until Natural Tomato Soluble Solids (NTSS) of puree reaches to the target NTSS of 8–16%. Puree transferred to the vacuum kettle evaporator was condensed to paste until the paste reaches the target NTSS, of 24–35%.

Table 27 Difenoconazole and metabolite residues in processed tomato products (Report No.: T003262-03)

Location Year (Variety) Trial No.	Application					PHI, days	Sample analysed	Residue, mg/kg			
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha			Parent	T	TA	TAA
GAP, USA	0.13				0.52	0					
Visalia, CA 2004 (H-9557)	0.13	4	100	76- 89	0.52	7	Pre- process	0.09	< 0.01	0.01 (< 0.01)	< 0.01

Location Year (Variety) Trial No.	Application					PHI, days	Sample analysed	Residue, mg/kg			
	kg ai/ha	n	Vol. (L/ha)	B B C H	Total/ season, kg ai/ha			Parent	T	TA	TAA
WC-FR-04-5222											
						7	Paste	0.11 <i>PF</i> =1.22	< 0.01	0.06 (0.02)	< 0.01
						7	Puree	0.05 <i>PF</i> =0.56	< 0.01	0.02 (< 0.01)	< 0.01
Visalia, CA 2004 (H-9557) WC-FR-04-5222	0.64- 0.65	4	100	76- 89	2.6	7	Pre- process	0.35	< 0.01	0.03 (< 0.01)	< 0.01
						7	Paste	0.62 <i>PF</i> =1.77	< 0.01	0.16 (0.02)	< 0.01
						7	Puree	0.17 <i>PF</i> =0.49	< 0.01	0.04 (< 0.01)	< 0.01
Glenn, CA 2004 (H-9557) WD-FR-04-5225	0.12- 0.13	4	200		0.50	0	Pre- process	0.18	< 0.01	< 0.01	< 0.01
						0	Paste	0.38 <i>PF</i> =2.11	< 0.01	0.05 (< 0.01)	< 0.01
						0	Puree	0.11 <i>PF</i> =0.61	< 0.01	0.02 (< 0.01)	< 0.01
Glenn, CA 2004 (H-9557) WD-FR-04-5225	0.63- 0.65	4	200		2.6	0	Pre- process	1.4	< 0.01	0.04 (< 0.01)	< 0.01
						0	Paste	1.9 <i>PF</i> =1.36	< 0.01	0.13 (< 0.01)	< 0.01
						0	Puree	0.77 <i>PF</i> =0.55	< 0.01	0.07 (< 0.01)	0.01 (< 0.01)

Potatoes (wet peel, flake and chip)

A processing study was conducted on treated tubers from one residue trial (Trial No. ID19, Idaho, USA). Potatoes were treated post-harvest with a spray application directed to tubers falling from a conveyor belt. The applications were made with a spray solution containing difenoconazole, fludioxonil and azoxystrobin at a rate of 3.5–3.6, 4.5 and 4.5 g ai/t tubers, respectively. Bulk tuber samples (~ 113 kg) were collected after the test substance had dried (0 day) and used for processing. Processing was conducted according to commercial processing practices.

Potato tubers were washed and representative samples were removed and returned to storage for chip processing. The remaining tubers were steam peeled and scrubbed. The peel was collected, and the peeled tubers were hand trimmed as necessary. The trimmings were added to the collected peel and both were hydraulically pressed to produce the wet peel sample, which was placed in frozen storage.

The peeled tubers were sliced into slabs, washed in cold water, and pre-cooked at 70 to 77 °C for 20 minutes in a steam-jacketed kettle. The pre-cooked tuber slabs were cooled to less than 32 °C for approximately 20 minutes and then steam-cooked at 94 to 100 °C for 40 to 42 minutes. The cooked tuber slabs were mashed in a grinder and mixed with an emulsion of pre-weighed food additives. The cooked mash was dried into a thin sheet, which was broken into large flakes by hand and then fed into a press for milling into potato flakes. After drying on a fluidized bed-dryer, to remove excess moisture, the potato flake samples were placed into frozen storage.

The tubers retained for chips were removed from storage. The tubers were peeled, trimmed and cut into thin slice. The slices were placed in a tub of hot water to remove free starch, drained, and then fried at 163 to 191 °C for approximately 120 seconds. The fried chips were drained, salted and placed in frozen storage for later analysis.

Table 28 Difenoconazole and metabolite residues in processed potato products (Report No.: TK0003297)

Location Year (Variety) Trial No.	Application				WHP, days	Sample analysed	Residue, mg/kg			
	Method ^a	n	Del. rate (l/t)	g ai/t			Parent	T	TA	TAA
GAP, USA, for post-harvest treatment	In line aqueous spray	1		3.5						
Kimberly, ID2009 (Russet Burbank) ID19	Conveyor belt	1	2	3.5- 3.6	0	Pre- processing	0.41	< 0.01	< 0.02	< 0.01
					0	Flake	< 0.01 PF=< 0.024	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
					0	Chip	0.03 PF=0.073	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
					0	Wet peel	1.3 PF=3.17	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01

Ginseng (dried-, red ginseng, the extracts)

Ginseng was treated four times with SC 10 formulation (% w/w) at a rate of 0.0054 kg ai/hL at 10 day intervals. The fresh ginseng was then harvested at 14-day PHI. Two processing studies (Study No. 09072-944 and 09072-945) were conducted in 2010, in the same manner with the method described in 2010 JMPR evaluation.

Briefly, washed ginseng (RAC, ginseng treated with tap water to remove soil particles) was dried in hot air to produce dried ginseng (water content, 8.0% and 9.6% in each study). The washed ginseng was steamed, dried in hot air, and dried again under sunlight to produce red ginseng (water content, 9.0% and 12.1% in each study).

Ethanol or water extracts of the dried and red ginseng were made by refluxing with ethanol (70%) or with water. The solvents were evaporated until the sugar content in the extract reached 65 or 72 °Brix. Water content in the dried extracted product was as follows: in two studies each, 38.5%, 40.2% in ethanol extract of dried ginseng, 48.5%, 36.8% in water extract of dried ginseng, 38.2%, 37.2% in ethanol extract of red ginseng and 53.4%, 35.9 % in water extract of red ginseng.

Table 29 Difenoconazole residues in processing ginseng products

Location Year (Variety) ^a	Application				PHI, days	Sample analysed	Residue, mg/kg		Study No.
	kg ai/hL	n	Interval days				Results	Mean	
GAP in Rep. of Korea	0.0054 ^b	5 ^b	10 ^b	14 ^b					
	0.0030 ^c	4 ^c	10 ^c	7 ^c					
Gongju, Chungnam 2009 ^d	0.0054	5	10	14		Fresh root		0.017	09072-945
						Dried ginseng	0.065 0.068 (2)	0.067 PF=3.9	
						Red ginseng	0.052 0.050 (2)	0.051 PF=3.0	
						Ethanol extract of dried ginseng	0.090 0.082 0.077	0.083 PF=4.9	
						Water extract of dried ginseng	< 0.007 (3)	< 0.007 PF=< 0.4	(?)
						Ethanol extract	0.069	0.070	

Location Year (Variety) ^a	Application			PHI, days	Sample analysed	Residue, mg/kg		Study No.
	kg ai/hL	n	Interval days			Results	Mean	
					of red ginseng	0.068 0.074	PF=4.1	
					Water extract of red ginseng	< 0.007 (3)	< 0.007 PF=< 0.4	(?)
Wonju, Gangwon 2009 ^d	0.0054	5	10	14	Fresh root		< 0.02	
					Dried ginseng	0.067 (2) 0.063	0.066 PF=>3.3	
					Red ginseng	< 0.04 (3)	< 0.04	
					Ethanol extract of dried ginseng	0.070 (2) 0.073	0.071 PF=>3.6	
					Water extract of dried ginseng	< 0.04 (3)	< 0.04	
					Ethanol extract of red ginseng	0.10 (2) 0.097	0.099 PF=>5.0	
					Water extract of red ginseng	< 0.04 (3)	< 0.04	
Icheon, Gyunggi 2009 ^d	0.0054	5	10	14	Fresh root		< 0.02	08072-051
					Dried ginseng	0.11 (2) 0.13	0.12 PF=>6.0	
					Red ginseng	0.097 (2) 0.10	0.098 PF=>5.0	
					Ethanol extract of dried ginseng	0.37 0.36 0.38	0.37 PF=>18.5	
					Water extract of dried ginseng	< 0.04 (3)	< 0.04	
					Ethanol extract of red ginseng	0.21 (2)	0.21 PF=>10.5	
					Water extract of red ginseng	< 0.04 (3)	< 0.04	
Chungju, Chungbuk 2009 ^d	0.0054	5	10	14	Fresh root		0.006	09072-944
					Dried ginseng	0.012 (2) 0.013	0.012 PF=2.0	
					Red ginseng	0.011 (3)	0.011 PF=1.8	
					Ethanol extract of dried ginseng	0.017 (2) 0.016	0.016 PF=2.7	
					Water extract of dried ginseng	0.016 0.015 0.014	0.015 PF=2.5	
					Ethanol extract of red ginseng	0.012 (2) 0.011	0.012 PF=2.0	
					Water extract of red ginseng	0.012 (3)	0.012 PF=2.0	
Goesan, Chungbuk 2009 ^d	0.0030	4	10	7	Fresh root		0.04	08082-016
					Dried ginseng	0.072 0.067 0.068	0.069 PF=1.7	
					Red ginseng	0.037 0.035 0.038	0.037 PF=0.9	
					Ethanol extract of dried ginseng	< 0.07 (3)	< 0.07 PF=<1.8	
					Water extract of dried ginseng	< 0.07 (3)	< 0.07 PF=<1.8	

Location Year (Variety) ^a	Application			PHI, days	Sample analysed	Residue, mg/kg		Study No.
	kg ai/hL	n	Interval days			Results	Mean	
					Ethanol extract of red ginseng	< 0.07 (3)	< 0.07 PF=<1.8	
					Water extract of red ginseng	< 0.007 (3)	< 0.007 PF=< 0.2	
Chungju, Chungbuk 2010	0.0054	5	10	14	Fresh root		0.044	09072-944
					Dried ginseng	0.13 (2) 0.14	0.13 PF=3.0	
					Red ginseng	0.089 0.093 0.095	0.092 PF=2.1	
					Ethanol extract of dried ginseng	0.18 0.17(2)	0.17 PF=3.9	
					Water extract of dried ginseng	0.19(3)	0.19 PF=4.3	
					Ethanol extract of red ginseng	0.11(3)	0.11 PF=2.5	
					Water extract of red ginseng	0.12(3)	0.12 PF=2.7	
Gongju, Chungnam 2010	0.0054	5	10	14	Fresh root		0.03	09072-945
					Dried ginseng	0.10 0.097 0.11	0.10 PF=3.3	
					Red ginseng	0.093 0.094 0.096	0.094 PF=3.1	
					Ethanol extract of dried ginseng	0.21(2) 0.20	0.21 PF=7.0	
					Water extract of dried ginseng	0.054 0.055(2)	0.055 PF=1.8	
					Ethanol extract of red ginseng	0.20(2) 0.21	0.20 PF=6.7	
					Water extract of red ginseng	0.047 0.046(2)	0.046 PF=1.5	

^a *Panax ginseng* C.A. Mey. (Violet-stem variant)

^b GAP for SC 10 (% w/w)

^c GAP for SC 10.7 (% w/w) as of 2009. Presently the formulation composition is changed into 11.3 (% w/w). In the only one trial (Study No. 08082-016), the SC 10.7 formulation was applied.

^d Studies evaluated by the 2010 JMPR

Table 30 Summary of processing factors for difenoconazole estimated by the JMPR Meetings

Raw agricultural commodity	Processed commodity	Calculated processing factors ^a	Pf (best estimate)
Orange	Oil	42.7, 50.7	47
	Dried pulp	4.0, 4.0	4.0
	Juice	< 0.01, < 0.09	< 0.01
Apple	Juice	< 0.01, < 0.01, < 0.02, 0.03, <1.0, <1.0	0.03
	Wet pomace	6.67, 8.90, 10.0, 12.4	9.5
Grape	Raisin	1.01, 1.4, 2.84, 4.31	2.1
	Juice	0.46, 0.46, < 0.5	0.46
Tomato	Paste	1.22, 1.36, 1.77, 2.11	1.6
	Puree	0.49, 0.54, 0.55, 0.56, 0.58, 0.61, 0.74, 1.00	0.57
Potato	Flake	< 0.024	< 0.024
	Chip	0.073	0.073
	Wet peel	3.17	3.2

Raw agricultural commodity	Processed commodity	Calculated processing factors ^a	Pf (best estimate)
Ginseng ^b	Dried ginseng	1.7, 2.0, 3.0 , 3.3 , 3.9	
	Red ginseng	0.9, 1.8, 2.1 , 3.0, 3.1	
	Ginseng, dried including red ginseng	0.9, 1.7, 1.8, 2.0, 2.1 , 3.0 , 3.0 , 3.1 , 3.3 , 3.9	2.6
	Ethanol extract of dried ginseng	<1.8, 2.7, 3.9 , 4.9, 7.0	
	Water extract of dried ginseng	< 0.4, < 1.8, 1.8 , 2.5, 4.3	
	Ethanol extract of red ginseng	< 1.8, 2.0, 2.5 , 4.1, 6.7	
	Water extract of red ginseng	< 0.2, < 0.4, 1.5 , 2.0, 2.7	
	Ginseng, extracts	< 0.2, 1.5 , <1.8, <1.8, <1.8, 1.8 , 2.0, 2.0, 2.5 , 2.5, 2.7 , 2.7 , 3.9 , 4.1, 4.3 , 4.9, 6.7 , 7.0	7.0

^a Bold letter value refers to Pf derived by the present Meeting. The others came from the previous JMPR reports.

^b For ginseng, the 2010 JMPR derived only one Pf, 3.3 for dried ginseng, due to an uncertainty of the dataset.

APPRAISAL

Difenoconazole was first evaluated by the JMPR in 2007 for toxicology when an ADI of 0–0.01 mg/kg bw and an ARfD of 0.3 mg/kg bw were established. In 2007 and 2010, the JMPR evaluated for residues and recommended numerous maximum residue levels. The compound was listed by the Forty-fourth Session of the CCPR for residue evaluation for additional MRLs by the JMPR in 2013.

The residue is defined, for plant commodities, as parent difenoconazole for compliance with the MRL and for estimation of dietary intake. For animal commodities, it is defined as sum of difenoconazole and 1-[2-chloro-4-(4-chloro-phenoxy)-phenyl]-2-(1,2,4-triazol)-1-yl-ethanol (CGA 205375), expressed as difenoconazole, for compliance with the MRL and for estimation of dietary intake. The residue is fat soluble.

The present Meeting received residue trial information on citrus fruits, pome fruits, grapes, Japanese persimmon, bulb vegetables, brassica vegetables, fruiting vegetables, ginseng and post-harvest treated potato. Further, processing studies on oranges, apples, grapes, tomatoes, potatoes and ginseng were provided. According to a request from the Forty-fourth Session of the CCPR, the Meeting re-evaluated the ginseng processing studies evaluated in 2010 to estimate MRLs complying with the new classification for processed products.

Methods of analysis

The analytical methods used for the determination of difenoconazole in samples from supervised trials, had already considered by the JMPR in 2007 and 2010. The methods are based on LC-MS/MS and GC-NPD determination and the limits of quantitation were 0.01 mg/kg. The validity of the analytical results was supported by validation data on representative crops and results of concurrent recovery studies.

The methods used for ginseng and the processed products were also considered by the 2010 JMPR. The limits of quantitation for difenoconazole based on GC-ECD were between 0.003 and 0.007 mg/kg and concurrent recoveries ranged between 86% and 113%.

Difenoconazole in Japanese persimmon were extracted with acetone and partitioned with dichloromethane. The LOQ by GC-ECD determination was 0.02 mg/kg and concurrent recoveries ranged from between 88% and 107%.

The Meeting additionally received information on analytical methods used for the determination of triazole metabolites 1, 2, 4-triazole, triazole alanine and triazole acetic acid residues in the same plant commodity samples from the supervised trials. The methods involved extraction with organic solvents, SPE clean-up and/or derivatization steps, partition with ethyl acetate and

determination by LC-MS/MS. The limits of quantitation for all metabolites were 0.01 mg/kg and procedural recoveries ranged from 70% to 115%.

Stability of residues in stored analytical samples

The 2007 JMPR concluded that difenoconazole was stable for 2 years in most plant commodities when deep frozen. This covered the stability of difenoconazole in samples from the supervised trials. New data on ginseng and Japanese persimmon were provided. The storage stability tests were conducted simultaneously with storage of field trial sample for 4–31 days in ginseng and the products and for 51 days in Japanese persimmon. The results indicated that residues in the samples were stable during the storage period.

Results of supervised residue trials on crops

Citrus fruits

Difenoconazole is registered in the USA for use on citrus fruits at a GAP of 4×0.14 kg ai/ha (total seasonal rate of 0.56 kg ai/ha), 7 day interval and a PHI of 0 days. Residue trials on citrus fruits were conducted in the USA, matching the critical GAP. Residue concentrations of difenoconazole in citrus fruit, determined on a whole fruit basis, were: 0.11, 0.13, 0.13, 0.14, 0.15, 0.15, 0.23, 0.26 and 0.37 mg/kg in oranges (n=9); 0.17, 0.38 mg/kg in mandarin (n=2); 0.49 mg/kg in tangerine (n=1); 0.075, 0.09, 0.11, 0.13, 0.18 and 0.18 mg/kg in grapefruit (n=6); 0.09, 0.16, 0.17, 0.19 and 0.24 mg/kg in lemons (n=5).

The Meeting noted that as the GAP in USA was for citrus fruits and that the medians of data sets for oranges, mandarins, grapefruits and lemons differed by less than 5-fold, agreed to consider a group maximum residue level. In deciding on the data set to use for estimating a group maximum residue level, given a Kruskal-Wallis H-test indicated that the residue populations were not different, it was agreed to combine the results to give a data set of: 0.075, 0.09, 0.09, 0.11, 0.11, 0.13, 0.13, 0.13, 0.14, 0.15, 0.15, 0.16, 0.17, 0.17, 0.18, 0.18, 0.19, 0.23, 0.24, 0.26, 0.37, 0.38 and 0.49 mg/kg (n=23) for citrus.

The Meeting agreed to estimate a maximum residue level of 0.6 mg/kg, an STMR of 0.16 mg/kg and an HR of 0.49 mg/kg for whole citrus fruits.

Pome fruits

Difenoconazole is registered in the USA for use on pome fruits at a GAP of 5×0.078 kg ai/ha (total seasonal rate of 0.37 kg ai/ha), 7 day intervals and a PHI of 14 days. Residue trials on apple and pear were conducted in the USA and complied with the US GAP.

Residues in apples were (n=13): 0.02, 0.07, 0.07, 0.08, 0.13, 0.16, 0.21, 0.25, 0.28, 0.37, 0.38, 0.39 and 0.47 mg/kg.

Residues in pears were (n=6): 0.07, 0.12, 0.12, 0.14, 0.19 and 0.27 mg/kg.

A national use pattern in the Republic of Korea permits up to five foliar applications of difenoconazole WP 10 (% w/w) on Japanese persimmon at a rate of 0.0054 kg ai/L with 10 day intervals and a PHI of 7 days. Six trials were conducted in the Republic of Korea in 2011 (3) and 2012 (3) matching the critical GAP.

However, all trials were conducted with the same variety. In each year, three trials were performed at the same dates of application and under the same weather conditions, thus the trials were not considered as independent. As a result the Meeting considered that for this evaluation, only two residue values (0.37, 0.43 mg/kg) were available. In addition, the GAP differed from that of the US GAP for pome fruits. Consequently, the persimmon residue values could not be combined with residues from apple and pear.

The Meeting noted that the GAP in USA was for pome fruits and that the medians of the apple and pear data sets differed by less than 5-fold and agreed to consider a group maximum residue

level. In deciding on the data set to use for estimating a group maximum residue level, since a Mann-Whitney U-test indicated that the residue populations for apple and pear were not different it was agreed to combine the results to give a data set of: 0.02, 0.07 (3), 0.08, 0.12 (2), 0.13, 0.14, 0.16, 0.19, 0.21, 0.25, 0.27, 0.28, 0.37, 0.38, 0.39 and 0.47 mg/kg (n=19) for pome fruits group.

The Meeting estimated a maximum residue level of 0.8 mg/kg, an STMR of 0.16 mg/kg and an HR of 0.47 mg/kg for pome fruits. The Meeting withdrew its previous recommendation of 0.5 mg/kg for pome fruits.

Grapes

A national use pattern in the USA permits up to four foliar applications of difenoconazole EC 250 (250 g/L) on grapes at a rate of 0.13 kg ai/ha (total seasonal rate of 0.52 kg ai/ha) with 10 days interval and a PHI of 7 days. Twelve trials conducted in the USA matched the critical GAP, of which two trials were not considered independent as they were carried out on the same variety at a nearby location (experiencing the same weather conditions) and shared the same dates of application. In addition, one trial was excluded as it was carried out with a grape variety for which use was not allowed.

Residues in grapes were (n=10): 0.11, 0.17, 0.19, 0.23, 0.40, 0.64, 0.65, 0.67, 1.3 and 1.5 mg/kg.

The 2007 JMPR estimated a maximum residue level of 0.1 mg/kg for grapes, based on residue trials conducted in southern Europe matching Italian GAP (four applications to grape vines with a spray concentration of 0.005 kg ai/hL with a PHI of 21 days).

As the US use pattern is considered the more critical GAP than the Italian GAP, the Meeting recommended a maximum residue level of 3 mg/kg, an STMR of 0.52 mg/kg and an HR of 1.5 mg/kg for grapes, using residue data from the USA. The Meeting withdrew its previous recommendation of 0.1 mg/kg for grapes.

Bulb vegetables

Onion, bulb

A national use pattern in the USA permits up to four foliar applications of difenoconazole EC 250 (250 g/L) on bulb onions at a rate of 0.13 kg ai/ha (total seasonal rate of 0.52 kg ai/ha), with a 7 day interval and a PHI of 7 days.

Residues in onion, bulb were (n=8): < 0.01 (3), 0.01, 0.02, 0.02, 0.03 and 0.07 mg/kg.

Based on the residue values, the Meeting estimated a maximum residue level of 0.1 mg/kg, an STMR of 0.015 mg/kg and an HR of 0.07 mg/kg for onion, bulb.

Spring onion

A national use pattern in the USA permits up to three foliar applications of difenoconazole EC 250 (250 g/L) on green onions including spring onions at a rate of 0.13 kg ai/ha (total seasonal rate of 0.38 kg ai/ha), with 7 days interval and a PHI of 7 days. Three trials conducted in the USA matched the critical GAP.

Residues in whole spring onion were (n=3): 2.3, 2.8 and 3.8 mg/kg.

The Meeting estimated a maximum residue level of 9 mg/kg, an STMR of 2.8 mg/kg and an HR of 3.8 mg/kg for spring onions.

Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead cabbages

A national use pattern in the USA permits up to four foliar applications of difenoconazole EC 250 (250 g/L) on Brassica (cole) leafy vegetables at a rate of 0.13 kg ai/ha (total seasonal rate of

0.52 kg ai/ha) with 7 days interval and a PHI of 1 day. Six trials on head cabbage and broccoli each were conducted in the USA according to the critical US GAP.

Residues in head cabbage with wrapper leaves were (n=6): 0.09, 0.30, 0.34, 0.46, 0.94 and 1.3 mg/kg.

Residues in broccoli (head and stem) were (n=6): 0.15, 0.32, 0.32, 0.35, 0.37 and 0.53 mg/kg.

Based on GAPs of various European countries, the 2007 JMPR recommended a maximum residue level of 0.2 mg/kg for Brussels sprouts, head cabbage and cauliflowers, respectively, and 0.5 mg/kg for broccoli. As the USA GAP allows a shorter PHI (1 day) than the European GAP, the Meeting decided to use the US trials for maximum residue level estimation.

The Meeting noted that the GAP in USA was for Brassica vegetables and that the medians of the two data sets differed by less than 5-fold and agreed to consider a group maximum residue level. In deciding on the data set to use for estimating a group maximum residue level, since a Mann-Whitney U-test indicated that the residue populations for head cabbage and broccoli were not different, it was agreed to combine the results to give a data set of: 0.09, 0.15, 0.3, 0.32, 0.32, 0.34, 0.35, 0.37, 0.46, 0.53, 0.94 and 1.3 mg/kg (n=12) for Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead cabbages.

The Meeting estimated a maximum residue level of 2 mg/kg, an STMR of 0.35 mg/kg and an HR of 1.3 mg/kg for the crop group, Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead cabbages. The meeting withdrew its previous recommendations for Brussels sprouts, Head cabbage and Cauliflowers of 0.2 mg/kg and for Broccoli of 0.5 mg/kg.

Fruiting vegetables, Cucurbits

Melons

A national use pattern in the USA permits up to four foliar applications of difenoconazole EC 250 (250 g/L) on cucurbit vegetables at a rate of 0.13 kg ai/ha (total seasonal rate of 0.52 kg ai/ha), 7 day interval and a PHI of 0 days. Six trials on cantaloupe conducted in the USA were provided for this Meeting. Five trials were performed according to the US critical GAP, however in one trial the harvest was made 4 days after the last application.

Residues in whole melon were (n=5): 0.06, 0.08, 0.14, 0.19 and 0.35 mg/kg.

The Meeting estimated a maximum residue level 0.7 mg/kg, an STMR of 0.14 mg/kg and an HR of 0.35 mg/kg for melons, except watermelon.

Cucumber, summer squash

A national use pattern in the USA permits up to four foliar applications of difenoconazole EC 250 (250 g/L) on cucurbit vegetables at a rate of 0.13 kg ai/ha (total seasonal rate of 0.52 kg ai/ha), 7 day interval and a PHI of 0 days. Six trials on gherkins and five trials on summer squash were provided to the Meeting. The trials were conducted in the USA complied with the critical US GAP.

Residues in gherkin were (n=6): < 0.01, 0.01, 0.03, 0.04, 0.04 and 0.15 mg/kg.

Residues in summer squash were (n=5): < 0.01, 0.02, 0.05, 0.06 and 0.06 mg/kg.

The Meeting noted that the GAP in USA is for fruiting vegetables, cucurbits with edible peel and that the medians of the two data sets differed by less than 5-fold and agreed to consider a group maximum residue level. In deciding on the data set to use for estimating a group maximum residue level, since a Mann-Whitney U-test indicated that the residue populations for gherkin and summer squash were not different it was agreed to combine the results to give a data set of < 0.01, < 0.01, 0.01, 0.02, 0.03, 0.04, 0.04, 0.05, 0.06, 0.06 and 0.15 mg/kg (n=11) for fruiting vegetable, cucurbits with edible peel.

The Meeting estimated a maximum residue level of 0.2 mg/kg, an STMR of 0.04 mg/kg and an HR of 0.15 mg/kg for fruiting vegetables, cucurbits with edible peel (cucumber, gherkin and summer squash).

Fruiting vegetables, other than Cucurbits

A national use pattern in the USA permits up to four foliar applications of difenoconazole EC 250 (250 g/L) on fruiting vegetables (tomatoes and peppers) at a rate of 0.13 kg ai/ha (total seasonal rate of 0.52 kg ai/ha), 7 day interval and a PHI of 0 days. Trials conducted in the USA (11 trials for tomatoes, six trials for sweet peppers, three trials for chili pepper) were provided to the current Meeting. The trials were performed according to the critical US GAP.

Residues in tomato were (n=11): 0.01, 0.10, 0.11, 0.11, 0.14, 0.15, 0.16, 0.26, 0.27, 0.39 and 0.39 mg/kg.

Residues in sweet pepper were (n=6): 0.06, 0.10, 0.11, 0.14, 0.14 and 0.18 mg/kg.

Residues in chili pepper were (n=3): 0.10, 0.16 and 0.26 mg/kg.

Residue data for sweet pepper and chili pepper was combined for mutual support. Further, the Meeting noted that the GAP in USA was for fruiting vegetable other than cucurbits and that the medians of the two data sets differed by less than 5-fold and agreed to consider a group maximum residue level. In deciding on the data set to use for estimating a group maximum residue level, as a Mann-Whitney U-test indicated that the residue populations for tomatoes and peppers were similar, it was agreed to combine the results to give a data set of 0.01, 0.06, 0.10(3), 0.11 (3), 0.14 (3), 0.15, 0.16, 0.16, 0.18, 0.26, 0.26, 0.27, 0.39 and 0.39 mg/kg (n=20) for fruiting vegetables other than cucurbits.

The 2007 JMPR recommended a maximum residue level of 0.5 mg/kg for tomato from eleven trials conducted on tomatoes in Europe (France, Greece, the UK, Spain) matching the Italian GAP (2 applications at 0.13 kg ai/ha with a PHI of 7 days). However, the GAP of the USA was considered to be the critical GAP.

Therefore, based on the combined dataset on tomato and peppers from the US trials the Meeting estimated a maximum residue level of 0.6 mg/kg, an STMR of 0.14 mg/kg and an HR of 0.39 mg/kg for fruiting vegetables other than cucurbits except sweet corn and mushrooms. The Meeting withdrew its previous recommendation for tomatoes of 0.5 mg/kg.

Furthermore, the Meeting estimated a maximum residue level of 5 mg/kg, an STMR of 1.1 mg/kg and an HR of 1.8 mg/kg for chili peppers dried.

Potato (post-harvest treatment)

A national use pattern in the USA permits a single post-harvest application of difenoconazole to potatoes at a rate of 3.19 g ai/t tubers with in an line aqueous spray application using T-jet controlled droplet applicator (CDA) or similar application system. The US GAP does not specify a withholding period.

Residue trials on potatoes involving post-harvest application were conducted at five sites in different regions of the USA. In the trials, difenoconazole FS 360 (360 g/L) was applied once to potatoes as a post-harvest treatment at a rate of 3.5–3.8 g ai/t tubers, spraying directly to tubers falling from a conveyor belt or moving along a roller table. Post-harvest treated tubers were then collected on the day of treatment (0 day) once the test substance had dried. In decline studies, tubers were stored for up to 231 days in typical storage conditions of 5–10 °C.

At one site, potato tubers were cut at the field site. At another one site, in addition to a conveyor belt treatment, three additional application methods (surface, spray chamber and brush table) were utilized. The two methods using surface spraying and spray chamber did not comply with US GAP.

Therefore, in total five trials matching US GAP were available for use in estimating a maximum residue level.

In the USA, a pre-harvest application using difenoconazole formulation is also authorized on potatoes. No residue was detected in pre-treatment samples.

Residues in potatoes from post-harvest treatment (n=5): 0.61, 0.87, 1.2, 1.3 and 1.9 mg/kg.

The Meeting estimated a maximum residue level of 4 mg/kg, an STMR of 1.2 mg/kg and an HR of 1.9 mg/kg for post-harvest treated potato. The Meeting withdrew its previous recommendation of 0.02 mg/kg for potato that had been based on the residues resulting from pre-harvest treatment.

Ginseng

The maximum GAP in the Republic of Korea allows five applications of difenoconazole SC 10 (% w/w) on ginseng at a rate of 0.0054 kg ai/hL, with a 10 day interval and a PHI of 14 days.

Two trials, using ready to harvest ginseng plantations (5 years old), were conducted in the Republic of Korea, complying with the maximum GAP. The resulting residues were: 0.030 and 0.044 mg/kg.

Of five trials evaluated by the 2010 JMPR, four trials matched the maximum GAP of the Republic of Korea. Thus the residues were (n=6): 0.006, 0.017, < 0.02, < 0.02, 0.030 and 0.044 mg/kg.

The Meeting estimated a maximum residue level 0.08 mg/kg, an STMR of 0.02 mg/kg and an HR of 0.044 mg/kg for ginseng. The Meeting withdrew its previous recommendation of 0.5 mg/kg for ginseng.

Animal feed

Residue information on animal feeds was not provided to the current Meeting.

Fate of residues during processing

The Meeting received information on the fate of difenoconazole residues during the processing of oranges, apples, grapes, tomatoes, potatoes and ginseng. The following table summarizes processing factors, STMR-Ps and HR-Ps estimated by the Meeting.

Raw agricultural commodity	Processed commodity	Pf (best estimate)	RAC STMR/HR	STMR-P/HR-P
Citrus	Citrus juice	< 0.01	0.16	0.002
	Citrus oil	47		7.5
	Citrus dry pulp	4.0		0.64
Pome fruit	Apple juice	0.03	0.16	0.005
	Apple pomace, wet	9.5		1.5
Grape	Raisin	2.1	0.52/1.5	1.1/3.2
	Juice	0.46		0.24
Tomatoes	Paste	1.6	0.14	0.22
	Puree	0.57		0.08
Potato	Flakes	< 0.024	1.2	0.029
	Chips	0.073		0.088
	Peel, wet	3.2		3.8
Ginseng	Dried including red ginseng	2.6	0.02/0.044	0.052/0.11
	Extracts	7.0	-	0.14

For dried grapes (raisin), the Meeting estimated a maximum residue level of 6 mg/kg, based on the processing factor of 2.1 for raisins and the maximum residue level of 3 mg/kg for grapes.

The Meeting re-calculated a processing factor for dried ginseng including processing study results for red ginseng, for a processing factor of 2.6. Based on the processing factor of 2.6 and a maximum residue level of 0.08 mg/kg for the ginseng raw commodity, the Meeting recommended a maximum residue level of 0.2 mg/kg for ginseng, dried including red ginseng. For ginseng extracts, applying the calculated processing factor of 7.0, a maximum residue level of 0.6 mg/kg was estimated.

Residues in animal commodities

Estimated dietary burdens of farm animals

Dietary burden calculations for beef cattle and dairy cattle and poultry are provided below. The dietary burdens were estimated using the OECD diets listed in Appendix IX of the 2009 edition of the FAO Manual.

Potential feed items include: almond hulls, apple pomace, bean forage, cabbages, head, carrot culls, citrus dried pulp, grape pomace, dry, pea vines, potato culls, potato process waste (wet peel), rape seed fodder, rape seed meal, soya bean seed, sugar beet leaves or tops, sunflower seed meal, wheat straw and fodder.

The Japanese animal diet contained only soya bean seed and rape seed meal of those commodities for which the JMPR estimated highest and median residues. The residues in the two commodities resulted in an animal dietary burden of less than 0.01 ppm on dry matter basis, therefore those values are not included in the summary table.

	Livestock dietary burden, difenoconazole, ppm of dry matter diet					
	US-Canada		EU		Australia	
	max	mean	max	mean	max	mean
Beef cattle	12.56	11.42	17.88 ^a	15.30 ^b	11.39	10.80
Dairy cattle	4.87	4.36	14.91 ^c	12.37 ^d	11.31	10.71
Poultry, broilers	0.01	0.01	0.96	0.61	0.01	0.01
Poultry, layers	0.01	0.01	1.89 ^e	1.11 ^f	0.01	0.01

^a Highest maximum beef or dairy cattle dietary burden suitable for maximum residue level estimates for mammalian meat and edible offal

^b Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat and edible offal

^c Highest maximum dairy cattle dietary burden suitable for maximum residue level estimates for milk

^d Highest mean dairy cattle dietary burden suitable for STMR estimates for milk

^e Highest maximum broiler or layer poultry dietary burden suitable for maximum residue level estimates for poultry meat, edible offal and eggs

^f Highest mean broiler or layer poultry dietary burden suitable for STMR estimates for poultry meat, edible offal and eggs

Estimated residues in animal commodities

For MRL estimation, the residues in the animal commodities are the sum of difenoconazole and CGA 205375 (1-[2-chloro-4-(4-chloro-phenoxy)-phenyl]-2-(1, 2, 4-triazol)-1-yl-ethanol)) expressed as difenoconazole.

Cattle

The 2007 JMPR evaluated two animal transfer studies carried out with Holstein dairy cows administering difenoconazole at 1, 3, 10 ppm (study 1) or 1, 5, 15 ppm (study 2) in the dry-weight diet for 29–30 consecutive days. The Meeting concluded that the two feeding studies were generally in good agreement of transfer factors. Thus, the present Meeting used the study with the 5 and 15 ppm feeding levels as most closely bracketing the dietary burdens.

For maximum residue level estimation, the high residues in the tissues were calculated by interpolating the maximum dietary burden of 17.88 ppm (in 2010 it was 2.42 ppm) between the

relevant feeding levels (5 and 15 ppm) from the dairy cow feeding study and using the highest tissue concentrations from individual animals within those feeding groups.

The STMR values for the tissues were calculated by taking the STMR dietary burden of 15.30 ppm between the relevant feeding levels (5 and 15 ppm) from the dairy cow feeding study and using mean residue of the three animals.

The following table shows the expected residues in animal commodities.

	Feed level (ppm) for milk residues	Residues (mg/kg) in milk	Feed level (ppm) for tissue residues	Residues (mg/kg) in			
				Muscle	Liver	Kidney	Fat
Maximum residue level beef or dairy cattle							
Feeding study ^a	5	< 0.005	5	0.012	0.29	0.046	0.058
	15	0.013	15	0.058	0.80	0.14	0.16
Dietary burden and residue estimate	14.91	0.013	17.88	0.071	0.95	0.17	0.19
STMR beef or dairy cattle							
Feeding study ^b	5	< 0.005	5	0.012	0.25	0.043	0.046
	15	0.013	15	0.046	0.70	0.13	0.14
Dietary burden and residue estimate	12.37	0.011	15.30	0.047	0.71	0.13	0.14

^a Highest residues for tissues and mean residue for milk

^b Mean residues for tissues and milk

For muscle, the residues arising from dietary burdens of 17.88 ppm and 15.30 ppm were 0.071 mg/kg and 0.047 mg/kg, respectively. In fat, the residues arising from dietary burdens of 17.88 ppm and 15.30 ppm were 0.19 mg/kg and 0.14 mg/kg, respectively.

The residues in milk were 0.013 mg/kg and 0.011 mg/kg from dietary burdens of 14.91 ppm and 12.37 ppm, respectively.

For liver, the residues arising from dietary burdens of 17.38 ppm and 15.30 ppm were 0.95 mg/kg and 0.71 mg/kg, respectively. In kidney, the residues arising from dietary burdens of 17.88 ppm and 15.30 ppm were 0.17 mg/kg and 0.13 mg/kg.

The Meeting estimated a maximum residue level for difenoconazole in mammalian fat of 0.2 mg/kg. STMR and HR values for mammalian muscle and fat were estimated as 0.047 and 0.071 mg/kg in muscle, 0.14 and 0.19 mg/kg in fat, respectively.

For milk, the Meeting estimated a maximum residue level of 0.02 mg/kg and an STMR value of 0.011 mg/kg. Information on fat distribution in milk was not available.

The Meeting estimated a maximum residue level, an STMR value and an HR value for difenoconazole in mammalian edible offal of 1.5, 0.71 and 0.95 mg/kg, respectively, reflecting residues in liver of higher residue level.

The Meeting withdrew its previous recommendations on commodities of mammalian origin and milks.

Poultry

The 2007 JMPR evaluated a transfer study carried out with laying white leghorn hens. Four groups of 15 laying hens were fed rations treated with difenoconazole at 0.3, 1, 3 and 10 ppm for 28 consecutive days. Eggs were collected on 10 occasions for analysis (days 0 before treatment, 1, 3, 6, 9, 13, 16, 20, and 23). Poultry tissue and egg samples from the 0.3 ppm feeding group were not analysed because residues were at or below LOQ (< 0.01 mg/kg) in the 1 ppm feeding group. For poultry tissue, residues in 1 ppm feeding level were also not analysed as the residues in 3 and 10 ppm feeding levels were at or below LOQ (< 0.01 mg/kg).

	Feed level (ppm) for egg residues	Residues (mg/kg) in egg	Feed level (ppm) for tissue residues	Residues (mg/kg) in			
				Muscle	Liver	Skin	Fat
Maximum residue level broiler or laying hen							
Feeding study ^a	1	< 0.01	3	< 0.01	< 0.01	< 0.01	< 0.01
	3	0.046	10	< 0.01	< 0.01	< 0.01	< 0.01
Dietary burden and residue estimate	1.89	0.026	1.89	< 0.01	< 0.01	< 0.01	< 0.01
STMR broiler or laying hen							
Feeding study ^b	1	< 0.01	3	< 0.01	< 0.01	< 0.01	< 0.01
	3	0.032	10	< 0.01	< 0.01	< 0.01	< 0.01
Dietary burden and residue estimate	1.11	0.011	1.11	< 0.01	< 0.01	< 0.01	< 0.01

^a Highest residues for tissues and mean residues for egg

^b Mean residues for tissues and mean residues for egg

For poultry tissues, residues arising from the maximum dietary burden of 1.89 ppm were below LOQ (0.01 mg/kg). The Meeting confirmed the maximum residue level recommendation of < 0.01 mg/kg for poultry tissues (fat, edible offal). Further, the Meeting estimated an STMR value and an HR value, 0.001 mg/kg and 0.002 mg/kg, respectively, for the tissues (muscle, fat and edible offal).

For eggs, residues arising from dietary burdens of 1.89 ppm and 1.11 ppm were 0.026 mg/kg and 0.011 mg/kg. The Meeting estimated a maximum residue level of 0.03 mg/kg and an STMR value 0.011 mg/kg and an HR value of 0.026 mg/kg for eggs. The Meeting withdrew its previous recommendation for eggs of 0.01* mg/kg.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue concentrations listed below are suitable for establishing MRLs and for assessing IEDIs and IESTIs.

Definition of the residue (for compliance with the MRL and for estimation of dietary intake) for plant commodities: *difenoconazole*.

Definition of the residue (for compliance with the MRL and for estimation of dietary intake) for animal commodities: *sum of difenoconazole and 1-[2-chloro-4-(4-chloro-phenoxy)-phenyl]-2-(1,2,4-triazol)-1-yl-ethanol*, expressed as *difenoconazole*.

The residue is fat-soluble.

CCN	Commodity	Recommended MRL mg/kg		STMR or STMR-P	HR or HR-P
		New	Previous	mg/kg	mg/kg
VB 0040	Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead brassicas	2		0.35	1.3
VB 0400	Broccoli	W	0.5	0.065	0.41
VB 0402	Brussels sprouts	W	0.2	0.065	0.14
VB 0041	Cabbages, Head	W	0.2	0.035	0.19
VB 0404	Cauliflowers	W	0.2	0.02	0.10
FC 0001	Citrus fruits	0.6		0.16	0.49

CCN	Commodity	Recommended MRL mg/kg		STMR or STMR-P	HR or HR-P
		New	Previous	mg/kg	mg/kg
VC 0424	Cucumber	0.2		0.04	0.15
DF 0269	Dried grapes (=currants, raisins and sultanas)	6		1.1	3.2
MO 0105	Edible offal (Mammalian)	1.5	0.2	0.71	0.95
PE 0112	Eggs	0.03	0.01*	0.011	0.026
VO 0050	Fruiting vegetables , other than cucurbits, except sweet corn and mushroom	0.6	0.5 for tomato	0.14	0.39
VO 0448	Tomato	W	0.5		
VC 0425	Gherkin	0.2		0.04	0.15
VR 0604	Ginseng	0.08	0.5	0.02	0.044
DV 0604	Ginseng, dried including red ginseng	0.2		0.052	0.11
DM 0604	Ginseng, extracts	0.6		0.14	
FB 0269	Grapes	3	0.1	0.52	1.5
MM 0095	Meat (from mammals other than marine mammals)	0.2 (fat)	0.05 (fat)	0.047 (muscle) 0.14 (fat)	0.071 (muscle) 0.19 (fat)
VC 0046	Melons, except watermelon	0.7		0.14	0.35
ML 0106	Milks	0.02	0.005*	0.011	
VA 0385	Onion, Bulb	0.1		0.015	0.07
HS 0444	Peppers, Chili, dried	5		1.1	1.8
FP 0009	Pome fruits	0.8	0.5	0.16	0.47
VR 0589	Potato	4 Po	0.02	1.2	1.9
VA 0389	Spring Onion	9		2.8	3.8
VC 0431	Squash, Summer	0.2		0.04	0.15
JF 0226	Apple juice			0.005	
	Apple pomace, wet			1.5	
JF 0001	Citrus juice			0.002	
OR 0001	Citrus oil, Edible			7.5	
	Citrus pulp dry			0.64	
JF 0269	Grape juice			0.24	
	Grape pomace, dry			6.2	
	Potato chips			0.088	
	Potato flakes			0.029	
	Potato, wet peel			3.8	
VW	Tomato paste			0.22	

CCN	Commodity	Recommended MRL mg/kg		STMR or STMR-P	HR or HR-P
		New	Previous	mg/kg	mg/kg
	Tomato puree			0.08	
	Tomato juice			0.031	
	Tomato canned			0.01	
	Wine			0.094	

DIETARY RISK ASSESSMENT

Long-term intake

The ADI for difenoconazole is 0–0.01 mg/kg bw. The International Estimated Daily Intakes (IEDIs) for difenoconazole were estimated for the 13 GEMS/Food Consumption Cluster Diets using the STMR or STMR-P values estimated by the previous and present JMPR. The results are shown in Annex 3 of the 2013 JMPR Report. The IEDIs ranged 4–60% of the maximum ADI. The Meeting concluded that the long-term intake of residues of difenoconazole from uses considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The ARfD for difenoconazole is 0.3 mg/kg bw. The International Estimate of Short Term Intakes (IESTIs) for difenoconazole were calculated for the food commodities for which STMRs or HRs were estimated by the present Meeting and for which consumption data were available. The results are shown in Annex 4 of the 2013 JMPR Report. The IESTIs varied from 0–30% of the ARfD for children and 0–20% for the general population.

The Meeting concluded that the short-term intake of residues of difenoconazole from other uses that have been considered by the present Meeting is unlikely to present a public health concern.

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DIQUAT (031)

The first draft was prepared by Dr Dugald MacLachlan, Australian Government Department of Agriculture, Fisheries and Forestry

EXPLANATION

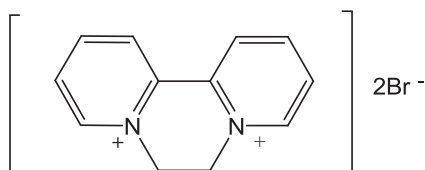
Diquat is an herbicide used in a variety of crops and was first reviewed by the 1970 JMPR. Diquat was scheduled at the Forty-fourth Session of the CCPR (2012) for periodic re-evaluation of toxicology and residues by the 2013 JMPR.

Diquat is a non-selective contact herbicide; the major use of which is for pre-harvest desiccation of a variety of crops. It is rapidly absorbed by green plant tissue and interacts with the photosynthetic process to produce compounds that destroy plant cells. It is inactivated on contact with soil and not taken up by plant roots. As a general herbicide diquat is used to control weeds before planting, before or just after crop emergence, and as a directed spray between the rows of established crops.

IDENTITY

Common name	Diquat
Chemical name	
IUPAC:	6,7 dihydrodipyrido[1,2-a:2',1'-c]pyrazinediium dibromide
CAS:	6,7-dihydrodipyrido[1,2-a:2',1'-c]pyrazinediium (8 & 9 CI)
CAS number:	2764-72-9 (diquat); 85-00-7 (diquat dibromide)
CIPAC Code:	55 (diquat); 55.303 (diquat dibromide)
Molecular formula:	C ₁₂ H ₁₂ N ₂ Br ₂ (diquat)
Molecular mass	344.05 (diquat), 184.2 (diquat ion)

Structural formula:

**Formulations**

Formulations	Active ingredient content
SL diquat	150–240 g ai/L
SL diquat and paraquat mixtures	45–135 g ai/L

Specifications

Specifications for diquat have been developed by FAO (2008).

PHYSICAL AND CHEMICAL PROPERTIES

Pure diquat dibromide as the monohydrate

Property	Results (method)	Reference
Appearance	Pure diquat dibromide is a yellow crystalline solid with no known characteristic odour	Wollerton, 1987; PP901/0024
Melting point	325 °C with decomposition	Wollerton, 1987; PP901/0024
Relative density	1.61 g/cm	Wollerton, 1987; PP901/0024
Vapour pressure	less than 10^{-8} kPa at 25 °C	Wollerton, 1987; PP901/0024
Henry's Law constant	An absolute value for Henry's Law Constant (H) cannot be calculated since pure diquat dibromide has no measurable vapour pressure. The value of H is estimated to be less than 5×10^{-12} Pa/m ³ /mol.	
Solubility in water including effect of pH	712 g/L at pH 5.2 (buffered water) 718 g/L at pH 7.2 (buffered water) 713 g/L at pH 9.2 (buffered water)	Wollerton, 1987; PP901/0024
Solubility in organic solvents (at 20 °C)	Methanol 25 g/L Acetone < 0.1 g/L Dichloromethane < 0.1 g/L Toluene < 0.1 g/L Ethyl acetate < 0.1 g/L Hexane < 0.1 g/L	Wollerton, 1987; PP901/0024
Partition coefficient n-octanol/water	log P _{ow} -4.6	Wollerton, 1987; PP901/0024
Hydrolysis	The hydrolysis of diquat was studied in the dark in sterile, aqueous buffered solutions at pH 4, pH 7 and pH 9 at 50 °C for 5 days. Diquat was shown to be hydrolytically stable under all the conditions tested in this study.	Dixon and Alderman, 2012; PP901_10823
Photolysis	The photolysis of diquat was investigated in sterile natural water under continuous irradiation from a xenon arc lamp simulating natural sunlight. Diquat was rapidly degraded, with only 15.8% parent compound remaining after 3 days irradiation. Degradation followed first-order kinetics with an estimated half-life of 31 hours (equivalent to 6.5 days of Tokyo spring sunshine, or 2 days summer sunlight at a latitude of 50 °N).	Oliver and Webb, 2005; PP901_1892
Dissociation constant	Not measureable	Wollerton, 1987; PP901/0024

Technical grade material

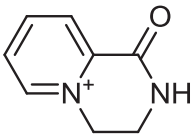
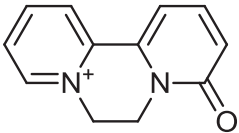
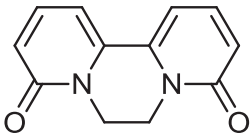
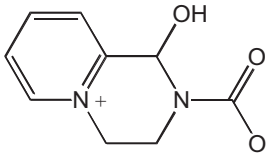
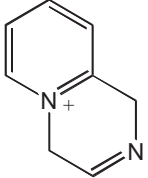
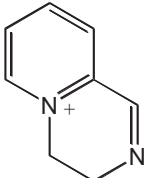
Property	Results (method)	Reference
Physical state, colour, and odour	Dark brown clear liquid with earthy odour	Wollerton, 1987; PP901/0024

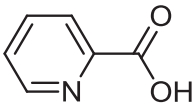
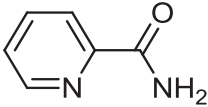
Property	Results (method)	Reference
Density at 25 °C	1.26 g/cm ³	Wollerton, 1987; PP901/0024
pH at 20 °C	6.68	Wollerton, 1987; PP901/0024
Surface tension at 20 °C	41.0 mN/m	Wollerton, 1987PP901/0024

METABOLISM AND ENVIRONMENTAL FATE

Metabolites are given various abbreviations and code numbers in the studies. Structures and abbreviations and codes are shown below.

Degradation compounds from metabolism of diquat in plants, animals, soil, or water

Compound Name	Structure	Found in:
TOPPS 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion R032245		Livestock, plants
Diquat monopyrindone SYN546442 R34908		Livestock, crops
Diquat dipyrindone R030740		Livestock, crops
1-hydroxy-3,4-dihydro-1H-pyrido[1,2-a]pyrazine-2-carboxylic acid		Photolysis
1,4-dihydro-pyrido[1,2-a]pyrazin-5-ylum		Photolysis
3,4-dihydro-pyrido[1,2-a]pyrazin-5-ylum		Photolysis

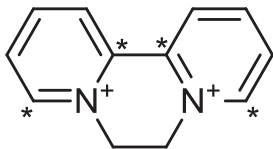
Compound Name	Structure	Found in:
Picolinic acid		Livestock, crops
Picolinamide		Livestock, crops

The identification of residue components in the animal and plant metabolism studies was achieved using authentic standards of the compounds involved.

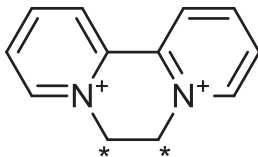
Animal metabolism

The Meeting received studies on the metabolism of diquat in rats, lactating goats and laying hens. The metabolism of only low levels of radioactivity are found in plant parts such as tubers that are not directly exposed to the spray in plants and animals was investigated using [^{14}C] diquat bromide. The structural formula and the positions of the ^{14}C label are shown below. The studies on rats were evaluated by the WHO Core Assessment Group.

*Label positions of diquat: marked as **



Ring-labelled diquat



Bridge-labelled diquat

Lactating goat

Wickstead and Lowrie (2012 PP901_10848) studied the metabolism of diquat in a lactating goat (53.5–58 kg bw; 2 kg milk/d) that was dosed orally via gelatin capsule once a day with ring labelled [^{14}C] diquat dibromide just after the morning milking for 7 consecutive days at the equivalent of 90 ppm in the feed (feed consumption 2.2 kg DM/d). Milk was collected twice daily and urine and faeces were collected daily. The goat was sacrificed approximately 12 h after the administration of the final dose and tissues taken post-mortem for quantification and analysis of radioactivity.

The radioactive residue in liquid samples was determined by direct liquid scintillation counting. Solid samples were homogenised frozen and the radioactive residue determined by combustion analysis followed by liquid scintillation counting. Milk, liver, kidney, composite muscle (forequarter, hindquarter and tenderloin in the ratio 4:4:1) and subcutaneous fat, sub-samples of were extracted three times (four times for fat) with 10% trichloroacetic acid. The resulting extracts were then further fractionated and subjected to chromatographic analysis by HPLC-MS/MS with concurrent radiodetection for identification/characterisation and quantification, respectively. The day 6 urine sample was analysed directly by LC-MS to provide further understanding of the biotransformation pathway.

The total recovery of dosed radioactivity was 97% with the majority of the radioactivity excreted in the faeces (84%) and only low levels (0.8%) in the urine. Approximately 12% remained in the gastrointestinal tract contents.

TRR in milk samples increased during the dosing period and reached a maximum of 0.015 mg equiv/kg in the milk collected at 156 hours (Day 7 pm) after the start of dosing. The large difference in TRR levels for samples collected at the morning and afternoon milkings is indicative of rapid elimination.

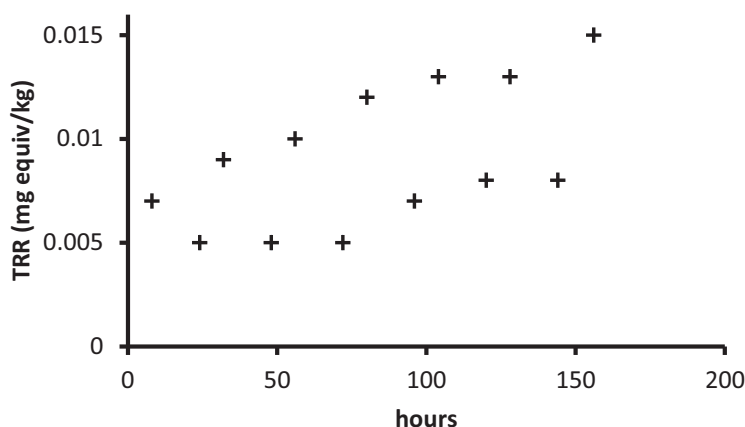


Figure 1 Radioactive residue in milk following dosing of a lactating goat once daily, equivalent to 90 ppm in the feed, for 7 consecutive days + morning samples, ● evening samples

Subsamples of day-4 to day-7 milk were separated by centrifugation into cream and skimmed milk; the fraction of cream residue to skimmed milk residue was between 0.57 and 0.67 in all samples suggesting the residues do not selectively partition into lipids.

Radioactive residues in tissues were low and ranged from 0.003 mg equiv/kg in the omental fat to 0.079 mg equiv/kg in the kidneys. Good extractability was achieved for the milk and muscle samples with greater than 90% TRR recovered in extracts. Extractability of radioactive residues from kidney and fat was approximately 80%TRR while the extractability from liver was slightly lower at 64% TRR.

The identified metabolites in the tissue, milk and urine samples are summarised in Table 1.

Table 1 Identification of radioactivity in goat tissue, milk and urine

Matrix	Milk	Liver	Kidney	Muscle	Subcutaneous Fat	Urine
TRR (mg equiv/kg)	0.012	0.052	0.079	0.010	0.016	—
			%TRR			
Extracted	94	64	83	91	80	

Matrix	Milk	Liver	Kidney	Muscle	Subcutaneous Fat	Urine
Diquat dipyrindone	82	33	29	46	20	16
Diquat monopyridone	ND	13	21	13	ND	19
Diquat	ND	22	4.3	ND	3.5	19
Unextracted	6.2	36	17	9.1	20	—

ND = not detected

The radioactivity remaining in liver and kidney after extraction with 10% trichloroacetic acid was further investigated using molecular weight/size exclusion filtration following treatment of the debris with sodium dodecyl sulphate. In liver, 9.2% TRR (0.005 mg equiv/kg) was characterised as having a molecular weight of < 3 kDa and a further 9.8% TRR (0.005 mg equiv/kg) > 3 kDa. In kidney, 1.2% TRR (0.001 mg equiv/kg) was characterised as < 3 kDa and a further 2.5% TRR (0.002 mg equiv/kg) > 3 kDa.

Laying hens

The metabolism of diquat in laying hens was studied by Leahey and Hemingway (1973, PP901/0464). Doses of ^{14}C -bridge labelled diquat were applied to the hen feed pellets and were administered orally once daily. Three experiments were carried out in this study, as follows:

Experiment 1

One hen was given a single oral dose of [^{14}C] diquat at a rate equivalent to 4–5 ppm in the diet and excreta collected for 3 days post dosing. Expired air was collected for 4 hours on day 1 and 7 hours on day 2 by drawing the air through ethanolamine traps.

Experiment 2

One hen was given five daily oral doses of [^{14}C] diquat at a rate equivalent to 4–5 ppm in the diet. Excreta and eggs were collected daily. The hen was sacrificed 7 days after the final dose, and samples of meat, fat, liver, kidney and lungs collected.

Experiment 3

One hen was given 14 daily oral doses of [^{14}C] diquat at a rate equivalent to 0.4–0.5 ppm in the diet. Excreta and eggs were collected daily. The hen was sacrificed 4 hours after the final dose, and samples of meat, fat, liver, kidney and blood collected.

TRR levels in the samples were determined by oxidative combustion followed by liquid scintillation counting (LSC) or by direct liquid scintillation counting. Dose feed pellets were analysed 1 and 28 days after treatment with [^{14}C] diquat. Pellets were extracted with water followed by 1 N HCl, and the combined extracts analysed by paper chromatography and by isotope dilution. Faeces samples were extracted by boiling with 2 M HCl, and the extracts analysed by paper chromatography against reference standards and by isotope dilution for diquat, diquat monopyridone and TOPPS. Fat was dissolved in a xylene solution for analysis by LSC. All other tissues were dried and analysed by sample oxidation. Eggs were separated into yolk and albumen. The egg yolks from experiments 2 and 3 were extracted by refluxing with 2 M HCl. Diquat, diquat monopyridone and TOPPS were isolated and analysed by isotope dilution.

The majority of the administered residue was rapidly excreted in hens. Extremely low residues of diquat or its metabolites were found in the tissues and eggs of poultry after continuous oral dosing with diquat.

In Experiment 1 after 3 days, 98% of dose was recovered in the excreta with almost none recovered in expired air traps.

In Experiment 2 after 8 days, 94% of dose was recovered in the excreta, most of which was unchanged diquat. The residue levels in eggs during and after dosing are shown in Figure 2. One week

after the final dose, very low radioactive residues were found in the tissues, indicating that neither diquat nor its metabolites accumulate in the hen. TRR in egg yolks from days 5 and 6 comprised 36–39% diquat, 54–61% diquat monopyridone and 6–7% TOPPS.

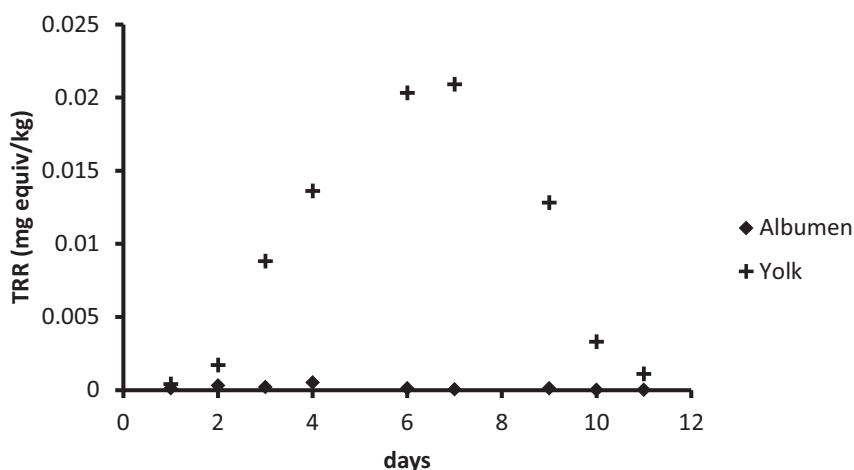


Figure 2 Radioactive residues in eggs following dosing of hens once daily, equivalent to 4–5 ppm in the feed, for 5 consecutive days

Table 2 Radioactive residues in hen tissues following oral administration of [^{14}C] diquat to a laying hen for 5 consecutive days at 4–5 ppm in the diet

Sacrifice time	TRR (mg equiv/kg)				
	Muscle	Fat	Liver	Kidney	Lung
5 days dosing + 7 days depletion)	< 0.0001	0.0008	0.0004	0.0035	0.0008

Residues in excreta were profiled. During the dosing period, unchanged diquat accounted for 75–80% of the excreted radioactivity. TOPPS (2%) and diquat dipyrindone (4%) were also detected.

In Experiment 3 very low TRR were detected in the egg albumen (0.00001–0.00012 mg equiv/kg) and yolk (0.0002–0.0032 mg equiv/kg) of eggs collected throughout the 14 day dosing period. Very low TRR were found in the tissues collected 4 hours after the final dose.

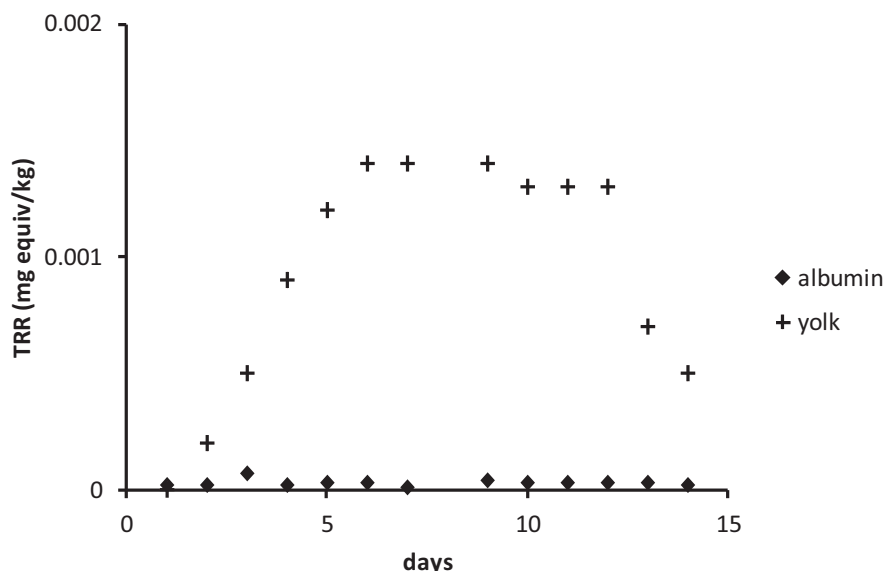


Figure 3 Radioactive residues in eggs following dosing of hens once daily, equivalent to 0.4–0.5 ppm in the feed, for 14 consecutive days (outlier at day 8 white 0.00012 mg equiv/kg and yolk 0.0032 mg equiv/kg not plotted)

The extractability of radioactivity from treated feed pellets declined with time after preparation and may have accounted in part for the unexpected decline in TRR for eggs. Yolk from day 9 + 10 eggs contained 26% diquat, yolks from day 7 contained 85% diquat monopyridone and egg yolks from day 11 contained 10% TOPPS.

Table 3 Radioactive residues in hen tissues following oral administration of [^{14}C] diquat to a laying hen for 14 consecutive days at 0.4–0.5 ppm in the diet

Sacrifice time	TRR (mg equiv/kg)					
	Muscle	Fat	Liver	Kidney	Lung	Blood
Day 14 (14 days dosing)	0.00019	0.00010	0.00042	0.00045	0.00016	0.00043

A later study French and Leahey (1988, RJ0622B Fujie 1988 addendum PP901/0470) also investigated the metabolism and distribution of [^{14}C] diquat in laying hens. Three laying hens were each given daily doses of ^{14}C -ring labelled diquat by oral gavage for 4 days at 2.4 mg/kg bodyweight/day equivalent to 32 ppm in the diet. Excreta and eggs were collected daily. The hens were sacrificed 18 hours after the last dose, and samples of liver, kidney, muscle and fat collected. Samples were stored at -18°C prior to analysis. TRR levels in the samples were determined by combustion followed by liquid scintillation counting (LSC) or by direct liquid scintillation counting (egg whites, extracts). Pooled tissue samples were extracted with acetonitrile. After solvent extraction, liver and kidney samples were subjected to a second extraction with 2 M HCl under reflux. Residues in liver and kidney extracts were characterized using HPLC and TLC against reference standards, and by isotope dilution.

Table 4 Radioactive residues in eggs and tissues following oral administration of [^{14}C] diquat to hens for 4 consecutive days at 32 ppm in the diet

Matrix	Radioactive residue (mg equiv/kg)
Egg yolk (day 2 ^a)	< 0.001
Egg white (day 2 ^a)	0.004
Liver	0.030–0.045
Kidney	0.042–0.058

Matrix	Radioactive residue (mg equiv/kg)
Muscle (leg and breast)	0.003
Fat (abdominal and subcutaneous)	0.004

^a All hens laid eggs at day 2 only

Radioactive residues in the muscle, fat and eggs were all < 0.01 mg/kg and were not analysed further. For liver, 76% of the radioactive residue was extracted with acetonitrile/water, and a further 22% TRR was extracted with 2 M HCl, total extracted 97%. The residue comprised mainly diquat, with small amounts of TOPPS, diquat monopyridone and diquat dipyrindone being identified. For kidney, 70% TRR was extracted with acetonitrile/water, and a further 28% TRR extracted with 2M HCl, total 98%. The residue in kidney was shown to comprise diquat and diquat monopyridone in similar amounts together with small amounts of TOPPS and diquat dipyrindone.

Table 5 Identification of the radioactive residues in liver and kidney following oral administration of [¹⁴C] diquat to hens for 4 consecutive days at 32 ppm in the diet

Matrix	liver	kidney
TRR (mg equiv/kg)	0.045	0.058
	%TRR	
Extracted	97	98
Diquat	48	12
TOPPS	1.8	3.9
Diquat monopyridone	3.9	15
Diquat dipyrindone	3.1	6.6
Unidentified in acetonitrile/water extract	27	37
Unidentified in 2 M HCl extract	13	24
Unextracted	2.6	1.9

In an additional study, Hughes and Leahey (1975, PP901/0461) studied the absorption, metabolism and distribution of incurred residues of [¹⁴C] diquat in laying hens. ¹⁴C-ring labelled diquat was sprayed onto mature barley plants at a rate equivalent to 1.1 kg ai/ha. After 4 days, the barley plants were harvested and the dried grain powdered and pelleted for dosing. One laying hen (hen 1) was given a single oral dose of treated grain pellets. A further two laying hens (hens 2 and 3) were each given 11 consecutive daily doses of treated grain pellets at a rate equivalent to 1–1.5 ppm in the diet. Excreta and eggs were collected daily. Hen 2 was sacrificed 7 days after the final dose and hen 3 was sacrificed 4 hours after the final dose. At sacrifice, samples of heart, liver, kidney, lungs, muscle and fat were collected.

TRR levels in the samples were determined by oxidative combustion followed by LSC or by direct liquid scintillation counting (diluted egg yolk and albumen, extracts). Samples of the pelleted barley grain were extracted by refluxing with 2 N HCl, and the extracts analysed for diquat and its photoproducts by paper chromatography against reference standards and by isotope dilution. Faeces samples from hen 1 and hen 2 (day 10) were extracted by refluxing with 2 N HCl, and the activity in the extract determined by LSC. The hen 2 (day 10) sample was analysed by paper chromatography against reference standards and by isotope dilution. Faeces samples from hens 2 and 3 were analysed by combustion. Egg yolk (hen 2, day 8) was extracted with ethyl acetate, and the extract analysed by LSC to determine the amount of radioactivity associated with fat. The egg yolk residue was purified by washing with 1 N HCl, 1 N NaHCO₃ and water, and combusted to determine the amount of radioactivity associated with protein.

The majority of the administered dose was excreted in the faeces. The transfer of residues to eggs and tissues was very low following repeated daily oral dosing. The maximum residues found in eggs albumen and yolk was 0.0006 and 0.0039 mg equiv/kg respectively. Residue levels in tissues were very low, with the highest residues being found in kidney (0.014 mg equiv/kg) and liver (0.0046 mg equiv/kg) at 4 hours after the final dose).

Table 6 Recovery of total radioactivity following oral administration of [^{14}C] diquat (incurred residues) to laying hens at a dose level of 1–1.5 ppm in the diet

Matrix	Recovery of radioactivity (% of dose)		
	Hen 1 (sacrificed 5 days after a single dose)	Hen 2 (sacrificed 7 days after 11 daily doses)	Hen 3 (sacrificed 4 hours after 11 daily doses)
Faeces	96	89	84
Eggs	–	0.08	0.05
TOTAL	96	89	84

Table 7 TRR in eggs following daily oral administration of [^{14}C] diquat (incurred residues) to laying hens for 11 consecutive days at a dose level of 1–1.5 ppm in the diet

	Radioactive residue (mg equiv/kg)			
	Hen 2 (sacrificed 7 days after 11 daily doses)		Hen 3 (sacrificed 4 hours after 11 daily doses)	
Day	Albumen	Yolk	Albumen	Yolk
1	0.0002	< 0.0005	< 0.0001	< 0.0005
2	0.0003	< 0.0005	0.0002	< 0.0005
3			0.0004	0.0009
5	0.0005	0.0011	0.0004	0.0017
6	0.0005	0.0019	0.0004	0.0025
7	0.0005	0.0034	0.0005	0.0030
8	0.0005	0.0037	0.0004	0.0033
10	0.0006	0.0038	am 0.0005 pm 0.0004	am 0.0035 pm 0.0034
11	0.0006	0.0038		
13	0.0004	0.0039		
14	0.0001	0.0030		
15	< 0.0001	0.0027		
17	< 0.0001	0.0025		
18 (inside hen)	< 0.0001	0.0015		

Table 8 Radioactive residues in tissues following daily oral administration of [^{14}C] diquat (incurred residues) to laying hens for 11 consecutive days at a dose level of 1–1.5 ppm in the diet

Animal ID (Sacrifice time)	Radioactivity residue (mg equiv/kg)					
	Muscle	Heart	Kidney	Lung	Liver	Fat
Hen 2 (sacrificed 7 days after last dose)	0.0002	0.0003	0.0012	0.0007	0.0004	0.0011
Hen 3 (sacrificed 4 hours after last dose)	0.0009	0.0008	0.014	0.0014	0.0046	0.0022

The residue in the treated grain, used to prepare the dose, was characterized.

Table 9 Characterization of radioactive residues in treated barley grain and hen faeces

Component	Residue in treated grain (% TRR)	Residue in hen 2 day 10 faeces (% TRR)
Diquat	17	16
TOPPS	8.7	3.6
Diquat monopyridone	1.1	2.4
Diquat dipyrindone	0.1	1.0
Picolinic acid	1.7	0.4
Picolinamide	1.0	0.5
Unidentified photoproducts	59	49
Unextracted	15	27

Analysis of the faeces from hen 2 (day 10) showed that the composition of the radioactivity in the faeces was fairly similar to the composition of the dose.

Radioactive residues in the egg albumen were very low and as a result no attempt was made to characterise the residue. The yolks from hen 2 (days 10, 11 and 13) were analysed. Diquat, TOPPS and diquat monopyridone were found to account for only a small part of the residue in egg yolk. The majority of the residue in egg yolk was found to be associated with fats and protein. This is in contrast to the study (French and Leahey, 1988; Report RJ0622B) where hens were dosed with [^{14}C] diquat only where diquat, TOPPS and diquat monopyridone accounted for almost all the radioactive residue in eggs.

Table 10 Characterization of radioactive residues in egg yolk following oral administration of [^{14}C] diquat and its photoproducts to a laying hen for 11 consecutive days at a dose level of 1–1.5 ppm in the diet

	Hen 2 Day 8 yolk	Hen 2 Day 10 yolk	Hen 2 Day 11 yolk	Hen 2 Day 13 yolk
TRR (mg equiv/kg)	0.0037	0.0038	0.0038	0.0039
		%TRR		
Diquat		0.9		
TOPPS			3.5	
Diquat monopyridone				3.0
Associated with fats	31			
Associated with protein	29			

Metabolic pathways in animals

Diquat is poorly absorbed following oral ingestion and is largely excreted in the faeces; residues in tissues, milk and eggs are low.

In the ruminant dosed with [^{14}C] diquat at the equivalent of 90 ppm in the diet for a period of 7 consecutive days and terminated 12 hours after the final dose, the recovery of ^{14}C was 97%. The majority of the radioactivity was found in the faeces and only 0.8% in the urine. Radioactive residues milk and tissues were low. In liver, diquat (22%), diquat monopyridone (13%) and diquat dipyrindone (33%) were the major components of the ^{14}C residue. In kidney the major components were diquat (4.3%), diquat monopyridone (21%), and diquat dipyrindone (29%). In milk the radioactive residue comprised almost entirely diquat dipyrindone. Radioactive residues in muscle and fat were very low comprising of diquat dipyrindone (20–46% TRR). Diquat represented 3.5% TRR in fat but was not found in muscle. In muscle diquat monopyridone represented 13% TRR and was not found in the fat sample.

In poultry dosed with diquat at 32 ppm in the diet for 4 days, the residues in eggs and tissues were low. The radioactive residue in liver was characterised as mainly diquat (48%), with small quantities of diquat monopyridone (3.9%), diquat dipyrindone (3.1%) and TOPPS (1.8%), also present. The radioactive residue in kidney was mainly comprised of diquat (12%) and diquat monopyridone (15%). Small quantities of diquat dipyrindone (6.6%) and TOPPS (3.9%) and were also present.

The metabolism of diquat in ruminants and laying hens is adequately understood. In both goats and hens diquat is oxidised to form diquat monopyridone and diquat dipyrindone. TOPPS is found as a minor metabolite in hens but was not detected in studies of the metabolism of diquat by goats or rats.

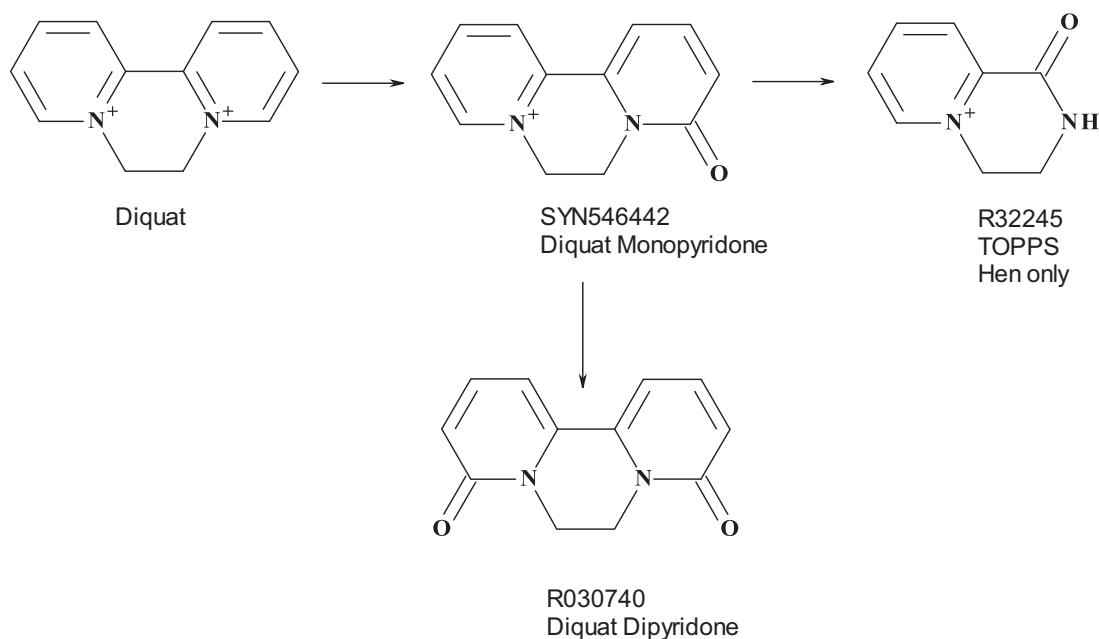


Figure 4 Proposed metabolic pathway for diquat in livestock (ruminant and poultry)

Plant metabolism

For weed control, diquat is applied either pre-emergent or inter row. On contact with the soil, diquat is strongly adsorbed by clay minerals and organic matter, reducing the availability of the chemical for degradation and uptake by plant roots. It is unlikely that soil residues will be taken up by the crops. Additionally diquat is used pre-harvest for crop desiccation with application at a time when plants are entering senescence and little diquat is expected to be translocated.

The metabolism of diquat in plants was studied in tomatoes (pre-emergent application) and in potatoes and rape plants (pre-harvest desiccation). Each study utilised ring-labelled diquat (as the dibromide salt).

Tomatoes

Derz (2012, A1412A_10298) studied the metabolism of diquat in tomatoes (var “Vitella”) following a single pre-emergence application to soil for the control of weeds. A single pre-emergence application at a nominal application rate of 1.0 kg diquat/ha (spray volume 300 L/ha) of an SL formulation was made to sandy loam soil into which tomato seeds had previously been sown. The tomato plants were maintained in a container in a glasshouse until maturity. Mature fruits, immature fruits, leaves and stems were harvested 112 days after application and were separately homogenised and radioactivity determined by combustion/LSC. TRR were 0.002 mg equiv/kg in tomato leaves and < 0.001 mg equiv/kg in mature fruits and due to the low levels were not analysed further.

The low levels detected in mature fruits and in leaves suggest that uptake of residues from soil into crops is negligible.

Potatoes

The metabolism of diquat in potato plants (var Belana”) following a desiccant use pattern was studied by Derz (2012 A1412A_10304). A single foliar application of an SL formulation of [¹⁴C] diquat dibromide was made to potato plants at growth stage BBCH 44–48 and at an application rate of 0.97 kg ai/ha in a spray volume of 400 L/ha. The potato plants were grown outdoors in a sandy loam soil and the tubers and haulm harvested 10 days and 20 days after application. Tubers were gently

wiped to remove the adhering soil, were washed with water and then peeled. After peeling, the potato flesh was washed again and the radioactivity in all wash solutions determined by LSC. The tuber flesh and skins were separately homogenised in a frozen state and the radioactivity determined by combustion/LSC.

The wash solutions were not analysed further since the radioactive residue present was determined to be extremely low, i.e., 0.0003 mg equiv/kg potato.

TRRs in tuber flesh were 0.029 and 0.032 mg equiv/kg for the samples taken after 10 and 20 days after application respectively. TRRs in tuber skins harvested after 10 and 20 days amounted to 0.044 and 0.039 mg equiv/kg, respectively. Sub-samples of tuber flesh and skins were extracted under reflux with water/sulphuric acid. Aliquots of the water / sulphuric acid extracts were centrifuged, adjusted to pH 9 and subjected to solid phase extraction.

The total extractability for all samples was very high with > 95% TRR extracted by a single water/sulphuric acid reflux. The levels of radioactivity that remained unextracted were low in all samples ($\leq 4.7\%$ TRR; ≤ 0.002 mg equiv/kg) and were not investigated further.

The principal component of the residue in the extracts was parent diquat representing $\geq 71.7\%$ TRR. No postulated metabolites of diquat were detected. A minor unassigned metabolite was observed during TLC analysis but only in potato flesh from the samples harvested 10 days after treatment and at very low levels, corresponding to 0.5% TRR (< 0.001 mg equiv/kg). No individual fraction contained $> 9.0\%$ TRR (0.003 mg equiv/kg).

The extracted radioactivity was analysed by chromatography. The identified components for tuber flesh and skins at each sampling interval are summarised in Table 11.

Table 11 Identification of radioactivity in potato tubers

	flesh		skins	
Days after application	10	20	10	20
TRR (mg equiv/kg) ^a	0.029	0.032	0.044	0.039
	%TRR			
Extracted	97	97	95	96
Diquat	79	74	72	73
Unassigned ^b	0.5	ND		
Baseline ^c	3.9	4.0	2.5	3.6
Remainder ^d	1.9	1.6	2.0	1.6
Other fractions ^e	9.1	6.6	7.2	4.1
Unextracted ^f	2.9	2.9	4.7	3.7
Losses/gains on fractionation ^g	2.9	11	12	14
Total	100	100	100	100

^a mg equiv/kg calculated directly from radioactivity extracted, radioactivity in the debris and specific activity.

^b Unassigned components which chromatographed away from the origin in 1D-TLC. In the 10 day sample this comprises of a single discrete component.

^c Polar material on origin of the radio-chromatogram using 1D-TLC.

^d The remainder comprises diffuse areas of radioactivity within the chromatogram which cannot be assigned to discrete radioactive components.

^e Extractable residues in 2–3 fractions per harvest timepoint that were not analysed and produced during processing that were too low for analysis. No single fraction comprised $> 9.0\%$ TRR (> 0.003 mg equiv/kg) in either harvest timepoint.

^f Radioactivity remaining in the debris after the water/sulphuric acid reflux extraction procedure.

^g The net cumulative incremental losses or gains during analysis, calculated as 100%—sum of all components.

The presence of diquat in tubers suggests translocation occurs though the levels are low.

Oilseed Rape

Derz (2012, A1412A_10305) also studied the metabolism of diquat in oilseed rape plants following use of diquat for pre-harvest crop desiccation. An SL formulation of [¹⁴C] diquat was applied as a single foliar application to oilseed rape plants (var “Belinda”) at growth stage BBCH 80–87 at an

application rate of 0.58 kg ai/ha and in a spray volume of 300 L/ha. The rape plants were grown outdoors in a sandy loam soil and the seed, pods and foliage were harvested 5 days after application. The seeds were homogenised in a frozen state to a powder and the radioactive residue determined by combustion/LSC. A sub-sample of seed was extracted sequentially once with hexane, using a Soxhlet-extractor, to remove the oil and then the remaining meal twice with water / sulphuric acid under reflux. Aliquots of the combined water / sulphuric acid extracts were centrifuged, adjusted to pH 9 and subjected twice to solid phase extraction (SPE) procedures.

TRR in the oilseed rape seed was 0.97 mg equiv/kg. Extractability was high with 82% TRR extracted from the seed. Significant radioactive residues were only extracted into the water/sulphuric acid extracts (82% TRR), while the initial hexane which contained the oil fraction only extracted 0.3% TRR.

The principal component of the residue in the meal, after extraction of the oil with hexane, was parent diquat representing 48% TRR. Diquat metabolites TOPPS and diquat monopyridone were observed at low levels corresponding to 7.8 and 2.0% TRR respectively. Minor unassigned components were observed representing in total 3.9% TRR (0.038 mg equiv/kg) but no individual component accounted for > 2% TRR (0.019 mg equiv/kg).

Unextracted radioactivity amounted to 17.9% TRR. A sub-sample of post-extraction solids was subjected sequentially to further extraction with acetonitrile/water (80/20), diluted acid and a surfactant solution. Each separate treatment step released radioactivity representing $\leq 2.0\%$ TRR and in total only a further 3.5% TRR was extracted leaving 10.1% TRR (0.098 mg equiv/kg) which was not investigated further.

The principal component of the residue in the meal after extraction of the oil was parent diquat with two diquat metabolites, TOPPS and diquat monopyridone, observed at low levels.

Table 12 Summary of total radioactive residues and extractability in rape seed treated with [^{14}C] diquat dibromide

TRR (mg equiv/kg) ^a	0.969
	%TRR
Extracted	73
Diquat	48
TOPPS	7.8
diquat monopyridone	2.0
Unassigned ^b	3.9
Baseline ^c	1.9
Remainder ^d	5.5
Other fractions ^e	4.2
Unextracted ^f	18
Losses/gains on fractionation ^g	8.9
Total	100

^a TRR determined by summation of radioactivity present in the extracts, filter and debris following solvent extraction.

^b Unassigned components which chromatographed away from the origin in 1D-TLC comprising at least three discrete components, none > 2% TRR; 0.019 mg equiv/kg.

^c Polar material on origin of the radio-chromatogram using 1D-TLC

^d The remainder comprises diffuse areas of radioactivity within the chromatogram which cannot be assigned to discrete radioactive components.

^e Extractable residues in 4 fractions produced during processing that were too low for analysis. No single fraction comprised > 2.2% TRR (> 0.021 mg equiv/kg).

^f Radioactivity remaining in the debris after the initial hexane and water/sulphuric acid reflux extraction procedures.

^g The net cumulative incremental losses or gains during analysis, calculated as 100%—sum of all components.

Table 13 Further characterisation of radioactive residues in rape seed post-extraction solids

Percentage of TRR in PES	17 (Sub-sample)
TRR (mg equiv/kg)	0.164

Percentage of TRR in PES	17 (Sub-sample)
Radioactive residues released by	% TRR
Acetonitrile/water 80/20	2.0
Dilute acid reflux (water/sulphuric acid)	1.4
2% (w/v) SDS solution in water	0.1
Filters used	1.0
Remaining unextracted	10
Losses on fractionation	2.4
Total	17

Metabolic Pathways in Crops

For weed control use, diquat is applied pre-emergent or as an inter-row spray; in this use diquat will inevitably reach the soil. There is no deliberate application to crop plants, and accidental application is avoided so far as possible by careful spraying and/or the use of shielded sprayers. There is effectively no direct application to plants. Once on the soil, diquat is strongly adsorbed by clay minerals and organic matter and largely unavailable for metabolism by soil organisms or uptake by plant roots. It is not expected that there would be any residues in crop commodities following weed control use of diquat.

In the tomato metabolism study where [^{14}C] diquat was applied to the soil as a single pre-emergent application, radioactive residues in leaves and mature fruits were very low, 0.002 and < 0.001 mg equiv/kg respectively.

Where diquat is used for desiccation of crops, the residues found in commodities that are not exposed to the spray (i.e. tubers) show only low levels of parent diquat with no degradation products were observed. Where direct spray could result in application to the commodity, other metabolites/degradates, i.e. TOPPS and diquat monopyridone are also found albeit at low levels (< 7.8% and 2.0% TRR respectively). The proposed transformation pathway for diquat following desiccation use is shown in Figure 5.

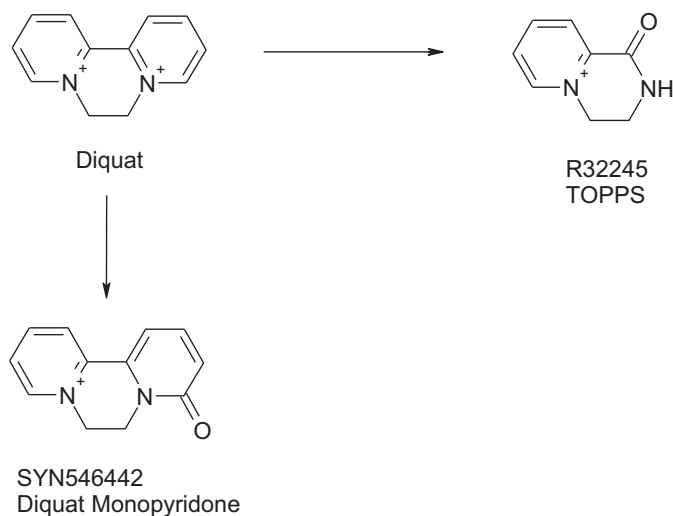


Figure 5 Proposed metabolic pathway for diquat in plants following pre-harvest desiccation use

Confined rotational crop studies

A confined rotational crop study was conducted on a sandy loam soil treated at 1.12 kg ai/ha with ^{14}C ring-labelled diquat (Lee 1989 PP901/0451). After intervals of 30, 120, and 365 days, carrots (var

Imperator), lettuce (var “Parris Island Romaine”) and wheat (var “Anza”) were planted and grown under greenhouse conditions to maturity. Plant samples were harvested at immature and mature stages for analysis. In most cases, the TRR in the mature plant were below the LOD (< 0.008 mg equiv/kg). The TRR was above the LOD in the carrot leaf at 365-days post- treatment (0.017 mg equiv/kg) and the wheat straw at 120- and 365-days post-treatment (0.022 and 0.024 mg equiv/kg, respectively). It is likely the radioactive residue in these plants, identified as parent diquat, is due to contamination with soil though not all the residues were removed with rinsing. Immature plants contained TRRs above LOD (0.035–0.090 mg equiv/kg) but these residues were not characterized since the immature plants are not a typical raw agricultural commodity. The bulk of the radioactivity was contained in the soil, mostly in the 0–7.6 cm soil depth (TRR 0.13–1.15 mg equiv/kg) with little observed in the 7.6–15 cm soil cores (0–0.047 mg equiv/kg).

Crops grown in soil containing [^{14}C] diquat showed negligible uptake of radioactivity. As such, crops grown in rotation with diquat-treated crops are not expected to contain residues of diquat or diquat degradation products.

Field Crop Rotational Studies

No field crop rotational studies were made available to the meeting. However, no residues are expected in rotational crops.

Environmental fate in soil

Route of Degradation in Soil

Aerobic degradation in soil

The rate and route of degradation of [^{14}C] diquat was investigated in four soils under aerobic conditions by Dixon (2012, PP901_10824). [^{14}C] Diquat was applied at a nominal rate equivalent to a single application of 0.54 kg ai/ha. The soil samples were incubated under aerobic conditions in the laboratory and maintained under moist, dark conditions at 20 °C for up to 120 days. Extraction was sequentially using calcium chloride solution, sulphuric acid (6 M) and finally water and acetone solutions. Additional samples for each soil type were incubated up to 364 days and the volatile radioactivity recovered in the liquid traps quantified to investigate the potential for further mineralisation to $^{14}\text{CO}_2$ beyond the normal study duration.

The mean total recoveries of radioactivity for the 0 to 120 DAT soil samples were between 93 and 103% of applied radioactivity (AR). The total extracted was high throughout the incubation period (from 97 to 99% AR at 0 DAT and 96 to 101% AR at 120 DAT). Of the extraction solutions, minimal radioactivity was extracted using calcium chloride solutions ($\leq 0.3\%$ extracted at 0 DAT).

Levels of parent compound decreased slowly over the incubation period from initial values of 96% to be 86–98% AR at 120 DAT. In addition to parent, four minor metabolites were present at levels $< 5\%$ AR; diquat monopyridone and three unknown compounds.

The unextracted radioactivity remained constant throughout the 120 DAT incubation period for the Gartenacker loam and 18 Acre sandy clay loam soils, ranging from 0.4 to 3.2% AR. Unextracted radioactivity at 7 days in the Marsillargues silty clay and North Dakota sandy clay loam soils were 9.5 and 8.1% AR, respectively, declining thereafter. Limited degradation to volatile products was observed with levels of $^{14}\text{CO}_2$ in traps totalling $< 5\%$ AR by the end of the study 36 DAT.

The rate of degradation was estimated using single first-order (SFO) kinetics. The DT_{50} values obtained are presented in Table 14.

Table 14 Summary of DT_{50} for diquat in the various culture systems at 10 mg diquat/L

Soil	DT_{50} (days)	Chi^2	r^2

Gartenacker (Switzerland, loam)	662	0.81	0.9109
18 Acres (UK, sandy clay loam)	> 1000 ^a	1.46	0.0702
Marsillargues (France, silty clay)	> 1000 ^a	4.16	0.0034
North Dakota (USA, sandy clay loam)	> 1000 ^a	3.05	0.0017

^a Although there was a small amount of degradation, calculated DT₅₀ values could not be differentiated from zero using SFO kinetics and therefore a default of 1000 days is proposed.

A number of studies assessed the degradation of diquat by soil bacteria and fungi and to enhance the understanding of the intrinsic biodegradability of diquat (Ricketts, 1997 PP901/0876; Kuet *et al.*, 2001a PP901/1321; Kuet and Pinheiro, 2001 PP901/0741; Kuet *et al.*, 2001b PP901/1244). The studies used a range of techniques including isolated soil bacterial cultures, aqueous soil extracts, isolated soil fungal species and a soil yeast culture (*Lipomyces starkeyi*). Diquat is rapidly and extensively degraded by soil micro-organisms, normally found in soil pore water, in the absence of soil, to give a small number of non-volatile degradation products (not identified), with mineralisation to CO₂. The DT₅₀ for degradation in soil solution is rapid at < 1 week.

Addition of clay minerals to the bacterial test system proportionately decreased the rate of diquat degradation, and ¹⁴CO₂ evolution, until the point when virtually all the diquat had adsorbed onto the clay, when degradation apparently ceased. This finding confirms that sorbed diquat is not available to biological degradation processes.

Mônego (2006, PP901/1977) studied the rate of degradation of [¹⁴C] diquat in four viable Brazilian soils: Argissolo Vermelho from Eldorado do Sul (sandy clay loam), Latossolo Vermelho from Nova Prata (clay), Neossolo from Osório (sand) and Gleissolo from Viamão (sandy loam) under aerobic laboratory conditions. The test was performed at 20 °C in the dark under aerobic conditions with soil moisture content at 40% of the maximum water holding capacity (MWHC). Diquat was applied to the soils at the rate of 0.5 kg ai/ha. The dissipation half-lives were calculated using nonlinear first-order regression and are summarised in Table 15.

Table 15 Dissipation half-lives (DT₅₀) for diquat in four soils from Brazil

Soil	k	Half-life (days)
Argissolo (sandy clay loam),	0.00071	976
Latossolo (clay)	0.00239	290
Neossolo (sand)	0.00148	468
Gleissolo (sandy loam)	0.00122	568
Mean		576

Diquat dissipation proceeded slowly in each soil. Unchanged diquat accounted for an average of 99%, 101%, 104% and 99% at day 0 to 86%, 77%, 80% and 83% at day 119 for Argissolo, Latossolo, Neossolo and Gleissolo soils, respectively. Other than diquat, only a single minor compound was detected in Argissolo, Neossolo and Gleissolo soils but accounted for less than 2.8% of the applied radioactivity at the end of the study.

The soil dissipation of diquat occurs at a very slow rate and is dependent on the equilibrium between sorbed and dissolved phases.

Aerobic degradation of TOPPS

Dixon and Dove (2012, CGA130327 10007) investigated the rate of degradation of [¹⁴C]-TOPPS in four soils under aerobic conditions. [¹⁴C]-TOPPS was applied at a nominal rate equivalent to a single application rate of 0.15 kg ai/ha. The microbial biomass at the end of the incubation period (120 DAT) was in the range 1.6 to 2.7% of organic carbon indicating that the soil supported a viable microbial population. The soil samples were maintained under moist, dark aerobic conditions at 20 °C for up to 120 days.

Levels of TOPPS decreased over the incubation period from initial values of 93–94% to 3.8–46% AR (Gartenacker and Marsillargues) and from 94–95% to 82–85% AR (18 Acres and White Swan). Limited mineralisation to $^{14}\text{CO}_2$ was observed in 18 Acres and White Swan soils, with maximum levels reaching 2.2% AR by the 120 DAT timepoint. However, significant levels of $^{14}\text{CO}_2$ were formed during the incubation period for Gartenacker and Marsillargues soils, with levels reaching 53 and 46% AR at 120 DAT, respectively, indicating that mineralisation is potentially a major route of degradation.

The TOPPS degradation data were modelled to obtain DT_{50} and DT_{90} values using SFO kinetics as listed in the table (Patterson 2012 CGA130327_10009). DT_{50} values range from 28 to 757 days with a geometric mean of 224 days.

Table 16 Dissipation half-lives for TOPPS in soil

Soil	DT_{50} (days)	DT_{90} (days)
18 Acres	750	> 1000
Gartenacker	27.8	92.4
Marsillargues	159	529
White Swan	757	> 1000

Anaerobic degradation

A number of studies have investigated the long-term dissipation of diquat in field soils (Wilkinson 1980 PP148/0662; Gowman *et al.*, 1980 PP148/0576; Cole *et al.*, 1986 PP148/0014; Dyson and Chapman 1986 PP901/0017). Dissipation of diquat was monitored following application of either a single dose of diquat at exaggerated application rates (UK and USA), or of repeat annual doses of diquat applied at normal field application rates (USA). These long-term studies indicate that the DT_{50} for the total diquat residue was in the range 10–20 years in the UK and 1–4 years in the USA.

Monitoring studies on diquat residues in soil after long-term treatment of various crops with diquat showed that soil residues were considerably lower than the 'theoretical' maximum that would be anticipated on the basis of the amount of diquat known to have been applied and assuming no degradation (Devine 2004, PP901/1604).

Surveys on sites using diquat as a desiccant in various crops were also carried out in Europe (Anderson and Earl 1996, PP901/0522). In a series of 39 trials, diquat residues were determined in a variety of soils 184–280 days after a single application of diquat in an SL formulation as a desiccant to a variety of crops (potatoes, oilseed rape, peas and sunflowers) at rates up to 1 kg ai/ha. The amount of diquat reaching the soil was substantially below the theoretical deposition rate based on the amount of diquat applied. The average loss of applied diquat by degradation on the plant and soil between application and sowing of the following crop was 75%. German trials (on potatoes, oilseed rape and fodder peas, treated at 0.5–0.6 kg ai/ha) showed a loss of diquat 268 days after application of 45–75%. Following application at rates of 0.5–1.0 kg ai/ha, the increases in diquat soil residues the following spring were less than 0.11 mg/kg and averaged only 0.03 mg/kg in the top 30 cm of soil.

Diquat in soil adsorbs strongly to clay materials, and is not bioavailable leading to persistence in soils. However, when released into solution diquat is available for microbial degradation. Diquat degrades very slowly in standard aerobic soil studies. Mineralisation to form CO_2 was demonstrated with the extent varying between soils. Diquat is persistent in the environment.

Soil photolysis

The photolysis of diquat was investigated on both dry and moist soil surfaces of one soil, Gartenacker (Switzerland, loam) by Dixon and Gilbert (2012, PP901_10832). Ring-labelled [^{14}C] diquat was applied at a rate equivalent to 0.54 kg ai/ha, to thin layers of either dry or moist soil in individual photolysis vessels. The treated soils were maintained at about 20 °C and continuously irradiated using light from a xenon arc lamp filtered to provide a spectral distribution close to natural sunlight, with a

mean light intensity of 24.3 W/m^2 for periods up to the equivalent of approximately 30 days summer sunlight.

The mean mass balance ranged from 97 to 101% for the irradiated samples and from 98 to 101% for the dark controls.

Dry layer tests

Only slight degradation occurred in the light and dark dry soil samples. Two minor degradation products, TOPPS and diquat monopyridone, were observed in the irradiated samples, individually accounting up to 0.9% AR.

Moist layer tests

Degradation was more significant in the light moist soil samples with only a small degree of degradation occurring in the dark moist soil samples. The major photolytic degradation product was TOPPS which reached a maximum of 9.9% AR after 30 days. Diquat monopyridone was also detected but was generally present at levels $< 1\%$ AR. A number of other minor degradation products were also detected. Unknown SP-1, present at between 5.2 and 5.4% after 30 days, was found to be composed of two components by TLC. The maximum level of either single component was 4.0% AR. Volatile radioactivity, confirmed as CO_2 , resulted mainly from irradiation of moist soil with levels of $^{14}\text{CO}_2$ reaching 7.2% AR by 30 DAT.

The maximum levels of unextracted residues were observed under light and moist conditions and were present up to a level of 3.1% AR after the 30-day incubation period.

In soil exposed to light, the main degradation pathway involved oxidation to diquat monopyridone and TOPPS. In dark samples, only oxidation to diquat monopyridone was observed. There was also photodegradation to a number of minor unknowns under moist light conditions. There was a small amount of mineralization to carbon dioxide.

The rate of degradation was estimated using single first-order (SFO) kinetics. Under the experimental conditions, photolytic DT_{50} values in dry soil and in moist soil were 237 and 37 days respectively (equivalent summer days for Europe and North America at latitudes 30° and 50°N). Degradation in the dark controls was significantly slower with DT_{50} for the dry and moist soils being 857 and > 1000 days, respectively.

Soil photolysis is not expected to be a significant route of diquat degradation.

Aqueous Photolysis

Oliver and Webb (2005, PP901/1892) studied the photolysis of diquat in sterile natural water (Middle Row Pond). Solutions containing $10 \mu\text{g } [^{14}\text{C}] \text{ diquat/mL}$ were continuously irradiated using light from a xenon arc lamp filtered to give a spectral distribution close to that of natural sunlight. The samples were maintained at 25°C and were irradiated for periods up to the equivalent of approximately 15 days Tokyo spring sunlight (equivalent to approximately 5 days of summer sunlight at latitude of 50°N).

The mean mass balance (across all samples) was 94% of the applied radioactivity. Diquat was rapidly degraded accounting for 16% AR after 3 days of continuous irradiation. The photo-degradation of diquat followed first-order kinetics with an estimated half-life of 31 hours under continuous irradiation, equivalent to approximately 6.5 days of Tokyo spring sunlight (or approximately 2 days of summer sunlight at a latitude of 50°N).

A number of photo-degradates were formed (> 8 HPLC peaks in samples at 2 and 3 days of irradiation). The most significant identified metabolite formed was TOPPS, reaching a level of 23% AR at 15 days irradiation. Traces of diquat monopyridone were also detected (maximum 4.3% AR after 3 days). A mixture of 1,4 dihydropyrido[1,2a]pyrazin-5-ylum and 3,4 dihydropyrido[1,2a]pyrazin-5-ylum was detected by LC-MS/MS analysis although levels were not determined. The majority of the remainder consisted of a polar component (representing a maximum

of 12% AR after 2 days of irradiation) identified as 1-hydroxy-3,4-dihydro-1H-pyrido[1,2-a]pyrazine-2-carboxylic acid. Trapped volatiles ($^{14}\text{CO}_2$) accounted for up to 3.8% AR during the irradiation period. No significant degradation was apparent in the dark controls indicating that the degradation in irradiated samples was the result of photodegradation only.

Aqueous photolysis of diquat is expected to be a significant route of degradation under environmental conditions.

RESIDUE ANALYSIS

Analytical methods

The analysis of diquat is complicated by its polar nature and similarity in properties to paraquat. Several different analytical methods have been reported for the analysis of residues of both compounds in plant materials, animal tissues, milk and eggs. Early methods used in field trials generally involve extraction of residues by reflux with sulphuric acid with clean-up on cation exchange columns. Detection was initially achieved spectrophotometrically following reduction with alkaline dithionite or sodium borohydride. In more recent methods, the diquat recovered from the cation exchange column is subjected to HPLC with NPD or UV detection. In the case of animal commodities, trichloroacetic acid is sometimes used in place of sulphuric acid for the extraction step.

The efficiency of the acid extraction step has been demonstrated during the metabolism studies where the majority of the total radioactive residue (TRR) was recovered in the aqueous acid extracts.

The most recent advance in methods has been the use of LC-MS/MS which allows for the clean-up steps to be omitted.

A brief description of the methods used in the residue trials is given in Table 17.

Table 17 Summary of major analytical methods used for the determination of diquat and metabolites in various matrices

Method/reference	Matrix	Extraction	Clean-up	Detection, LOQ
PPRAM 1	Plant commodities	Reflux 0.5 M H_2SO_4	Filter extract, percolate through cation exchange column, wash 2.5% NH_4Cl , elute saturated NH_4Cl . A portion is reduced with alkaline sodium dithionite.	Spectrophotometric detection, 350–450 nm LOQ 0.1–0.5 mg/kg
PPRAM 005/RAM 005	Plant commodities	<u>Oil seeds:</u> Remove oil by extracting with hexane. Then proceed as for other crops. <u>Other crops:</u> Reflux 0.5 M H_2SO_4	Filter extract, percolate through cation exchange column, wash 2.5% NH_4Cl , elute saturated NH_4Cl . A portion is reduced with alkaline sodium dithionite.	Spectrophotometric detection, 350–450 nm LOQ 0.05–0.1 mg/kg
RM5/RM5.5	Plant commodities	Reflux 18 N H_2SO_4	Filter extract, percolate through cation exchange column, wash 2.5% NH_4Cl , elute saturated NH_4Cl . A portion is reduced with alkaline sodium dithionite.	Spectrophotometric detection, 350–450 nm LOQ 0.02–0.05 mg/kg
RM5C	Plant commodities	Reflux 18 N H_2SO_4	Filter extract, percolate through cation exchange column, wash 2.5% NH_4Cl , elute saturated NH_4Cl . A portion is reduced with sodium borohydride.	GC-NPD LOQ 0.02 mg/kg
PPRAM 007	Liquid	Mix with cation	Place resin in a column and	Spectrophotometric detection

Method/reference	Matrix	Extraction	Clean-up	Detection, LOQ
	commodities (milk, water)	exchange resin and roll for 2 hours, decant the liquid and wash the resin 3× with deionised water	wash 2.5% NH ₄ Cl, elute saturated NH ₄ Cl. A portion is reduced with alkaline sodium dithionite.	(350–450 nm) LOQ 0.001–0.01 mg/kg
RAM 252 RAM 252/01 RAM 252/02	Plant commodities	Reflux 0.55 to 1 N H ₂ SO ₄ depending on matrix	Precipitation with EDTA may be used prior to clean-up using cation exchange. Filter extract, percolate through cation exchange column, sequentially wash with deionised water, 2 M HCl and 2.5% NH ₄ Cl. Elute using saturated NH ₄ Cl. A portion is reduced with alkaline sodium dithionite. If using HPLC, clean-up using C18 SPE cartridge	Spectrophotometric detection 350–450 nm (RAM 252) 2 nd derivative spectrophotometric detection (RAM 252/01) HPLC-UV 310 nm (RAM 252/02) LOQ 0.02–10 mg/kg
RAM272	Plant commodities	Reflux 0.55 to 1N H ₂ SO ₄ depending on matrix	<u>For oilseeds:</u> precipitation with EDTA is required prior to clean-up using cation exchange. <u>For all crops:</u> Filter extract, percolate through cation exchange column, sequentially wash with deionised water, 2M HCl and 2.5% NH ₄ Cl. Elute using saturated NH ₄ Cl. Clean-up the eluate on a preconditioned SPE cartridge.	Reversed-phase ion-pair HPLC-UV (310 nm) LOQ 0.01–0.05 mg/kg.
POPIT MET.021 Rev00	Citrus	Reflux 1 M H ₂ SO ₄	Filter extract, adjust to 100 mL. An aliquot is derivatised using potassium ferricyanide/NaOH and partitioned against CH ₂ Cl ₂ . The organic phase is evaporated and redissolved in CH ₃ CN/H ₂ O (1:1).	LC-MS/MS LOQ 0.02 mg/kg
GRM012.03A	Plant commodities	<u>Oilseeds:</u> Reflux 1M H ₂ SO ₄ <u>Other:</u> Reflux 1M H ₂ SO ₄ + octan-2-ol	Centrifuge if required. Aliquots (0.01 µL) are diluted with ammonium formate (250 mM) and CH ₃ CN.	LC-MS/MS LOQ 0.01 mg/kg
RM5B	Animal commodities	Reflux 18 N H ₂ SO ₄	<u>Fat:</u> Partition against hexane. <u>All samples:</u> Filter extract, percolate through cation exchange column, wash with H ₂ O, 2.5% NH ₄ Cl, elute saturated NH ₄ Cl. A portion is reduced with sodium borohydride.	GC-NPD LOQ 0.02 mg/kg
PPRAM 7	Animal commodities	Homogenise in ten times the volume CCl ₃ COOH (10%), centrifuge. Retain the liquid. Resuspend the pellet in CCl ₃ COOH (10%) and	Percolate through cation exchange column. Sequentially wash with H ₂ O, 2 N HCl, H ₂ O, 2.5% NH ₄ Cl, H ₂ O. Elute saturated NH ₄ Cl. A portion is reduced with alkaline sodium dithionite.	Spectrophotometric detection (350–450 nm) LOQ 0.01 mg/kg

Method/reference	Matrix	Extraction	Clean-up	Detection, LOQ
		centrifuge retaining the liquid.		
GRM012.02A	Animal commodities	Homogenise in ten times the volume CCl ₃ COOH (10%)	Centrifuge, aliquots (75 μ L) are diluted with ammonium formate (250 mM) and CH ₃ CN.	LC-MS/MS LOQ 0.005 mg/kg

Plant materials

PPRAM 1 (developed for paraquat and extended to diquat, PP148/0910, PP148/0972, PP148/0349, PP901/0478)

Samples are extracted by reflux in dilute (0.5 M) sulphuric acid solution to which a small amount of octan-2-ol is added (about 1:500 v/v). The filtered digest is percolated through a column of cation-exchange resin. The column is washed with aqueous ammonium chloride (2.5%) to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. A portion of the eluate is treated with alkaline sodium dithionite (0.2% w/v in 0.3 M NaOH) to reduce diquat to a free radical. Light absorption of the radical is measured spectrophotometrically between 350 and 450 nm. The absorption is compared to a reference solution prepared from saturated ammonium chloride and sodium dithionite. The spectra must be measured within 5 minutes of adding the dithionite. The LOQ was 0.01–0.05 mg/kg for diquat in crop matrices, depending on the crop.

Table 18 Recovery data for the determination of diquat obtained during carrot residue analysis (PP901/0636)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)
Carrot	0.10	97, 78, 82	3	86	12
Lettuce	0.50	75, 102, 75	3	84	19
Onion	0.10	74, 99, 76	3	83	17

Residue Analytical Method PPRAM 005/RAM 005(PP901/0230, PP901/0220)

For oil seeds: a preliminary hexane extraction is performed to remove oil before the acid extraction. All commodities: Samples are extracted by reflux in dilute (0.5 M) sulphuric acid solution. The filtered digest is neutralised and percolated through a column of cation-exchange resin. The column is washed with aqueous ammonium chloride (2.5%) to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. A portion of the eluate is treated with alkaline sodium dithionite (0.2%w/v in 0.3 M NaOH) to reduce diquat to a free radical. Light absorption of the radical is measured spectrophotometrically (350–450 nm). The LOQ was 0.01–0.1 mg/kg for diquat in crop matrices, depending on the crop.

Table 19 Recovery data for the determination of diquat using method PPRAM 5A/RAM 005 (PP901/0240, PP901/0671)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Potatoes	0.05	100, 80, 82, 76, 98	5	87	13	76–100
	0.10	95, 91, 84, 71, 92, 82, 76, 84, 68, 70, 81, 79, 76, 69, 81, 69	16	79	11	68–95
	0.20	61, 62, 69, 71, 68, 77, 60, 72, 76	9	68	9.2	60–77
	Overall		30	77	14	60–100
Grapes	0.05	87	1	–	–	–
	0.10	89	1	–	–	–

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
	Overall		2	88	—	87–88
Rape seed	0.05	87, 69	2	78	—	69–87
	0.10	89, 59	2	74	—	59–89
	0.20	88	1	—	—	—
	0.50	108	1	—	—	—
	Overall		6	83	21	59–108
Rape seed oil	0.10	87, 77	2	82	—	—
	0.20	80, 82, 88	3	83	5.0	80–88
	0.50	70	1	—	—	—
	Overall		6	81	8.3	70–88
Potatoes	0.01	89, 101	2	95	—	89–101
	0.10	84, 84	2	84	—	84
	0.50	88, 88	2	88	—	88
	Overall		6	89	7.0	84–101
Peas (seeds, fresh)	0.05	84, 85	2	85	—	84–85
	0.10	87, 84	2	86	—	84–87
	0.50	89, 92	2	91	—	89–92
	Overall		6	87	3.8	84–92
Beans (seeds, fresh)	0.05	88, 87	2	88	—	87–88
	0.10	81, 80, 85, 78	4	81	2.9	78–85
	0.50	84, 85, 91, 93	4	88	4.4	84–93
	Overall		10	85	5.6	78–93
Rape seed cake	0.10	72, 85	2	79	—	72–85
	2.0	70, 70	2	70	—	70
	10	73, 72	2	73	—	72–73
	Overall		6	74	7.7	84–92
Rape seed oil	0.05	88, 71	2	80	—	71–88
	0.10	81, 72	2	77	—	72–81
	0.50	73, 77	2	75	—	73–77
	Overall		6	77	8.5	71–88

Residue Analytical Method RM-5 (PP901/0594)

Samples are extracted by reflux in concentrated (18 N) sulphuric acid solution for 15 minutes. A small volume of octan-2-ol may be added to reduce foaming. Filter the digest. For oily crops, extract the filtered digest three times with benzene, retaining the aqueous phase. The filtered digest/aqueous phase is neutralised using 50% NaOH, EDTA (1 g) is added and the solution adjusted to pH 9 (10 M NaOH) and percolated through a column of cation-exchange resin. The column is washed with aqueous ammonium chloride (2.5%) to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. In method versions RM-5 and RM-5-5, a portion of the eluate is treated with alkaline sodium dithionite to reduce diquat to a free radical. Light absorption of the radical is measured spectrophotometrically (350–450 nm).

In method version RM-5C, reduction with dithionite was replaced by reduction with sodium borohydride and determination of the reduced diquat product was by GC-NPD in place of spectrophotometry.

The LOQ of the method was 0.02 mg/kg for diquat in crop matrices.

Table 20 Recovery data for the determination of diquat using method RM-5C, Report PP901/0238

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Potatoes	0.02	111, 117, 99	3	109	8.4	99–117
	0.10	88, 80, 86	3	85	4.9	80–88
	Overall		6	97	15	80–117
Tomatoes	0.02	109, 99, 106	3	105	4.9	99–109
	0.10	85, 86, 82	3	84	2.5	82–86
	Overall		6	95	12	82–109

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Lettuce	0.02	101, 119, 118	3	113	9.0	101–119
	0.10	85, 86, 82	3	84	2.5	82–86
	Overall		6	99	17	82–119
Oranges	0.02	98, 108, 97	3	101	6.0	97–108
	0.10	94, 92, 99	3	95	3.8	92–99
	Overall		6	98	5.7	92–108
Wheat grain	0.02	116, 107, 110	3	111	4.1	107–116
	0.10	74, 94, 102	3	90	16	74–102
	Overall		6	101	15	74–116

Residue Analytical Method PPRAM 007 (PP901/1005)

Aliquots of milk or water are mixed with cation-exchange resin by rolling for 2 hours. After allowing the resin to settle, the milk or water is decanted away from the resin and the resin washed three times with deionised water. The resin is then packed into a burette and the water allowed to percolate through. The resin column is washed with aqueous ammonium chloride (2.5%) to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. A portion of the eluate is treated with alkaline sodium dithionite to reduce diquat to a free radical. Light absorption of the radical is measured spectrophotometrically (350–450 nm). The LOQ of the method was reported to be 0.001 to 0.01 mg/kg for diquat in liquid matrices, depending on the sample volume used, however no data to support the LOQ was supplied.

Table 21 Diquat analytical method recovery data for method PPRAM 007 (PP901/1005)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Milk	0.001	85 88 90 94 100 85 100 100 100 100 100 100 100 91 108 100	16	96	7.1	85–108
	0.002	100 91 85 88 92 91 93 100 100 100 85 100 100 97	14	94	6.2	85–100
	0.003	83 90 93 89	4	89	4.7	83–90
	0.004	94 84	2			84–94
	0.008	80 81	2			80–81
Tissues ^a	0.01–0.2	NR	12	90		75–100

^a Tissues fortified and individual recovery values were not reported

Residue Analytical Method RAM 252 (PP901/0589)

Samples are extracted by reflux in dilute (0.55–1 M, depending on sample type) sulphuric acid solution. The filtered digest is neutralised using NaOH and percolated through a column of cation-exchange resin. For some crops an additional clean-up i.e. required where 5% (w/v) EDTA solution is added after the neutralisation step and the solution filtered prior to loading onto the cation exchange column. The column is washed with deionised water, hydrochloric acid (2 M), aqueous ammonium chloride (2.5%) and deionised water to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. A portion of the eluate is treated with alkaline sodium dithionite to reduce diquat to a free radical. Light absorption of the radical is measured using a scanning spectrophotometer in second-derivative mode (350–450 nm). Oilseeds may be analysed directly as whole, seeds or extracted with hexane and the cake and oil (from evaporation of the hexane extract) determined separately. The LOQ of the method ranged from 0.01 mg/kg to 10 mg/kg, depending on the matrix.

In an extension to the method (RAM 252/02) the sample is cleaned up using a C₁₈ SPE cartridge prior to analysis using HPLC-UV.

Table 22 Diquat procedural recovery data obtained in residue trials during 1989–1994 (PP901/0589, PP148/0350)

Matrix	Fortification Range (mg/kg)	n	Mean Recovery (%)	RSD (%)
Grape	0.05–0.1	2	100	5
Banana	0.05–0.2	10	92	3
Carrot	0.05–0.1	2	97	3
Onion	0.05–0.1	2	87	2
Lettuce	0.05–0.1	2	92	1
Pea seed	0.05–0.1	6	88	15
Pea haulm	0.1–20	6	90	6
Lentils	0.1	2	85	2
Linseed oil	0.1	2	72	8
Linseed cake	0.5–2.0	2	69	1
Sunflower oil	0.05–0.1	2	89	3
Sunflower cake	0.1–0.4	2	72	6
Potato	0.05–0.2	32	94	6
Barley grain	0.5–3.0	4	97	2
Barley straw	10–25	4	98	2
Oat grain	0.5–3.0	2	93	1
Oat straw	10–25	2	98	2
Wheat grain	0.1	4	82	4
Wheat straw	0.1–0.2	3	68	6
Rice grain	0.05–0.1	2	90	3
Rice straw	0.05–0.1	2	95	2
Maize cob	0.05–0.1	2	89	2
Maize silage	0.05–0.1	2	82	5
Coffee bean	0.05–0.5	8	80	4

The methods also refer to validation studies (M4895B and CEMR-322) conducted with earlier versions of the method and which remain applicable. These data are summarised above (under Method PPRAM 005).

Table 23 Recovery data for the determination of diquat using method RAM 252 (PP901/0742)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Potatoes	0.02	113, 69	2	91	–	69–113
	0.10	63, 72	2	68	–	63–72
	Overall		4	68	6	63–113
Pea seed	0.05	81, 79	2	80	–	79–81
	0.10	85, 77	2	81	–	77–85
	Overall		4	80	4	77–85
Bean seed	0.05	71, 73	2	72	–	71–73
	0.10	71, 71	2	71	–	71
	0.50	81, 82	2	82	–	81–82
	Overall		6	75	7	71–82

Residue Analytical Method RAM 272 (PP901/0226, PP901/0225)

Crop samples are extracted by reflux in dilute (0.55–1 M, depending on sample type) sulphuric acid solution. The filtered digest is neutralised and percolated through a column of cation-exchange resin. The column is washed with deionised water, hydrochloric acid (2 M), aqueous ammonium chloride (2.5%) and deionised water to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. An additional clean-up step using precipitation with EDTA is required prior to ion-exchange clean-up for oilseed crops. A portion (10 mL) of the eluate from the resin column is transferred to a pre-conditioned SPE cartridge (C₁₈) and eluted, collecting a portion of the second 5 mL for final determination. The analytical standards are cleaned-up in the same way to remove interferences arising from ammonium chloride. Diquat residues in the clean-up extracts are

determined using reversed-phase ion-pair HPLC with UV detection (310 nm). The LOQ of the method ranged from 0.01 to 0.05 mg/kg, depending on the matrix.

Table 24 Recovery data for the determination of diquat using method RAM 272, (PP901/0689, PP901/0244, ASF378/0002, PP901/1438)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Potatoes	0.01	93, 94, 94, 110	4	98	8	93–110
	0.10	88, 93, 106, 102	4	97	8	88–106
	0.5	95, 95	2	95	–	95
	Overall		10	97	7	88–106
Barley grain	0.02	95, 90, 90, 85	4	90	5	85–95
	0.10	80, 88, 83, 113	4	91	17	80–113
	1.0	91, 87	2	89	–	87–91
	Overall		10	90	10	80–113
Beans	0.05	88, 84, 86, 74	4	83	7	74–88
	0.10	86, 90, 90, 94	4	90	4	86–94
	0.50	96, 96	2	96	–	96
	Overall		10	88	7	74–96
Rape seed	0.05	78, 98, 92, 96	4	91	10	78–98
	0.10	95, 99	2	97	–	95–99
	0.50	92, 85	2	89	–	85–92
	2.0	93, 97	2	95	–	93–97
	Overall		10	93	7	78–99
Potatoes	0.01	89, 89, 90, 85	4	88	2.5	85–90
	0.05	69, 96	2	83	–	69–96
	0.2	94, 76	2	85	–	76–94
	Overall		8	86	11	76–96
Rape seed	0.05	67, 76, 78, 65	4	72	9.0	65–78
	0.25	58, 78, 87, 88	4	78	18	58–88
	1.0	80, 81	2	81	–	80–81
	Overall		10	76	13	78–99
Orange	0.01	99, 95, 94, 96, 88	5	94	3.6	88–99
	0.10	92, 91, 91, 92, 93	5	92	0.9	91–93
	Overall		10	93	2.7	88–99
Tomato	0.01	104, 78, 94, 100, 88	5	93	11.1	78–104
	0.10	97, 97, 98, 96, 94	5	96	1.6	94–98
	Overall		10	95	7.6	78–104
Rape seed	0.05	87, 92, 90, 91, 87	5	89	2.6	87–92
	0.50	89, 89, 87, 88, 88	5	88	0.9	87–89
	Overall		10	89	2.0	87–92
Straw	0.05	77, 71, 76, 75, 76	5	75	3.1	71–76
	0.50	72, 87, 78, 76, 85	5	80	7.9	72–87
	Overall		10	77	6.6	71–87
Potatoes	0.0025	91, 90	2	91	–	90–91
	0.005	84, 86	2	85	–	84–86
	0.01	89, 91	2	90	–	89–91
	Overall		6	89	3.3	84–91

Residue Analytical Method POPIT MET.021.Rev00 (PP148/3146)

Diquat is extracted from crop samples by reflux in dilute (1 M) sulphuric acid solution. After cooling, the extract is filtered and adjusted to a volume of 100 mL before an aliquot of the extract solution is derivatized with potassium ferricyanide/sodium hydroxide. The resulting solution is partitioned against dichloromethane. The organic phase is evaporated and redissolved in acetonitrile:water (1:1, v / v) for quantification by liquid chromatography with mass-selective triple-quadrupole mass-spectrometric detection (LC-MS/MS). The LOQ of the method was 0.02 mg/kg.

Table 25 Recovery data for the determination of diquat using method POPIT MET.021.Rev00 (PP148/3146)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Orange fruit	0.02	91, 88, 89, 89, 92, 96, 98	7	91	4.1	88–98
	0.2	83, 78, 79, 76, 74	5	78	4.3	74–83
	Overall		12	86	9.2	74–98
Orange juice	0.02	107, 104, 107, 91, 106, 86, 108	7	101	8.8	86–108
	0.2	97, 100, 106, 106, 109	5	104	4.8	97–109
	Overall		12	102	7.2	86–109

Residue Analytical Method GRM012.03A (PP901/0478, PP901/2096)

Samples are extracted by reflux in dilute sulphuric acid solution (3.75% v/v). Octan-2-ol may be added to reduce foaming. Extracts are centrifuged (if required) and aliquots (100 µL=0.01 g) are diluted with aqueous ammonium formate (250 mM) and acetonitrile. Final determination is by LC-MS/MS, primary 183–157 m/z and confirmatory 183–130 m/z transition data. The detector response was linear for solution concentrations ranging from 0.000005 to 0.005 µg/mL corresponding to sample concentrations of 0.005 to 0.16 mg/kg (r^2 1.000). Sample extracts (3.75% v/v H₂SO₄) were stable for at least 15 days when stored at < 7 °C. Final extracts (CH₃CN: pH 3.7 aqueous ammonium formate buffer 30:70 v/v) were stable for at least 8 days when stored at < 7 °C. Stock solutions of diquat in water were stable for at least 51 days when stored at < 7 °C. No significant enhancement or suppression of MS/MS response was detected for the matrices in Table 26. The LOQ of the method is 0.01 mg/kg for diquat in crop matrices.

It was noted that diquat absorbs strongly to glass and it is imperative to use disposable polypropylene labware (not Teflon). LC systems should be fitted with PEEK tubing rather than stainless steel to avoid Teflon or derivatized the glass silanols using trimethylsilane.

Table 26 Recovery data for the determination of diquat using method GRM012.03A (PP148/3147)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Primary transition m/z 183–157						
Sunflower seeds	0.01	93, 101, 100, 99, 93	5	97	4	93–101
	0.10	103, 105, 100, 97, 99	5	101	3	97–105
	Overall		10	99	4	93–105
Sunflower oil	0.01	87, 86, 90, 116, 89	5	93	13	86–116
	0.10	89, 119, 89, 89, 83	5	94	15	83–119
	Overall		10	94	14	83–119
Lettuce leaves	0.01	84, 80, 80, 87, 88	5	84	4	80–88
	0.10	86, 84, 92, 88, 83	5	87	4	83–92
	Overall		10	85	4	80–92
Cereal grains	0.01	112, 112, 98, 105, 100	5	105	6	98–112
	0.10	111, 111, 107, 108, 114	5	110	3	107–114
	Overall		10	108	5	98–114
Orange whole fruits	0.01	76, 76, 81, 79, 81	5	79	3	76–81
	0.10	83, 79, 85, 82, 78	5	82	4	78–85
	Overall		10	80	4	76–85
Hop fresh cones	0.01	81, 82, 77, 79, 77	5	79	3	77–82
	0.10	78, 82, 78, 80, 80	5	80	2	78–82
	Overall		10	79	2	77–82
Cabbages	0.01	91, 84, 84, 90, 89	5	88	4	84–91
	0.10	91, 95, 99, 100, 106	5	98	6	91–106
	Overall		10	93	8	84–106
Confirmatory Transition m/z 183–130						

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Sunflower seeds	0.01	96, 101, 109, 94, 90	5	98	7	90–109
	0.10	98, 99, 96, 97, 98	5	97	1	96–99
	Overall		10	98	5	90–109
Sunflower oil	0.01	88, 82, 87, 118, 75	5	90	18	75–118
	0.10	84, 122, 92, 89, 84	5	94	17	84–122
	Overall		10	92	17	75–122
Lettuce leaves	0.01	81, 78, 84, 88, 101	5	86	11	78–101
	0.10	82, 79, 80, 85, 82	5	81	3	79–85
	Overall		10	84	8	78–101
Cereal grains	0.01	110, 101, 96, 92, 110	5	102	8	92–110
	0.10	113, 109, 106, 110, 116	5	111	4	106–116
	Overall		10	107	7	92–116
Orange whole fruits	0.01	79, 77, 86, 84, 81	5	81	5	77–86
	0.10	84, 81, 82, 82, 79	5	82	2	79–84
	Overall		10	81	3	77–86
Hop fresh cones	0.01	78, 80, 75, 81, 79	5	79	3	75–81
	0.10	79, 85, 81, 77, 83	5	81	4	77–85
	Overall		10	80	4	75–85
Cabbages	0.01	96, 91, 97, 96, 112	5	98	8	91–112
	0.10	87, 94, 97, 97, 103	5	95	6	87–103
	Overall		10	97	7	87–112

In addition, a range of methods have been published in the scientific literature for the analysis of diquat in various crops that are similar to those reported above (Worobey 1993; Chichila and Walters 1991; Chichila and Gilvydis 1993; Aramendía *et al.*, 2006; King 1978; Calderbank and Yuen 1966; Tadeo *et al.*, 2000).

An LC-MS/MS method has been developed by Kolberg *et al.*, (2012). Homogenised samples (10 g for potato and 5 g for barley, pulses and other dry commodities are weighed into 50 mL centrifuge tubes and 100 µL of a 10 µg/mL internal standard mixture added. For the dry commodities, water (10 mL) is added and the slurry was allowed to stand for 10 min to allow the water to thoroughly wet the sample. Then 10 mL of extraction solution (MeOH (50%) + HCl 0.1 M in H₂O (50%)) is added and the mixture shaken for 2 min followed by heating at 80 °C in a water bath for 15 min after which the extracts are shaken vigorously and then cooled prior to centrifugation for 5 min at 4000 rpm. An aliquot is filtered through a syringe filter (0.45 µm) and analysed directly by LC-MS/MS (m/z 183/157). LOQs were 0.006 mg/kg for diquat in potatoes and barley. Mean recoveries in three different laboratories were 94 to 120% (n=5).

RESIDUES IN FOOD OF ANIMAL ORIGIN

Residue Analytical Method RM-5B

Samples are extracted by reflux in concentrated (18 N) sulphuric acid solution. Fat samples are initially cleaned-up by hexane partition. For all sample types, the filtered digest is then percolated through a column of cation-exchange resin. The column is washed with water and aqueous ammonium chloride (one-tenth saturated) to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. Diquat is reduced with sodium borohydride and determination of the reduced diquat product is by GC-NPD. The LOQ of the method is 0.02 mg/kg for diquat in animal matrices.

Table 27 Recovery data for the determination of diquat using method RM-5B-1 (PP901/0868)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Beef muscle	0.02	110, 115, 90	3	105	13	90–115
	0.10	101, 111, 101	3	104	5.5	101–111

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
	Overall		6	105	8.7	90–115
Beef liver	0.02	105, 50, 85	3	80	35	50–105
	0.10	103, 99, 114	3	105	7.4	99–114
	Overall		6	93	25	50–114
Beef fat	0.02	80, 90, 70	3	80	13	70–90
	0.10	76, 82, 66	3	75	11	66–82
	Overall		6	77	11	66–90
Beef kidney	0.02	120, 90, 100	3	103	15	90–120
	0.10	107, 84, 174 ^a	3	121	47	84–174
	Overall		5	100	14	84–120
Beef heart	0.02	87, 77, 89	3	84	7.6	77–89
	0.10	83, 88, 94	3	88	6.2	83–94
	Overall		6	86	6.7	77–94

^a Possibly double-fortified

Residue Analytical Method PPRAM 7 (PP901/1005)

Tissue samples (10–20 g) are homogenised in ten times the volume of trichloroacetic acid (10%). The homogenates are centrifuged and then the supernatant liquid decanted and retained. The precipitate is re-suspended in trichloroacetic acid (10%, 50 mL) and centrifuged again, decanting the supernatant and combining with the first. The de-proteinised extracts are then percolated through a column of cation-exchange resin. The column is washed with water, hydrochloric acid (2 N), water, aqueous ammonium chloride (2.5%) and water again to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. A portion of the eluate is treated with alkaline sodium dithionite to reduce diquat to a free radical. Light absorption of the radical is measured colourimetrically (350–450 nm). The LOQ of the method was 0.01 mg/kg for diquat in animal tissues.

Residue Analytical Method GRM012.02A (PP148/3006)

Samples are extracted by homogenisation in 10% w/v aqueous trichloroacetic acid. Extracts are centrifuged and aliquots (75 µL=0.005 g) are diluted with ammonium formate (250 mM) and acetonitrile (CH₃CN: pH 3.7 aqueous ammonium formate buffer 30:70 v/v). Final determination is by LC-MS/MS. The detector response was linear for the range 0.000025–0.015 µg/mL. No significant matrix effects were observed. Primary extracts were stable for at least 14 days when stored at < 7 °C. Final extracts were stable for at least 7 days under the same storage conditions. The LOQ of the method is 0.005 mg/kg for diquat in milk, eggs, muscle tissue, liver, kidney, fat and blood.

Table 28 Recovery data for the determination of diquat using method GRM012.02A(PP901/2097, PP148/3005)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Primary Transition m/z 183–157						
Cows' milk	0.005	108, 108, 102, 106, 113	5	107	4	102–113
	0.05	107, 108, 111, 112, 109	5	109	2	107–112
	Overall		10	108	3	102–113
Cow muscle	0.005	86, 92, 92, 92, 94	5	91	3	86–94
	0.05	87, 89, 86, 94, 91	5	89	4	86–94
	Overall		10	90	3	86–94
Cow liver	0.005	93, 97, 100, 92, 100	5	96	4	92–100
	0.05	106, 103, 110, 112, 112	5	108	3	103–112
	Overall		10	102	7	92–112
Cow kidney	0.005	85, 92, 89, 91, 95	5	90	4	85–95
	0.05	95, 96, 96, 91, 93	5	94	2	91–96
	Overall		10	92	4	85–96
Cow fat	0.005	88, 94, 90, 92, 85	5	90	4	85–94

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
	0.05	95, 94, 93, 88, 90	5	92	3	88–95
	Overall		10	91	4	85–95
Cows' blood	0.005	113, 112, 108, 101, 113	5	109	5	101–113
	0.05	110, 104, 109, 110, 113	5	109	3	104–113
	Overall		10	109	4	101–113
Hens' eggs	0.005	95, 100, 108, 102, 97	5	100	5	95–108
	0.05	106, 100, 107, 107, 114	5	106	5	100–114
	Overall		10	103	5	95–114
Confirmatory Transition m/z 183–130						
Cows' milk	0.005	104, 101, 105, 90, 108	5	102	7	90–108
	0.05	107, 106, 111, 116, 105	5	109	4	105–116
	Overall		10	105	6	90–116
Cow muscle	0.005	93, 80, 102, 94, 100	5	94	9	80–102
	0.05	101, 89, 89, 93, 89	5	92	6	89–101
	Overall		10	93	7	80–102
Cow liver	0.005	98, 105, 103, 108, 114	5	106	5	98–114
	0.05	110, 100, 110, 117, 108	5	109	5	100–117
	Overall		10	107	5	98–117
Cow kidney	0.005	93, 102, 95, 84, 90	5	93	7	84–102
	0.05	94, 93, 96, 87, 88	5	92	4	87–96
	Overall		10	92	6	84–102
Cow fat	0.005	84, 86, 93, 95, 83	5	88	6	83–95
	0.05	91, 92, 90, 87, 86	5	89	3	86–92
	Overall		10	89	5	83–95
Cows' blood	0.005	113, 107, 111, 106, 105	5	109	3	105–113
	0.05	109, 109, 98, 116, 105	5	107	6	98–116
	Overall		10	108	5	98–116
Hens' eggs	0.005	99, 112, 101, 107, 102	5	104	5	99–112
	0.05	104, 101, 110, 110, 117	5	109	5	101–117
	Overall		10	106	5	99–117

Extraction of residues from incurred residue samples

Potatoes

In the metabolism study employing a similar extraction procedure as analytical methods PPRAM 1, PPRAM005, RAM 252 and GRM012.03A (with the exception that the water content of the samples were not taken into consideration), the extractability of the radioactive residues from both potato flesh and skin was very high (> 95% TRR). Diquat was the only significant component present in the extracted material. The extraction using reflux with sulphuric acid/water is suitable for use in analytical methods for determining diquat.

Rape seed

In the metabolism study, the first water/sulphuric acid reflux extraction recovered approximately 70% TRR. Diquat accounted for 48% of the TRR.

Milk and tissues

The metabolism study utilised three sequential extractions (four for fat) with 10% trichloroacetic acid. The extraction procedure extracted 94% of radioactivity in milk with diquat accounting for 82% of the radioactivity. In tissues ≥ 80% of the radioactivity was extracted with the exception of liver which was lower at 63%. In tissues diquat was 20 to 46% of the radioactive residue. The extraction procedure is suitable for use in analytical methods and has been employed in PPRAM7 and GRM012.02A.

Chicken liver

A sub-sample of composited chicken liver from metabolism study was used for the radio-validation of method RM-5B-1. Extraction of diquat involves reflux with 18 N H₂SO₄. Diquat measured using method RM-5B-1 was 0.012 and 0.013 mg/kg. Recoveries for samples spiked at 0.05 and 0.1 mg/kg were 80 and 85% respectively. The metabolism study reported diquat level in liver to be 0.022 mg/kg which is similar to the values measured using method RM-5B-1 after correction for recovery (0.015–0.016 mg/kg).

Applicability of multi-residue methods

Incorporation of diquat into multiresidue screen is unlikely as extraction from crops generally requires reflux in an acid solution.

Stability of residues in stored analytical samples

The freezer storage stability of diquat in fortified plant, animal tissues, milk and eggs samples was studied. Residues were generally stable for the duration of the studies.

Stability of residues in plant products

Langridge (2007) studied the stability of diquat in spinach, wheat grain, oilseed rape seed, lentil, orange, potato and wheat straw under freezer storage conditions for up to 24 months. These include representatives of the four crop types, predominantly water-, oil-, protein- and starch-containing materials. Crop samples (10 g of spinach, wheat grain, oilseed rape seed, lentil, whole orange, potato and wheat straw) were separately weighed into polypropylene extraction vessels and fortified with known amounts of a standard solution of diquat in water at a target rate of 0.2 mg/kg. The fortified samples were sealed (after allowing any solvent to evaporate) and gently shaken to distribute the analyte before being stored in a temperature monitored freezer at < -18 °C. Method GRM012.03A was used to determine diquat in the crop commodities.

There was no significant decrease (> 30% as compared to the initial value) in the observed residues of diquat in spinach, wheat grain, oilseed rape seed, lentil, whole orange, potato and wheat straw when stored deep frozen at < -18 °C for a period of at least 24 months.

Table 29 Storage stability results for samples spiked with diquat at 0.2 mg/kg.

Commodity	Storage Period (months)	Concentration (mg/kg)	Mean Procedural Recovery (%) ^a
Spinach	0	0.22, 0.21, 0.22	107
	3	0.18, 0.18	98
	6	0.21, 0.20	94
	12	0.24, 0.22	116
	18	0.19, 0.21	105
	24	0.17, 0.18	91
Wheat grain	0	0.22, 0.22, 0.20	104
	3	0.19, 0.20	95
	6	0.19, 0.19	94
	12	0.19, 0.23	109
	18	0.18, 0.19	88
	24	0.19, 0.18	97
Wheat straw	0	0.21, 0.21, 0.21	110
	3	0.18, 0.17	85
	6	0.18, 0.19	100
	12	0.23, 0.22	110
	18	0.19, 0.17	97
	24	0.18, 0.17	91
Rape seed	0	0.21, 0.21, 0.22	104
	3	0.23, 0.25	107
	6	0.20, 0.19	92

Commodity	Storage Period (months)	Concentration (mg/kg)	Mean Procedural Recovery (%) ^a
	12	0.23, 0.22	109
	18	0.21, 0.19	105
	24	0.15, 0.15	69
Lentils	0	0.21, 0.23, 0.22	104
	3	0.14, 0.15	70
	6	0.17, 0.17	80
	12	0.18, 0.19	90
	18	0.17, 0.19	94
	24	0.16, 0.15	69
Orange fruit	0	0.21, 0.21, 0.21	107
	3	0.18, 0.18	95
	6	0.20, 0.20	103
	12	0.22, 0.22	114
	18	0.19, 0.19	86
	24	0.17, 0.17	80
Potato tubers	0	0.22, 0.19, 0.20	100
	3	0.18, 0.21	92
	6	0.20, 0.21	103
	12	0.17, 0.19	78
	18	0.19, 0.20	98
	24	0.20, 0.19	89

^a Mean of two recoveries

USE PATTERNS

Diquat is a non-volatile herbicide with two principal modes of use:

desiccant use as a harvest aid

weed-control use, before planting or around and between the rows of established crops.

Diquat is fast-acting and effectiveness varies with weed species; repeat applications may be necessary on certain perennial weeds while annual weeds are generally destroyed with one application.

Table 30 presents a summary of relevant GAP. The table is divided into two parts, desiccation uses where diquat is applied deliberately and directly to the target crop and weed-control uses where diquat is applied to weed plants and is not allowed to come into contact with the crop plants.

Table 30 Selected registered uses of diquat (SL formulations)

Crop	Country	Application				PHI (days)
		Method	Rate kg ai/ha	Water L/ha	No or/ Season max kg ai/ ha	
Desiccant or	harvest aid					
Beans	Austria	Broadcast	0.6		1	5
Beans	Brazil	Broadcast	0.3–0.4	200–300	1	7
Beans	Canada	Broadcast	0.30–0.41	225–550	1	4
	Canada	Aerial	0.41–0.55	45		
Beans	France	Broadcast	0.6	> 300	1	
Beans	Germany	Broadcast	0.6	400–800	1	5
Beans	Slovakia	Broadcast	0.5–0.8	200–600	1	6–10
Beans	UK	Broadcast	0.60	200–500	1	7–10
Lentils	Canada	Broadcast	0.3–0.41	225–550	1	4
	Canada	Aerial	0.41–0.55	45		
Peas	Slovakia	Broadcast	0.5–0.8		1	6
Peas	Canada	Broadcast	0.30–0.41	225–550	1	4
	Canada	Aerial	0.41–0.55	45		
Peas	France	Broadcast	0.6	> 300	1	4
Peas	UK	Broadcast	0.40–0.60	200–500	1	7–10

Crop	Country	Application				PHI (days)
		Method	Rate kg ai/ha	Water L/ha	No or/ Season max kg ai/ ha	
Potato (consum.)	Austria	Broadcast	0.5		1	10
Potato	Brazil	Broadcast	0.3–0.5	200–300	1	7
Potato	Canada	Broadcast	0.41–0.84	550–1000	2	
Potato	Germany	Broadcast	0.5 –1.0	400–800	1 at 0.5 or 2 max 1.0/year	10
Potato	Netherlands	Broadcast	0.5–0.8	200–500	1/ max 0.8 or 2/max 1.0/year	
Potato	Spain	Broadcast	0.6–0.8	300–1000	1	15
Potato	UK	Broadcast	0.80–1.0	200–400	1/ max 0.8;or 2/ max 1.0/year	0, 14 (if potatoes to be stored)
Potato	USA	Broadcast	0.28–0.56	47–187	2/1.12	7
Rape seed	Austria	Broadcast	0.4– 0.6	500–1000	1	5
Rape seed	Canada	Broadcast	0.30–0.41	225–550	1	14
Rape seed	UK	Broadcast	0.60	250–500	1	7–10
Rape seed	USA	Broadcast	0.42–0.56	140	1	7
Rape seed	Germany	Broadcast	0.4–0.6	400–800	1	5
Soya bean	Brazil	Broadcast	0.2–0.4	200–300	1	7
Soya bean	Bulgaria	Broadcast	0.6		1	7
Soya bean	Canada	Broadcast	0.41–0.56	225–500	1	4
Soya bean	Slovakia	Broadcast	0.6		1	6
Sunflower	Slovakia	Broadcast	0.3–0.6	200–600	1	6
Sunflower	Canada	Broadcast	0.30–0.41	225–550	1	15
Weed control						
Apple (and other fruit trees)	Canada	Broadcast	1.1	225–675	1	0
Apple (and other fruit trees)	USA	Foliar	0.42–0.56	> 140	1	365
Banana/plantain	Belize	Broadcast	0.2–0.6	250–300		0
Banana/plantain	Costa Rica	Broadcast	0.2–0.6	250–300		0
Banana/plantain	Dominican Republic	Broadcast	0.2–0.6	250–300		0
Banana/plantain	El Salvador	Broadcast	0.2–0.6	250–300		0
Banana/plantain	Guatemala	Broadcast	0.2–0.6	250–300		0
Banana/plantain	Nicaragua	Broadcast	0.2–0.6	250–300		0
Banana/plantain	Panama	Broadcast	0.2–0.6	250–300		0
Cashew	Dominican Republic	Broadcast	0.2–0.6	250–300		0
Carrot	Slovakia	Broadcast	0.8	200–600	1	7
Carrot	Spain	Broadcast	0.3–0.8		1	0
Citrus	Brazil	Broadcast	0.3–0.5	200–300	1	14
Citrus	Costa Rica	Broadcast	0.2–0.6	325–570		0
Citrus	Dominican Republic	Broadcast	0.2–0.6	325–570		0
Coffee	Belize	Broadcast	0.2–0.6	325–570		0
Coffee	Brazil	Broadcast	0.3–0.5	200–300	1	16
Coffee	Costa Rica	Broadcast	0.6	325–570		0
Coffee	Dominican Republic	Broadcast	0.2–0.6	325–570		0
Coffee	El Salvador	Broadcast	0.2–0.6	325–570		0
Coffee	Guatemala	Broadcast	0.2–0.6	325–570		0
Coffee	Nicaragua	Broadcast	0.2–0.6	325–570		0
Coffee	Panama	Broadcast	0.2–0.6	325–570		0
Pome fruit	Slovakia	Broadcast	0.6–1.0		1	
Row crops	Spain	Broadcast	0.3–0.45	300–600	1	15 ^a
Strawberry	Sweden	Broadcast	0.5		1 before flowering or after harvest	n/a ^b
Stone fruit	Slovakia	Broadcast	0.8–1.0		1	

Crop	Country	Application				PHI (days)
		Method	Rate kg ai/ha	Water L/ha	No or/ Season max kg ai/ ha	
General weed control (pre-plant or post-emergence incl carrots)	Spain	Broadcast	0.3–0.8	300–600	1	–

^a Use a spray protector (shield)

^b Use a spray shield

RESULTS OF SUPERVISED RESIDUE TRIALS ON CROPS

Diquat is a non-selective herbicide that is highly active against growing weeds. The Meeting received information on supervised field trials for diquat on the following crops or crop groups:

Commodity	Table No.
Citrus fruit	Table 32
Pome fruit	Table 33
Strawberries	Table 34
Banana	Table 35
Tomato	Table 36
Pulses	Tables 38–45
Carrots	Table 46
Potato	Tables 47–48
Rape seed	Tables 49–50
Sunflowers	Table 51
Coffee (beverage seeds)	Table 52
Animal feed	Tables 53–56

Trials were generally well documented with laboratory and field reports; trials from the 1980s followed the standards of those times. Laboratory reports included method validation with procedural recoveries from spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analyses or duration of residue sample storage were also provided. Although trials included control plots, no control data are recorded in the tables except where residues in control samples exceeded the LOQ. Control samples are indicated in the summary tables with a "c". Unless stated otherwise, residue data are recorded unadjusted for recovery.

Residues and application rates have generally been rounded to two significant figures or, for residues near the LOQ, to one significant figure. Residue values from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels. Those results included in the evaluation are underlined.

Conditions of the supervised residue trials were generally well reported in detailed field reports. Most trial designs used non-replicated plots. Most field reports provided data on the sprayers used, plot size, field sample size and sampling date.

Table 31 Summary of sprayers, plot sizes and field sample sizes in the supervised trials

Crop	Location	Year	Sprayer	Plot size	Sample size	Sample to analysis interval (days)
Orange	Brazil	1987-2003	CO ₂ backpack sprayer	4×15 m ² to 100 m ²	Not reported to 3 kg	294-346 d
Apple	UK	1998-1999	CO ₂ backpack sprayer with lance, Motor knapsack sprayer with single nozzle lance	4.1×2.0 m ² (4 trees) to 2×5.8 m ²	Not reported	98 to < 215 d
Apple	Austria, France, Hungary, Spain, Italy	2010	CO ₂ backpack sprayer, air-assisted backpack sprayer	4-10 trees	2.0-3.0 kg (12-30 fruit)	< 149 d
Banana	Costa Rica, Guatemala, Ecuador	1992	Hand held knapsack sprayer	2.3×2.5 m ² - 30×50 m ²	12 fruit	< 4 months
Strawberry	UK	2000	CO ₂ backpack sprayer with lance + shield	6×5 m ² - 7.5×5 m ²	Not reported	< 30 d
Coffee	Costa Rica, Guatemala	1993	Hand held knapsack sprayer	Not reported to > 10 plants	1 kg beans	< 5 months
Tomato	Spain, France, Italy	2009	Air-assisted backpack sprayer, flat fan nozzle	10×2.4 m ² - 25×3 m ²	1.6-3.5 kg	< 8 months
Tomato	France, Italy, Spain	2010	Air-assisted backpack sprayer, flat fan nozzle	10×2.4 m ² - 20×5 m ²	1.6-3.5 kg	< 7 months
Bean fodder dry	Germany	1984-1985	Boom sprayer, knapsack sprayer, tractor mounted sprayer	2×4 m ² , 4 reps - 4.5×150 m ²	0.8-1.3 kg	< 243 d
Bean	USA	1994	Broadcast	3×9.1 m ² - 4.9×61 m ²	1.1-1.8 kg	212-347d
Pea	France	1981	Not reported	Not reported	Not reported	< 173d
Pea fodder	Germany	1984	Knapsack sprayer, tractor mounted sprayer	2.5×10 m ² 6 reps	1 kg	< 508 d
Pea fodder	Germany	1984	Knapsack sprayer	1.5×10 m ² 4 reps - 25×25.2 m ²	1 kg	< 508 d
Pea	Denmark	1986	Knapsack sprayer	37.5m ² - 5×12m ²	Not reported	< 170 d
Pea	UK	1990			> 0.5kg	< 242 d
Pea	UK	1992	Knapsack sprayer		0.5-1kg	< 126 d
Pea	USA	1994	Broadcast	3×30 m ² - 4.9×61 m ²	> 1.1kg	145 - 357 d
Lentil	Canada	1989	Not reported to aerial	Not reported	> 1 kg	7 months
Lentil	USA	1994	Broadcast	3.7×9.1 m ² - 6.1×15 m ²	> 1kg	< 318 d
Soy bean	France	1985	Knapsack sprayer (Cristal)	30×2.2 m ²	Not reported	< 10 months
Soy bean	France	1994	Knapsack sprayer	15×2 m ² - 20×3.5 m ²	> 1kg	< 246 d
Soy bean	USA	1987	CO ₂ backpack sprayer, farm sprayer, Tractor mounted offset sprayer	1.5×15 m ² - 780 m ²	Not reported	< 136 d
Carrot	Germany	1983-1984	Knapsack sprayer with bar, sprayer with shield, Sprinkler watering can, sprinkler with shield, Sprinkler bar	20 m ² - 2.8×20 m ²	> 0.8kg	< 179 d
Carrot	Italy	1993	Knapsack sprayer with bar, sprayer with shield	Not reported	> 02kg	< 179 d
Potato	Austria, France	2009	Backpack sprayer	17×3 m ² - 25×3 m ²	> 2kg	< 7 months
Potato	UK, France, Austria	2010	Backpack sprayer	10×3 m ² - 30×3 m ²	> 2.4kg	< 3 months

Crop	Location	Year	Sprayer	Plot size	Sample size	Sample to analysis interval (days)
Potato	France, Italy, Spain	2009	Backpack sprayer	17×3 m ² - 10×6 m ²	> 2kg	< 3 months
Potato	France, Italy, Spain	2010	Backpack sprayer	Not reported - 20×2.25 m ²	> 2kg	< 6 months
Potato	USA	1994	Backpack sprayer	3×15 m ² - 4×37 m ²	Not reported	196-260 d
Rape	Austria, France, Italy	2009	Backpack sprayer	20×6 m ²	> 0.5kg	< 365 d
Rape	Austria	2009	Backpack sprayer	17×3 m ² - 80×3 m ²	> 0.5kg	< 365 d
Rape	Spain, France, Italy	2010	Backpack sprayer	10×3 m ² - 10×6 m ²	> 0.5kg	< 185 d
Rape	USA	2009-2010	Backpack sprayer, tractor mounted sprayer, bicycle sprayer	8.2×12.2 m ² to 136×26 m ²		< 789 d
Sunflower	France	1993-1994	Backpack sprayer			< 266 d
Sunflower	France	2004	Backpack sprayer			< 76 d

Where duplicate field samples from an unreplicated plot were taken at each sampling time and were analysed separately, the mean of the two analytical results was taken as the best estimate of the residues in the plot and only the means are recorded in the tables. Similarly where samples were collected from replicate plots the mean result is reported (see general consideration JMPR 2010).

Citrus fruits

Two trials in 1988 and 1989 were conducted using diquat formulated as a soluble concentrate (SL). Applications were made close to commercial harvest of the citrus fruit, as appropriate for weed control. Orange fruit were sampled 14 days after application. Sample size and storage conditions were not reported.

Table 32 Residues of diquat in orange fruit (directed sprays for weed control)

Location, year, variety	Form	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Gelria–Holambra-SP Brazil 1988 (Pera Natal)	200SL	1	0.5	400		fruit	14	< 0.01	A1412A_10320
	200SL	1	1.0	400		fruit	14	< 0.01	
Sr. Geraldo Van Broke –Holambra SP Brazil 1989 (Pera Natal)	200SL	1	0.5	300		fruit	14	< 0.01	A1412A_10321
	200SL	1	1.0	300		fruit	14	< 0.01	
Estrada da Cachoeira, Holambra-SP Brazil 2003 (Pera Coroa)	200SL	1	0.5	100	BBCH 81–89	Fruit Juice	14	< 0.02 < 0.02	A1412A_10251
	200 SL	1	1.0	100	BBCH 81–89	Fruit Juice	14	< 0.02 < 0.02	

Pome fruits

Twelve supervised residue trials with diquat on apples were conducted in Europe between 1998 and 2010. In these trials, diquat was formulated as an SL formulation applied once at a rate of 1.0 kg ai/ha to the area around the base of the trees, well away from the fruit. All applications included an appropriate locally-typical adjuvant (wetter) at the recommended rate. In four trials from 1998–1999,

applications were made late in the growing season, at the time of harvest (0-day PHI). In eight trials from 2010, applications were made early in the growing season of the apples, as appropriate for weed control. Consequently, PHIs ranged from 0 to 171 days. Mature apple fruit were sampled at normal commercial harvest (BBCH growth stages 85–89) and stored frozen until analysis. Samples of apples were stored for a maximum of 215 days. Residues of diquat in apple samples were determined using methods RAM 272/02 or GRM012.03A.

Table 33 Residues of diquat in apple fruit (directed sprays for weed control)

Location, year, variety	Form	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
West Malling, Kent UK 1998 Discovery	200SL	1	1.0	200	BBCH 87	Fruit	0	< 0.05	PP901/0345 + 0.1% v/v Agral 90
Sittingbourne, Kent UK 1998 Bramley	200SL	1	1.0	200	BBCH 87	Fruit	0	< 0.05	PP901/0345 + 0.1% v/v Agral 90
Blean, Kent UK 1999 Cox	200SL	1	1.0	310	BBCH 87	Fruit	0	< 0.01	PP901/0349 + 0.1% v/v Agral 90
Little Witley, Hereford & Worcester UK 1999 Golden Delicious	200SL	1	0.96	288	BBCH 87	Fruit	0	< 0.01	PP901/0349 + 0.1% v/v Agral 90
Buchkirchen, Upper Austria, Austria 2010 Golden Delicious	200SL	1	1.1	328	BBCH 11–56	Fruit	150	< 0.01	A1412A_10290 + Neowett (Isotridecanol-polyglycolether) was used at a rate of 0.04% v/v
Burgundy France 2010 Gloster	200SL	1	0.95	332	BBCH 11	Fruit	171	< 0.01	A1412A_10290 LI700 added as a wetter (0.5% v/v)
Burgundy France 2010 Pinova	200SL	1	1.0	356	BBCH 11	Fruit	161	< 0.01	A1412A_10290 LI700 = added as a wetter (0.5% v/v)
Horvátzsidány Vas Vas, Hungary 2010 Gala Must	200SL	1	0.974	341	BBCH 11–15	Fruit	137	< 0.01	A1412A_10290 Silwet L-77
Lleida Spain 2010 Granny Smith	200SL	1	1.03	350	BBCH 11	Fruit	149	< 0.01	A1412A_10294 Agral 0.3%
Lleida Spain 2010 Golden Reinders	200SL	1	1.0	350	BBCH 11	Fruit	148	< 0.01	A1412A_10294 Agral 0.3%
Nîmes Languedoc-Roussillon France 2010 Fuji	200SL	1	1.1	372	BBCH 10–11	Fruit	145	< 0.01	A1412A_10294 LI700 added as a wetter (0.5% v/v)
Verzuolo (CN) Piedmont Italy 2010 Gala	200SL	1	0.94	330	BBCH 11	Fruit	137	< 0.01	A1412A_10294 Etravon used as an adjuvant.

Strawberry

Three supervised trials were carried out on protected strawberries during 2000 in the UK. In each trial one application of an SL formulation was made at a rate of 0.85 to 0.92 kg ai/ha at BBCH 57–60.

Samples of strawberries were taken at normal harvest 47 to 50 days after the application and were stored frozen for up to one month prior to analysis. Residues of diquat in strawberries were determined by ion-pair high performance liquid chromatography using method RAM 272/02.

Table 34 Residues of diquat in strawberries ^a grown under cover (inter-row directed sprays for weed control)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Sevenoaks Kent UK 2000 Elsanta	1	0.85	213	BBCH 57–60	Fruit	50	< 0.05	PP901/0724
Maidstone Kent UK 2000 Elsanta	1	0.92	230	BBCH 57–60	Fruit	48	< 0.05	PP901/0724
Hereford Herefordshire UK 2000 Elsanta	1	0.86	215	BBCH 58–60	Fruit	47	< 0.05	PP901/0724

^a Applications pre-flowering and used a spray shield

Banana

Eight supervised trials were conducted on bananas during 1992 and 1993, three in Costa Rica, three in Guatemala and two in Ecuador. Trials in Costa Rica and Guatemala consisted of two plots, one receiving three applications of diquat a SL formulation at a rate of 0.6 kg ai/ha and the other receiving two applications of a formulation also containing paraquat at a rate of 0.15 kg diquat/ha, at intervals of 29 to 33 days. The trials in Ecuador also consisted of two plots, both treated three times at intervals of 28 days at rates of either 0.2 or 0.4 kg ai/ha. The three trials conducted in Guatemala included an adjuvant “Agral” in each application and the two trials in Ecuador included “Agral 90” in each application according to local practice. Applications were sprayed directly to the soil around the plants according to commercial practices. Samples of mature banana bunches were collected immediately after the spray dried and also after 3 days for the trials in Costa Rica and Ecuador. On sampling, bananas were washed by immersion in water for 5–10 minutes according to local practices. All samples were stored frozen until analysis. Residues of diquat in banana samples were determined using method RAM 005/01.

Table 35 Residues of diquat in banana (directed sprays for weed control)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
San Jose, Costa Rica 1992	3	0.15	168	250 cm	Fruit	0	< 0.05	PP901/0359 05CR
		0.15	168	250 cm	Fruit	3	< 0.05	
		0.15	168	250 cm				
	3	0.60	168	250 cm	Fruit	0	< 0.05	
		0.60	168	250 cm	Fruit	3	< 0.05	
		0.60	168	250 cm				
San Jose, Costa Rica 1992	3	0.15	168	250 cm	Fruit	0	< 0.05	PP901/0359 21CR
		0.15	168	250 cm	Fruit	3	< 0.05	
		0.15	168	250 cm				
	3	0.60	168	250 cm	Fruit	0	< 0.05	
		0.60	168	250 cm	Fruit	3	< 0.05	
		0.60	168	250 cm				
San Jose, Costa Rica 1992	3	0.15	168	250 cm	Fruit	0	< 0.05	PP901/0359 24CR
		0.15	168	250 cm	Fruit	3	< 0.05	
		0.15	168	250 cm				
	3	0.60	168	250 cm	Fruit	0	< 0.05	
		0.60	168	250 cm	Fruit	3	< 0.05	
		0.60	168	250 cm				

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Morales Izabel Guatemala 1992 Grand Nine	3	0.15	444	250 cm	Fruit	0	< 0.05	PP901/0359 + Agral 0.1% 109GUA
		0.15	444	250 cm	Fruit	3	< 0.05	
		0.15	444	250 cm				
	3	0.60	444	250 cm	Fruit	0	< 0.05	
		0.60	444	250 cm	Fruit	3	< 0.05	
		0.60	444	250 cm				
Morales Izabel Guatemala 1992 Grand Nine	3	0.15	444	250 cm	Fruit	0	< 0.05	PP901/0359 + Agral 0.1% 110GUA
		0.15	444	250 cm	Fruit	3	< 0.05	
		0.15	444	250 cm				
	3	0.60	444	250 cm	Fruit	0	< 0.05	
		0.60	444	250 cm	Fruit	3	< 0.05	
		0.60	444	250 cm				
Morales Izabel Guatemala 1992 Grand Nine	3	0.15	220	250 cm	Fruit	0	< 0.05	PP901/0359 + Agral 0.1% 111GUA
		0.15	220	250 cm	Fruit	3	< 0.05	
		0.15	220	250 cm				
	3	0.60	220	250 cm	Fruit	0	< 0.05	
		0.60	220	250 cm	Fruit	3	< 0.05	
		0.60	220	250 cm				
Guayas Ecuador 1992 Giant Cavendish	3	0.20	400		Fruit	0	< 0.05	PP901/0358 + Agral 0.1% RESREG1
		0.20	400					
		0.20	400					
	3	0.40	400		Fruit	0	< 0.05	
		0.40	400					
		0.40	400					
Guayas Ecuador 1992 Giant Cavendish	3	0.20	400		Fruit	0	< 0.05	PP901/0358 + Agral 0.1% RESREG2
		0.20	400					
		0.20	400					
	3	0.40	400		Fruit	0	< 0.05	
		0.40	400					
		0.40	400					

Tomato

Eight supervised residue trials were conducted in Europe during 2009 and 2010 where diquat was applied for weed control between the rows of tomato plants (inter-row application). In the trials, diquat as a SL formulation was applied once at a rate of 0.8 kg ai/ha. All applications included an appropriate adjuvant (wetter) at the recommended rate. Four of the trials contained additional plots treated with diquat pre-emergence with tomatoes sampled at normal commercial harvest 92 to 118 days after application. Samples of tomatoes were stored frozen for a maximum of 8 months. Tomato samples were analysed for residues of diquat using method GRM012.03A.

Table 36 Residues of diquat in field tomato (inter-row directed sprays for weed control)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Trajano, Sevilla Spain 2009 Juncal	1	0.85	431	BBCH 74–76	Fruit	0	< 0.01	A1412A_10282 + 0.3% v/v Agral
					Fruit	3	< 0.01	
					Fruit	7	< 0.01	
					Fruit	15	< 0.01	
					Fruit	21	< 0.01	
Lebrija Sevilla Spain 2009 Juncal	1	0.88	444	BBCH 74–76	Fruit	0	< 0.01	A1412A_10282 + 0.3% v/v Agral
					Fruit	3	< 0.01	
					Fruit	7	< 0.01	
					Fruit	15	< 0.01	
					Fruit	21	< 0.01	
Languedoc-Roussillon France 2009 Valina	1	0.85	850	BBCH 73–82	Fruit	0	0.05	A1412A_10282 + 0.5% v/v LI 700
					Fruit	3	< 0.01	
					Fruit	7	0.04	
					Fruit	15	< 0.01	
					Fruit	20	< 0.01	
							< 0.01	

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Castagnito d'Alba Cuneo Piedmont Italy 2009 H3402	1	0.82	308	BBCH 83	Fruit Fruit Fruit Fruit Fruit	0 3 7 14 21	0.20 0.06 0.03 < 0.01 < 0.01 < 0.01	A1412A_10282 + 0.3% v/v Etravon
Languedoc-Roussillon France 2010 Valina	1	0.81	354	BBCH 71–81	Fruit	15	< 0.01	A1412A_10296 + 0.5% v/v LI700
Castagnito d'Alba Piedmont Italy 2010 Red Pear	1	0.87	380	BBCH 83	Fruit	15	< 0.01 ^A	A1412A_10296 + Etravon
Losa del Obispo Valencia Spain 2010 Sahel	1	0.84	367	BBCH 72–76	Fruit	15	< 0.01	A1412A_10296 + 0.3% v/v Agral
Lliria Valencia Spain 2010 Valenciano	1	0.83	363	BBCH 74–79	Fruit	15	< 0.01	A1412A_10296 + 0.3% Agral

^a Spray screen used during application to protect tomato plants

Table 37 Residues of diquat in field tomato (pre-emergent use for weed control)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Languedoc-Roussillon France 2009 Valina	1	0.84	368	BBCH 00	Fruit	116	< 0.01	A1412A_10282 + LI 700
Castagnito d'Alba Cuneo Piedmont Italy 2009 H3402	1	0.78	293	BBCH 07	Fruit	102	< 0.01	A1412A_10282 + Etravon
Languedoc-Roussillon France 2010 Valina	1	0.86	375	BBCH 01–07	Fruit	92	< 0.01	A1412A_10282 + LI 700
Castagnito d'Alba Piedmont Italy 2010 Red Pear	1	0.82	358	BBCH 03	Fruit	118	< 0.01	A1412A_10282 + Etravon

Pulses

Beans, dry

Eight supervised trials were conducted on dried beans without pods (field and fodder beans) in Germany during 1984 and 1985. Each trial received a single application of a diquat SL formulation at 0.6 kg ai/ha. Mature beans were collected from 3 to 13 days after treatment. The seeds were separated from the pods and samples were frozen until analysis. Storage periods ranged up to 243 days (8 months). Residues of diquat were determined using method PPRAM 5. Mean procedural recoveries were 59–64% for samples fortified at 0.1–0.2 mg/kg. The data are not suitable for estimating maximum residue levels.

Table 38 Residues of diquat in bean (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Oldenburg Germany 1984 Hara	1	0.60	600	PH ^a	Seed	5 8 13	< 0.02 < 0.02 < 0.02	PP901/0312
Wankendorf Germany 1984 Hara	1	0.60	600	PH	Seed	5 7 9	< 0.02 < 0.02 0.03	PP901/0312
Mörstadt Germany 1984 Kristal	1	0.60	600	PH	Seed	4	< 0.02	PP901/0312
Rheinhessen Germany 1984 Kristal	1	0.60	600	PH	Seed	5 7	< 0.02 < 0.02	PP901/0312

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Wankendorf Germany 1984 Hara	1	0.60	600	BBCH 88	seed	5 7 11	0.08 0.07 0.09	PP901/0312
Lüneburg Germany 1985 Hara	1	0.60	600	BBCH 88	seed	5 7 10	0.15 0.09 0.14	PP901/0312
Bottenbach Germany 1985 Kristall	1	0.60	600	BBCH 86–88	seed	3 5 8	< 0.02 0.03 0.05	PP901/0312
Kappellen-Drusweiler Germany 1985	1	0.60	600	BBCH 88	seed	3 5 7	0.04 0.08 0.06	PP901/0312

^a PH Pre-harvest

Eight supervised trials were conducted in the USA in 1994 where diquat SL formulation was applied to mature bean plants as a desiccant 4 days prior to harvest of bean seeds. Dry bean samples were taken by hand or mechanically and maintained frozen until analysis. The maximum period of storage was 338 days. Samples were analysed for residues of diquat using method RAM 252/01.

Table 39 Residues of diquat in bean (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Visalia CA USA 1994 Greencrop	1	0.42	91	PH crop fully mature, pods drying	seed	4	< 0.05	PP901/0325
Ault CO USA 1994 Bill Z	1	0.42	93	PH crop mature	seed	4	< 0.05	PP901/0325
Jerome ID USA 1994 Pinto Vofi 196	1	0.42	76	PH crop mature	seed	4	< 0.05	PP901/0325
Bridgeport MI USA 1994 Blackhawk	1	0.42	92	PH crop mature	seed	4	< 0.05 ^a	PP901/0325
Hutchinson MN USA 1994 Montcalm	1	0.42	89	PH crop mature, pods yellow	seed	4	< 0.05	PP901/0325
Madrid NE USA 1994 Vaccaro	1	0.42	93	PH crop mature	seed	4	< 0.05	PP901/0325
Fabius NY USA 1994 Light Red Kidney	1	0.42	93	PH crop mature	seed	4	< 0.05	PP901/0325
Northwood ND USA 1994 Norstar	1	0.42	94	PH crop near maturity, 70% defoliated	seed	4	< 0.05	PP901/0325

^a Bridgeport MI USA site received 18 mm rain on the day after application

Peas, dry

Seventeen supervised trials on dry peas were conducted in Europe from 1981 to 1992. One trial was carried out in France, seven in Germany, five in Denmark and four in the UK. A single application of an SL formulation of diquat was applied to dry pea plants 4 to 14 days prior to harvest. Mature peas were collected and the seeds were separated from the pods. Seeds, haulm and pods were analysed for residues of diquat using method PPRAM 5 or PPRAM 5A. Samples were stored frozen at about – 20 °C prior to analysis. The maximum period of frozen storage was reported as 508 days (16 months). Mean procedural recoveries for the 1981 France trials were approximately 61% for samples fortified at 0.5 mg/kg. The data from the 1981 trials are not suitable for estimating maximum residue levels.

Table 40 Residues of diquat in peas dry (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Saint Vigor Bernay France 1981 Final	1	0.60	500	Dry pod	seed	5	< 0.05 ^a	PP901/0306 0.5 mg/kg 61% seed; 2 mg/kg 41% pods Corrected recovery
Emanville Bernay France 1981 Final	1	0.60	500	Dry pod	seed	4	< 0.05	PP901/0306 0.5 mg/kg 61% seed; 2 mg/kg 41% pods Corrected rec + Sporader
Matougues Rheims France 1981 Amino	1	0.60	500	Dry pod	seed	8	< 0.05	PP901/0306 0.5 mg/kg 61% seed; 2 mg/kg 60% vines. Corrected rec. no control
	1	0.60	500	Dry pod	seed	17	< 0.05	+ Sporader
Neufelize Rheims France 1981 Rondo	1	0.60	500	Dry pod	seed	17	< 0.05	PP901/0306 0.5 mg/kg 61% seed; 2 mg/kg 60% vines Corrected rec. + Sporader
Wankendorf Germany 1984	1	0.60	600	PH	seed	4 7 10	0.05 0.03 0.05	PP901/0311
Neustadt/Holst Germany 1984	1	0.60	600	PH	seed	5 7 11	< 0.02 0.03 < 0.02	PP901/0311
Morstadt bei Worms Germany 1984 Stehgold	1	0.60	600	PH	seed	5 7 12	0.10 0.10 0.07	PP901/0311
Bröthen/Büchen Germany 1985 Columba	1	0.60	600	PH	seed	5 7 9	0.06 0.04 0.04	PP901/0311
Neustadt/Holst Germany 1985 Birte	1	0.60	600	PH	seed	5 7 10	0.05 0.04 0.04	PP901/0311
Dierbach Germany 1985 Stehgolt	1	0.60	600	PH	seed	3 5 7	0.07 0.06 0.06	PP901/0311
Kapellen-Drusweiler Germany 1985 Bodil	1	0.60	600	PH	seed	3 6 8	0.12 0.13 0.15	PP901/0311
Oberndorf-Hochmössingen Germany 1985 Stehgold	1	0.60	600	PH	Seed	7	0.04	PP901/0311
Slagelse Denmark 1986 Bodil (app 28/7)	1	0.60	400	yellowing	seed	0 3 7 9 14	0.10 0.03 0.04 0.05 0.05	PP901/0315 Day 0 seed 54% moisture
Slagelse Denmark 1986 Bodil (app 6/8)	1	0.60	400	yellowing	seed	0 3 7 9 13	0.03 < 0.02 < 0.02 < 0.02 < 0.02	PP901/0315 Day 0 seed 32% moisture
Slagelse Denmark 1986 Bodil (app 8/8)	1	0.60	400	yellowing	seed	0 3 7 11 14	0.02 < 0.02 < 0.02 < 0.02 < 0.02	PP901/0315 Day 0 seed 14% moisture
Olstykke Denmark 1986 Bodil (app 5/8)	1	0.60	400	yellowing	seed	0 3 7 10 14	0.09 0.03 0.02 0.03 0.03	PP901/0315 Day 0 seed 51% moisture

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Olstykke Denmark 1986 Bodil (app 8/8) unclear not two apps? Subsampled for analysis	1	0.60	400	yellowing	seed	0 3 7 10 14	0.09 < 0.02 < 0.02 < 0.02 < 0.02	PP901/0315 Day 0 seed 25% moisture
Dorrington Lincolnshire UK 1990 Helka	1	0.53	300	PGRO/Knott 301–302	seed	5	0.04	PP901/0319 + Agral
Warwickshire UK 1990 Princess	1	0.53	300	PGRO/Knott 301–303	seed	10	0.04	PP901/0319 + Agral
Icklingham East Anglia UK 1990 Solara	1	0.53	300	PGRO/Knott 301–302	seed	8	< 0.03	PP901/0319 + Agral
Dorrington Lincolnshire UK 1992 Baroness	1	0.26	200	PGRO/Knott 301–302	seed	4	< 0.05	PP901/0322 + Agral
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	+ Agral
Welton Cuff Lincolnshire UK 1992 Progreta	1	0.26	200	PGRO/Knott 301–302	seed	4	< 0.05	PP901/0322 + Agral
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	+ Agral
Sandy Gate Lincolnshire UK 1992 Princess	1	0.26	200	PGRO/Knott 301–302	seed	4	< 0.05	PP901/0322 + Agral
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	+ Agral

Six supervised trials were conducted in the USA in 1994. Diquat was applied as a single application of an SL formulation at 0.42 kg ai/ha. Diquat applications were made to mature pea plants as a desiccant, 4 days prior to harvest of pea seeds. Dry pea samples were taken by hand or mechanically and maintained frozen at –20 °C until analysis. The maximum period of storage was 356 days. Samples were analysed for residues of diquat using method RAM 252/01.

Table 41 Residues of diquat in peas dry (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Visalia CA USA 1994 Progress #9	1	0.42	90	Mature	Seed	4	0.05	PP901/0324 + NIS
Nezperce ID USA 1994 Columbia	1	0.42	93	Mature	Seed	4	0.09	PP901/0324 + NIS
Milton-Freewater OR USA 1994 Columbia	1	0.42	93	Mature	Seed	4	0.56	PP901/0324 + NIS
Mercedes TX USA 1994 Tracer	1	0.42	84	Mature	Seed	4	0.40 c0.06	PP901/0324 + NIS small sample size 0.23 kg
Walla Walla WA USA 1994 Columbia	1	0.42	93	Mature	Seed	4	0.11	PP901/0324 + NIS
Ridgefield WA USA 1994 Yellow Spring	1	0.42	82	Mature	Seed	4	0.05	PP901/0324 + NIS

Lentils, dry

Fourteen trials on lentils were conducted in Canada and the USA. All trials received one application of diquat as an SL formulation at 0.4 or 0.42 kg ai/ha for broadcast application or 0.55 kg ai/ha for aerial applications. In some trials, a separate plot was treated with 2× application rates. Samples of lentil seeds were collected mechanically or by hand and stored frozen until analysis. The maximum period of frozen storage was about 12 months, though storage duration was not reported for study CRR114. Residues of diquat on lentil seeds from trials in the US were analysed using method RAM 252/01 while PPRAM 5A (modified as method 107) was used for the Canadian trials. Field trial reports were not available and analytical recoveries for the 1989 Canadian trials were 52–71%, mean 60% and, as such, the trials are not suitable for estimation of maximum residue levels. The description of the 1982 field trials was not adequate and there were no reports for the analytical phase. The trials are not suitable for use in maximum residue estimation.

Table 42 Residues of diquat on lentils—ground application (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Manitoba Canada 1989	1	0.40	225	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	PP901/0318
	1	0.80	225	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	
Manitoba Canada 1989	1	0.40	225	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	PP901/0318
	1	0.80	225	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	
Manitoba Canada 1989	1	0.40	225	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	PP901/0318
	1	0.80	225	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	
Manitoba Canada 1989	1	0.55	110	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	PP901/0318
	1	1.1	110	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	
Manitoba Canada 1989	1	0.55	110	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	PP901/0318
	1	1.1	110	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	
Manitoba Canada 1989	1	0.55	110	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	PP901/0318
	1	1.1	110	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	
Worley ID USA 1994 Brewers	1	0.42	90	Harvest aid	Seed	4	0.54	PP901/0323
	1	0.42	90	Harvest aid	Seed	4	0.21	PP901/0323

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Northwood ND USA 1994 Eston	1	0.42	94	Harvest aid	Seed	4	< 0.05	PP901/0323 pods still yellow, not mature at application. 14 mm rain between application and harvest
Waitsburg WA USA 1994 Baby Brown-Brewers	1	0.42	93	Harvest aid	Seed	4	0.06	PP901/0323
	1	0.42	93	Harvest aid	Seed	4	0.13	PP901/0323

Table 43 Residues of diquat on lentils—aerial application (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	PP901/0318 ^a
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	5	< 0.05	PP901/0318
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	5	< 0.05	PP901/0318
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	3	< 0.05	PP901/0318
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	5	< 0.05	PP901/0318
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	PP901/0318
Davidson, Saskatchewan Canada 1982 Chilean	1	0.28 ^b	20		Seed	12	0.16	
Davidson, Saskatchewan Canada 1982 Laird	1	0.56	45		Seed	8	0.113	
Rocanville, Saskatchewan Canada 1982 Laird	1	0.42	34		Seed	8	0.095	
Rocanville, Saskatchewan Canada 1982 Eston	1	0.42	34		Seed	10	0.09	
Delmas, Saskatchewan Canada 1982 Chilean	1	0.55	45		Seed	4	0.045	
North Battleford, Saskatchewan Canada 1982 Laird	1	0.55	45		Seed	6	0.043	
North Battleford, Saskatchewan Canada 1982 Laird	1	0.55	45		Seed	9	0.036	
Moose Jaw, Saskatchewan Canada 1982 Eston	1	0.56	45		Seed	6	0.135	
Moose Jaw, Saskatchewan Canada 1982 Laird	1	0.56	45		Seed	7	0.11	
Rosetown, Saskatchewan Canada 1982 Laird	1	0.56	45		Seed	10	0.08	
Wisetown, Saskatchewan Canada 1982 Chilean	1	0.56	23		Seed	19	0.133	

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Cupar, Saskatchewan Canada 1982 Laird	1	0.63	45		Seed	6	0.10	
Sedley, Saskatchewan Canada 1982 Laird	1	0.63	45		Seed	14	0.093 c0.06	

^a No field report just protocol summary

^b Data sheet suggests two applications made by aircraft from opposite directions so 0.56 kg ai/ha?

Rocanville, application dates about 1 week apart

North Battleford—different farms, dates

Moose Jaw—different variety, applications different as 1 week apart

Davidson—different variety, applications different as 1 week apart

Soya beans, dry

Four supervised trials on soya beans using diquat as a desiccant were conducted in Europe (France) during 1985 and 1994. Samples were maintained at -20 °C for periods up to 246 days, though the storage interval was not included in report R 2-FP. Diquat residues were determined by analytical method PPRAM 5 or RAM 252/01.

Table 44 Residues in soya beans (pre-harvest desiccation) Europe

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Villemur France 1985 Sloan	1	0.60	300	Yellow leaves	Seed	0 2 5 6 8	0.63 0.37 < 0.1 < 0.1 < 0.1	PP901/0310
	1	0.80	300	Yellow leaves	Seed	0 2 5 6 8	0.91 0.21 < 0.1 < 0.1 < 0.1	
	1	0.60	300	Yellow leaves	Seed	0 2 5 6 8	0.62 < 0.1 < 0.1 < 0.1 < 0.1	
	1	0.80	300	Yellow leaves	Seed	0 2 5 6 8	0.59 < 0.1 < 0.1 < 0.1 < 0.1	
Avignon France 1994 Goldor	1	0.60		Mature	Oil Cake Seed	4	< 0.05 0.06 0.06 ^a	PP901/0328
Blois France 1994 Maple Arrow	1	0.60		Mature	Oil Cake Seed	4	< 0.05 < 0.05 < 0.05 ^A	PP901/0328

^a Calculated residue (from separate oil and meal determinations)

Seven supervised trials using diquat as a desiccant on soya beans were conducted in various locations in the US in 1987. Samples were maintained in freezers at -20 °C for periods up to 136 days until analysis. Diquat residues were determined by analytical method RM-5C.

Table 45 Residues in soya beans (pre-harvest desiccation) USA

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg) ^a	Reference
Proctor AR USA 1987 Asgrow 5980	1	0.56	187	Harvest aid	Seed	7	0.09 0.08 (0.08)	PP901/0316
Lafayette IN USA 1987 Williams 82	1	0.56	153	Harvest aid	Seed	7	< 0.01 < 0.01 (≤ 0.01)	PP901/0316
Hollande MN USA 1987 NK 1346	1	0.56	187	Harvest aid	Seed	7	0.15 0.16 (0.16)	PP901/0316
Greenville MS USA 1987 Centennial	1	0.56	187	Harvest aid	Seed	7	0.02 < 0.01 (0.02)	PP901/0316
Oregon MO USA 1987 Asgrow 3127	1	0.56	219	Harvest aid	Seed	7	0.04 0.03 (0.04)	PP901/0316
Columbus OH USA 1987 Zane	1	0.56	281	Harvest aid	Seed	10	0.03 0.03 (0.03)	PP901/0316
Dallas Center IA USA 1987 Asgrow 2187	1	0.56	187	Harvest aid	Seed	7	0.03 0.02 (0.02)	PP901/0316

^a Replicate field samples collected from the same plot, mean in brackets

Carrots

Six supervised trials on carrots were conducted in Germany during 1983–1984. An SG formulation of diquat and paraquat was applied two or three times at rates of 0.71 to 0.98 kg ai/ha. Applications were made inter-row for the control of weeds. An additional trial on carrots was conducted in Italy during 1993 where a single application of an SL formulation of diquat was made between the crop rows at 0.8 kg ai/ha. Samples were stored frozen for up to 256 days. Residues of diquat from the trials in Germany were analysed using method PPRAM 1A or PPRAM 1B and in the Italy trial using method RAM 005/01.

Table 46 Residues in carrots (directed inter-row application for weed control). Trials at Lüneburg Germany 1983, Freisbach Germany 1984 and Lombardo Italy 1993 used spray shields.

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Lüneburg Germany 1983 Caramba	2 (37)	0.75 0.75	2500 1250	14 days before harvest	Roots	0 4 9 14 22	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	PP901/0636
	2 (37)	0.75 0.75	2500 1250	14 days before harvest	Roots	0 4 9 14 22	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	
Steinfeld Germany 1983 Nantaise	2 (19)	0.75 0.75	3250 2350	9 days before harvest	Roots	0 4 9 14 21	< 0.02 < 0.02 < 0.02 0.02 < 0.02	PP901/0636
Büchen Germany 1984 Caramba	2 (21)	0.75 0.75	2500 2500	5–10 cm 30–35 cm	Roots	0 4 6 14 21	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	PP901/0630
Lüneburg Germany 1984 Lange Rote	3 (24 20)	0.75 0.75 0.75	2500 2500 2500	20 cm 30 cm 45 cm	Roots	0 4 9 14	0.01 0.01 0.01 0.02 c0.01	PP901/0630

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Freisbach Germany 1984 Tip Top	1	0.75	1200	40–45 cm	Roots	0 4 8 13 19	< 0.01 0.01 0.01 0.01 0.01	PP901/0630
Montanaso Lombardo Italy 1993 Nantese	1	0.80	500	PH	Roots	1 7 13 20	< 0.02 < 0.02 < 0.02 < 0.02	PP901/0285

Lüneburg Germany 1983 Caramba, appears to be one trial at same location, similar application dates

Potatoes

Sixteen supervised residue trials were conducted on potatoes in Europe during 2009 and 2010. An SL formulation of diquat was applied once at a rate of 1.0 kg ai/ha. A wide range of potato types was used in these trials from early-maturing to late-maturing varieties. Samples of potatoes were stored for a maximum of 8 months. Potato samples were analysed for residues of diquat using method GRM012.03A.

Table 47 Residues of diquat in potatoes following pre-harvest use.

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Bruck an der Leitha Austria 2009 Maxilla	1	1.0	300	BBCH 93	Tubers	0 3 8 10 15	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10276
Reichersberg Austria 2009 Albatros	1	0.95	286	BBCH 47–48	Tubers	0 3 7 10 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10276
Chassenet France 2009 Mona Lisa	1	1.0	262	BBCH 48–49	Tubers	0 3 7 10 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10276
Chapelle de Guinchay France 2009 Charlotte	1	0.98	244	BBCH 47–48	Tubers	0 3 7 10 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10276
Sutton Bridge Lincolnshire UK 2010 Maris Piper	1	1.0	209	BBCH 48–49	Tubers	10	0.01	A1412A_10295
Thelnetham Norfolk UK 2010 Melody	1	1.0	207	BBCH 48	Tubers	10	0.01	A1412A_10295
La Chapelle de Guinchay France 2010 Bintje	1	1.0	260	BBCH 46–48	Tubers	10	0.01	A1412A_10295
Rohrau Austria 2010 Pluto	1	1.1	321	BBCH 48	Tubers	10	0.02	A1412A_10295
Midi-Pyrénées France 2009 Spunta	1	0.96	241	BBCH 43–49	Tubers	0 3 7 10 14	< 0.01 0.02 ^a < 0.01 < 0.01 < 0.01	A1412A_10277
Nîmes France 2009 Mona Lisa	1	0.99	247	BBCH 48–55	Tubers	0 3 7 10 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10277

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Azzano d'Ash Italy 2009 Marabel	1	0.96	288	BBCH 47	Tubers	0 3 7 11 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10277
Villena Spain 2009 Desiree	1	1.0	280	BBCH 46–47	Tubers	0 3 7 10 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10277
Nîmes Languedoc-Roussillon France 2010 Mona Lisa	1	1.1	278	BBCH 48–49	Tubers	10	< 0.01	A1412A_10291
Ges Midi-Pyrénées France 2010 Agata	1	1.0	257	BBCH 91	Tubers	10	0.01	A1412A_10291
Cervesina Lombardy Italy 2010 Hermes	1	0.95	238	BBCH 91	Tubers	10	< 0.01	A1412A_10291
Albacete Spain 2010 Hermes	1	1.0	280	BBCH 48–49	Tubers	10	< 0.01	A1412A_10291

^a Mean of two determinations on single sample (individual values not reported)

Eight supervised trials using diquat as a desiccant for potatoes were conducted in various locations in the US in 1994. Potato tubers were collected 7 days after the last application. Samples were maintained in freezers at –20 °C from 196 to 260 days prior to extraction. Diquat residues were determined using analytical method RAM 252/01.

Table 48 Residues in potatoes following pre-harvest desiccation use

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Visalia CA USA 1994 Russet Burbank	2 (5)	0.56 0.56	136 135	Mature Mature	Tubers	7	< 0.05	PP901/0286
Platteville CO USA 1994 Ranger	2 (5)	0.56 0.56	136 136	Mature Mature	Tubers	7	< 0.05	PP901/0286
Caldwell ID USA 1994 Shipody	2 (5)	0.56 0.56	185 185	Green beginning to go down Green	Tubers	7	< 0.05 0.06 (0.05)	PP901/0286
Presque Isle ME USA 1994 Atlantic	2 (6)	0.56 0.56	168 245	Tubers 5.1–7.0 cm Tubers 5.1–7.0 cm	Tubers	7	< 0.05	PP901/0286
Northwood ND USA 1994 Russet Burbank	2 (6)	0.56 0.56	187 93.5	Nearing crop maturity Nearing crop maturity	Tubers	7	< 0.05	PP901/0286
Waterloo NY USA 1994 Monona	2 (5)	0.56 0.56	180 263	Tubers 7.6–10.2 cm Tubers 7.6–10.2 cm	Tubers	6	0.07 0.05 (0.06)	PP901/0286
Ontario OR USA 1994 Russet Burbank	2 (5)	0.56 0.56	184 184	Mature Desiccated	Tubers	7	< 0.05	PP901/0286
Arlington WI USA 1994 Atlantic	2 (5)	0.56 0.56	152 152	Mature Mature	Tubers	7	< 0.05	PP901/0286

Rape seed

Sixteen supervised residue trials were conducted on oilseed rape in Europe during 2009 and 2010. A diquat SL formulation was applied once at a rate of 0.6 kg ai/ha. Samples of rape seed and plants were

stored for a maximum of 12 months. Samples were analysed for residues of diquat using method GRM012.03A.

Table 49 Residues in rape seed (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Burgenland Austria 2009 NK Petrol	1	0.63	314	BBCH 88	Seed	0	0.53	A1412A_10278 + Neo Wett
						1	0.09	
						3	0.07	
						5	0.07	
						7	0.07	
					Remaining plant	0	2.2	
						1	0.40	
						3	0.11	
						5	0.19	
						7	< 0.01	
Gemeinlebern Austria 2009 NK Petrol	1	0.65	323	BBCH 87–88	Seed	0	0.23	A1412A_10278 + Neo Wett
						1	0.42	
						3	0.43	
						5	0.39	
						7	0.42	
					Remaining plant	0	4.1	
						1	0.78	
						3	1.7	
						5	0.97	
						7	1.3	
La Chapelle de Guinchay France 2009 Hexagone	1	0.62	258	BBCH 87–89	Pods	0	31	A1412A_10278 + LI700
					Pods	1	8.1	
					Pods	3	2.8	
					Seed	5	0.10	
					Seed	7	0.05	
					Remaining plant	0	8.7	
						1	5.0	
						3	7.5	
						5	0.18	
						7	3.8	
Nancelle Burgundy France 2009 Exocet	1	0.62	256	BBCH 87–88	Pods	0	21	A1412A_10278 + LI700
					Pods	1	8.3	
					Pods	3	1.6	
					Seed	5	0.08	
					Seed	7	0.07	
					Remaining plant	0	8.6	
						1	3.5	
						3	1.2	
						5	1.6	
						7	1.1	
La Chapelle de Guinchay France 2010 PR44W29	1	0.62	620	BBCH 89	Seed	4	0.03	A1412A_10292 + LI700
Söpte Vas Hungary 2010 Ontario	1	0.56	281	BBCH 88–89	Seed	5	0.02	A1412A_10292 + Silwet Top
Stowbridge Norfolk UK 2010 D06	1	0.61	205	BBCH 88–89	Seed	5	0.12	A1412A_10292 + Activator 90
Stetchworth Suffolk UK 2010 Castille	1	0.63	209	BBCH 88–89	Seed	5	0.05	A1412A_10292 + Activator 90
Albacete Spain 2009 Dante	1	0.60	288	BBCH 87–89	Seed	0	1.2	A1412A_10279 + Agral
					Seed	1	2.6	
					Seed	3	0.15	
					Seed	5	0.02	
					Seed	7	0.03	
					Remaining plant	0	17	
						1	8.1	
						3	4.7	
						5	3.1	
						7	2.5	

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Alessandria Piedmont Italy 2009 Makila	1	0.57	285	BBCH 89	Pods Pods Seed Seed Seed	0 1 3 5 8	14 7.1 0.56 0.38 0.21	A1412A_10279 + Etravon
					Remaining plant	0 1 3 5 8	6.5 3.2 3.0 1.8 1.2	
Savés Ger Haute-Garome France 2009 ES Anabal	1	0.58	243	BBCH 87–89	Pods Pods Pods Seed Seed	0 1 3 5 7	4.3 1.6 0.85 0.06 0.04	A1412A_10279 + LI700
				BBCH 87–89	Remaining plant	0 1 3 5 7	11 11 3.2 2.0 0.35	
Nîmes Languedoc-Roussillon France 2009 ES Acaba	1	0.58	192	BBCH 87–89	Pods Pods Pods Seed Seed	0 1 3 5 7	1.2 0.73 0.23 0.27 0.14	A1412A_10279 + LI700
				BBCH 87–89	Remaining plant	0 1 3 5 7	16 17 7.6 2.2 2.7	
Albacete Spain 2010 Grizzly	1	0.61	255	BBCH 82–83	Seed	5	0.33	A1412A_10293 + Agral
Nîmes Languedoc-Roussillon France 2010 ES Akaba	1	0.66	273	BBCH 83–87	Seed	4	0.45	A1412A_10293 + LI700
Gers Midi Pyrénées France 2010 ES Annibal	1	0.65	270	BBCH 87–89	Seed	5	0.22	A1412A_10293
Asti Piedmont Italy 2010 Pioneer PR4SD03	1	0.61	253	BBCH 95	Seed	5	0.44	A1412A_10293 + Etravon

Nine supervised residue trials were conducted on oilseed rape (Canola) during 2009 and 2010. In these trial an SL formulated was applied once at a rate of 0.56 kg ai/ha. Samples of rape seed were stored for a maximum of 26 months. Samples were analysed for residues of diquat using method GRM012.03A (modified).

Table 50 Residues in rape seed (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg) ^a	Reference
Sanford NC USA 2009 DK 1369	1	0.54	145	Seed formation	Seed	6	0.51 0.53 (0.52)	ASF886_50000 + Induce
Minot ND USA 2009 Liberty Link 8440	1	0.54	191	Podding	Seed	8	0.71 0.74 (0.72)	ASF886_50000 + Preference
Minot ND USA 2009 Roundup Ready DKL 30–42	1	0.56	200	Podding	Seed	8	0.48 0.49 (0.48)	ASF886_50000 + Preference
Prosser WA USA 2009 Rapier	1	0.53	231	Podding	Seed	8	0.05 0.07 (0.06)	ASF886_50000 + Ad-Wet 90
Moxee WA USA 2009 67007	1	0.52	203	seed	Seed	8	0.23 0.24 (0.24)	ASF886_50000 + 90 Plus

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg) ^a	Reference
Brookings SD USA 2009 Freedom 84501	1	0.53	192	60–70% seed turned brown	Seed	6	0.27 0.34 (0.30)	ASF886_50000 + Induce
Brookings SD USA 2009 Freedom 84501	1	0.53	191	60–70% seed turned brown	Seed	5 7 10 15	0.46 0.48 (0.47) 0.49 0.36 (0.42) 0.48 0.44 (0.46) 0.44 0.40 (0.42)	ASF886_50000 + Induce
Aurora SD USA 2009 InVigor 8440	1	0.53	233	Ripening (60% ripened)	Seed	6	0.29 ^b 0.30 ^b (0.30)	ASF886_50000 + Induce
Kimberly ID USA 2009 Sunrise	1	0.53	246	Mature (70% brown)	Seed	6	0.78 0.86 (0.82)	ASF886_50000 + Activator 90

^a Replicate field samples collected from the same plot, mean in brackets)

^b Mean of duplicate analyses (individual results not reported)

Sunflowers

Ten trials on sunflowers were conducted in France using diquat as a desiccant or harvest aid. All treated plots received one application of diquat as an SL formulations at the rate of 0.6 kg ai/ha. Sunflower heads were collected 5 to 7 days after treatment and either shelled by hand or threshed by combine. Samples were stored frozen for 7 months prior to analysis. Sunflower seeds were fractioned into oil and cake components, analysing each component separately and calculating residues in the seed using weight ratios of oil to cake, which were roughly 40% to 60%, respectively. Residues of diquat from the 1993 and 1994 trials were analysed using methods RAM 005/01 and method RAM 252/01, respectively. Residues of diquat in the 2004 trials were analysed using RAM 252/02 and RAM 272/02.

Table 51 Residues of diquat in sunflower seed (pre-harvest desiccation) (residue levels reported for sunflower seeds were calculated from residues in oil and cake and the weight ratios of the components in each sample analysed)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Coulombs France 1993 Eurosol	1	0.60	300	When bracts become dark	Seed Oil Cake	6	0.15 ^{a,b} < 0.05 (66) 0.14 (34)	PP901/0424
Marchezais France 1993 Eurosol	1	0.60	300	When bracts become dark	Seed Oil Cake	7	0.11 ^{a,b} < 0.05 (65) 0.10 (35)	PP901/0424
Chambray Les Tours France 1993 Eurosol	1	0.60	300	When bracts become dark	Seed Oil Cake	7	0.11 ^{a,b} < 0.05 (58) 0.11 (42)	PP901/0424
Joue Les Tours France 1993 Eurosol	1	0.60	300	When bracts become dark	Seed Oil Cake	5	0.19 ^{a,b} < 0.05 (54) 0.22 (46)	PP901/0424
Marchezais France 1994 Eurosol	1	0.60		When bracts become dark	Seed Oil Cake	7	0.08 ^{a,b} < 0.05 0.06	PP901/0426
Coulombs France 1994 Eurosol	1	0.60		When bracts become dark	Seed Oil Cake	7	0.46 ^{a,b} < 0.05 0.46 c0.05	PP901/0426
Oyre France 1994 Albena	1	0.60		5.2–5.3 “Code Binoire Cetiom”	Seed Oil Cake	7	0.41 ^{a,b} < 0.05 0.39	PP901/0426

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Chatellerault France 1994 Santa Fe	1	0.60		5.2–5.3 “Code Binoire Cetiom”	Seed Oil Cake	7	0.54 ^{a, b} < 0.05 0.50 c0.05	PP901/0426
Monferran Saves France 2004 Melody	1	0.63	317	BBCH 85–87	Seed Oil Cake	7	0.06 ^a < 0.05 (32) 0.07 (68)	PP901/1769 +Agral
	1	0.57	283	BBCH 85–87	Seed Oil Cake	7	0.09 ^a < 0.05 (42) 0.12 (58)	+Agral
Correlles Beaujolais France 2004 All Star	1	0.57	287	BBCH 87–89	Seed Oil Cake	7	0.06 ^a < 0.05 (47) 0.07 (53)	PP901/1769 +Agral
Francheleins France 2004 Pegasol	1	0.62	312	BBCH 87–89	Seed Oil Cake	7	< 0.05 ^a < 0.05 (49) < 0.05 (51)	PP901/1769 +Agral
Brie France 2004 Aurasol	1	0.58	291	BBCH 87–88	Seed Oil Cake	7	0.10 ^a < 0.05 (43) 0.13 (57)	PP901/1769 +Agral
Taize France 2004 Dymec	1	0.59	297	BBCH 87	Seed Oil Cake	7	0.07 ^a < 0.05 (40) 0.09 (60)	PP901/1769 +Agral

^a Calculated residue from separate oil and meal determinations, values in brackets are percentage yield of oil and cake from seed

^b Residues corrected for recovery

Coffee

Table 52 Residues of diquat in coffee (directed sprays for weed control)

Location, year variety	No	kg ai/ha	L/ha	GS	Sample ^a	PHI (d)	Diquat (mg/kg)	Reference
La Luisa, Costa Rica 1993 Catuai Rojo	3 (36 97)	0.15 0.15 0.15		160 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B
	3 (36 97)	0.60 0.60 0.60		160 cm	Fruit	0 3	< 0.05 < 0.05	
La Margarita, Costa Rica 1992 Catuai Rojo	3 (34 30)	0.15 0.15 0.15		160 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B
	3 (34 30)	0.60 0.60 0.60		160 cm	Fruit	0 3	< 0.05 < 0.05	
Juan Vinas, Costa Rica 1992 Caturra	3 (32 34)	0.15 0.15 0.15		170 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B
	3 (32 34)	0.60 0.60 0.60		170 cm	Fruit	0 3	< 0.05 < 0.05	
Retalhuleu Guatemala 1992 Caturra	3 (30 31)	0.15 0.15 0.15		200 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B + Agral
	3 (30 31)	0.60 0.60 0.60		200 cm	Fruit	0 3	< 0.05 < 0.05	
Retalhuleu Guatemala 1992 Catimor 5269	3 (30 30)	0.15 0.15 0.15		300 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B + Agral
	3 (30 30)	0.60 0.60 0.60		300 cm	Fruit	0 3	< 0.05 < 0.05	

Location, year variety	No	kg ai/ha	L/ha	GS	Sample ^a	PHI (d)	Diquat (mg/kg)	Reference
Quetzaltenango Guatemala 1992 Catuai	3 (30 30)	0.15 0.15 0.15		300 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B + Agral
	3 (30 30)	0.60 0.60 0.60		300 cm	Fruit	0 3	< 0.05 < 0.05	

^a Coffee pods were pulped, fermented, the beans washed with water and dried.

Animal feed stuffs

Legume Animal Feeds

Diquat is used as a desiccant in the following crops and is applied shortly before harvest to dry the plants and facilitate harvest therefore, in addition to seeds, the derived animal feed commodities are straw and hay.

Dry beans-straw

Table 53 Residues of diquat in bean straw

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Visalia CA USA 1994 Greencrop	1	0.42	91	crop fully mature, pods drying	straw	4	9.4 9.0 (9.2)	PP901/0325
Ault CO USA 1994 Bill Z	1	0.42	93	crop mature	straw	4	6.2	PP901/0325
Jerome ID USA 1994 Pinto Vofi 196	1	0.42	76	crop mature	Straw	4	6.3	PP901/0325
Bridgeport MI USA 1994 Blackhawk	1	0.42	92	crop mature	Straw	4	7.8	PP901/0325
Hutchinson MN USA 1994 Montcalm	1	0.42	89	crop mature, pods yellow	Straw	4	5.5	PP901/0325
Madrid NE USA 1994 Vaccaro	1	0.42	93	crop mature	Straw	4	1.8	PP901/0325
Fabius NY USA 1994 Light Red Kidney	1	0.42	93	crop mature	Straw	4	9.8	PP901/0325
Northwood ND USA 1994 Norstar	1	0.42	94	crop near maturity, 70% defoliated	Straw	4	5.5	PP901/0325

Table 54 Residues in pea straw (haulm)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat ion (mg/kg)	Reference
Dorrington Lincolnshire UK 1990 Helka	1	0.53	300	PGRO/Knott 301-302	Haul m	5	<u>3.6</u> ^a c0.05	PP901/0319 +Agral
Warwickshire UK 1990 Princess	1	0.53	300	PGRO/Knott 301-303	Haul m	10	2.1 ^a	PP901/0319 +Agral
Icklingham East Anglia UK 1990 Solara	1	0.53	300	PGRO/Knott 301-302	Haul m	8	3.6 ^a c0.25	PP901/0319 +Agral
Dorrington Lincolnshire UK 1992 Baroness	1	0.26	200	PGRO/Knott 301-302	Haul m	4	8.3	PP901/0322 +Agral
	1	0.53	200	PGRO/Knott 301-302	Haul m	4	14	
	1	0.53	200	PGRO/Knott 301-302	Haul m	4	<u>18</u>	
Welton Cuff Lincolnshire UK 1992 Progreta	1	0.26	200	PGRO/Knott 301-302	Haul m	4	5.5	PP901/0322 +Agral

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat ion (mg/kg)	Reference
	1	0.53	200	PGRO/Knott 301-302	Haul m	4	12	+Agal
	1	0.53	200	PGRO/Knott 301-302	Haul m	4	<u>14</u>	
Sandy Gate Lincolnshire UK 1992 Princess	1	0.26	200	PGRO/Knott 301-302	Haul m	4	9.4	PP901/0322 +Agral
	1	0.53	200	PGRO/Knott 301-302	Haul m	4	<u>25</u>	
	1	0.53	200	PGRO/Knott 301-302	Haul m	4	20	+Agal

^a Recovery residues corrected for residue measured in the corresponding unfortified control sample

Table 55 Soya bean forage

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Avignon France 1994 Goldor	1	0.60		Mature	Forage	4	10 (23 ppm)	PP901/0328
Blois France 1994 Maple Arrow	1	0.60		Mature	Forage	4	6.0 (9 ppm)	PP901/0328

ppm = dry weight basis

Though described in the report as fodder, the water content of the plant samples was around 50% (estimated, as the residues increased by 1.5–2.3 times on oven drying), corresponding to forage as defined in the OECD animal feedstuffs table (56% dry matter).

Table 56 Lentil fodder

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Portage La Prairie, Manitoba Canada 1993 Eston	1	0.55	200	Lower 1/3 pods brown, mid 1/3 yellow	Fodder	5 + 2	10 (14 ppm) c0.12	RJ1895B
	1	1.1	200	Lower 1/3 pods brown, mid 1/3 yellow	Fodder	5 + 2	14 (19 ppm) c0.12	
Saskatoon, Saskatchewan Canada 1993 Laird	1	0.55	199	Lower/mid 1/3 pods brown, upper 1/3 yellow	Fodder	6	20 (28 ppm) c0.22	
	1	1.1	199	Lower/mid 1/3 pods brown, upper 1/3 yellow	Fodder	6	53 (74 ppm) c0.22	
Saskatoon, Saskatchewan Canada 1993 Eston	1	0.55	199	Lower/mid 1/3 pods brown, upper 1/3 yellow	Fodder	6	39 (49 ppm) c0.07	
	1	1.1	199	Lower/mid 1/3 pods brown, upper 1/3 yellow	Fodder	6	74 (92 ppm) c0.07	

ppm = dry weight basis

Saskatoon site, same location, same application date, harvest date

FATE OF RESIDUES IN STORAGE AND PROCESSING

Data are available to demonstrate the stability of diquat under conditions more extreme than those encountered in commercial food processing. Residue analytical methods for diquat in crops extract diquat from crop matrices by reflux in aqueous acid. At these concentrations of acid used pHs are low (< 0) and reflux temperatures are above 100 °C. Under these conditions there was no evidence of

degradation with acceptable mean recovery efficiencies obtained for diquat. Diquat is hydrolytically stable under conditions of extreme acidity and elevated temperature that might be encountered in commercial food processes.

The effect of processing on the level of diquat-derived residues was also investigated for soya beans to oil and rape seed to oil.

As a measure for the transfer of residues into processed products, a processing factor was used, which is defined as

$$PF = \frac{\text{Total residue in processed product (mg/kg}^{-1}\text{)}}{\text{Total residue in raw agricultural commodity (mg/kg}^{-1}\text{)}}$$

A concentration of residues takes place when $PF > 1$.

Soya beans

One application of diquat was made to soya beans (*var* Asgrow 2187) at a rate of 2.8 kg ai/ha seven days before normal commercial harvest. At harvest, samples of treated and untreated seed were collected and transported frozen to the processing facility. The beans were dried in a forced-air oven to achieve the optimal moisture content for hull removal (10%). The conditioned beans were cracked and the hulls removed by aspiration. After hulling the kernels were pre-heated to 74 °C and flaked by rolling to a thickness of 0.2–0.3 mm. Flaked kernels were solvent extracted using hot (63 °C) hexane for six cycles (3 hours). After draining the solvent, the flakes were dried using warm air for a further 4 hours to produce solvent-extracted meal. The miscella (oil and hexane mixture) was separated by evaporation, during which the crude oil reaches 85 °C temperature. Crude oil was sampled and the hexane discarded. Crude oil was refined by mixing crude oil with sodium hydroxide for 90 minutes at 20–24 °C and 20 minutes at 63–67 °C. After allowing to settle for an hour at 60–65 °C, the oil was refrigerated for at least 12 hours before the refined oil was decanted and filtered. The fraction remaining is the soapstock. Refined oil and soapstock were sampled.

The balance study achieved overall diquat mass balances of 141 and 131% for oil production. Residues and processing factors are presented in Table 57.

Table 57 Diquat residues in soya beans and processed commodities (PP901/0442)

Trial	Sample	Residue (mg/kg)	PF
Iowa 1987 R010 Run 1	Soya bean (RAC) ^a	0.24	–
	Soya bean (RAC) ^b	0.25	–
	Hulls	0.65	2.6
	Solvent-extracted Meal	0.18	0.7
	Crude Oil	< 0.01	< 0.04
	Soapstock	0.02	0.1
	Refined Oil	< 0.01	< 0.04
Iowa 1987 R010 Run 2	Soya bean (RAC) ^a	0.25	n/a
	Soya bean (RAC) ^b	0.14	n/a
	Hulls	0.50	3.6
	Solvent-extracted Meal	0.14	1.0
	Crude Oil	< 0.01	< 0.07
	Soapstock	0.03	0.2
	Refined Oil	< 0.01	< 0.07

^a Soya bean sample collected from the field

^b Soya bean sample collected from the bulk samples prior to processing

Rape seed

A processing study was performed for rape seed. Two residue trials on rape were conducted in northern France and the United Kingdom during 2011. One application of diquat was made to rape at

a rate of 2.0 kg ai/ha five days before normal commercial harvest. Rape seed was processed into refined oil. Two balance and two follow-up design tests were conducted, one balance study and one follow-up study on seed from each field trial. The process was representative of commercial oilseed rape processing.

Seed with non-optimal moisture content was dried until the optimal moisture content for pressing (6–10%) was achieved. The conditioned seed was cleaned manually using a sieve to remove parts of coarse stalks and weed seeds to produce cleaned seed. The rape seed was crushed to break the testa (seed coat) and flakes sampled. A screw press was used to separate the seed into a liquid phase (crude oil) and a solid phase (press cake). If required (depending on the pressing qualities of the seed), a heated press head was used. Crude oil and press cake were sampled. The press cake for solvent extraction was transferred to a small technical extraction plant. The first extraction step used n-hexane circulated through the press cake for about 2 hours at approximately 60 °C. After the circulation time, the solvent-oil-mixture (miscella) was pumped into a distillation vessel and after distillation, the extracted oil and the distilled n-hexane was transferred back to the press cake for a second extraction step. Fresh n-hexane was added and a second extraction performed under the same conditions as the first extraction. A second distillation was conducted as above, after which the remaining solvent was removed from the oil by rotary evaporation at 80 °C. Solvent-extracted oil and solvent-extracted meal were sampled. Before refining, crude oil (from screw pressing) from each sample was mixed with the corresponding solvent-extracted oil. The combined oil was sampled and then filtered. Refining of the crude oil included hydration, desliming (degumming), neutralisation, washing, drying, bleaching, filtration and deodorization steps, after which the refined oil was sampled. On completion of processing, samples were frozen immediately and stored below -18 °C.

Two balance and two follow-up processing studies were conducted where oilseed rape plants were treated with diquat and the harvested seeds processed by industrial processes into rape-seed oil. The procedures used closely mimicked industrial oil production processes. Good mass balances of diquat were achieved. Residues in processed commodities were reduced from those in raw rape seed, with processing factors from 0.17 to 0.76 in solvent-extracted meal and < 0.01 to < 0.03 in refined oil. Residues in by-products were also reduced from those in raw rape seed, with processing factors of 0.23 and 0.82 in press cake, 0.63 and 0.61 in crude oil and < 0.01 and < 0.03 in solvent-extracted oil. Only in waste (course plant debris and weed seeds) did residues increase, to 20 and 41 mg/kg in the two studies.

Residues of diquat (ion) were measured using method GRM012.03A. From receipt at the analytical facility, except for sample preparation and the removal of a sub-sample for analysis, the samples were stored frozen at or below -18 °C. Samples were stored frozen for a maximum period of 223 days from sampling to analysis and residues in the processed products are deemed to be stable over the storage period.

The balance study achieved overall diquat mass balances of 141 and 131% for oil production. The residues and processing factors found in the processed samples are presented in Table 58.

Table 58 Diquat residues in oilseed rape and processed commodities with corresponding processing factors

Country Year Trial	Crop Part	Diquat residue (mg/kg)	PF
France 2011 SRFR11-004-37HR	Rape Seed (RAC)	0.70	–
	Cleaned Seed	0.11	0.16
	Waste	20	29
	Flakes	0.17	0.24
	Press Cake	0.16	0.23
	Crude Oil	0.44	0.63
	Solvent-extracted Oil	< 0.01	< 0.01
	Solvent-extracted Meal	0.12	0.17
	Combined Oil	0.15	0.21
	Hydration Watery Phase	0.03	0.04

Country Year Trial	Crop Part	Diquat residue (mg/kg)	PF
	Desliming Watery Phase	< 0.01	< 0.01
	Soapstock	< 0.01	< 0.01
	Washing Water	< 0.01	< 0.01
	Refined Oil	< 0.01	< 0.01
France 2011 SRFR11-004-37HR (Follow-up study)	Rape Seed (RAC)	1.05	–
	Solvent-extracted Meal	0.21	0.20
	Refined Oil	< 0.01	< 0.01
United Kingdom 2011 SRUK11-003-37HR	Rape Seed (RAC)	0.38	–
	Cleaned Seed	0.24	0.63
	Waste	41	108
	Flakes	0.37	0.97
	Press Cake	0.31	0.82
	Crude Oil	0.23	0.61
	Solvent-extracted Oil	< 0.01	< 0.03
	Solvent-extracted Meal	0.29	0.76
	Combined Oil	0.11	0.29
	Hydration Watery Phase	0.02	0.05
	Desliming Watery Phase	< 0.01	< 0.03
	Soapstock	< 0.01	< 0.03
	Washing Water	< 0.01	< 0.03
	Refined Oil	< 0.01	< 0.03
United Kingdom 2011 SRUK11-003-37HR (follow-up study)	Rape Seed (RAC)	0.31	–
	Solvent-extracted Meal	0.18	0.58
	Refined Oil	< 0.01	< 0.03

Sunflower

No formal processing studies have been carried out for sunflower seeds. However, in ten supervised trials where diquat was applied as a desiccant or harvest aid, oil was extracted from seeds and residues were determined in the separated oil and cake fractions. All residues of diquat in the oil were below the LOQ (< 0.05 mg/kg). Residues of diquat concentrated in sunflower cake by a mean factor of 1.2. Residues did not concentrate in the oil.

Table 59 Diquat residues in sunflower oil and cake following application as a desiccant in France

Trial	Diquat residues (mg/kg)			PF		Reference
	Seed ^a	Oil	Cake	Seed to oil	Seed to cake	
S.215.94	0.08	< 0.05	0.08	< 0.6	1.0	PP901/0426
S.216.94	0.46	< 0.05	0.60	< 0.1	1.3	
S.622.94	0.41	< 0.05	0.50	< 0.1	1.2	
S.623.94	0.54	< 0.05	0.64	< 0.1	1.2	
CEMS-2362A	0.06	< 0.05	0.07	< 0.8	1.2	PP901/1769
CEMS-2362B	0.09	< 0.05	0.12	< 0.6	1.3	
CEMS-2362C	0.06	< 0.05	0.07	< 0.8	1.2	
CEMS-2362D	< 0.05	< 0.05	< 0.05	< 1.0	1.0	
CEMS-2362E	0.10	< 0.05	0.13	< 0.5	1.3	
CEMS-2362F	0.07	< 0.05	0.09	< 0.7	1.3	

^a Calculated from oil and cake residues

Livestock feeding studies

Dairy cow feeding study

The transfer of diquat residues from feed to tissues and milk of dairy cows was studied using incurred residues (Edwards *et al.*, 1976). A 2-hectare field of grass was sprayed with diquat at 4 kg ai/ha. The treated grass was harvested after 4 days of sunny, dry and warm weather and processed to grass nuts.

Levels of diquat in the grass nuts were 209 ppm after production and before study start and showed no decline in concentration during storage under ambient conditions.

Lactating cows (Friesian, 3 to 7 years, 394 to 559 kg, three per dose rate) were fed diets containing fresh grass and a mixture of treated (209 ppm diquat) and untreated grass. Mean daily feed consumption during the exposure period was 9.9 kg DM fresh grass and 8.8–9.1, 8.1–9.1, 9.0–9.1 and 5.3–7.6 kg grass nuts/cow for groups 1, 2, 3 and 4 respectively. Mean daily milk yield during the exposure period was 7 to 18 kg/cow/day. Based on mean daily feed consumption, the exposure was equivalent to 18, 50 and 84 ppm in the feed. Cows were milked twice daily and morning milk combined with milk from previous evening and three samples retained per week (Monday, Wednesday and Friday). Two cows per dose group were sacrificed after 30 days of dosing and samples of liver, kidney, fat and muscle (cardiac, pectoral and adductor) collected. The actual interval between last dosing and sacrifice was not reported. The remaining cow per dose group was fed untreated grass nuts and sacrificed after a further seven days.

Samples of feed and tissues were stored frozen for up to 4 weeks prior to analysis while milk samples were stored frozen for a maximum of 1 week. Feed samples (pelleted grass) were analysed for diquat using the analytical method PPRAM-5 to confirm the dose level of diquat in the feed. Milk samples were analysed for diquat using analytical method PPRAM-7 while samples of liver, kidney, fat and muscle were analysed for diquat using the analytical method TBM/3 (method adapted to determine diquat by monitoring the absorption at 379 nm).

There were no residues of diquat at or above the LOQ (0.001 mg/kg) in any of the milk samples from any of the dose groups, throughout the duration of the study. There were no residues of diquat at or above the LOQ (0.01 mg/kg) in any of the tissue samples (liver, kidney, fat and muscle) from any of the dose groups, throughout the duration of the study.

Table 60 Diquat residues in bovine milk and tissues

Matrix	18 ppm	50 ppm	84 ppm
Milk	< 0.001	< 0.001	< 0.001
Liver	< 0.01	< 0.01	< 0.01
Kidney	< 0.01	< 0.01	< 0.01
Fat	< 0.01	< 0.01	< 0.01
Muscle	< 0.01	< 0.01	< 0.01

Laying hen feeding study

A transfer study was conducted in White Leghorn chickens (1.70–1.82 kg bw, 28 weeks old) where laying hens were fed for 21 or 28 days on diets containing 1, 5 or 10 ppm diquat in the feed (Lai *et al.*, 1977). Each group were fed with basal feed treated with a known amount of diquat dibromide monohydrate. The dose level for each group was adjusted by mixing treated and untreated feed to obtain concentrations of diquat in feed on a dry weight basis of 1.0, 5.0 and 10 ppm. Mean daily food consumption during dosing period was 116–128 g/hen/day for the control group and 117–125, 112–141 and 109–140 g/hen/day for the 1, 5 and 10 ppm feed level groups respectively. The efficiency of egg production was not affected by the dosing with mean egg production during dosing period of 89–96% for the control group and 86–98%, 90–98% and 91–99% for the 1, 5 and 10 ppm feed level groups respectively. Eggs were collected daily and retained for analysis from days 1, 7, 14, 21, 28 and also day 35 (after a depuration period of 7 days). Eggs from each dose group were pooled for each day of sampling. Ten chickens from each group (excluding control Group 1) were sacrificed after 21 days and 28 days of treatment and after 7 days of depuration (study day 35). Samples of liver, muscle, heart, gizzard, skin and fat were collected from all sacrificed animals. The period of storage prior to analysis was not reported.

No residues of diquat were detected (< 0.005 mg/kg) in any of the egg, fat, muscle, liver or heart samples. With the exception of a residue of 0.006 mg/kg at the highest treatment rate on day 21, no detectable residues (< 0.005 mg/kg) were found in any of the chicken skin samples. Residues in gizzard reached a maximum of 0.019 mg/kg at day 21 in the birds dosed at the equivalent of 10 ppm,

were 0.018 mg/kg at day 28, declined during depuration to < 0.005 mg/kg, though a residue of 0.006 mg/kg remained in the 5 ppm group.

Table 61 Summary of diquat residues (mg/kg) in hen egg and tissues at end of dosing (day 28) ^a

Matrix	1 ppm	5 ppm	10 ppm
Egg	< 0.01 ^b (< 0.01, < 0.01)	< 0.01 ^b (< 0.01, < 0.01)	< 0.01 ^b (< 0.01, < 0.01)
Liver	< 0.01 ^b (< 0.01, < 0.01)	< 0.01 ^b (< 0.01, < 0.01)	< 0.01 ^b (< 0.01, < 0.01)
Muscle	< 0.01 ^b (< 0.01, < 0.01)	< 0.01 ^b (< 0.01, < 0.01)	< 0.01 ^b (< 0.01, < 0.01)
Heart	< 0.01	< 0.01	< 0.01
Gizzard	< 0.01 ^b (< 0.01, < 0.01)	< 0.01 ^b (0.011, 0.007)	0.02 ^b (0.015, 0.021)
Skin	< 0.01	< 0.01	< 0.01
Fat	< 0.01 ^b (< 0.01, < 0.01)	< 0.01 ^b (< 0.01, < 0.01)	< 0.01 ^b (< 0.01, < 0.01)

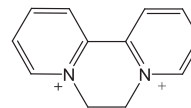
^a LOD = 0.005 mg/kg, LOQ = 0.01 mg/kg.

^b Mean of duplicate determinations

APPRAISAL

Diquat is a non-selective contact herbicide with uses on many crops. Diquat has been evaluated several times by the JMPR with the initial evaluation in 1970 and the latest in 1994. Diquat was scheduled at the Forty-fourth Session of the CCPR (2012) for periodic re-evaluation of toxicology and residues by the 2013 JMPR.

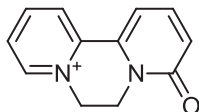
The Meeting received information on the metabolism of diquat in animals, on crops, methods of residue analysis, freezer storage stability, GAP information, supervised residue trials, fate of residue during storage and processing, and livestock feeding studies.



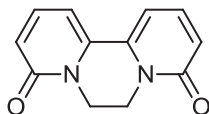
Diquat is 6,7-dihydrodipyrido[1,2-a:2',1'-c]pyrazinediium dibromide.

Metabolites referred to in the appraisal are addressed by their common names:

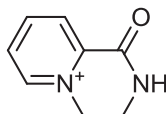
Diquat monopyridone



Diquat dipyridone



TOPPS



Animal metabolism

Metabolism of diquat in goats and hens involves formation of diquat dipyridone and diquat monopyridone. TRR are expressed in terms of diquat ion.

In a study where a lactating goat was orally treated once daily for 7 consecutive days with ring labelled [¹⁴C]-diquat at a dose equivalent to 90 ppm in the feed, approximately 97% of the administered dose was recovered with the majority in the excreta (84% faeces, < 1% urine) or gastrointestinal tract (12%). The radioactivity in the tissues ranged from 0.003 in fat to 0.079 mg equiv/kg in kidney. TRR values in milk were up to 0.015 mg equiv/kg during the dosing period with

levels not reaching a plateau after seven days of dosing. Major components of the ^{14}C residues were unchanged diquat ion (liver 22% TRR), diquat dipyrindone (kidney 29% TRR, liver 33% TRR, muscle 46% TRR, fat 20% TRR, milk 82% TRR) and diquat monopyridone (kidney 21% TRR, liver 13% TRR, muscle 13% TRR).

Laying hens were orally treated once daily in experiments where a single hen received a single dose at 4-5 ppm, five daily doses at 4-5 ppm or 14 doses daily doses at 0.4-0.5 ppm. By three days after administering the last dose the majority (> 94%) of the dose was recovered in the excreta. Radioactivity in tissues of hens dosed at 0.4-0.5 ppm ranged from 0.00010 mg equiv/kg in fat to 0.00045 mg equiv/kg in kidney. The ^{14}C levels in egg whites and yolks reached a plateau of 0.00003 and 0.00014 mg equiv/kg respectively by seven days of dosing. Yolk from day 9+10 eggs contained diquat ion (26% TRR), yolks from day 7 contained diquat monopyridone (85% TRR) and egg yolks from day 11 contained TOPPS (10% TRR).

In another study laying hens were each given daily doses of ^{14}C -ring labelled diquat by oral gavage for 4 days at the equivalent of 32 ppm in the diet. At sacrifice 18 hours after the last dose, radioactive residues in the muscle, fat and eggs were all < 0.01 mg equiv/kg. Levels of radioactivity in liver and kidney were 0.045 and 0.058 mg equiv/kg respectively with unchanged diquat (liver 48% TRR, kidney 12% TRR) and diquat monopyridone (liver 3.9% TRR, kidney 15% TRR) the main residue components. Minor components identified were TOPPS (liver 1.8% TRR, kidney 3.9% TRR) and diquat dipyrindone (liver 3.1% TRR, kidney 6.6% TRR).

In an additional study laying hens fed a diet containing powdered grain harvested from barley plants treated with [^{14}C]-diquat, the dose was equivalent to 1 to 1.5 ppm in the feed for 11 consecutive days with hens sacrificed 4 hours or 7 days after the last exposure. The major components of the ^{14}C in the grain were diquat ion (17% TRR) and TOPPS (8.7% TRR). Most of the administered dose was recovered in the excreta (84-89%) with less than 0.1% recovered in eggs. Radioactive residues in egg white reached a plateau by day 5 of dosing with a maximum level of 0.0006 mg equiv/kg while egg yolk reached a plateau by day 8 with a maximum residue of 0.0039 mg equiv/kg. In tissues at sacrifice 4 hours after last exposure, ^{14}C residues were highest in kidney (0.014 mg equiv/kg) and much lower in muscle and fat at 0.0009 and 0.0022 mg equiv/kg respectively. Diquat ion was a minor component of the ^{14}C residues in egg yolk at 0.9% TRR with TOPPS and diquat monopyridone present at 3.5 and 3.0% TRR respectively.

Metabolism in laboratory animals (rat) was summarized and evaluated by the WHO panel of the JMPR in the present meeting. The metabolism of diquat in ruminants and laying hens is adequately understood. In both goats and hens diquat is oxidised to form diquat monopyridone and diquat dipyrindone. TOPPS is found as a minor metabolite (< 10% TRR) in hens but was not detected in studies of the metabolism of diquat by goats or rats.

Plant metabolism

Diquat is used for two different situations:

Directed sprays for weed control (crop not intentionally treated)

Use as a crop desiccant to facilitate crop harvest (crop treated)

Plant metabolism studies were conducted with diquat to investigate these two situations.

Application prior to crop emergence

A single application of ^{14}C -diquat was made to soil into which tomato seeds had been sown prior to emergence. Residues in mature fruit and leaves harvested 112 days after application were < 0.001 and 0.002 mg equiv/kg respectively and were not analysed further.

Crop desiccation

The use of diquat as a pre-harvest desiccant was investigated in potato and rape following foliar spray application to the crop. Since the plants are senescent at the time of application or die quickly after application, metabolism is essentially stopped and translocation from the treated parts of the crops

into other plant parts such as seeds and roots is reduced. Following use as a crop desiccant, diquat ion was the major component of the ^{14}C residue in the skin and flesh of potato tubers accounting for more than 70% of TRR with no other individual component comprising more than 10% TRR. The major component in rape seed harvested from crops, following pre-harvest desiccation, was diquat ion at 48% TRR with smaller amounts of TOPPS (7.8% TRR) and diquat monopyridone (2.0% TRR).

The metabolism of diquat by plants is well understood. Following directed application to weeds using shielded sprayers there is minimal contact of the crop with diquat. A portion of the spray will reach the soil, but as described later, diquat is strongly absorbed by soil components such that it is largely unavailable for uptake by plant roots.

Following use as a pre-harvest desiccant, diquat ion is the major component of the ^{14}C residue in those parts exposed to direct sprays with TOPPS and diquat monopyridone present as minor components. Only low levels of radioactivity are found in plant parts such as potato tubers that are not directly exposed to the spray (< 0.05 mg equiv/kg).

Environmental fate

The Meeting received information on soil aerobic metabolism, soil photolysis and aqueous hydrolysis properties of [^{14}C]-diquat. Studies were also received on the behaviour of [^{14}C]-diquat in a rotational crop situation.

Diquat residues are persistent in soils, however residues in soil are strongly bound to soil components and not available for uptake by plants. As such, residues in soil should not contribute significantly to the residues in succeeding crops.

In soil incubation studies under aerobic conditions in the dark, diquat disappeared with a half-life that was > 290 days. In the absence of soil, diquat was rapidly and extensively degraded by soil micro-organisms normally found in soil pore water to give a small number of non-volatile degradation products (not identified) with mineralisation to CO_2 . The DT₅₀ for degradation in solutions of soil micro-organisms is rapid at < 1 week. Addition of clay to these solutions essentially stopped further degradation confirming that sorbed diquat is not available for biological degradation.

The degradation product TOPPS is also persistent in soils. Studies on the aerobic soil degradation of the diquat metabolite TOPPS estimated DT₅₀ values for degradation of 28 to 757 days.

Soil photolysis has negligible effect on degradation. In a study with application of ^{14}C -diquat on the surface of a sterilised loam soil, the DT₅₀s for photolytic degradation on dry and wet soil were 237 and 37 days respectively.

In a study of aqueous photolysis the DT₅₀ for degradation was 31 hours. The major degradation product was TOPPS with smaller amounts of diquat monopyridone and 1-hydroxy-3,4-dihydro-1H-pyrido[1,2-a]pyrazine-2-carboxylic acid formed.

In a confined rotational crop study with wheat, lettuce and carrot, a plot of sandy loam soil was treated with [^{14}C]-diquat at the equivalent of 1.1 kg ai/ha and crops sown 30, 120 and 365 days. At normal commercial harvest, crops grown in soil containing ^{14}C -diquat showed negligible uptake of radioactivity (TRR up to 0.02 mg equiv/kg). Residues above the LOD of 0.008 mg equiv/kg could have been due to contamination with adhering soil. Crops grown in rotation with diquat-treated crops are not expected to contain residues of diquat ion or diquat degradation products. Diquat residues in soil should contribute little to residue levels in rotational crops.

Methods of analysis

The Meeting received description and validation data for analytical methods for residue analysis of diquat in various plant and animal commodities. Early methods used in field trials generally involved extraction of residues by reflux with sulphuric acid with clean-up on cation exchange columns. Following reduction of diquat ion with alkaline dithionite or sodium borohydride, detection was initially achieved spectrophotometrically (350–450 nm). In more recent methods the diquat ion recovered from the cation exchange column is subjected to HPLC-UV or GC-NPD for quantitation. In

the case of animal commodities, trichloroacetic acid is sometimes used in place of sulphuric acid for the extraction step. LOQs were in the range 0.01 to 0.1 mg/kg.

The most recent advance in methods has been the use of LC-MS/MS which allows for the clean-up steps to be omitted with LOQs of 0.005 mg/kg for animal commodities, 0.006 mg/kg for potato and barley and 0.02 mg/kg for citrus.

The efficiency of the acid extraction step has been demonstrated during the metabolism studies where the majority of the total radioactive residue (TRR) was recovered in the acid extracts.

Multi-residue methods are currently not validated for diquat.

Stability of pesticide residues in stored analytical samples

The Meeting received information on the stability of diquat in samples of commodities from crops stored frozen.

Diquat is stable for at least 24 months in homogenised samples of spinach, wheat grain, wheat straw, rape seed, lentils, orange fruit and potato tubers fortified with diquat and stored frozen.

The periods of demonstrated stability cover the frozen storage intervals used in the residue studies.

Definition of the residue

In metabolism studies of diquat in goats and hens diquat ion was a significant component of the residue in hen (48% TRR liver; 12% TRR kidney) and goat (22% TRR liver; 4.3% TRR kidney) tissues. Other major components were diquat monopyridone (13% TRR liver; 13% muscle) and diquat dipyrindone (33% TRR liver; 29% kidney; 20-46% muscle and fat; > 80% milk) with small amounts of TOPPS (1.8% liver; 3.9% kidney) formed in hens. Radioactivity in egg yolks comprised mostly diquat monopyridine (up to 85% TRR) and diquat ion (up to 26% TRR) with smaller amounts of TOPPS (up to 10%TRR).

The major components of the residue in livestock are diquat ion, diquat monopyridone and diquat dipyrindone and should be considered for inclusion in the residue definition for compliance with MRLs and estimation of dietary intake in animal commodities. However, at realistic livestock exposures no residues of diquat ion, diquat monopyridone or diquat dipyrindone are expected. Additionally, current analytical methods for tissues have only been validated for determination of residues of diquat. Noting the above, the Meeting considered diquat ion to be a suitable as a residue definition for compliance with MRLs and estimation of dietary intake for animal commodities.

The log P_{ow} for diquat is -4.6 suggesting diquat residues are not fat soluble. There was only a small difference in residue levels in muscle and fat confirming diquat ion does not preferentially partition into fat and that the residue should not be classed as fat soluble. The Meeting decided that residues of diquat are not fat soluble.

Diquat is used on crops for two different situations:

Directed sprays or pre-emergent application for weed control (crop not intentionally treated)

Use as a crop desiccant to facilitate crop harvest (crop treated)

No residues are expected in situations where crops are not directly sprayed (directed sprays for weed control, pre-emergent or pre-sowing applications). The conclusion is supported by the results of confined crop rotation studies where soil residues were not taken up by crops.

Following use as a crop desiccant, diquat ion was the major component of the residue in flesh and skins of potato tubers and in rape seeds accounting for more than 70% of TRR in potatoes and 48% TRR in rape seeds. TOPPS was also detected in rape seed but represented less than 10% of the TRR. In plants, the majority of diquat-related residues in crops are accounted for in the previous residue definition; diquat ion.

Based on the above the Meeting confirmed the previous residue definition for compliance with MRLs and estimation of dietary intake for plant commodities.

Definition of the residue for compliance with MRL and estimation of dietary intake (animal and plant commodities): *diquat ion*

The residue is not fat soluble.

Results of supervised residue trials on crops

The Meeting received supervised residue trial data for diquat on citrus fruits, pome fruits, strawberries, banana, tomato, pulses, carrots, potatoes, rape, sunflower and coffee as well as for some animal feed commodities.

As no data were available for alfalfa fodder, barley, maize, oats, rice, sorghum and wheat the Meeting agreed to withdraw previous recommendations for these commodities.

A range of uses for diquat involve the application to weeds growing under trees in a variety of countries. The Meeting noted the results of soil aerobic metabolism and confined rotational crop studies that show that diquat in soil is not available for plant uptake. As application to weeds growing under trees is not expected to result in residues in harvested commodities the Meeting decided to evaluate the use on tree crops together, using the data on the crops supplied as mutual support for recommendations for those commodities with approved use-patterns. Diquat is approved for weed control in citrus fruit (Brazil, Costa Rica, Dominican Republic), pome fruit (Slovakia), banana/plantain (Belize, Costa Rica, Dominican Republic, El Salvador, Guatemala, Nicaragua, Panama), cashews (Dominican Republic), coffee (Belize, Brazil, Costa Rica, Dominican Republic, El Salvador, Guatemala, Nicaragua, Panama), stone fruit (Slovakia) and also apple and other fruit trees (Canada, USA).

Tree crops (application to weeds)

Field trials involving citrus orchards where diquat was applied to weeds were conducted in Brazil and were available to the Meeting.

The GAP for citrus in Brazil is application directed to weeds at 0.5 kg ai/ha with a PHI of 14 days. In the trials matching this GAP diquat residues in ranked order were (n=3): < 0.01 (2), < 0.02 mg/kg. Residues in trials on citrus that utilized rates higher than permitted in Brazil were < 0.01 (2) mg/kg.

Field trials involving apples were conducted in Europe were made available to the Meeting. The GAP for apples in Slovakia is application directed to weeds at 1.0 kg ai/ha with a PHI not specified (unnecessary). In twelve trials matching this GAP and with PHIs ranging from 0 to 171 days residues were (n=12): < 0.01 (10), < 0.05 (2) mg/kg.

Diquat is permitted to be used for weed control in banana plantations in various countries of central America (Belize, Costa Rica, Dominican Republic, El Salvador, Guatemala, Nicaragua, Panama) with an application rate of 0.6 kg ai/ha and no PHI required. In six trials from Costa Rica, Ecuador and Guatemala that matched GAP residues were < 0.05 mg/kg.

Diquat is approved in a range of Central and South American countries for weed control in coffee plantations including Belize, Brazil, Costa Rica, Dominican Republic, El Salvador, Guatemala, Nicaragua and Panama with maximum application rate of 0.5–0.6 kg ai/ha and a PHI typically 0 days. In trials from Costa Rica and Guatemala residues in coffee beans were < 0.05 (6) mg/kg.

The Meeting concluded that residues of diquat are not expected in harvested commodities from tree crops when application is to the weeds. The Meeting considered an LOQ of 0.02 mg/kg achievable and decided to estimate an STMR of 0 mg/kg, an HR of 0 mg/kg and a maximum residue level of 0.02 (*) mg/kg for citrus fruit, pome fruit, banana and coffee beans and to extrapolate the values to cashew apple (including cajou), cashew nuts and stone fruit.

*Berries and other small fruit (application to weeds)**Strawberries*

Trials were available from the UK. The GAP for strawberry in Sweden is a single application to weeds at 0.5 kg ai/ha before flowering or after harvest (use of spray shield) with no PHI required.

Residues in three trials from the UK at > 1.4 times the GAP of Sweden were: < 0.05 (3) mg/kg.

The Meeting utilized trials approximating the GAP of Sweden to estimate a maximum residue level for strawberries. Noting the exaggerated rates used in the three trials, the long interval between application and harvest and the requirement for a physical barrier when spraying, the Meeting estimated a maximum residue level of 0.05 * mg/kg, an STMR of 0 mg/kg and an HR of 0 mg/kg for strawberries.

Fruiting vegetables other than Cucurbits

Diquat is permitted to be used for weed control in row crops (includes tomatoes) in Spain with an application rate of 0.45 kg ai/ha and using spray protectors or shields, PHI 15 days.

Only one trial utilized a spray screen. The application rate was 2 times the GAP of Spain and residues were < 0.01 mg/kg. In another seven trials where the application rate was 2 times the maximum application rate of Spain and that did not use a spray shield the residues were also < 0.01 (7) mg/kg. The Meeting considered there is no expectation of residues above the LOQ for tomatoes and agreed to extrapolate the conclusion to fruiting vegetables other than cucurbits except sweet corn and fungi.

The Meeting estimated a maximum residue level of 0.01* mg/kg, an STMR of 0 mg/kg and an HR of 0 mg/kg for fruiting vegetables, other than cucurbits (except sweetcorn, fungi and mushrooms).

Pulses (pre-harvest desiccation)

Residue data from trials in common beans were made available from Germany and the USA for pre-harvest desiccation. The use pattern in Germany is 0.6 kg ai/ha with a PHI of 5 days. Analytical recoveries reported for trials from Germany on beans were low making the trials unsuitable for estimating maximum residue levels. The use pattern in Canada is for pre-harvest desiccation of beans at up to 0.41 kg ai/ha for ground application and 0.55 kg ai/ha for aerial application with a PHI of 4 days. In eight trials conducted in the USA approximating Canadian GAP residues were < 0.05 (8) mg/kg. The Meeting estimated an STMR of 0.05 mg/kg and a maximum residue level of 0.05* mg/kg for beans, dry replacing the previous recommendation of 0.2 mg/kg.

In Canada, diquat is permitted for pre-harvest desiccation of peas at up to 0.41 kg ai/ha for ground application and 0.55 kg ai/ha for aerial application with a PHI of 4 days. In five trials conducted in the USA approximating Canada GAP residues were: 0.05, 0.05, 0.09, 0.11 and 0.56 mg/kg. The Meeting considered five trials insufficient to estimate a maximum residue level for peas dry.

Pre-harvest desiccation sprays are permitted in Slovakia on peas at up to 0.8 kg ai/ha with a PHI of 6 days. In nine trials conducted in Europe, residues following a pre-harvest desiccation application at 0.6 kg ai/ha and after a 6 day PHI were: 0.03, 0.04, 0.04, 0.04, 0.05, 0.05, 0.06, 0.10, 0.15 mg/kg. The Meeting estimated an STMR of 0.05 mg/kg and a maximum residue level of 0.3 mg/kg for peas, dry confirming the previous recommendation.

In Canada, pre-harvest desiccation sprays are permitted in lentils at up to 0.41 kg ai/ha for ground application and 0.55 kg ai/ha for aerial application with a PHI of 4 days. In three trials conducted in USA with application at 0.42 kg ai/ha residues were < 0.05, 0.13 and 0.54 mg/kg at 4 days after application. The Meeting considered three trials insufficient to estimate a maximum residue level for diquat in lentils and withdrew its previous recommendation of 0.2 mg/kg.

In Canada, pre-harvest desiccation sprays are permitted in soya beans at up to 0.56 kg ai/ha with a PHI of 4 days. In seven trials conducted in USA at 0.56 kg ai/ha residues were < 0.01, 0.02, 0.03, 0.03, 0.04, 0.09, 0.16 mg/kg in samples harvested 7 to 10 days after application. The Meeting noted there was little decline in residues between 4 and 10 days and decided to use the data to estimate an STMR of 0.03 mg/kg and a maximum residue level of 0.3 mg/kg for soya beans (dry) replacing its previous recommendation of 0.2 mg/kg.

Carrots (directed application for weed control)

In Spain diquat is approved for general weed control in row crops including carrots (GAP: 0.45 kg ai/ha using spray protectors, PHI 15 days). In three trials in Germany and Italy that used spray shields and with application rates that were two times GAP of Spain residues were: 0.01, < 0.02, < 0.02 mg/kg.

The Meeting considered three trials insufficient to estimate a maximum residue level for carrots.

Potato (pre-harvest desiccation)

Diquat is approved for pre-harvest desiccation of potato crops in various countries. Pre-harvest desiccation use-patterns approved in various countries include Austria (GAP: 0.5 kg ai/ha, PHI 10 days), Brazil (GAP 0.5 kg ai/ha, PHI 7 days), Canada (GAP 2×0.84 kg ai/ha, PHI 0 days), Germany (GAP: 1 kg ai/ha, PHI 10 days), the Netherlands (GAP: 0.8 kg ai/ha, max 2 sprays and 1 kg ai/ha per crop, PHI 0 days), Spain (GAP: 0.8 kg ai/ha, PHI 15 days), the UK (GAP: 1.0 kg ai/ha, max 2 sprays and 1 kg ai/ha per crop, PHI 0 days or 14 days if storing potatoes) and the USA (GAP: 0.56 kg ai/ha, PHI 7 days).

In trials in Europe approximating the GAP of the UK residues were: < 0.01 (10), 0.01, 0.01, 0.01, 0.01, 0.02, 0.02 mg/kg.

In trials conducted according to the GAP of USA residues were: < 0.05 (6), 0.06, 0.06 mg/kg.

Using the residue data from the USA, the Meeting estimated an STMR of 0.05 mg/kg, an HR of 0.06 mg/kg and a maximum residue level of 0.1 mg/kg for potato replacing the previous recommendation of 0.05 mg/kg.

Rape seed, (pre-harvest desiccation)

Diquat is approved for pre-harvest desiccation of oilseed rape in Austria (GAP: 0.6 kg ai/ha, PHI 5 days), Canada (GAP: 0.41 kg ai/ha, PHI 14 days), Germany (GAP: 0.6 kg ai/ha, PHI 5 days), the UK (GAP: 0.6 kg ai/ha, PHI 7-10 days) and the USA (GAP: 0.56 kg ai/ha, PHI 7 days).

Residues in rape seeds from trials conducted in Europe approximating German GAP were (n=12): 0.02, 0.03, 0.03, 0.05, 0.06, 0.07, 0.08, 0.10, 0.12, 0.22, 0.27, 0.33, 0.38, 0.42, 0.44, 0.45 mg/kg.

In trials approximating GAP in the USA total residues in rape seeds were (n=9): 0.06, 0.24, 0.30, 0.30, 0.46, 0.48, 0.52, 0.72, 0.82 mg/kg.

The Meeting considered the trials from the USA would lead to the higher maximum residue level and estimated an STMR of 0.49 mg/kg and a maximum residue level of 1.5 mg/kg for rape seed replacing its previous recommendation of 2 mg/kg.

Sunflower seed (pre-harvest desiccation)

Diquat is approved for pre-harvest desiccation of sunflowers in Canada (GAP: 0.41 kg ai/ha, PHI 15 days) and Slovakia (GAP: 0.6 kg ai/ha, PHI 6 days). Residues in trials from France approximating Slovakian GAP were (n=13): < 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.11, 0.15, 0.19, 0.41, 0.46, 0.54 mg/kg.

The Meeting estimated an STMR of 0.11 mg/kg and a maximum residue level of 0.9 mg/kg for sunflower seed replacing its previous recommendation of 1 mg/kg.

Animal feeds

Pea fodder (pre-harvest desiccation)

Residue levels occurring in pea straw were evaluated. In four trials conducted in the UK approximating GAPs in Austria (0.6 kg ai/ha, PHI 5 days) and France (0.6 kg ai/ha, PHI 4 days) residues in pea straw were 3.6, 14, 18, 25 mg/kg all on an as received basis. The Meeting estimated median and highest residues of 16 and 25 mg/kg on an as received basis for residues of diquat in pea straw.

The Meeting estimated a median residue of 16 mg/kg, a highest residue of 25 mg/kg (both on an as received basis) and a maximum residue level of 50 mg/kg for pea fodder (on a dry weight basis).

The Meeting received two trials conducted in France that measured residues in soya bean forage. The meeting considered two trials insufficient to make recommends for soya bean forage.

Fate of residues during processing

The Meeting received information on the fate of incurred residues of diquat during the processing of soya bean, oilseed rape/canola and sunflower seeds. Studies of the hydrolysis of diquat under a range of conditions showed diquat is stable.

Summary of selected processing factors for diquat

Raw commodity	Processed commodity	Individual PF	Best estimate PF	STMR _{RAC} (mg/kg)	STMR _{RAC} × PF (mg/kg)
Soya bean	Hulls	2.6 3.6	3.1	0.03	0.093
	Meal	0.7 1.0	0.85		0.0255
	Oil	< 0.04 < 0.07	< 0.055		< 0.00165
Rape/canola	Meal	0.17 0.20 0.58 0.76	0.39	0.49	0.19
	Oil	< 0.01 < 0.01 < 0.03 < 0.03	< 0.02		< 0.0098
Sunflower seed	Oil	< 0.1 < 0.1 < 0.1 < 0.5 < 0.6 < 0.6 < 0.7 < 0.8 < 0.8 < 1	< 0.6	0.11	< 0.066
	Cake	1 1 1.2 1.2 1.2 1.2 1.3 1.3 1.3 1.3	1.2		0.132

Residues are not expected in oils obtained from treated crops.

Residues in animal commodities

Farm animal feeding studies

The Meeting received information on the residue levels arising in tissues and milk when dairy cows were fed a diet containing incurred residues of diquat at dietary levels of 18, 50 and 84 ppm for 30 consecutive days. There were no residues of diquat at or above the LOQ (0.001 mg/kg) in any of the milk samples from any of the dose groups, throughout the duration of the study. There were no residues of diquat at or above the LOQ (0.01 mg/kg) in any of the tissue samples (liver, kidney, fat and muscle) from any of the dose groups.

The Meeting also received information on the residue levels arising in tissues and eggs, when laying hens were fed a diet containing diquat at total dietary levels of 1, 5 and 10 ppm diquat for 21 or 28 consecutive days. No residues of diquat above the LOQ (< 0.01 mg/kg) were found in any of the egg, fat, muscle, skin, liver or heart samples.

Animal commodity maximum residue levels

Dietary burden calculations for beef cattle and dairy cattle and poultry are provided below. The dietary burdens were estimated using the OECD diets listed in Appendix IX of the 2009 edition of the FAO Manual.

Summary of livestock dietary burden (ppm of dry matter diet)

	US-Canada		EU		Australia		Japan	
	max	mean	Max	Mean	max	Mean	max	Mean
Beef cattle	0.12	0.09	7.3	4.7	28 ^a	18 ^c	0.09	0.09
Dairy cattle	2.9	1.9	8.7	5.6	20 ^b	13 ^d	0.09	0.09
Poultry Broiler	0.06	0.06	0.11	0.10	0.08	0.08	0.04	0.04
Poultry Layer	0.06	0.06	2.9 ^e	1.9 ^{f g}	0.08	0.08	0.05	0.05

^a Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian meat

^b Highest maximum dairy cattle dietary burden suitable for MRL estimates for mammalian milk

^c Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat.

^d Highest mean dairy cattle dietary burden suitable for STMR estimates for milk.

^e Highest maximum poultry dietary burden suitable for MRL estimates for poultry meat and eggs.

^f Highest mean poultry dietary burden suitable for STMR estimates for poultry meat.

^g Highest mean poultry dietary burden suitable for STMR estimates for poultry eggs.

Animal commodity maximum residue levels

The Meeting concluded that at the maximum estimated dietary burdens for cattle of 28 ppm and 2.9 ppm for poultry no residues are expected in tissues, milk and eggs.

The Meeting estimated HR and STMR values of 0 for milk, muscle, edible offal and fat. The Meeting estimated the following maximum residue levels: milk 0.001* mg/kg; meat (mammalian except marine mammals) 0.01* mg/kg and edible offal 0.01* mg/kg to replace its previous recommendations of: milk 0.01 mg/kg; meat (mammalian except marine mammals) 0.05 mg/kg and edible offal 0.05 mg/kg.

For poultry no residues are expected. The Meeting estimated the following maximum residue levels for poultry commodities: poultry meat 0.01* mg/kg; poultry edible offal 0.01* mg/kg and eggs 0.01* mg/kg to replace its previous recommendations of: eggs 0.05 mg/kg; poultry meat 0.05 mg/kg and poultry edible offal 0.05 mg/kg.

The Meeting estimated the following STMR values: poultry meat 0 mg/kg; poultry fat 0 mg/kg; poultry edible offal 0 mg/kg and eggs 0 mg/kg.

RECOMMENDATIONS

On the basis of the data obtained from supervised residue trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue for compliance with MRL and for estimation of dietary intake (for animal and plant commodities):

Definition of the residue for compliance with MRL and estimation of dietary intake (for animal and plant commodities): *Diquat ion*.

The residue is not fat soluble.

Table of recommendations

Commodity		Recommended MRL (mg/kg)		STMR or STMR-P (mg/kg)	HR, HR-P, highest residue (mg/kg)
CCN	Name	New	Previous		
AL 1020	Alfalfa fodder	W	100		

Commodity		Recommended MRL (mg/kg)		STMR or STMR-P (mg/kg)	HR, HR-P, highest residue (mg/kg)
CCN	Name	New	Previous		
FI 0327	Banana	0.02*		0	0
GC 0640	Barley	W	5		
VD 0071	Beans (dry)	0.05	0.2	0.05	
FT 2352	Cajou (pseudofruit)	0.02 *		0	0
FT 0292	Cashew apple	0.02 *		0	0
TN 0292	Cashew nut	0.02 *		0	0
FC 0001	Citrus fruits	0.02 *		0	0
SB 0716	Coffee beans	0.02 *		0	
MO 0105	Edible offal (mammalian)	0.01 *	0.05	0	0
PE 0112	Eggs	0.01 *	0.05	0	0
VO 0050	Fruiting vegetables, other than cucurbits (except sweetcorn, fungi and mushrooms)	0.01*		0	0
VD 0533	Lentil (dry)	W	0.2		
GC 0645	Maize	W	0.05		
MM 0095	Meat (from mammals other than marine mammals)	0.01*	0.05	0	0
ML 0106	Milks	0.001*	0.01	0	0
GC 0647	Oats	W	2		
VD 0072	Peas (dry)	0.3	0.2	0.05	
AL 0072	Pea fodder	50		16	25
FP 0009	Pome fruits	0.02*		0	0
VR 0589	Potato	0.1	0.05	0.05	0.06
PM 0110	Poultry meat	0.01*	0.05	0	0
PO 0111	Poultry, Edible offal of	0.01*	0.05	0	0
SO 0495	Rape seed	1.5	2	0.49	
GC 0349	Rice	W	10		
CM 0649	Rice, Husked	W	1		
CM 1205	Rice, Polished	W	0.2		
GC 0651	Sorghum	W	2		
VD 4521	Soya bean (dry)	0.3	0.2	0.03	
FS 0012	Stone fruits	0.02*		0	0
FB 0275	Strawberry	0.05 *		0	0
SO 0702	Sunflower seed	0.9	1	0.11	
OC 0172	Vegetable oils, Crude	W	0.05		
	Vegetables (except as otherwise listed)	W	0.05		
GC 0654	Wheat	W	2		

Commodity		Recommended MRL (mg/kg)		STMR or STMR-P (mg/kg)	HR, HR-P, highest residue (mg/kg)
CCN	Name	New	Previous		
CM 0654	Wheat bran, Unprocessed	W	2		
CF 1211	Wheat flour	W	0.5		
CF 1212	Wheat wholemeal	W	2		

Table of recommendations

Commodity		STMR or STMR-P (mg/kg)	HR-P or highest residue (mg/kg)
CCN	Name		
	Rape seed meal	0.19	
OR 0495	Rape seed oil, edible	0.0098	
	Sunflower seed cake/meal	0.132	
OR 0702	Sunflower seed oil, edible	0.066	
	Soya bean hulls	0.093	
	Soya bean meal	0.0255	
OR 0541	Soya bean oil, refined	0.00165	

DIETARY RISK ASSESSMENT

Long-term intake

The WHO Panel of the 2013 JMPR established an Acceptable Daily Intake (ADI) of 0–0.006 mg/kg bw for diquat.

The evaluation of diquat resulted in recommendations for MRLs and STMR values for 30 raw and processed commodities. Where data on consumption were available for the listed food commodities, dietary intakes were calculated for the 13 GEMS/Food Consumption Cluster Diets. The results are shown in Annex 3 of the 2013 JMPR Report.

The IEDIs in the thirteen Cluster Diets, based on the estimated STMRs were 0–4% of the maximum ADI (0.006 mg/kg bw). The Meeting concluded that the long-term intake of residues of diquat from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The WHO Panel of the 2013 JMPR established an Acute Reference Dose (ARfD) of 0.8 mg/kg bw for diquat. The IESTIs represented 0% of the ARfD of 0.8 mg/kg bw.

The Meeting concluded that the short-term intake of residues of diquat resulting from uses that have been considered by the JMPR is unlikely to present a public health concern.

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A1412A_10304	Derz K.	2012a	Diquat: Metabolism in Potato. Syngenta. Fraunhofer Institute, Schmallenberg, Germany, SYN-005/7-08/B. GLP, Unpublished. Syngenta File No A1412A_10304
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PP148/0017	Dyson J, Chapman P	1995	Diquat: Long/Term High/Rate Trial. Frensham UK 1971-1991. Fate of soil residues. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, TMJ3431B. Not GLP, Unpublished. Syngenta File No PP148/0017
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PP901/0319	Earl M.	1991	Diquat: Residues in Peas from Trials carried out in the United Kingdom during 1990. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M5373B. GLP, Unpublished. Syngenta File No PP901/0319
PP901/0322	Earl M., Hall G.	1994	Diquat: Residue Levels in Peas from Trials Carried Out in the United Kingdom During 1992. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ1502B. GLP, Unpublished. Syngenta File No PP901/0322
PP901/0478	Edwards M, HaywardG, Ward R, Iswaran T	1972	Diquat: Residue and Toxicology Trials with Cows Fed Treated Grass. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, AR2653A. Not GLP, Unpublished. Syngenta File No PP901/0478
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PP901/0470 addendum	Fujie G.	1988	Addendum to "Diquat - Quantification and Characterisation of Radioactive Residues in Hen Tissues and Eggs" (ICI Project No. PP901AA01). Chevron Chemical, Richmond, USA. Chevron Chemical, Richmond, USA, R010/ICIVAL. GLP, Unpublished. Syngenta File No: Included in PP901/0470
PP901/0868	Fujie G.	1987	Validation Of Residue Analytical Method RM/5B-1 For Diquat In Animal Tissues. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, R-10RM5B1MV. GLP, Unpublished. Syngenta File No PP901/0868
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PP148/0576	Gowman MA, Riley D, Newby SE	1980	Paraquat and Diquat: Long-term High-rate Trial Frensham UK, 2. Persistence and Movement in Soil and Glasshouse Bioassays. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ0014B. Not GLP, Unpublished. Syngenta File No PP148/0576
PP901/0461	Hughes H., Leahey J.	1975	Diquat: Residues Resulting in the Eggs and Tissues of Hens Dosed with 14C-Diquat Desiccated Barley Grain. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, AR2581B. Not GLP, Unpublished. Syngenta File No PP901/0461
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PP901/0349	Jones S.	2000	Diquat: Residue Levels in Apples from Trials carried out in the UK during 1999. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, CEMR-1101. GLP, Unpublished. Syngenta File No PP901/0349

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PP901/0312	Kennedy S.	1986	Diquat: Residues in Fodder Beans From Trials Carried Out During 1984 and 1985 in West Germany. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M4170B. GLP, Unpublished. Syngenta File No PP901/0312
PP901/0311	Kennedy S.	1985	Diquat: Residues in Fodder Peas From Trials Carried Out During 1984 and 1985 in West Germany. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M4137B. GLP, Unpublished. Syngenta File No PP901/0311
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A1412A_10290	Langridge G.	2011	Diquat: Residue Study on Apples in Northern France, Austria and Hungary in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4622. GLP, Unpublished. Syngenta File No A1412A_10290

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A1412A_10295	Langridge G.	2011c	Diquat: Residue Study on Potatoes in Northern France, Austria and the United Kingdom in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4671. GLP, Unpublished. Syngenta File No A1412A_10295
A1412A_10291	Langridge G.	2011d	Diquat: Residue Study on Potatoes in Southern France, Spain and Italy in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4672. GLP, Unpublished. Syngenta File No A1412A_10291
A1412A_10292	Langridge G.	2011e	Diquat: Residue Study on Oilseed Rape in Northern France, Hungary and the United Kingdom in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4659. GLP, Unpublished. Syngenta File No A1412A_10292
A1412A_10293	Langridge G.	2011f	Diquat: Residue Study on Oilseed Rape in Southern France, Spain and Italy in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4660. GLP, Unpublished. Syngenta File No A1412A_10293
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PP901/0464	Leahey J.	1973	Diquat: A Study of the Metabolism and Residues in Hens and their Eggs. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, AR2438B. Not GLP, Unpublished. Syngenta File No PP901/0464
432113	Leary J., Slagowski J.	1970	Analysis of Diquat Residues - Method RM-5, Analysis of Diquat Residues - Method RM-5-5, Analysis of Diquat Residues in Water - Method RM-5W-1. Syngenta Crop Protection, Inc., Greensboro, USA. Chevron Chemical, Richmond, USA, 8613239 A. Not GLP, Unpublished. Syngenta File No 432113
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PP901/0630	Massey J	1987	Paraquat/Diquat: Residues in Carrots from Trials Carried Out in West Germany During 1984. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M4417B. GLP, Unpublished. Syngenta File No PP901/0630
PP901/0315	Massey J.	1987	Diquat: Residues in Peas from Trials Carried out in Denmark During 1986. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M4459B. GLP, Unpublished. Syngenta File No PP901/0315
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PP901/0724	Nagra B., Kingdom N.	2001	Diquat and Paraquat: Residue Levels in Protected Strawberries from Trials conducted in the UK during 2000. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-1301. GLP, Unpublished. Syngenta File No PP901/0724
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PP901/0742	Reichet N	1996	Determination of Diquat & Paraquat in Potato, Pea Seed, Bean Seed & Soil Validation of the Methods RAM 252/01 & RAM 253/01. Syngenta Crop Protection AG, Basel, Switzerland. Institut Fresenius, Taunusstein, Germany, IF-94/21111-00. GLP, Unpublished. Syngenta File No PP901/0742
PP901/0876	Ricketts D.	1997	Diquat- Microbial Degradation. Zeneca Agrochemicals, Jealott's Hill, United Kingdom. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RIC3794. GLP, Unpublished. Syngenta File No PP901/0876
PP901/0325	Roper EM	1995	Diquat: Magnitude of the Residues of Diquat in Dry Beans From Trials Conducted in the USA During 1994 (WRC-95-058). Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RR 95-033B. GLP, Unpublished. Syngenta File No PP901/0325
PP901/0324	Roper EM	1995a	Diquat: Magnitude of the Residues of Diquat on Dry Peas From Trials Conducted in the USA During 1994 (WRC-95-071). Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RR 95-046B. GLP, Unpublished. Syngenta File No PP901/0324
PP901/0323	Roper EM	1995b	Diquat: Magnitude of the Residues on Lentils From Trials Conducted in the USA During 1994 (WRC-95-063). Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RR 95-038B. GLP, Unpublished. Syngenta File No PP901/0323
PP901/0286	Roper EM	1995c	DIQUAT: Magnitude of the Residues of Diquat on Potatoes From Trials Conducted in the USA During 1994 (WRC-95-053). Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RR 95-029B. GLP, Unpublished. Syngenta File No PP901/0286
A1412A_10320	Suchek E., Kamienski V.	1989	Residual analysis of Diquat in samples of citrus (oranges) Certificate 39510-A. Syngenta, 39510-A. Not GLP, Unpublished. Syngenta File No A1412A_10320
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	Tadeo JL, Sánchez-Brunete C, Pérez RA, Fernández MD	2000	Analysis of herbicide residues in cereals, fruits and vegetables. Journal of Chromatography A 882:175-191
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PP148/0662	Wilkinson W.	1980	Paraquat and Diquat: Long-term High-rate Trial, Frensham, UK.1. Management of site, effects on crops and weeds and residues in crops. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ0013B. Not GLP, Unpublished. Syngenta File No PP148/0662
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	Worobey BL.	1993	Liquid chromatographic method for determination of diquat and paraquat herbicides in potatoes: collaborative study. J AOAC Int. 76:881-887.

DITHIANON (180)

The first draft was prepared by Dr U Banasiak, Delegate for Federal Institute for Risk Assessment, Berlin, Germany

EXPLANATION

The fungicide dithianon was first evaluated by the JMPR in 1992 (T, R). The compound was evaluated for toxicology by the 2010 JMPR within the periodic review programme of the CCPR. The periodic review for residues was scheduled at the 39th Session of the CCPR for the 2012 JMPR but postponed to be evaluated by the 2013 Meeting.

The Meeting received information from the manufacturer on physical and chemical properties, metabolism studies on plants and animals, analytical methods, supervised residue trials data, processing studies as well as use pattern.

IDENTITY

Common name: Dithianon

Chemical name:

IUPAC: 5,10-Dihydro-5,10-dioxonaphtho-[2,3-beta]-1,4-dithiine-2,3-dicarbonitrile

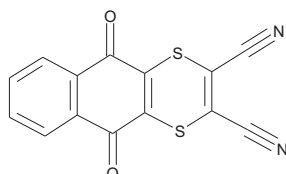
CA: 5,10-Dihydro-5,10-dioxonaphtho[2,3-beta]-1,4-dithi-in-2,3-dicarbonitrile

CAS number: 3347-22-6

CIPAC number: 153

Molecular formula: C₁₄H₄N₂O₂S₂

Structural formula:



Molecular mass: 296.3

Minimum purity: active substance (ai) manufactured 930 g/kg

Formulations

Dithianon is available in numerous commercial formulations in different formulation types (SC, WDG, WP) in many countries.

PHYSICAL AND CHEMICAL PROPERTIES

Dithianon, the pure and the technical grade active ingredient are thermally stable solids. The compound is poorly soluble in water and hexane and soluble in toluene, dichloromethane and acetone. It hydrolyses rapidly under neutral or alkaline conditions, is not explosive, not self-igniting and does not burn. The physical and chemical properties of dithianon are shown in detail in Table 1 (ai = pure active ingredient, TC = technical material, purity in percent (%)).

Table 1 Physical and chemical properties of dithianon

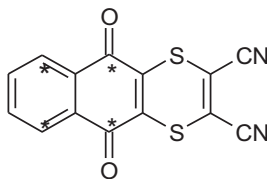
	Guideline or method	Test material purity and specification	Findings and comments	Report
Melting point	OECD 102	ai 99.3% TC 96.9%	range of 215–216 °C 218.5 °C	DT-303-001 2005/1007543
Temperature of	OECD 102	TC 96.9%	222 °C, immediately after melting.	2005/1007543

	Guideline or method	Test material purity and specification	Findings and comments	Report
decomposition				
Relative density (D ₄ ²⁰)	OECD 109 EEC A3	ai 99.3% TC 95.5%	1.576 1.52	DT-308-001 DT-308-007
Vapour pressure	OECD 104	ai 99.3% TC 96.9%	2.71 × 10 ⁻⁹ Pa at 25 °C. < 1 × 10 ⁻¹⁰ Pa at 20 and 25 °C.	DT-306-001 2005/1007543
Henry's law constant			Henry's Law constant at 20 °C: H < 1.347 × 10 ⁻⁷ (Pa × m ³ /mol).	2005/1038558
Colour and physical state	EPA Guideline OPPTS 830.6302 830.6303	ai 99.9% TC 95.5%	Solid, powdery, fibrous, fine-crystalline dark-brown Solid, powdery, fine-crystalline, medium-brown	DT-390-070 DT-390-069 DT-390-068 DT-390-067
Odour	EPA Guideline OPPTS 830.6304	ai 99.9% TC 95.5%	characteristic musty-organic smell	DT-390-071 DT-390-066
UV/VIS, IR, NMR, MS spectra	Standard UV, IR, NMR, MS Methodology OECD 101	ai 99.0% ai 98.6%	MS, NMR, IR, UV spectra consistent with the assigned structure, UV spectra are dependent on the pH of the environment UV absorption (extinction coefficient ε): pH 6.2 λ nm ε (l × mol ⁻¹ cm ⁻¹) 199 22380 218.2 13635 250.0 15110 290.5 8724 350 7207 pH 1.3 λ nm ε (l × mol ⁻¹ cm ⁻¹) 199 18102 215.5 8767 237 9820 290.5 5100 342 4489 pH 12.8 λ nm) ε (l × mol ⁻¹ cm ⁻¹) 218 22186 242.3 15350 270 23196 290.5 15055 364 17179	DT-360-012 2008/1028546
Solubility in water including effect of pH at 20 °C	OECD 105	ai 99.3% TC 96.9%	pH 5: 0.27 mg/L pH 7: 0.14 mg/L pH 9: 0.19 mg/L pH 4: 0.31 mg/L pH 7: 0.38 mg/L pH 9: 0.36 mg/L deionized water 0.22 mg/L	DT-311-001 2005/1008916
Solubility in organic solvents at 20 °C	OECD 105 flask method and EPA Guideline 63-8	ai 99.3%	expressed as g of ai soluble in 1000 mL solvent: hexane: 0.0096 toluene: 15.9 dichloromethane: 20.1 methanol: 0.8 acetone: 17.6 ethyl acetate 7.7	DT-312-001
Solubility in organic solvents at 20 °C	EC Council Directive 92/69/EEC, A.6	TC 95.5%	expressed as g of TC soluble in 1000 mL of solvent: hexane: 0.00877 toluene: 14.7	DT-312-002

	Guideline or method	Test material purity and specification	Findings and comments	Report
			dichloromethane:25.1 methanol: 0.815 acetone: 22.2 ethyl acetate: 10.6	
n-Octanol/water partition coefficient at 20 °C	OECD 107 flask method	ai 99.3%	log P _{OW} : > 3.34	DT-315-002
n-Octanol/water partition coefficient at 20 °C	92/69/EEC A.8 OECD 107 HPLC method	TC 91.6%	log P _{OW} : 3.2	DT-315-003
Hydrolysis rate at 20 °C	SETAC Guideline, Part 9 and OECD 111	[5,6,9,10- ¹⁴ C]-dithianone, radio-chemical purity: >98%	expressed as DT ₅₀ values: pH 5: 10.7 d pH 7: 0.6 d pH 9: 9.8 min	DT-322-008
Hydrolytic degradation at different pH and temperatures	OECD 111	[5,6,9,10- ¹⁴ C]-dithianone	expressed as DT ₅₀ values: pH 4: 11.6 d ^{50°C} , 4.9 d ^{60°C} , 1.8 d ^{70°C} pH 7: 6.3 h ^{30°C} , 1.5 h ^{40°C} , 0.5 h ^{50°C} pH 9: 0.2 h ^{15°C} , 0.1 h ^{25°C}	DT-322-006
Photochemical degradation at 20 °C in sterile pH 4 buffer	SETAC Guideline, Part 10 and OECD GD 97/21(1997)	[5,6,9,10- ¹⁴ C]-dithianone, radio-chemical purity: >98%	expressed as DT ₅₀ values: < 0.05 d Degradation to multiple photo-products including carbon dioxide. 3 major degradate fractions: phthalic acid DT ₅₀ = 16.0 d, phthaldialdehyde DT ₅₀ = 1.4 d, 1,2-benzenedimethanol DT ₅₀ = 4.8 d	DT-324-003
Quantum yield at pH 4 and 20 °C	OECD GD 97/21(1997)	[5,6,9,10- ¹⁴ C]-dithianone, radio-chemical purity: >98%	x 10 ⁻³ mol/einstein, expressed as DT ₅₀ value: 0.5 h (1 st order kinetic model)	DT-324-002
Flammability	EEC A.10	TC 95.5%	Non-flammable	DT-330-005
Explosive	EEC A.14	TC 95.5%	Non- explosive	DT-334-003
Surface tension at 20 °C	EEC A.5	TC 95.5%	72.7 mN/m	DT-340-001
Oxidizing	EEC A.17	TC 93.5%	No oxidizing	DT-356-001

METABOLISM AND ENVIRONMENTAL FATE

The metabolism and distribution of dithianon in plants and animals was investigated using the [5,6,9,10-]¹⁴C-labelled compound or, in some studies, a [5,6,9,10-]¹³C/¹⁴C-labelled compound.

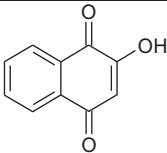
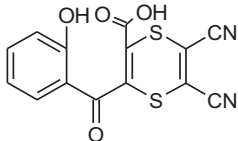
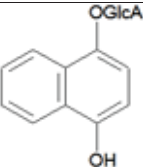


* Denotes position(s) of carbon-¹³ label and position(s) of carbon-¹⁴ label

Chemical names, structures and code names of metabolites and degradation products of dithianon are summarized in Table 2.

Table 2 Code names, chemical names and structures of dithianon related substances

Compound Code	Chemical Name	Chemical Structure
BAS 216 F (AC 37114) D0	5,10-Dihydro-5,10-dioxonaphtho[2,3- <i>b</i>]-1,4-dithiin-2,3-dicarbonitrile (Dithianon)	
D1	5,10-Dihydroxy-5,10-dioxonaphtho-[2, 3- <i>b</i>]-1,4-dithiin-2,3-dicarbonitrile	
D2 (CL1025, Reg. No. 4107273)	1,4-Naphthoquinone	
D3	5,10-Dihydroxy [2',3',5,6]-[1,4]-dithiino-[2, 3- <i>c</i>]-isothiazole-3-carbonitrile	
D4 (CL 66629, Reg. No. 31062)	Dibenzo-[<i>b,i</i>]-thianthrene-5,7,12,14-tetrone	
D5	4,11-Dithia-2-aza-cyclopenta [<i>b</i>]-anthracene-1,3,5,10-tetraone	
D8 (CL 902198, Reg. No- 4110933)	4,9-Dihydro-4,9-dioxonaphtho [2,3- <i>b</i>]-thiophene-2,3-dicarbonitrile	
D15 (CL902200, Reg. No. 4110934)	5,10-Dihydro-5,10,dioxonaphtho[2,3- <i>b</i>]-1,4-dithiin-2,3-dicarboxylic acid diamide	
D19	5,10-Diacetoxynaphtho[2,3- <i>b</i>]-1,4-dithiin-2,3-dicarbonitrile	
D21	2,3-Dihydroxy-1,4-naphthoquinone	
D27	2-Oxa-4,11-dithia-cyclopenta [<i>b</i>]-anthracene-1,3,5,10-tetraone	
ROI 14 (R2, Reg. No. 4005234)	Phthalic acid	

Compound Code	Chemical Name	Chemical Structure
ROI 6 (R1, CL 231509)	2-Hydroxy-1,4-naphthoquinone	
CL 1017911 (Reg. No. 4110904)	5,6-Dicyano-3-(2-hydroxybenzoyl)-1,4-dithiine-2-carboxylic acid	
M216F020	glucuronic acid conjugate of 1,4-dihydroxynaphthalene	

Animal metabolism

The metabolism of dithianon has been studied in laboratory rats, goats and hens.

Rats

Rat metabolism studies were evaluated by the WHO Core Assessment Group of the 2010 JMPR. A summary of the rat metabolism is given below:

At tested doses of 10 and 50 mg/kg bw, orally administered dithianon was about 40–50% absorbed in rats. The majority of the administered dose was recovered in Faeces (64.0–72.2%) and in urine (26.7–31.4%). Dithianon was extensively metabolized according to the following key transformation steps: oxidation of the sulphur atoms, cleavage of the dithiine ring, reduction of the 1,4-naphthoquinone moiety and further glucuronidation, as well as substitution of the carbonitrile moieties by amino and carboxy groups. The only metabolite in rat urine at a level greater than 2% was M216F020 (glucuronic acid conjugate of 1,4-dihydroxynaphthalene).

Lactating goats

The fate of dithianon in lactating goats was investigated by Cheng (1990, DT-440-006 and 1992 DT-440-008) and Webb and Richardson (1994, DT-440-011).

Study 1 [Cheng 1990, DT-440-006; Cheng 1992, DT-440-008]

One lactating goat each was dosed by capsule at a daily nominal rate of 6 mg (equiv. to 2.5 mg/kg feed) and 60 mg ¹⁴C-dithianon (equiv. to 28 mg/kg feed) for five days. One animal was assigned as control. Milk, urine and faeces were sampled during the course of the study and liver, kidney, muscles and fat were obtained after the end of the experiment.

Solid matrices were homogenized under frozen conditions followed by sample combustion. Faeces were homogenized with deionized H₂O, whereas the liquid samples (urine, blood, bile, milk and cage wash) were homogenized without any additional additives and finally combusted. Radioactivity was determined using liquid scintillation counter (LSC).

Each matrix was blended with a mixture of chloroform, methanol and with a buffer of either 0.1 M potassium phosphate (pH 5) or 0.1 M ammonium acetate (pH 5). The volume ratios of solvents were depending on the matrix adjusted and sample was blended again. The mixture was centrifuged and the resulting layers were transferred to separate containers. The extraction was repeated on the remaining solid. The chloroform fractions of the tissues were rotary-evaporated to dryness; and the residue was partitioned between hexane and acetonitrile. The aqueous/methanol and organic-soluble

fractions were concentrated before analysis. After extraction, the remaining solid was dried, and aliquots were combusted to obtain material balances of radioactivity for each examined sample.

Extracted ^{14}C -dithianon from the goat milk, bile, excreta and tissues were subjected to high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC) to determine the metabolite profiles. Urine was hydrolysed using aryl sulfatase and β -glucuronidase and analysed by HPLC and TLC techniques. The total radioactive residues (TRR) in mg/kg and% of the total applied radioactivity (TAR) in goat tissue and milk after administration of ^{14}C -radiolabelled dithianon are shown in Tables 3 and 4.

Table 3 Total radioactivity residue levels in goat tissue, milk and excreta (DT-440-006, DT-440-008)

Matrix	Goat 1 (6 mg/animal/day)		Goat 2 (60 mg/animal/day)	
	TAR, %	TRR, mg/kg	TAR, %	TRR, mg/kg
Bile	< 0.01	0.332	0.04	2.883
Blood	ND	ND	< 0.01	0.162
Fat (omental)	ND	ND	< 0.01	0.014
Fat (renal)	< 0.01	0.003	< 0.01	0.013
Faeces	50.2 ^a	NA	53.7 ^{a)}	NA
Kidney	0.04	0.065	0.03	0.489
Liver	0.07	0.019	0.07	0.174
Milk	0.03 ^a	NA	0.07 ^{a)}	NA
Muscle (round)	ND	ND	< 0.01	0.013
Urine	27.9 ^a	NA	24.2 ^{a)}	NA
Total	78.2	-	78.1	-

^a For details see Table 4

Table 4 Total radioactivity residue levels in goat milk and excreta (DT-440-006, DT-440-008)

Collection time	Goat 1 (6 mg/animal/day)		Goat 2 (60 mg/animal/day)	
	TAR, %	TRR, mg/kg	TAR, %	TRR, mg/kg
Milk				
Day 0 am	ND	ND	ND	ND
Day 0 pm	ND	ND	< 0.01	0.021
Day 1 am	ND	ND	< 0.01	0.018
Day 1 pm	< 0.01	0.002	< 0.01	0.030
Day 2 am	ND	ND	< 0.01	0.021
Day 2 pm	< 0.01	0.002	< 0.01	0.029
Day 3 am	< 0.01	<0.001	< 0.01	0.022
Day 3 pm	< 0.01	0.003	< 0.01	0.027
Day 4 am	ND	ND	< 0.01	0.019
Sacrificed at day 4	< 0.01	0.002	< 0.01	0.024
Total	0.03	-	0.07	-
Faeces				
Day 0 am	ND	not applicable	ND	not applicable
Day 0 pm	0.06		ND	
Day 1 am	7.79		7.51	
Day 1 pm	2.21		3.50	
Day 2 am	10.34		10.70	
Day 2 pm	3.56		3.94	
Day 3 am	8.62		9.30	
Day 3 pm	4.06		3.30	
Day 4 am	11.13		12.40	
Sacrificed at day 4	3.04		3.01	
Total	50.2	-	53.7	-
Urine				
Day 0 am	ND	not applicable	ND	not applicable
Day 0 pm	3.55		no sample	
Day 1 am	2.78		4.97	
Day 1 pm	4.07		3.37	
Day 2 am	2.16		2.45	
Day 2 pm	4.00		3.25	

Collection time	Goat 1 (6 mg/animal/day)		Goat 2 (60 mg/animal/day)	
	TAR, %	TRR, mg/kg	TAR, %	TRR, mg/kg
Milk				
Day 3 am	2.76		2.30	
Day 3 pm	3.43		3.03	
Day 4 am	2.64		2.33	
Sacrificed at day 4	2.11		2.10	
Sacrificed at day 4 (Cage wash)	0.39		0.42	
Total	27.9	-	24.2	-

Sacrificed at day 4: Milk, urine and Faeces produced after last dose and before sacrifice

The nature of radioactive residues in lactating goat dosed with 60 mg radiolabeled ^{14}C -dithianon/day was investigated by separation of radioactive residues into organo-soluble (non-polar), aqueous/methanol-soluble (polar) and non-extracted (bound/conjugated) fractions.

The results are shown in Tables 5 and 6 as well as were described below:

In liver, several radioactive components were detected by HPLC analysis. The concentration of each component was low, with the highest being 0.02 mg/kg for the polar (aqueous-soluble component A-4). TLC analysis of the organic-soluble extract revealed several components. One component (accounted 0.96% of TRR) was presumably identified as parent dithianon.

In kidney, several radioactive components were detected by HPLC analysis. The highest concentrations were detected in the aqueous-soluble extract and were identified as A-2 (0.03 mg/kg) and A-3 (0.03 mg/kg), respectively. One component was identified as dithianon (2.32% of TRR in the kidney sample).

In milk, several radioactive components were detected by HPLC analysis and all had radioactive concentrations less than 0.01 mg/kg. A component in the organic-soluble extract was identified as dithianon and accounted for 8.2% of TRR in the milk sample.

HPLC analysis of bile indicated the presence of several radioactive components. The major components were identified as A-2, A-3, A-4, and A-5. The percentage of the samples radioactivity that these components constituted ranged from 12.1% to 30.8%. Dithianon accounted for 2.19% of the TRR in the bile sample.

In Faeces, several radioactive residue components were detected by analysis of the aqueous-soluble and the organic-soluble extracts. All components constituted less than 5% of TRR. Dithianon accounted for 3.27% of TRR in Faeces sample.

HPLC analysis of urine indicated the presence of two major radioactive components, identified as A-2 and A-3. Each component constituted 21.1% and 37.0% of TRR, respectively. A minor component was identified as dithianon (1.7% of TRR).

Table 5 Distribution of radioactivity in goat tissues after treatment with 60 mg/goat/day (DT-440-006, DT-440-008)

	Liver		Kidney		Muscle	
	mg/kg	%	mg/kg	%	mg/kg	%
Total radioactive residues (TRR)	0.174	100	0.489	100	0.013	100
Extracted radioactive residues (ERR)	0.08	49.4	0.256	52.4	0.004	32.0
Aqueous/MeOH	0.057	32.5	0.229	46.8	0.003	24.4
Dithianon	ND	ND	0.0114	2.32	---	NA
Component A-1	ND	ND	0.0127	2.60	---	NA
Component A-2	< 0.01	3.87	0.0330	6.74	---	NA
Component A-3	0.0166	9.56	0.0305	6.23	---	NA
Component A-4	0.0211	12.1	0.0166	3.39	---	NA
Component A-5	0.0125	7.18	0.0186	3.80	---	NA
Component A-6	< 0.01	1.27	< 0.01	1.48	---	NA
Component A-7	ND	ND	ND	ND	ND	ND

Total radioactive residues (TRR)	Liver		Kidney		Muscle	
	mg/kg	%	mg/kg	%	mg/kg	%
	0.174	100	0.489	100	0.013	100
Component A-8	ND	ND	ND	ND	ND	ND
Chloroform	---	16.9	---	5.59	0.001	7.59
Hexane	0.013	7.4	0.008	1.7	---	NA
Acetonitrile	0.016	9.01	0.023	4.79	---	NA
Dithianon	< 0.01	0.96	---	NA	---	NA
Component B-1	< 0.01	0.88	---	NA	---	NA
Component B-2	< 0.01	2.06	---	NA	---	NA
Component B-3	< 0.01	0.77	---	NA	---	NA
Component B-4	< 0.01	0.40	---	NA	---	NA
Component B-5	ND	ND	---	NA	---	NA
Component B-6	ND	ND	---	NA	---	NA
Component B-7	ND	ND	---	NA	---	NA
Component B-8	ND	ND	---	NA	---	NA
PES	0.095	54.7	0.36	73.6	0.012	95.2

ERR: extracted radioactive residue (sum of all extracted fractions)

Table 6 Distribution of radioactivity in goat milk, bile and excreta (DT-440-006, DT-440-008)

Total radioactive residues (TRR)	Milk		Bile		Urine		Faeces	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
	0.024	100	2.89	100	12.8	100	5.18	100
Extracted radioactive residues (ERR)	0.018	76.8	3.04	105	13.2	103	2.55	49.2
Aqueous/MeOH	0.011	48.0	2.67	92.2	13.1	102	1.42	27.5
Dithianon	---	ND	0.063	2.19	0.217	1.70	0.169	3.27
Component A-1	---	ND	ND	ND	0.558	4.36	ND	ND
Component A-2	< 0.01	9.34	0.486	16.8	2.701	21.1	0.066	1.28
Component A-3	< 0.01	10.4	0.350	12.1	4.736	37.0	0.121	2.34
Component A-4	< 0.01	7.17	0.850	30.8	0.573	4.48	0.202	3.89
Component A-5	< 0.01	4.85	0.529	18.3	0.634	4.95	0.246	4.74
Component A-6	---	ND	0.156	5.39	0.303	2.37	0.141	2.73
Component A-7	ND	ND	ND	ND	0.174	1.36	0.199	3.85
Component A-8	ND	ND	ND	ND	0.054	0.43	0.054	1.05
Chloroform	---	28.8	---	12.8	---	1.0	---	21.7
Hexane	0.001	6.08	NA	NA	NA	NA	0.054	1.04
Acetonitrile	0.004	16.3	0.37	12.8	0.117	0.91	0.672	13.0
Dithianon	< 0.01	8.20	ND	ND	---	NA	0.042	0.81
Component B-1	< 0.01	4.47	ND	ND	---	NA	ND	ND
Component B-2	< 0.01	1.48	ND	ND	---	NA	0.0307	0.59
Component B-3	ND	ND	< 0.01	6.14	---	NA	0.046	0.89
Component B-4	ND	ND	< 0.01	5.79	---	NA	0.0431	0.83
Component B-5	ND	ND	ND	ND	---	NA	0.071	1.37
Component B-6	ND	ND	ND	ND	---	NA	0.0616	1.19
Component B-7	ND	ND	ND	ND	---	NA	0.127	2.45
Component B-8	ND	ND	ND	ND	---	NA	0.087	1.68
PES	0.005	20.2	NA	NA	NA	NA	2.54	49.1

For further characterization the urine sample was subjected to an enzymatic cleavage experiment. The HPLC results of the β -glucuronidase and sulfatase treatment of urine are summarized in Table 7.

Table 7 HPLC metabolite profiles of goat urine, enzymatic treatment (DT-440-006, DT-440-008)

Component	TRR,%				
	Urine native	Urine β -glucuronidase	Urine control	Urine Sulfatase	Urine Control
Dithianon	1.70	6.75	1.96	4.03	2.48
A-1	4.36	1.44	2.35	3.43	14.1

Component	TRR,%				
	Urine native	Urine β -glucuronidase	Urine control	Urine Sulfatase	Urine Control
A-2	21.2	9.24	13.5	17.7	27.1
A-3	37.0	16.0	28.3	19.7	27.1
A-4	4.48	12.0	6.28	11.0	19.4
A-5	4.95	13.9	5.23	10.6	6.90
A-6	2.37	6.74	2.77	5.66	3.01
A-7	1.36	3.93	1.79	2.46	1.67
A-8	0.425	2.75	ND	2.14	ND

Study 2 [Webb and Richardson, 1994, DT-440-011]

One lactating goat was dosed by capsule at a daily nominal rate of 60 mg $^{13}\text{C}/^{14}\text{C}$ -dithianon (equivalent to 25 mg/kg feed) for 5 consecutive days. Animals were sacrificed 6 hours post dose 5. The radiochemical purity was determined to be > 97% over the dosing period. The carbon-13 isotope abundance was 42.6%. Milk, urine and Faeces were sampled during the course of the study and liver, kidney, muscles and fat were obtained after the end of the experiment. Solid matrices were analysed by means of sample combustion. Radioactivity in liquid samples was measured by liquid scintillation counters (LSC). The results for TRR and of TAR are shown in Tables 8 and 9.

Table 8 Total radioactive residues in tissues and milk after administration of 60 mg/goat/day over 5 days (DT-440-011)

Goat matrix	TRR, mg/kg
Liver	0.157
Kidney	0.475
Muscle (fore leg)	0.012
Muscle (hind leg)	0.014
Subcutaneous fat	0.074
Renal fat	0.009
Whole milk ^{a)}	0.016
Cream ^{a)}	0.016
Curds ^{a)}	0.031
Whey ^{a)}	0.005
Bile	1.84
Plasma	0.199
Whole blood	0.135

^{a)} Sampled on day 5 in the morning (5 am)

Table 9 Total balance results after administration of 60 mg/goat/day over 5 days (DT-440-011)

Goat sample/time (hour)	TAR,%
Urine	
Day 1 (0-12)	2.32
Day 2 (0-24)	3.53
Day 3 (0-48)	7.5
Day 4 (0-72)	11.9
Day 5 (0-96)	16.9
Urine/Day 5 (0-102)	18.1
Faeces	
Day 2 (0-24)	7.15
Day 3 (0-48)	17.6
Day 4 (0-72)	30.7
Day 5 (0-96)	43.9
Faeces/Day 5 (0-102)	47.4
Cage wash	

Goat sample/time (hour)	TAR, %
Day 0 am	0.53
Tissue	0.09
Carcass	0.80
GI tract	27.3
Total	
Day 2 (0-24)	10.6
Day 3 (0-48)	24.0
Day 4 (0-72)	41.5
Day 5 (0-96)	59.7
Total/Day 5 (0-102)	94.2

Different extraction approaches were used in order to extract radioactive material from the different matrices:

Liver and kidney were extracted via methanol and chloroform and partitioned by KCl into chloroform, aqueous and methanol/water phases. The chloroform fraction was dried and partitioned into hexane and acetonitrile phases. The volume of the methanol/water phase was reduced; the methanol was removed and radioactive substances were extracted using ethyl-acetate. The acetonitrile and ethyl acetate phases were combined and concentrated (representing the organic phase).

The extraction of muscle samples was done using chloroform/methanol following an aqueous KCl partitioning into a chloroform, methanol/water and final aqueous phase.

Fat was extracted with dichloromethane. The revealed extract was dried and partitioned into an acetonitrile and a hexane phase.

After extraction, the samples of liver and kidney were treated with enzymes (pepsin, glucuronidase, sulfatase and pancreatin), acid and/or alkali hydrolysis to release the non-extracted radioactivity. Aliquots of the hydrolysate and remaining pellet were analysed by combustion and/or LSC. Liquid samples were analysed by a number of TLC and HPLC systems.

The distribution of TRR in tissues (as results of the solvent extraction) and in milk is summarized in Table 10. Solvent extraction of tissues afforded between 27.3% (0.043 mg/kg) and 49.1% (0.077 mg/kg) of the ^{14}C -residues in liver (total residue 0.157 mg/kg), 40.6% (0.193 mg/kg) of the ^{14}C -residues in kidney (total residue 0.475 mg/kg), 20% (0.003 mg/kg) of the ^{14}C -residues in muscle (total residue 0.013 mg/kg), 26.1% (0.019 mg/kg) of the ^{14}C -residues in fat (total residue 0.074 mg/kg) and 78.39% (0.012 mg/kg, 96 h sample) of the ^{14}C -residues in whole milk (total residue between 0.003 and 0.018 mg/kg). Non-extracted residues accounted for 72.7% (0.114 mg/kg) of the liver residue, 59.4% (0.282 mg/kg) of the kidney residues, 80% (0.01 mg/kg) of the muscle residue, 73.9% (0.055 mg/kg) of the fat residue and 21.7% (0.003 mg/kg) of the milk residue (96–102 h value).

Table 10 Distribution of radioactivity in goat tissues (DT-440-011)

TRR	Liver		Kidney		Muscle		Fat		Milk	
	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
	0.157	100	0.475	100	0.013	100	0.074	100	0.016	100
ERR	0.043	27.3	0.193	40.6	0.003	20.0	0.019	26.1	0.012	78.3
Hexane phase	0.008	5.6	0.013	2.7						
Organic phase ^{a)}	0.019	12.0	0.038	8.0						
Aqueous phase	0.009	5.6	0.121	25.5						
Chloroform phase					11.2	0.0015				
Methanol/water phase					9.6	0.0012				
Final aqueous phase					0.9	0.0001				
Hexane phase							0.002	2.2		
Acetonitrile phase							0.017	23.0		
PES	0.114	72.7	0.282	59.4	0.010	80.0	0.055	73.9	0.003	21.7

^a Acetone, cyclohexane, dichloromethane

Chromatography of the extracted radioactivity revealed metabolites with a wide range of polarity. HPLC analysis proved to be the most efficient in terms of resolution of components. Comparison of the organic and aqueous phases using HPLC reverse phase system indicated that there were some similarities in the metabolite profiles for liver, kidney, urine and bile however the profiles were very complex, containing numerous metabolites (> 20 compounds in the organic phase and > 6 compounds in the aqueous phase). The quantitation of such complex mixtures was difficult due to the low concentration of radioactive residues and the incomplete resolution of all components, no single metabolite in these extracts was > 0.05 mg/kg. No parent was present in the extracts and none of the metabolites were identified. The metabolites did not appear to match any of the reference chemicals. No chromatographic profiling of the muscle, fat or milk extracts was carried out because of the low concentrations of metabolites.

The enzymatic hydrolysis of the PES was carried out as follows: After solvent extraction, unreleased radioactivity present in liver was partly solubilized by treatment with pepsin, (25% of the unextracted radioactivity) or base (NaOH, up to 67%). Pancreatin treatment of the residuum from base solubilisation afforded 52% of the remaining radioactivity. Base treatment solubilised 49% of the unextracted radioactivity in the RRR of kidney. Incubation in pH 7.5 buffer of the residuum from base solubilisation afforded 49% of the remaining radioactivity. Chromatographic profiles of the solubilised radioactivity were obtained but it was not possible to identify any of the components. No metabolic pathway can be directly derived since none of the metabolites being present could be identified.

In this study, a further experiment to demonstrate the reactivity of dithianon with nucleophiles (commonly thiols in the form of proteins and peptides such as glutathione) was undertaken *in vitro*. Glutathione and N-acetylcysteine were shown to react very quickly with dithianon when incubated in pH 6.5 buffers at 37 °C without the intermediacy of facilitating enzymes such as glutathione transferase. This experiment indicated that the reaction of dithianon with glutathione and protein thiol groups *in vivo* will be virtually instantaneous. Thus, the metabolism of dithianon was likely to have been initiated by the opening of the dithiine ring by endogenous thiols (e.g. glutathione). The reaction with protein thiol groups accounts for the high levels of unextracted radioactivity found in the tissues. Following the ring opening reaction, further biotransformation via, for example, the glutathione pathway will have produced the very complex metabolite mixtures seen during the chromatographic analysis of the tissue extracts and the analysis of urine and bile.

Laying hens

The absorption, distribution, excretion of dithianon in laying hens was studied by Cheng (1990, 1992).

Cheng, 1990, DT-440-005; Cheng, 1992, DT-440-007

Two groups of laying hens, five hens per group, were treated orally once daily for 5 consecutive days with gelatin capsules containing the test substance. Animals were sacrificed 6 hours after the last dose. One group of hens was treated at a nominal dose level of 0.36 mg/day and the other group was treated at a nominal dose level of 3.6 mg/day. A third group of 5 hens served as the control group and was treated with empty capsules. The doses of dithianon were equivalent to a nominal dose rate of 3 and 30 mg/kg in the feed based on a projected average feed consumption of 120 g per hen per day. The actual doses of dithianon administered were 0.396 mg/day and 3.99 mg/day, respectively, equivalent to 3.57 mg/kg and 38.7 mg/kg in the feed.

Excreta from each group were collected daily. Eggs were collected twice daily (am and pm) during the dosing period. The 'pm-eggs' were refrigerated and added to the 'am-collections' the following morning. The eggs were separated into yolks and whites, which were stored separately. All samples were pooled according to day, sample matrix and subset, and then weighed. Approximately 6 hours after administration of the last dose, the animals were sacrificed. A sample of heparinized blood

was taken from each animal. Tissue samples [skin adhering to fat, breast muscle, thigh muscle, kidneys (both), liver, fat (abdominal)] and gastrointestinal (GI) tract, GI tract contents, and shelled eggs in oviduct (if present) were collected. Blood was refrigerated until analysis; all other samples were stored at or below 0 °C.

All measurements of radioactivity in liquid samples were analysed directly by LSC. Radioactivity in solid samples was determined by combustion followed by LSC. Tissue samples (kidney, liver, thigh muscle, breast muscle, and abdominal fat, skin with fat and GI tract) were homogenized while frozen, and triplicate aliquots were weighed for combustion. Excreta samples were homogenized with water (1:1 w/v), and triplicate aliquots were weighed for combustion. Triplicate aliquots of blood samples were weighed for combustion. Egg white and egg yolk were homogenized separately, and triplicate aliquots were weighed for LSC. Post-extracted solid samples were combusted prior to analysis by LSC.

Tissues, egg yolk, blood, and excreta from chickens (high dose group; 38.7 mg/kg feed) were extracted for metabolite profiling. Extraction procedures were carried out with a mixture of chloroform, methanol and water. The chloroform-soluble fraction was separated from the methanol:water fraction and each was concentrated to dryness. The organo-soluble (chloroform) residue was reconstituted in hexane and re-extracted with acetonitrile. The hexane and acetonitrile fractions were separated for radioanalysis. The water soluble fraction (methanol:water) residue was reconstituted in water. The extracted ^{14}C residues were analysed by TLC and high performance liquid chromatography (HPLC). Fractions of the HPLC eluate were collected, and each was analysed directly by LSC.

As shown in Table 11, following oral administration of ^{14}C -dithianon to laying hens, the overall recoveries of radioactivity were approximately 93.9% and 94.6% of the total applied radioactivity (TAR) for the low and high dose groups, respectively. The elimination rate of radioactivity in excreta was rapid and constant. Approximately 90% of TAR was eliminated in excreta by 6 hours after the last dose. The majority of the radioactivity was in excreta (approximately 90% TAR), GI tract contents (3.4% to 4.8% TAR), GI tract (0.6% TAR), liver (0.03% TAR), and kidneys (0.02% TAR). All of the eggs together contained less than 0.01% of the dose administered, most of which was retained in the yolk.

Table 11 Material balance after administration of ^{14}C -dithianon to laying hens (DT-440-005)

Matrix	TAR,%	
	Low dose (3.57 mg/kg)	High dose (38.7 mg/kg)
Eggs yolk	0.006	0.009
Eggs white	ND	0.002
Organs and tissues		
Muscle (breast)	< 0.01	< 0.01
Muscle (thigh)	< 0.01	< 0.01
Kidneys	0.02	0.02
Liver	0.03	0.03
Fat (abdominal)	ND	< 0.01
Skin with fat	0.01	< 0.01
Blood	0.02	0.02
GI Tract	0.56	0.57
GI Tract (contents and wash)	3.35	4.79
Excreta	90.0	89.2
Total	93.9	94.6

Total radioactive residues (TRR) in tissues, excreta and eggs are given in Table 12. Reported values are based on direct analysis by combustion and LSC.

Table 12 TRR in eggs and tissues of laying hens treated with ^{14}C -dithianon (DT-440-005)

Matrix	Low dose (3.57 mg/kg)	High dose (38.7 mg/kg)
	TRR, mg/kg	TRR, mg/kg
Egg yolks, day 0	ND	ND

Matrix	Low dose (3.57 mg/kg)	High dose (38.7 mg/kg)
	TRR, mg/kg	TRR, mg/kg
Egg yolks, day 1	ND	ND
Egg yolks, day 2	ND	0.003
Egg yolks, day 3	< 0.001	0.025
Egg yolks, day 4	0.003	0.051
Egg yolks, sac, day 4 ^{a)}	0.005	0.075
Egg white, day 0	ND	ND
Egg white, day 1	ND	ND
Egg white, day 2	ND	0.003
Egg white, day 3	ND	0.004
Egg white, day 4	ND	0.004
Egg white, sac, day 4	ND	0.004
Egg, day 0 ^{b)}	ND	ND
Egg, day 1 ^{b)}	ND	ND
Egg, day 2 ^{b)}	ND	0.006
Egg, day 3 ^{b)}	< 0.001	0.029
Egg, day 4 ^{b)}	0.003	0.055
Egg, sac, day 4 ^{b)}	0.005	0.081
Muscle (breast)	0.002	0.013
Muscle (thigh)	0.002	0.022
Abdominal fat	ND	0.014
Liver	0.017	0.178
Kidney	0.042	0.339
Skin with fat	0.005	0.039
GI tract	0.138	1.519
GI tract, contents and wash	0.387	5.537

^a Sac day 4: eggs in the oviduct taken about 6 hours after sacrifice

^b TRR values for egg yolk and white combined

The extraction procedure served to characterize the radioactivity in each sample as organo-soluble (non-polar), aqueous : methanol-soluble (polar), and non-extracted residues. The distribution of radioactivity in eggs, tissues and excreta from the high dose group is summarized in Table 13. The results for partitioning of the chloroform-soluble residues between hexane and acetonitrile are presented in Table 14 for egg yolks, skin with fat, liver and kidney. Acetonitrile-hexane partitioning of the chloroform-soluble residues in muscle, abdominal fat, blood and excreta was not performed.

Table 13 TRR extracted in eggs, tissues and excreta of laying hens after dosing with ¹⁴C-dithianon, equivalent to 38.7 mg/kg in the feed (DT-440-007)

Matrix	TRR ^a , mg/kg	Chloroform TRR, mg/kg (%)	Aqua methanol TRR, mg/kg (%)	ERR ^b TRR, mg/kg (%)	PES ^c TRR, mg/kg (%)	Recovery ^d TRR, mg/kg (%)
Egg yolks (last day)	0.078	0.010 (12.4)	0.027 (34.5)	0.037 (46.9)	0.042 (53.5)	0.079 (101)
Muscle	0.022	0.003 (12.6)	0.012 (55.7)	0.015 (68.3)	0.008 (35.0)	0.023 (103)
Skin with fat	0.041	0.004 (10.8)	0.027 (64.8)	0.031 (75.6)	0.011 (27.7)	0.042 (103)
Liver	0.186	0.029 (15.6)	0.105 (56.5)	0.134 (72.1)	0.046 (24.7)	0.180 (97)
Kidney	0.378	0.025 (6.6)	0.254 (67.1)	0.279 (73.7)	0.126 (33.3)	0.405 (107)
Blood	0.275	0.013 (4.73)	0.103 (37.6)	0.116 (42.3)	0.162 (58.8)	0.278 101
Excreta, pool (last day)	20.1	1.81 (8.99)	13.7 (68.0)	15.48 (77.0)	7.14 (35.5)	22.6 (113)

^a TRR values measured directly by combustion and LSC

^b ERR: Extracted radioactive residue (sum of chloroform and methanol: water extracts)

^c PES: Post-extraction solids remaining after extraction

^d Sum of TRR in all extracts and PES

Table 14 Distribution of ^{14}C -dithianon-derived chloroform-soluble tissue residues between hexane and acetonitrile (DT-440-007)

Matrix	TRR ^a , mg/kg	Chloroform-soluble TRR, mg/kg (%)	Hexane-soluble TRR, mg/kg (%)	Acetonitrile-soluble TRR, mg/kg (%)
Egg yolks (last day)	0.078	0.010 (12.4)	0.008 (9.9)	0.002 (2.5)
Skin with fat	0.041	0.004 (9.8)	0.002 (4.9)	0.002 (4.9)
Liver	0.186	0.029 (15.6)	0.012 (6.5)	0.016 (8.6)
Kidney	0.378	0.025 (6.6)	0.012 (3.3)	0.012 (3.3)

^a TRR values measured directly by combustion and LSC

The findings of the characterization of metabolites (components) are summarized in Table 15 for liver, kidney, skin with fat and egg yolk. Additionally, for all matrices including blood and excreta the results are described as follows:

Of the pooled egg yolks TRR (0.078 mg/kg), 46.9% (0.037 mg/kg) were extracted and 53.5% (0.042 mg/kg) were un-extracted. The aqueous:methanol-soluble extract accounted for 34.5% (0.127 mg/kg) of the egg yolk residue. Component C-14 (10.5%, 0.008 mg/kg) was the most abundant metabolite in the egg yolk. Other metabolites found in this fraction were component C-10 (5.72%, 0.004 mg/kg) and C-11 (2.16%, 0.002 mg/kg). Following solvent partitioning of the chloroform-soluble residue (12.4%, 0.010 mg/kg), the hexane-soluble fraction accounted for 9.9% of the TRR (0.008 mg/kg) and the acetonitrile fraction accounted for 2.5% (0.002 mg/kg).

Of the TRR in skin with adhering fat (0.041 mg/kg), 75.6% (0.031 mg/kg) were extracted and 27.7% (0.011 mg/kg) were not extracted. The aqueous:methanol-soluble fraction accounted for 65.8% (0.027 mg/kg) and contained the highest percentage of component C-10 (36%, 0.015 mg/kg). Also detected was C-14 (3.51%, 0.001 mg/kg). Solvent partitioning of the chloroform-soluble fraction (9.8%, 0.004 mg/kg) resulted in hexane- and acetonitrile-soluble fractions, each containing 4.9% TRR (0.002 mg/kg).

Of the TRR in liver (0.186 mg/kg), 72.1% (0.134 mg/kg) were extracted and 24.7% (0.046 mg/kg) were un-extracted. The chloroform-soluble fraction accounted for 15.6% (0.029 mg/kg) and the aqueous:methanol-soluble fraction accounted for 56.5% (0.105 mg/kg). Following the acetonitrile/hexane partitioning of the initial chloroform-soluble residue, six components were detected in the acetonitrile fraction (8.6%, 0.016 mg/kg). C-5 amounted to 1.32% (0.002 mg/kg), C-3 accounted for 1.42% (0.003 mg/kg) and C-4 accounted for 0.62% (0.001 mg/kg). The concentrations of components C-1, C-6 and C-7 were < 0.5% (< 0.001 mg/kg). Three components were found in the liver aqueous:methanol fractions, C-10 (18.9%, 0.035 mg/kg), C-11 (1.13%, 0.002 mg/kg) and C-13 (1.59%, 0.003 mg/kg).

Of the TRR in kidney (0.378 mg/kg), 73.7% (0.279 mg/kg) were extracted and 33.3% (0.126 mg/kg) were un-extracted. The chloroform-soluble fraction accounted for 6.6% (0.025 mg/kg), and the aqueous:methanol fraction accounted for 67.1% (0.254 mg/kg). Following the acetonitrile/hexane partitioning of the initial chloroform-soluble residue, five minor components were detected in the acetonitrile fraction (3.3%, 0.012 mg/kg). Component C-4 accounted for 0.72% (0.003 mg/kg), C-3 for 0.52% (0.002 mg/kg), and C-5 for 0.66% (0.002 mg/kg). The concentrations of components C-1 and C-2 were less than 0.2%. Four components were found in the aqueous:methanol fraction: C-10 accounted for 11.1% (0.042 mg/kg), C-14 (7.26%, 0.027 mg/kg), C-12 (5.14%, 0.019 mg/kg) and C-11 (0.71%, 0.03 mg/kg).

Low levels of radioactive residues were found in muscle (0.022 mg/kg). Of the TRR, 68.3% (0.015 mg/kg) was extracted and 35% (0.008 mg/kg) was un-extracted. The nature of the extracted residue was not characterized.

Of the excreta TRR, 77.0% of the TRR were extracted of which 9% was recovered as chloroform-soluble and 68% were recovered as aqueous:methanol-soluble. Six compounds were found in the chloroform extract. One was identified as dithianon and accounted for 0.44% (0.087 mg/kg). The other components found in the chloroform-soluble fraction were: C-4 (1.65%, 0.332 mg/kg), C-3 (1.90%, 0.382 mg/kg), C-5 (0.641%, 0.129 mg/kg), and C-1 (0.183%, 0.037 mg/kg). Five components were found in the aqueous:methanol-soluble fraction. These were C-14 (8.52%, 1.71 mg/kg), C-10 (6.39%, 1.28 mg/kg), C-12 (5.64%, 1.13 mg/kg), C-13 (4.3%, 0.864 mg/kg), and C-11 (3.16%, 0.635 mg/kg).

Of the TRR in blood (0.275 mg/kg), 42.3% (0.116 mg/kg) were extracted and 58.8% (0.162 mg/kg) were not extracted. Two components were found in the chloroform extract (4.73%, 0.013 mg/kg), corresponding to C-4 (3.1%, 0.008 mg/mg), and C-5 (0.41%, 0.001 mg/kg). One component was found in the aqueous-methanol extract (37.6%, 0.103 mg/kg), corresponding to C-10 (28.2%, 0.002 mg/kg).

The metabolites were not identified.

Table 15 HPLC metabolite profile of tissues and egg yolk of chickens (DT-440-007)

Component	Liver replicate 1		Liver replicate 4		Kidney replicate 2		Kidney replicate 2 ^a		Skin with fat		Egg yolk	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
	0.186	100	0.186	100	0.378	100	0.378	100	0.041	100	0.078	100
Dithianon	ND	ND	ND	ND	ND	ND	-	-	-	-	-	-
C-1	<0.001	0.189	<0.001	0.275	<0.001	0.177	<0.001	0.139	-	-	-	-
C-2	ND	ND	ND	ND	<0.001	0.155	ND	ND	-	-	-	-
C-3	0.003	1.42	0.001	0.618	0.002	0.519	0.001	0.305	-	-	-	-
C-4	0.002	1.20	0.002	1.27	0.003	0.720	0.002	0.474	-	-	-	-
C-5	0.002	1.32	<0.001	0.312	0.002	0.655	<0.001	0.055	-	-	-	-
C-6	<0.001	0.353	<0.001	0.364	ND	ND	<0.001	0.060	-	-	-	-
C-7	<0.001	0.22	<0.001	0.155	ND	ND	ND	ND	-	-	-	-
C-8	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	-
C-9	ND	ND	ND	ND	ND	ND	0.003	0.852	-	-	-	-
C-10	-	-	0.035	18.9	0.042	11.1	-	-	0.015	36.0	-	5.72
C-11	-	-	0.002	1.13	0.003	0.711	-	-	ND	ND	ND	2.16
C-12	-	-	ND	ND	0.019	5.14	-	-	ND	ND	ND	ND
C-13	-	-	0.003	1.59	ND	ND	-	-	ND	ND	ND	ND
C-14	-	-	ND	ND	0.027	7.27	-	-	0.001	3.51	0.008	10.5

^a Repeated analysis

- Not analysed

ND not detected

Plant metabolism

The metabolism of dithianon has been studied in citrus, apples, spinach and wheat.

Oranges

The metabolism of dithianon in citrus was investigated by Hubert (1991, 1992), Mayo (1994), Schlueter and Memmesheimer (1994, including an amendment by Schlueter, 1996) and finally by Schlueter (1998).

Hubert, 1991, DT-640-015; Hubert, 1992, DT-640-016 (amendment to DT-640-015)

A single orange tree was treated with ¹⁴C-dithianon at a specific activity of 49.4 μ Ci/mg. The test plot consisted of an area of the test tree (ca. 1.2 m $\times$ 1.2 m) containing 50 fruits and the surrounding foliage. The test solution was applied three times as a foliar spray at the rate of 1.87 kg ai/ha. Applications were made when the oranges were approximately 2.5 cm in diameter and at

approximately 30-day intervals after that. Fruit and foliage were sampled at each spray application (pre- and post-application sampling) and at full commercial maturity.

The oranges sampled at full commercial maturity were rinsed with dichloromethane and the rinse was analysed. Orange (whole fruit, peel, pulp) and leave samples were homogenized frozen (liquid nitrogen) and analysed by means of oxidative combustion followed by a measurement using liquid scintillation counting. Extensive extraction and fractionation procedures (using chloroform, acidic acetone, dichloromethane and methanol as solvents) were applied in conjunction with two-dimensional thin-layer chromatography for characterization of ^{14}C -residues in peel, pulp and final harvest fruit rinse. The TRR in fruits and foliage are presented in Table 16. The reported LOD by LSC was 0.022 mg/kg (based on a calculation using 0.2 g as a representative sample weight and a specific activity of 7820). The highest concentration of radioactivity (3280 mg/kg) was found in foliage samples taken from the treated plants at the 31-day post application sampling point. The highest concentration in the whole oranges from treated plants was 92.8 mg/kg found in oranges harvested at day 60. The TRR in peel, pulp and rinse at final harvest was 17.6, 0.85 and 109 mg/kg, respectively, based on the individual matrix masses. The concentrations are 5.9, 0.92 and 64.4 mg/kg, respectively, when based on the mass of whole oranges. The results of the distribution of TRR of the acidic acetone fraction are provided in Table 17.

Table 16 TRR in fruit and foliage of oranges after application of ^{14}C -dithianon (DT-640-015)

Sample	Sampling point	Day	TRR (mg equivalents/kg)
Foliage	Pre application	0	< 0.022
	Post application		954
	Pre application	31	1010
	Post application		3280
	Pre application	60	2800
	Post application		782
	Final harvest	121	1430
Whole fruit	Pre application	0	< 0.022
	Post application		19.1
	Pre application	31	10.5
	Post application		68.8
	Pre application	60	35.6
	Post application		92.8
Peel	Final harvest	121	17.6
Pulp	Final harvest	121	0.85
Rinse	Final harvest	121	109

Table 17 Distribution of TRR in oranges treated with ^{14}C -dithianon (DT-640-015, DT-640-016)

Classification	TRR in surface rinse		Peel		Pulp	
	%	mg equiv./kg	%	mg equiv./kg	%	mg equiv./kg
Dithianon	88.0	62.5	ND	ND	ND	ND
Unknowns ^a			1.8	1.3	0.47	0.32
Polar origin	2.3	1.7	2.1	1.5	0.33	0.24
Diffuse ^b			0.91	0.64	NA	NA
Total	90.3	64.2	4.8	3.44	0.8	0.56

^a Multiple components; no assignment could be made.

^b Radioactivity that is not found in discrete zones / spots.

Mayo, 1994, DT-640-018; Schlueter and Memmesheimer, 1994, DT-640-020; Schlueter, 1996, DT-123-045 (amendment to DT-640-020), Schlueter, 1998, DT-123-066

Mature oranges were treated two times with $^{13}\text{C}/^{14}\text{C}$ -dithianon (treatment interval: 4 weeks) at a specific activity of 27.8 $\mu\text{Ci}/\text{mg}$. ^{13}C -labelling was used in order to facilitate mass-spectroscopic identification of unknown metabolites and fragments by their characteristic $^{12}\text{C}/^{13}\text{C}$ -mass doublets. An air brush sprayer was used to apply test material to the 30 fruit on the tree. Each fruit was sprayed to

almost run-off. During the application, the leaves adjacent to the fruit were also sprayed. The nominal application rate was 0.44 kg ai/ha (actual 0.39 kg ai/ha). Samples were taken 2 weeks and 4 weeks after the last application. Upon arrival in the lab, oranges were stored frozen until analysis. In the 1994 studies (DT-640-018, DT-640-020), two oranges from the first and five oranges from the second sampling occasion were randomly selected and analytically processed as follows:

The weight of the oranges was determined and residues were washed from the surface by submerging the samples two times in dichloromethane/acetic acid (1000:1) and one time in acetone/acetic acid (1000:1) at solvent temperatures of -20 °C.

Following surface extraction and after peeling the oranges, the peel and pulp samples were separately homogenized. The peel was extracted two times with dichloromethane/acetic acid (1000:1) followed by one extraction step using acetone/acetic acid (1000:1). The radioactivity in the extracts was determined by LSC, all peel extracts were combined according to sampling date and solvent and investigated further by TLC.

Equal amounts of the peel extracts and the third surface rinse (acetone/0.1% acetic acid) were combined, concentrated and diluted with acidified deionized water and the aqueous solution extracted 3 × with dichloromethane. The radioactivity in the organo-soluble (dichloromethane) and water-soluble fraction was determined by LSC.

Different metabolite fractions from the organo-soluble radioactivity were purified by TLC and HPLC and partly further investigated by TLC. The polar components of the water-soluble radioactivity were further subjected to a derivatization with pentafluorobenzyl bromide. An aliquot of the aqueous layer was evaporated nearly to dryness using a rotary evaporator. After the addition of tetrabutylammonium-fluoride in a Na₂HPO₄/KH₂PO₄-buffer (pH 8) and a mixture of pentafluorobenzyl bromide in dichloromethane solution, the reaction mixture was sonicated for 1 hour. Thereafter, the solution was subjected to partitioning with dichloromethane and analysed by TLC.

Following determination of the radioactivity by combustion analysis and liquid scintillation counting, aliquots of the non-extractable peel residues were subjected to enzyme cleavage using protease. The reaction mixtures were filtered, the undigested residue was washed with buffer solution and freeze dried. After the determination of radioactivity the buffer solution was subjected to a further partitioning with dichloromethane. Finally, the organic layer was investigated by TLC.

The pulp was analysed in the same way as described for the peel. For thin-layer chromatographic (TLC) purposes of metabolite identification, reference compounds were co-chromatographed with the surface rinse and extractable residues from peel and pulp.

In the 1998 study (DT-123-066), the samples out of the 1994 study (DT-640-020) were re-analysed to characterize and to identify metabolites occurring in and on the peel of mature oranges. After initial storage stability investigations using the same extraction procedures, the remaining oranges (28 DAT) were further investigated using the following techniques:

Thin layer chromatography using normal phase and reversed phase (RP-18) plates

Liquid/liquid partition experiments

Reversed phase HPLC of the organo soluble peel extracts

Purification of fractions, components by solid phase extraction (SPE, C 18), HPLC semi-and preparative TLC fractionation, gel chromatography (2 different gel systems)

HPLC-MS investigations

Hydrolytic cleavage reactions using hydrochloric acid.

The TRR in the surface, peel and pulp of oranges treated with ¹³C/¹⁴C-dithianon are shown in Table 18. After two applications of radio-labelled dithianon on mature oranges, most of the radioactivity was found in the surface wash. On oranges sampled 2 weeks after application the TRR accounted 94.2% and after 4 weeks 87.25% of the TRR. After peeling, the radioactivity accounted

between 5.44% (2 weeks after application) and 12% (4 weeks after application) in the peel as well as between 0.36% (2 weeks after application) and 0.75% (4 weeks after application) in the pulp. Generally, half of the radioactivity was detected in the extractable portion and the remaining radioactive material was bound to the PES fractions.

Table 18 TRR in orange matrices after two applications of $^{13}\text{C}/^{14}\text{C}$ -dithianon (DT-640-020)

Sample	Surface ^a	Peel ^b			Pulp		
		extracted	PES	total	Extracted	PES	Total
2 weeks after application (values = mean of 2 oranges)							
Amount, µg	771.3	22.6	22.3	44.9	1.6	1.1	2.7
TRR, mg equiv./kg	4.213	0.122	0.121	0.243	0.009	0.007	0.016
TRR%	94.20	2.73	2.71	5.44	0.21	0.15	0.36
Total TRR in whole oranges, mg equiv./kg	4.47						
Total TRR, %	100						
4 weeks after application (values = mean of 5 oranges)							
Amount, µg	928.5	73.5	53.9	127.4	3.2	4.9	8.0
TRR, mg equiv./kg	4.590	0.362	0.270	0.632	0.016	0.024	0.039
TRR, %	87.25	6.88	5.12	12.01	0.30	0.45	0.75
Total TRR in whole oranges, mg equiv./kg	5.26						
Total TRR, %	100						

^a 1st and 2nd surface rinse

^b 3rd surface rinse, 1st and 2nd peel extraction

In 1998, the residues of ^{14}C -dithianon were re-analysed (oranges from 4 weeks post applications only). No significant differences between the first and the second determination of radioactive residues were found. The measured data sets of the second analysis in comparison to the previous results are summarized in Table 19. The results of distribution and characterization of radioactive residues compartments as surface wash, peel and pulp are summarized in Table 20.

Table 19 TRR, comparison of the results reported in 1994 (DT-640-020) and in 1998 (DT-123-066)

Matrix	TRR, % (analysed 1994)	TRR, % (re-analysed 1998)
1 st surface rinse	85.6	82.2
2 nd surface rinse	1.6	2.0
3 rd surface rinse	2.2	2.3
1 st Peel extraction	3.0	2.6
2 nd Peel extraction	1.7	0.3
3 rd Peel extraction	Not analysed	2.1
Pulp extraction	0.3	0.4
PES (peel)	5.1	7.1
PES (pulp)	0.45	0.9
Total extracted radioactivity	94.4	92.0
Total non-extracted radioactivity	5.6	8.0

Table 20 Characterization of ^{14}C -dithianon-derived radioactive residues in oranges (DT-123-066)

Residue fractions		TRR	
		%	mg/kg
TRR in whole sample		100.0	5.261
TRR in the wash and extracts		94.4	4.967
Surface rinse ^{a)}	Components in wash	87.3	4.590
	Dithianon	80.3	4.222
	Others	6.99	0.368
Peel extracts ^{b)}	Components in peel extract	6.88	0.362
	Organo-soluble fraction ^{d)}	4.14	0.218
	Dithianon (component by HPLC)	0.27	0.014
	Pe01 (4 components by TLC)	1.05	0.055

Residue fractions		TRR	
		%	mg/kg
	Pe02 (baseline radioactivity by TLC)	0.61	0.032
	Pe03 (2 components by TLC)	0.97	0.051
	Pe04 (baseline radioactivity by TLC)	0.68	0.036
	Pe05 (8 components by HPLC including BAS 216 F)	0.65	0.034
	Pe06 (baseline radioactivity by TLC)	0.19	0.010
	Water-soluble fraction ^{c, b)}	2.74	0.144
	Organo-soluble fraction (6 components by TLC) ^{d)}	1.52	0.080
	Water-soluble fraction	1.22	0.064
Pulp extracts ^{c)}	Components in pulp extract ^{c)}	0.30	0.015
	Organo-soluble fraction (4 components by TLC) ^{d)}	0.10	0.005
	Water-soluble fraction ^{d)}	0.20	0.010
Total identified dithianon (80.3% surface rinse, 0.27% peel extract)		80.5	4.236
PES peel	Peel	5.12	0.270
	Organo-soluble fraction (multiple components) of enzyme digest (Pronase E) ^{d)}	0.19	0.010
	Water-soluble fraction of enzyme digest (Pronase E) ^{d)}	2.98	0.157
	Undigested	1.98	0.104
PES pulp	Pulp	0.45	0.024

^{a)} Combined residues from surface washes with dichloromethane/0.1% acetic acid

^{b)} Combined residues from peel extracts with dichloromethane/0.1% acetic acid and acetone/0.1% acetic acid surface wash

^{c)} Combined residues from pulp extracts

^{d)} Dichloromethane fraction (organo-soluble) from solvent partitioning

^{e)} Water-soluble fraction from solvent partitioning

^{f)} The fraction was derivatized with pentafluorobenzyl bromide, then solvent partitioned

Thin-layer chromatography of surface washes showed that the major radioactive component (approximately 92%) was the parent dithianon. This corresponds to approximately 80% of the TRR. The surface washes of the radioactive residues obtained from the five treated oranges collected 28 days after treatment contained 87% of the total terminal residue. TLC and HPLC analysis showed that 92% of the radioactivity recovered in the dichloromethane/0.1% acetic acid rinses (or 80% TRR, 4.22 mg/kg) was unchanged dithianon. The identification was confirmed by mass spectrometry.

Initial TLC investigations of the peel extracts showed the presence of mainly polar compounds and a proportion of radioactivity migrating with reference compound dithianon. In order to separate the polar and the less polar fractions, equal amounts of the peel extracts and the third surface acetone/acetic acid extract were combined and subjected to a partitioning with dichloromethane and water. Approximately 60% of the radioactivity contained in the combined peel extracts proved to be organosoluble. The TLC of the organic layer revealed three prominent metabolite fractions (Pe01, Pe03 and Pe05, corresponding to 0.055 mg/kg, 0.051 mg/kg and 0.034 mg/kg, respectively), which were isolated from the TLC-plates and further investigated. One- and two-dimensional thin-layer chromatography revealed that the radioactivity contained in fractions Pe01 and Pe03 did not represent single metabolites but a number of more or less polar degradation products: TLC investigations of fraction Pe01 indicated the presence of at least 4 different compound fractions none of which exceeded 0.018 mg/kg (0.34% TRR). Furthermore, the TLC-chromatogram of fraction Pe03 showed at least two metabolite fractions representing only 0.17% and 0.75% of the TRR (0.009 mg/kg and 0.040 mg/kg). In the case of Pe05 a small amount of unchanged dithianon was identified (0.014 mg/kg) by LC/MS investigations following purification by HPLC.

The radioactive residues remaining in the aqueous solution after the above mentioned partitioning were further subjected to derivatization with pentafluorobenzyl bromide. As a result, approximately 56% of the originally water-soluble residue could additionally partitioned into dichloromethane. TLC investigations of the organic layer revealed the presence of several product fractions, which did not exceeded 0.045 mg/kg or 0.86% of the TRR.

The non-extracted peel residues, which amounted approximately 5.12% of the TRR (0.27 mg/kg) were subjected to enzyme cleavage reaction. After incubating aliquots of the non-

extracted peel residues with pronase E, about 62% of the original non-extracted radioactivity was found in the buffer solution. Further partitioning of the aqueous solution with dichloromethane proved 0.01 mg/kg of the radioactivity to be organosoluble whereas 0.157 mg/kg remained in the aqueous solution. TLC investigations of the organosoluble compounds again revealed the presence of several products. Also in this case, all metabolite fractions represented only traces of the radioactivity found on or in whole oranges (0.001–0.005 mg/kg).

Radioactive residues found in pulp at 28 days after application accounted for 0.75% of the TRR (0.039 mg/kg). After homogenization and extraction of the pulp samples, only 0.30% of the TRR (0.015 mg/kg) proved to be extracted and 0.45% (0.024 mg/kg) as non-extracted. Also in this case, the combined pulp extracts were subjected to a partitioning with dichloromethane and water in order to separate the polar and the less polar metabolite fractions. A portion of 34% of the radioactivity, originally in the pulp extracts, was transferred into the organic layer, whereas 66% remained in the aqueous solution. The TLC investigations of the organosoluble compounds revealed the presence of different metabolite fractions, each representing only traces of the terminal radioactive residue (< 0.002 mg/kg).

From all results obtained in the course of the DT-123-066 (1998) and the previous study DT-640-020 (1994), it can be stated that the main portion of the TRR found on or in whole oranges treated with $^{13,14}\text{C}$ -dithianon, remained on the surface of the fruits (87%). Furthermore, the majority of this surface residue (approximately 80% of the TRR) was still the unchanged parent compound. The remaining radioactive residues, ca. 12% (6.9 ERR + 5.12 PES) of TRR in the peel and ca. 0.8% (0.3% ERR + 0.45% PES) of TRR in the pulp, was composed of a large number of mostly polar compounds none of which can be considered major.

Apple

The fate of dithianon was characterized in apples by Hawkins (*et al.* 1991) and Mayo (1993). Apple trees grown outdoor were treated with 100 μL droplets of a formulation that contained ^{14}C -labelled dithianon at a concentration between 0.07% and 0.1%. The number of applications ranged from 1 to 4 and 5 treatments. Apples and leaves were harvested directly after the application as well as 21 days after successive 2-weekly ^{14}C -dithianon applications or 15 days after 5 successive 2-weekly ^{14}C -dithianon applications.

The samples (apples and leaves) were surface washed (within 1 hour after harvesting) by soaking in dichloromethane with 0.1% acetic acid. Surface wash was repeated three times and combined for measurement of radioactivity. A fourth surface wash was carried out with acetone with 0.1% acetic acid. Apples were subsequently peeled and the peel and flesh extracted separately by homogenizing with acetone, centrifugation, and separation of the extract from the residue. Washes, extracts and post-extracted residues were analysed for total radioactive residues (TRR) by liquid scintillation counting (LSC) and combustion. The TRR was determined as the sum of the total radioactivity in the surface rinse, the extracts and the post-extracted residues of the remaining plant parts after combustion. Thin layer chromatography (TLC) on normal phase and reverse phase TLC plates was used for the characterization and identification of the ^{14}C -dithianon-derived residues in the washes and extracts the apples and leaves. For measurement of proportions of radioactive components, radio-chromatograms of TLC plates were obtained. To aid in the identification, the radioactive samples were co-chromatographed with appropriate reference compounds and these were located by quenching of a fluorescent indicator under UV light at 254 nm.

The radioactive residues in treated apples and leaves, expressed in mg/kg dithianon equivalents and as portion of the applied dose of ^{14}C -dithianon are summarized in Table 21. TRR after 4 to 5 application of dithianon onto apple fruits and leaves were determined to be between 2.6 and 5.4 mg/kg in apple fruits and in leaves between 217 to 485 mg/kg.

Table 21. Radioactive residues in apples and leaves after treatment with ^{14}C -dithianon, mean values $\pm$ SD (DT-640-013).

Sampling interval	Fruits		Leaves	
	TRR, mg/kg	TAR, %	TRR, mg/kg	TAR, %

1 hour after 1 st application	Not reported	91.9	Not reported	92.7
21 days after 4 th application	5.4 ± 2.5	69.6 ± 8.4	217 ± 72	49.3 ± 9.6
15 days after 5 th application	2.6 ± 0.7	61.3 ± 1.6	485 ± 118	41.2 ± 6.6

Most of the recovered radioactivity was found in washed surface fraction of both apple fruit (81.4% to 89.7% of TRR) and leaves (90.3% to 94.0% of TRR) (see Table 22).

Table 22 Distribution of radioactivity in apple matrices after application of ¹⁴C-dithianon (DT-640-013)

Sample	TRR, %	
	Mean	± SD
Apple fruit (21 days after 4 applications)		
Surface wash 1 – 3	89.7	6.0
Surface wash 4	0.5	0.2
Peel extract	1.3	0.3
Flesh extract	1.3	0.8
Peel (PES)	1.1	0.9
Flesh (PES)	6.2	4.0
Apple fruit (15 days after 5 applications)		
Surface wash 1 – 3	81.4	2.4
Surface wash 4	2.8	0.2
Peel extract	2.3	0.4
Flesh extract	2.7	1.0
Peel (PES)	1.3	0.7
Flesh (PES)	9.4	1.4
Apple leaf (21 days after 4 applications)		
Surface wash 1 – 3	90.3	4.6
Surface wash 4	0.7	0.2
Extract	1.0	0.4
PES	8.1	4.7
Apple leaf (15 days after 5 applications)		
Surface wash 1 – 3	94.0	0.6
Surface wash 4	0.2	0.0
Extract	0.6	0.1
PES	5.1	0.6

The nature of ¹⁴C-dithianon residues in various apple matrices was characterized by TLC. TLC of surface washes showed that the major radioactive component was co-chromatographed with the parent dithianon. The parent accounted for means of 72.7% to 82.0% (apples) and 69.7% to 85.7% (leaves) of the TRR corresponding to 2 to 4 mg/kg (apples) and 151 to 415 mg/kg (leaves), respectively (see Table 23). Only dithianon could be identified in the extracted residues.

Table 23 Characterization of ¹⁴C-dithianon-derived radioactive residues in apples (DT-640-013)

Residue fractions		TRR				TRR			
		21DAT4 ^d		21DAT4		15DAT5		15DAT5	
		Fruit		Leaves		Fruit		Leaves	
		%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
TRR in whole sample		100	5.40	100	217	100	2.6	100	485
TRR in wash + extracts		92.8	5.01	92.0	199.5	89.2	2.3	94.8	459.8
Surface wash ^a	Components:								
	Dithianon	82.0	4.43	69.7	151	72.7	1.89	85.7	415
	TLC Baseline ^b	6.1	0.33	18.2	39	6.7	0.17	5.7	28
	Others	1.6	0.09	2.4	5	1.8	0.05	2.7	13
Extract	Components:								
	Dithianon	ND		ND		ND		ND	
	Others	2.6	0.14 ^c	0.9	2	5.0	0.13 ^c	1.6	3
Total identified		82.0	4.43	69.7	151	72.7	1.89	85.7	415
PES		7.3	0.39	8.1	18	10.4	0.44	5.1	15.6

^a Combined residues from washes with dichloromethane/0.1% acetic acid and acetone/0.1% acetic acid

^b For both the 21DAT4 and 15DAT5 samples, this residue fraction consisted of at least two components, each at ≤ 0.24 mg/kg ($\leq 5\%$ TRR) in apples, and ≤ 29 mg/kg ($\leq 13\%$ TRR) in leaves

^c Peel and flesh

^d 21DAT4: 21 days after 4 treatments

Spinach

A greenhouse study was conducted in 1999 by van Dijk (2000, DT-640-023) to elucidate the metabolic fate of dithianon in spinach.

For the study, three plastic containers (70 cm $\times$ 50 cm; soil depth: 40 cm), each providing an application area of 0.35 m², were filled with silt loam soil and were sown within a depth of 2-3 cm with 43 g of spinach seeds per m² or 15 g/container. Two containers were established for treatment with a WP formulation of ¹⁴C-dithianon (plot A) and one container (plot B) for treatment with the blank formulation to provide control samples.

¹⁴C-labelled dithianon at the 5, 6, 9 and 10 positions of the naphthoquinone ring (specific activity 1.569 MBq/mg, radiochemical purity 98.1%) was mixed with ¹³C-labelled dithianon (purity 98.1%), also labelled at the 5, 6, 9 and 10 positions, and non-labelled ¹²C-dithianon (purity 99.9%) to yield material with a specific activity of 0.092 MBq/mg (5526 dpm/ μ g; or 2.49 μ Ci/mg).

The ¹³C-dithianon was added as a mass marker to aid in mass spectrometric analysis and identification of the radioactive residues derived from dithianon in the spinach samples. The labelled material, hereafter is referred to as ¹⁴C-dithianon.

Three applications of test substance, formulated as a WP with blank formulation were made over plot A at 38 days (early 6-leaf stage), 51 days (6–8-leaf stage) and 61 days (8-leaf stage) after sowing at nominal dose rates of 1 kg ai/ha/application. Spinach samples (above-ground parts) were collected on the day of the first, second, and third application, and 20 days after the third application. The spinach plants in Plot B (control) were treated with the blank formulation.

All plant samples were analysed for TRR by combustion and LSC. The TRR values for the whole plant samples were determined by summing the radioactive residue in the surface rinses with the radioactive residue in the rinsed plant samples. The radioactive residue in the rinsed plant is referred to as the post rinse residue (PRR). ¹⁴C-dithianon-derived residues in the spinach samples in the surface rinse and extracts of the PRR were taken for characterization and identification by TLC (normal and reversed phase) and reversed phase HPLC by co-chromatography with reference compounds and, where possible, by mass spectrometry. The limit of quantitation of the radioassay for the determination of the TRR was validated at 0.01 mg/kg by combustion of control spinach (0.5 g) fortified with 25 dpm of ¹⁴C-dithianon. The TRR in spinach leaf, expressed as mg/kg equivalents of ¹⁴C-dithianon, are summarized in Table 24.

Table 24 TRR in spinach samples following three applications of ¹⁴C-dithianon (DT-640-023).

Sampling Interval		TRR in mg/kg and (%)		
Days After Sowing (Growth Stage)	DAT ^a	Total (unwashed spinach)	Rinse	Rinsed Spinach (PRR) ^b
38 (early 6-leaf stage)	0DAT1	91.4 (100)	86.4 (94.6)	4.93 (5.4)
51 (6-8 leaf stage)	0DAT2	112.7 (100)	103.1 (91.5)	9.58 (8.5)
61 (8 leaf stage)	0DAT3	305.8 (100)	292.9 (95.8)	12.9 (4.2)
81 (final harvest)	20DAT3	149.5 (100)	143.9 (96.2)	5.67 (3.8)

^a DAT denotes days after treatment; for example, 20DAT3 denotes 20 days after treatment three

^b PRR: post rinse residues (TRR in the rinsed spinach)

The results showed that the surface rinse accounted for $> 90\%$ of the TRR and the post rinse residue (PRR) accounted for $< 9\%$ TRR at each sampling interval. During the three treatments, the PRR concentrations increased from 4.93 mg/kg after the first treatment to 12.89 mg/kg after the third

treatment. Because of the growth that increased plant mass, the PRR decreased from 12.89 mg/kg on the day of third treatment to 5.67 mg/kg 20 days later.

The post rinse residues (PRR) in spinach from all sampling intervals accounted for 3.8–8.5% of the TRR, with the majority of the radioactivity released by exhaustive extractions (3.4–7.5% TRR released by extractions). The extraction steps included aqueous acetonitrile, enzymatic treatment (pronase and cellulase), and reflux with methanol/ammonia (8 : 2) all in the presence of 0.1% acetic acid. The non-extracted PRR residue was very low, accounting for $\leq 1\%$ TRR at all sampling intervals. Extraction results of the incurred radioactivity in the spinach forage derived from ^{14}C -dithianon are summarized in Table 25. At harvest, 20 days after the third application, radioactivity in the three extracts ranged from 0.9–1.5% TRR (1.36–2.18 mg/kg).

Table 25 Distribution of ^{14}C -dithianon-derived radioactive residues in spinach (DT-640-023)

Main fractions	TRR,% (mg/kg)			
	0DAT1 ^a	0DAT2	0DAT3	20DAT3
TRR in whole unwashed sample	100 (91.36)	100 (112.68)	100 (305.77)	100 (149.53)
Surface rinse	94.6 (86.44)	91.5 (103.1)	95.8 (292.88)	96.21 (143.87)
ERR ^b	5.10 (4.66)	7.47 (8.42)	3.88 (11.88)	3.41 (5.10)
Extracts/washes ^c	1.27 (1.16)	1.11 (1.25)	1.19 (3.64)	1.04 (1.56)
Enzymatic treatment	3.15 (2.88)	4.70 (5.30)	0.86 (2.63)	1.46 (2.18)
Base/acid hydrolysis (reflux)	0.68 (0.62)	1.66 (1.87)	1.52 (4.65)	0.91 (1.36)
Others	NP	NP	031 (0.65)	NP
PES	0.29 (0.27)	1.03 (1.16)	0.33 (1.01)	0.38 (0.57)

^a DAT: Days After Treatment; for example, 0DAT1 denotes 0 days after first treatment.

^b ERR: Extractable Radioactive Residue (sum of all treatments from extraction, enzymatic treatment, hydrolysis and others).

^c Sequential extraction and washes of post-rinse residue (PRR) followed by enzyme treatment and base/acid hydrolysis.

NP: Not performed

The surface rinses and selected extracts were analysed by TLC, reversed phase HPLC, and mass spectrometry, where appropriate. The radioactivity recovered in the surface rinse was due exclusively to parent compound for all sampling intervals. The identification of parent was confirmed by HPLC, TLC, GC-MS and EI-MS (electron impact/mass spectrometry). The radioactivity profiles of the residues extracted from the surface rinsed spinach at the different growth stages and treatment timings were qualitatively similar.

For all sampling intervals, dithianon accounted for 92–96% of the TRR and was identified in the surface rinse. The extractable residues contained at least 14 ‘Regions Of Interest’ (ROIs), five of them being very polar, occurring in amounts of 0.1–0.5% of TRR at harvest. No dithianon was detected in the extracted residues at any of the growth stages and treatment timings. By HPLC and TLC analysis of the spinach extracts with the reference compounds, ROI 6 was identical to reference compound 2-hydroxy-naphthoquinone (R1, CL 231509). ROI 7 was identical to reference compound 5,10-dioxo-5,10-dihydro-naphtho[2,3-b]-1,4-dithiin-2,3-dicarboxylic acid diamide (D15, CL 902200). ROI 14 was contained a minor sub-fraction identical to reference compound phthalic acid (R2). A summary of the quantified and identified radioactive residues in spinach samples collected at harvest (20 days after the third application, 20DAT3) is provided in Table 26.

Table 26 Identification and quantification of ^{14}C -dithianon derived radioactive residues in spinach, 20DAT3 (DT-640-023)

Fraction	Component identified	TRR	
		%	mg/kg
Whole unwashed sample		100	149.53
Surface rinse ^a		96.2	143.87
Extract ^b		3.41	5.10
Rinse	Dithianon	96.2	143.87
Extract	ROI 1	0.11	0.16
	ROI 2	0.10	0.14

Fraction	Component identified	TRR	
		%	mg/kg
	ROI 3, ROI 4, ROI 5	0.33	0.50
	ROI 6 (identified as R1, CL 231509)/ ROI 7 (identified as D15, CL 902200)	0.26	0.39
	ROI 8	0.14	0.20
	ROI 9	0.15	0.23
	ROI 10	0.23	0.34
	ROI 11	0.08	0.13
	ROI 12, ROI 13	0.42	0.64
	ROI 14 (identified as R2)	0.54	0.80
	Others (unresolved)	0.59	0.91
Total Identified		97	145
PES	Unknown	0.38	0.57

^a Residue from rinse

^b Residue from extracts/washes, enzyme and base treatment

The main residue component in spinach, accounting for more than 90% of the TRR, was unchanged parent compound. In the post rinse spinach residues, no parent was detected. Besides multiple polar minor unknown components, metabolites identified by co-chromatography with the authentic reference compounds were 2,3-dicarboxylic acid diamide derivative (D15; CL 902200), 2-hydroxy-naphthoquinone (R1; CL 231509) and phthalic acid [benzyl 1, 2-dicarboxylic acid, (R2)]. This indicated that absorbed dithianon, which accounted for 3.8–8.5% of the TRR, was completely metabolized by the spinach plants.

In summary, besides the multiple unidentified polar minor components, based on the metabolites that were identified and characterized in spinach plants, the metabolism of dithianon in spinach first undergoes hydrolysis of the cyano groups to yield the diacid diamide (CL 902200). Further aromatic oxidation of the sulfur atoms and cleavage of the dithiine ring followed by hydroxylation of the naphthoquinone ring to yield metabolite CL 231509. The naphthoquinone undergoes further aromatic oxidation and cleavage to yield phthalic acid. The proposed metabolic pathway in spinach is shown in Figure 1.

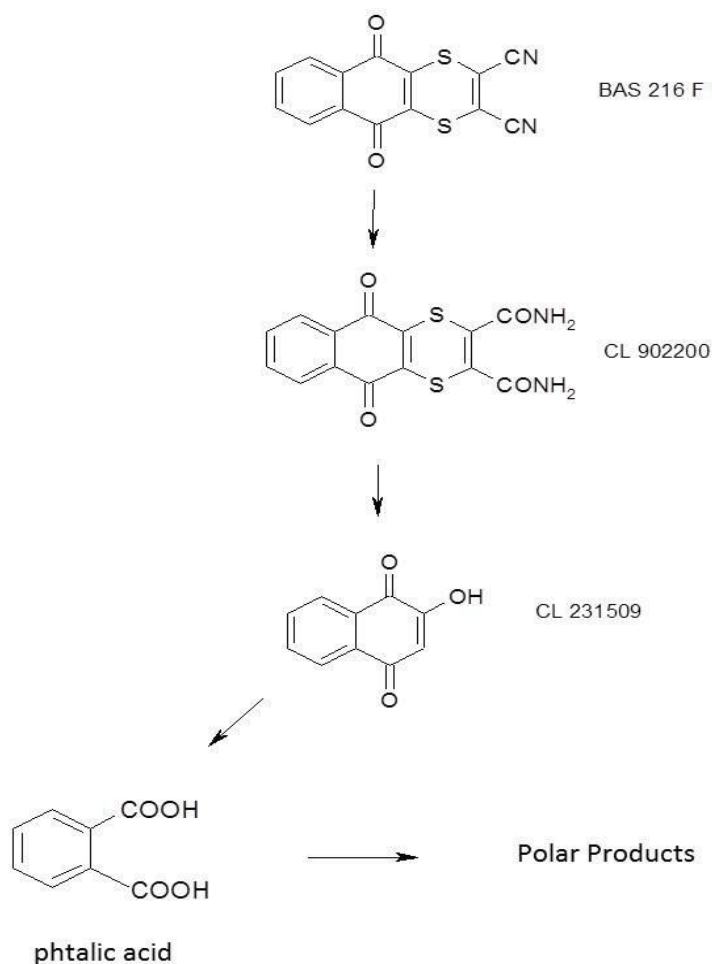


Figure 1 Proposed metabolic pathway of ¹⁴C-dithianon (BAS 216 F) in spinach (DT-640-023).

Wheat

The metabolism of dithianon in wheat was investigated by Mayo (1994, DT-640-019), Schlueter and Grahl, 1994 (1994/7001689), Schlueter, 1996 (DT-640-021, amendment to report 1994/7001689), Schlueter, 1998 (DT-640-017) and Hawkins, 1991 (DT-640-014).

Mayo, 1994, DT-640-019

A field study was conducted in 1992 to characterize the nature of dithianon and its metabolites in spring wheat. For the preparation of the test substance, the materials were mixed to provide ¹²C- and ¹³C-dithianon in a 1:1 ratio and ¹⁴C-dithianon at a nominal specific activity of 30 μ Ci/mg. The plants had been treated at two growth stages, "Zadoks 59" and "Zadoks 61" (equivalent to BBCH 59 and 61). The application rate was at both sprayings equivalent to 1.5 kg ai/ha. Samples of wheat were taken at 2 hours after the second application (0 days), at 20 days after and finally at 35 days after the second application. At 0 and 21 days, the plants were separated into stems and ears and at 35 days into grain, husk and straw.

Schlueter and Grahl, 1994, 1994/7001689; Schlüter, 1996, DT-640-021 (amendment to 1994/7001689)

The wheat samples generated in report DT-640-019 were further investigated. The samples were washed with acetonitrile/hydrochloric acid and the washings were removed by centrifugation. The plant material was homogenized and extracted with acetonitrile/hydrochloric acid and the extracts were removed. The surface rinse and extracts were analysed for TRR by LSC, the non-extracted residues were analysed by combustion followed by LSC. The surface rinse and extracts were partitioned with hexane/ethyl acetate, dichloromethane and dichloromethane/diethyl ether. The radioactive dithianon-derived residues in the wheat extracts were analysed by TLC and reversed phase HPLC. The TRR in all plant parts were determined as the sum of the TRR of the extracts and the non-extracted residues. The non-extracted residues were subjected to a variety of hydrolysis and extraction procedures to release additional radioactivity. The extracted plant material was further treated with acidic, basic and enzymatic cleavage and with selective extraction of main wheat cell wall components. The TRR in wheat samples, expressed as mg/kg equivalents of ^{14}C -dithianon, are summarized in Table 27.

Table 27 TRR in wheat samples following 2 applications of ^{14}C -dithianon at 1.5 kg ai/ha per application (1994/7001689; DT-640-021)

Sampling time (DAT) ^a	Sample type	TRR in mg/kg
0DAT2	Immature stems	61.0
	Immature ears	51.9
20DAT2	Immature stems	74.9
	Immature ears	67.6
35DAT2	Mature straw	68.1
	Mature grain	1.9
	Husks	60.6

^a DAT: days after treatment; for example, 20DAT2 denotes twenty days after treatment two.

The distribution of radioactivity in the extracts of immature and mature wheat commodities is provided in Table 28. For all samples, the surface rinsed residues were partitioned using hexane followed by dichloromethane/ethyl acetate, resulting in 21–48% TRR recovered in the hexane fraction, 27–44% TRR recovered in the dichloromethane/ethyl acetate fraction, and 0.2–2% TRR remaining in the water-soluble fraction. The extracted residues of all samples were also sequentially partitioned using hexane followed by dichloromethane/ethyl acetate. Following partitioning of the surface rinse and the extracts of the wheat samples, the major portion of the extractable residues was partitioned into organic layers.

Table 28 Distribution of ^{14}C -derived radioactive residues in wheat (1994/7001689; DT-640-021)

Fraction	TRR, % (mg/kg)						
	0DAT2 ^a		20DAT2		35DAT2		
	Stems	Ears	Stems	Ears	Straw	Husks	Grain
Whole sample	100 (61.0)	100 (51.9)	100 (74.9)	100 (67.6)	100 (68.1)	100 (60.6)	100 (1.9)
Surface rinse ^b	80.5 (49.1)	87.4 (45.3)	65.1 (48.8)	66.7 (45.1)	57.3 (39.0)	50.8 (30.8)	55.9 (1.0)
Hexane-soluble fraction	35.8 (21.9)	48.3 (25.1)	23.1 (17.3)	34.1 (23.1)	24.2 (16.5)	23.7 (14.3)	21.4 (0.4)
Dichloromethane/ethyl acetate-soluble fraction	44.4 (27.0)	38.7 (20.1)	41.7 (31.2)	32.4 (21.9)	32.3 (22.0)	26.5 (16.1)	33.0 (0.6)
Water-soluble fraction	0.3 (0.2)	0.3 (0.2)	0.3 (0.2)	0.2 (0.1)	0.8 (0.5)	0.6 (0.4)	1.5 (<0.1)
Extract ^c	9.3 (5.7)	4.4 (2.3)	8.3 (6.2)	14.4 (9.7)	12.8 (8.7)	16.2 (9.8)	8.5 (0.2)
Hexane-soluble fraction	2.5 (1.5)	0.5 (0.3)	1.6 (1.2)	3.6 (2.5)	2.9 (1.9)	3.8 (2.3)	1.4 (<0.1)
Dichloromethane/ethyl acetate-soluble fraction	6.4 (3.9)	3.7 (1.9)	6.4 (4.8)	10.4 (7.0)	9.5 (6.5)	11.5 (7.0)	6.3 (0.1)
Water-soluble fraction	0.4 (0.2)	0.2 (0.1)	0.4 (0.3)	0.4 (0.2)	0.5 (0.3)	0.8 (0.5)	0.8 (<0.1)
ERR ^d	89.8 (54.8)	91.8 (47.6)	73.4 (55.0)	81.1 (54.8)	70.1 (47.7)	67.0 (40.6)	64.4 (1.2)
PES ^{e, f, g, h, i}	10.2 (6.2)	8.2 (4.3)	26.6 (19.9)	18.9 (12.8)	29.9 (20.4)	33.0 (20.0)	35.7 (0.7)

^a DAT: Days After Treatment; for example, 20DAT2 denotes twenty days after second treatment

^b Surface rinse with acetonitrile/concentrated hydrochloric acid (99:1, v/v) at -20 °C; residues in surface rinse were

solvent partitioned as indicated

^c Extract 2 × with acetonitrile/concentrated hydrochloric acid (99:1, v/v); residues in extract were solvent partitioned as indicated

^d ERR: Extracted Radioactive Residue (sum of surface rinse and fractions)

^e PES: Post Extraction Solids

^f For 0DAT2 wheat, 18% of RRR in stems and 21% of RRR in ear was released by acid hydrolysis

^g For 20DAT2 wheat, 41% of RRR in stems and 27% of RRR in ears was released by acid hydrolysis

^h For 35DAT2 wheat, 17% of the RRR in straw, 24% of the RRR in husk and 57% of the RRR in grain was released by acid hydrolysis

ⁱ For 35DAT2 straw, 32-39% of the RRR was released by base hydrolysis, versus 20% RRR released by pronase E, 13% RRR released by cellulase, and 10% RRR released by pectinase

The non-extracted residues amounted to 30, 33, and 36% of the TRR in the straw, husk and grain, respectively. Radioactivity remaining in the non-extracted plant material of all samples was subjected to acid hydrolysis, which released approximately 20–60% of the radioactivity.

The PES-fractions of samples taken 35 days after the second application (35 DAT2) were further analysed. Non-extracted residues in wheat straw were subjected to alkaline hydrolysis, which released approximately 30–40% of the radioactivity. Furthermore, the PES-fractions of straw and grain were additionally subjected to sequential enzymatic treatments (pronase E, cellulase and pectinase). For the PES of wheat straw, 3% of the TRR was associated with the pectin, 11% TRR was associated with the lignin, 5% TRR was associated with the non-cellulosic polysaccharides, and 3% TRR was associated with cellulose. The corresponding results for the PES of wheat grain were 15, 16, 2, and 3% TRR, respectively. Results from the further treatments of the non-extracted residues in wheat straw and grain are presented in Table 29.

Table 29 Further extraction of wheat straw and grain (35DAT2) treated with ¹⁴C-dithianon (1994/7001689; DT-640-021)

Fraction	TRR, % (mg/kg)	
	Straw	Grain
Whole sample	100 (68.1)	100 (1.9)
Surface rinse	57.3 (39.0)	55.9 (1.0)
Extract	12.8 (8.7)	8.5 (0.2)
PES	29.0 (20.4)	35.6 (0.7)
Sequential treatment of PES ^a		
Na ₂ EDTA (pectin fraction)	2.5 (1.7)	14.6 (0.28)
Dimethyl sulfoxide/35 °C (lignin fraction)	8.2 (5.60)	12.0 (0.23)
Dimethyl sulfoxide/80 °C (lignin fraction)	2.7 (1.9)	3.5 (0.07)
Concentrated NH ₃ (non-cellulose polysaccharide fraction)	4.6 (3.1)	2.2 (0.04)
Residual radioactivity from NH ₃ -extraction	11.9 (8.2)	3.3 (0.06)
Schweizer's reagent ^b (cellulose fraction)	3.1 (2.1)	3.2 (0.06)
Residual radioactivity from Schweizer's reagent ^b	13.6 (9.3)	2.4 (0.05)

^a PES: radioactive residues in post extraction solids described in Table 27

^b Schweizer's reagent: saturated solution of copper hydroxide in concentrated ammonium hydroxide

Schlueter and Varga, 1998, DT-640-017

The wheat samples generated in 1992 by Mayo (1994, DT-640-019) were further investigated in order to quantify, characterize and identify metabolites occurring in and on wheat. Focus of the additional study was on further investigations of the extractable radioactivity.

In order to prove the storage stability, the TRR, the extraction behaviour and the distribution of the radioactivity in the extracts were investigated and compared with the previous study. When the additional investigations started, the samples had been stored for a period of 32 months. Samples of plant material were washed with acetonitrile/hydrochloric acid and the washings were removed by centrifugation. The plant material was homogenized and extracted with acetonitrile/hydrochloric and

the extracts were removed. The surface rinse and extracts were analysed for TRR by LSC, the non-extracted residues were analysed by combustion followed by LSC. The surface rinse and extracts were sequentially partitioned with hexane, dichloromethane/ethyl acetate and ethyl acetate. The extracts have been further and extensively characterized using as techniques:

TLC using normal phase and reversed phase (RP-18) plates

Reversed phase HPLC

Liquid/liquid partition experiments

Purification of fractions by HPLC fractionation

Derivatization with pentafluorobenzyl bromide

HPLC-MS

In order to prove the storage stability of the samples under investigation, the samples were first subjected to the same work-up procedures. The results of the investigations are summarized in Table 30. The data indicate that the samples had been stable over the period of storage. In deviation to the study of 1994 (1994/7001689; DT-640-021), no further characterization work of the non-extracted radioactivity has been carried out.

Table 30 Distribution of ^{14}C -dithianon derived radioactive residues from wheat (DT-640-017)

Fraction	TRR, mg/kg (%)						
	0DAT2		20DAT2		35DAT2		
	Stems	Ears	Stems	Ears	Straw	Husks	Grain
Whole sample	50.72 (100)	57.67 (100)	79.78 (100)	79.43 (100)	48.14 (100)	92.43 (100)	2.20 (100)
Surface rinse	36.25 (71.5)	47.61 (82.5)	52.58 (65.9)	56.02 (70.5)	29.71 (61.7)	57.08 (61.8)	1.25 (56.7)
Organo-soluble fraction	36.08 (71.1)	47.45 (82.3)	51.90 (65.1)	55.77 (70.2)	29.44 (61.2)	56.50 (61.1)	1.21 (55.0)
Water-soluble fraction	0.17 (0.3)	0.15 (0.3)	0.68 (0.9)	0.24 (0.3)	0.27 (0.6)	0.59 (0.6)	0.04 (1.8)
Extract	9.93 (19.6)	5.66 (9.8)	4.99 (6.3)	12.26 (15.4)	3.02 (6.3)	14.63 (15.8)	0.34 (15.4)
Organo-soluble fraction	9.63 (19.0)	5.44 (9.4)	4.80 (6.0)	11.71 (14.7)	2.91 (6.0)	13.94 (15.1)	0.32 (14.5)
Water-soluble fraction	0.30 (0.6)	0.21 (0.4)	0.20 (0.2)	0.55 (0.7)	0.11 (0.2)	0.69 (0.7)	0.02 (0.9)
ERR	46.19 (91.1)	53.26 (92.3)	57.57 (72.2)	68.27 (85.9)	32.73 (68.0)	71.71 (77.6)	1.59 (72.1)
PES	4.54 (8.9)	4.41 (7.7)	22.20 (27.8)	11.16 (14.1)	15.41 (32.0)	20.72 (22.4)	0.61 (27.9)

During the conduct of the plant metabolism studies, more experience was gained with regard to the instability of dithianon in plant extracts (especially under alkaline conditions). Dithianon was found to be unstable during concentration using a rotary evaporator, but also during TLC analyses under normal phase conditions. In deviation to the studies performed before specific consideration was given to the sensitive and careful work-up of the sample material. Reducing purification and concentration procedures to the minimum extent minimized any artificial degradation of dithianon. Due to this fact, higher amounts of the parent were found in the 1998 study. The TRR partitioned into the organic layers were further subjected to TLC and HPLC investigations. The results of these investigations are shown in Table 31.

Table 31 Quantification of dithianon and unknown extracted residues recovered in wheat matrices (DT-640-017)

Sample		Dithianon		Remaining radioactivity	
DAT ^{a)}	Matrix	mg/kg	% of TRR	mg/kg	% TRR
0	stem	40.46	79.8	5.74	11.2
	ears	48.21	83.5	5.06	8.7
20	stem	52.46	65.7	5.11	6.5
	ears	60.75	76.5	7.52	9.4
35	straw	29.67	61.6	3.05	6.3
	grain	1.13	50.9	0.46	21.2
	husk	61.12	66.1	10.59	11.4

^{a)} DAT: Days After last Treatment

Besides the parent compound fraction, considerable amounts of radioactivity (up to approximately 10% TRR) proved to be spread over the total length of run (in the case of TLC analysis) or elute constantly from the column (in the case of HPLC) without any single major substance peak. Due to this fact, the extracts obtained after sample homogenization were chosen for further characterization or identification of the fractions (metabolites) M1 to M4. The quantitation of the metabolites M1 to M4 in the extracts is shown in Table 32.

Table 32 Quantification of fractions M1 - M4 contained in the 2nd extracts of wheat commodities (DT-640-017)

Days		Residues mg/kg (% TRR)						
		0		20		35		
Matrix		Stems	Ears	Stems	Ears	Straw	Grain	Husk
Fraction M1		NQ	0.2 (0.4)	0.38 (0.5)	0.66 (0.8)	0.21 (0.4)	0.02 (0.8)	0.61 (0.7)
Fraction M2		NQ	NQ	NQ	NQ	NQ	0.01 (0.6)	NQ
Fraction M3		0.5 (1.0)	0.79 (1.4)	0.42 (0.5)	1.08 (1.4)	0.27 (0.6)	0.07 (3.3)	1.02 (1.1)
Fraction M4		NQ	NQ	NQ	0.38 (0.5)	NQ	0.01 (0.6)	NQ

NQ: not quantified

In the extracts obtained after sample homogenization, four fractions (M1 - M4) were found which amounted to $\geq 3.3\%$ TRR. HPLC isolation and purification of these metabolites was attempted. In the course of these attempts, the main fractions (M1 and M3) proved to be of considerable instability again. Therefore, the four fractions were directly subjected to HPLC/MS without any further purification but no interpretable results were obtained. Since M3 is the most abundant peak, it was additionally subjected to derivatization with pentafluorobenzyl bromide. Following this procedure, about 92% of the residue could be partitioned into dichloromethane. HPLC investigations of the organic layer revealed the presence of at least four product fractions which either indicates artificial degradation of the metabolite occurring during the isolation and/or the derivatization procedure itself. The occurrence of more than one derivative could also result that peak M3 consists of more than one component. No further investigation of the products formed was carried out.

Hawkins et al., 1991, DT-640-014

Winter wheat has grown in an outdoor environment. A plot of 1 m² was sprayed with ¹⁴C-diathinon formulated as SC when the wheat was at approximately growth stage Zadoks 39. The second treatment was carried out 19 days after the first spray (Zadoks 59). The application rate at both sprayings was 150 mg/m², equivalent to 1.5 kg ai/ha. Samples were taken 2 hours after the second spray (0 days) and then at 14 and 39 days post treatment and finally the whole crop at 31 days after the second spray. At 0 and 14 days, the wheat was separated into stems and ears and at 39 and 51 days into grain, husk and straw.

At 0 days, TRR in ears and stems were 29.76 mg/kg and 18.46 mg/kg respectively and at 14 days 12.27 mg/kg and 7.92 mg/kg respectively. TRR in grain, husk and straw were 0.303 mg/kg,

21.72 mg/kg and 16.2 mg/kg respectively at harvest (51 days). The TRR in grain analysed after 2 months storage at -15 °C was 0.431 mg/kg. The samples were washed with acetonitrile/hydrochloric acid cooled to -20 °C to remove surface residues. After the washes, the samples were macerated with acetonitrile/hydrochloric acid at -20 °C. The results are summarized in Table 33.

Table 33 TRR in washes and extracts of wheat matrices after the last 2 applications of ¹⁴C-dithianon (DT-640-014)

Sample		Wash		Extract		Residues remaining	
Day	Type	mg/kg	%	mg/kg	%	mg/kg	%
0	Ears	24.98	83.9	3.79	12.7	0.99	3.3
	Stems	15.54	84.2	1.77	9.6	1.14	6.2
14	Ears	9.41	76.7	2.10	17.1	0.76	6.2
	Stems	6.10	77.0	1.06	13.4	0.76	9.6
39	Grain	0.146	48.2	0.066	21.8	0.091	30.0
	Straw	10.36	64.0	3.04	18.8	2.81	17.3
	Husk	14.20	65.4	4.91	22.6	2.61	12.0
51	Grain (A)	0.248	49.8	0.069	13.9	0.181	36.3
	Straw	19.44	34.5	14.91	26.5	22.0	39.0
	Husk	18.25	46.2	9.66	24.4	11.63	29.4
51	Grain (B)	0.211	49.0	0.058	13.5	0.162	37.6

Grain (A): sample A was analysed at harvest time

Grain (B): sample B was analysed 2 months after harvest

Residues remaining (PES): TRR in the wheat matrices remaining after washing and extracting with acetonitrile/hydrochloric acid at -20 °C.

The harvest samples of grain, straw and husk were extracted further with acetonitrile/hydrochloric acid, 2 × methanol and methanol/hydrochloric acid at room temperature. These further extracts accounted for 18.4%, 17.8% and 18.0% of TRR in grain, straw and husk, respectively. The residues remaining in the samples after these further extractions accounted for 16.5% (0.083 mg/kg), 16.7% (9.42 mg/kg) and 13.7% (5.42 mg/kg) of the TRR for grain, straw and husk respectively.

The characterization of the radioactivity in the washes and extracts of wheat matrices have been examined by TLC. At all times the major component was unchanged dithianon. At harvest dithianon represented 53.5% of TRR in grain after extraction and ca. 65% of the TRR in the extract. For husk and straw, dithianon represented 55.6% and 45.9% of the TRR in the sample after extraction and 63% each of TRR in the extract.

Environmental fate in soil and water-sediment systems

The FAO Manual (FAO, 2009) explained the data requirements for studies of environmental fate. The focus should be on those aspects that are most relevant to MRL setting. For dithianon, supervised residue trials data were received for foliar spray on permanent crops such as citrus fruits, tree nuts, pome fruits, stone fruits, grapes and hops. Therefore, according to the FAO manual, neither environmental fate nor rotational crops studies are required. For information on hydrolysis and photolysis see chapter “Physical and chemical properties”, Table 1.

RESIDUE ANALYSIS

Analytical methods

The Meeting received descriptions and validation data for analytical methods for residues of dithianon in plant and animal commodities. Residue analytical methods for dithianon rely on HPLC with UV-detection or LC/MS-MS for plants and HPLC with electrochemical detection or LC-MS/MS for animal matrices. Typical LOQs achieved for plant and animal commodities fall in the range of 0.01–0.05 mg/kg. Methods have been subjected to independent laboratory validation.

Plant commodities

Dithianon is used since more than 30 years as fungicide in fruit, vegetables and cereals crops. In this time period, many residue analytical methods have been developed. The HPLC methods described in this section were performed over the past 20 years; they have been used for the analysis of the samples generated during the supervised field trials, processing fraction studies and storage stability tests (see Table 34). New methods have been developed from 2006 to 2011 and are based on LC-MS/MS and also include a second transition as confirmatory technique (see Tables 35 – 37). The analysis of the most recent supervised field trials and studies on residues in processed commodities occurred with method No. L0152/01, which is, with the exception of minor modifications, identical to method SOP-PA.0281. The further developments of SOP-PA.0281 have been performed to include the degradation product CL 1017911, known from the hydrolysis study at exaggerated temperatures in buffer solutions, in the analytical method. With this elaborated method further information can be obtained on the presence/absence of CL 1017911 on RAC and processed products (see Table 38).

The analytical methods are described briefly as follows:

Grapes, juice, wine, beer, method no. RLA 12616V (Smalley 2001, DT-244-065 including amendments 1 and 2)

Analyte: Dithianon Method: HPLC-UV D LOQ: 0.01 mg/kg
 Description: Dithianon is extracted from the grape and processed commodities with concentrated hydrochloric acid/acetonitrile 1:2 (v/v). After further washing with acetonitrile, the extract is subjected to liquid-liquid partitioning with dichloromethane. The dried residue is reconstituted in acidic methanol (1% acetic acid) and a portion cleaned up using gel permeation chromatography (GPC) with acidic methanol (0.06% acetic acid) as the eluant. The collected solution is evaporated to approximately 0.5 ml and re-dissolved in acetonitrile/water/acetic acid (60:38:2). Quantitative determination is carried out by HPLC (column: Luna Phenyl Hexyl) with UV detection, using acetonitrile/water/acetic acid (60:38:2) as mobile phase. Specificity of the method may be confirmed using a diode array detector.

Apples and processed commodities, method no. RLA 12616.03V (Smalley 2001, DT-244-068 including amendments 1 and 2)

Analyte: Dithianon Method: HPLC-UV D LOQ: 0.01 mg/kg
 Description: Dithianon is extracted from the apple with concentrated hydrochloric acid/acetonitrile 1:2 (v/v) as described above for grapes (DT-244-065)

Grapes, must, wine, method no. FAMS 028-02 (Weitzel, 1996, DT-244-054)

Analyte: Dithianon Method: HPLC-UV D LOQ: 0.01 mg/kg must, wine; 0.02 mg/kg grapes
 Description: Dithianon is extracted from the grapes, must and wine with concentrated hydrochloric acid/acetonitrile 1:2 (v/v). After further washing with acetonitrile the extract is subjected to liquid-liquid partitioning with dichloromethane. After evaporation of the organic phase, the residue is reconstituted in acidic methanol (1% acetic acid) and a portion cleaned up using gel permeation chromatography (GPC) with acidic methanol (0.01 M of acetic acid in methanol) as the eluant. The collected solution is evaporated to 0.5 ml and redissolved in methanol/acetic acid (99:1, v/v). Quantitative determination is carried out by HPLC (column: Nucleosil100-phenyl) with UV detection, using acetonitrile/ water/acetic acid (575:423:2, v/v) as mobile phase.

Apple, method number FAMS 028-02 (Weitzel, 1996, DT-244-055)

Analyte: Dithianon Method: HPLC-UV D LOQ: 0.02 mg/kg
 Description: Dithianon is extracted from the apple with concentrated hydrochloric acid/acetonitrile 1:2 (v/v) as described above for grapes (DT-244-054).

Grapes, method number HUK 460/38 (Todd, 1992, DT-244-045)

Analyte: Dithianon Method: HPLC-UV D LOQ: 0.05 mg/kg grapes
 Description: Dithianon is extracted from grapes with concentrated acetic acid/acetonitrile 1:15 (v/v). After further washing with acetonitrile, a second extraction was conducted with concentrated acetic acid/acetonitrile

1:15 (v/v). Aliquot of the extract is subjected to two times liquid-liquid partitioning using n-hexane, hydrochloric acid, water and sodium chloride. The n-hexane solution is concentrated to approximately 0.5 mL on a rotary evaporator and the residue is reconstituted in acidic dichloromethane (1%) and subjected to column chromatography using activated silica gel and acidic dichloromethane as the eluant. The collected solution is evaporated to 0.5 mL and re-dissolved in methanol/acetic acid (99:1, v/v). Quantitative determination is carried out by high pressure liquid chromatography (HPLC) with UV detection, using acetonitrile/methanol/water/acetic acid (55:10:35:1, v/v) as mobile phase.

Apple and pear, method number HUK 460/38 (Jones, 1989, DT-244-037)

Analyte: Dithianon Method: HPLC-UV D LOQ: 0.05 mg/kg
 Description: Dithianon is extracted from the apple with concentrated hydrochloric acid/acetonitrile 1:2 (v/v) as described above for grapes (DT-244-045).

Must, red and white wine, method number FAMS 009-01, HUK 460/55-01R (Curl, 1992, DT-244-048)

Analyte: Dithianon Method: HPLC-UV D LOQ: 0.05 mg/kg
 Description: Dithianon is extracted from must and wine, acidified with concentrated hydrochloric acid and extracted 4 times with n-hexane. The organic fraction is reduced in volume to near dryness and re-dissolved in 0.1% acetic acid in dichloromethane and subjected to column chromatography using activated silica gel and acidic dichloromethane as the eluant (0.1%). The collected organic solution is evaporated to 0.5 ml and re-dissolved in methanol/acetic acid (99:1, v/v).

Apples, grapes, lettuce, whole oranges, wheat grain, rape seed, hops, method number SOP-PA.0281 (Class and Richter, 2006, 2006/1032406;

Analyte: Dithianon Method: LC-MS/MS LOQ: 0.01 mg/kg, except hops LOQ: 1 mg/kg
 Description: The analyte is extracted from the plant materials with acetonitrile/water/2 N HCl (70/25/5, v/v/v). A portion of the extract is centrifuged and an aliquot of the supernatant is diluted for determination by LC/MS-MS, monitoring for each analyte two parent-daughter ion transitions (MRMs). The first transition is used for quantitation whereas the second can be used for confirmatory purposes.

Wheat, sunflower, lettuce, green-apple, hops, ILV of SOP-PA.0281 (Jones, 2007, 2007/1017102; Bross, 2010, 2010/1062111)

Analyte: Dithianon Method: LC-MS/MS LOQ: 0.01 mg/kg, except hops LOQ: 1 mg/kg
 Description: The analyte was extracted from the homogenized plant materials with acetonitrile/water/HCl. A portion of the extract was centrifuged and an aliquot of the supernatant was diluted for determination by LC-MS/MS, monitoring each analyte with at least two parent-daughter ion transitions (MRMs).

Citrus, apple, grape, wine, plum, method number L0152/01 (Lehmann, 2011, 2010/1021354)

Analytes: Dithianon, CL 1017911 Method: LC-MS/MS LOQ: 0.01 mg/kg
 Description: The analytes were extracted from the homogenized plant materials with acetonitrile/water/2N HCl. A portion of the extract was centrifuged and an aliquot of the supernatant was diluted for determination by LC-MS/MS, monitoring for each analyte at least two parent-daughter ion transitions (MRMs).

Table 34 Recovery data from the internal (LV) and independent laboratory validation testing (ILV) for dithianon in plant commodities

Matrix	Analyte	Study	Fortification level, mg/kg	Recovery, %		RSD, %	N	Report
				mean	Range			
Apples	Dithianon	ILV	0.01	76	64-83	10	5	DT-244-068
			1.0	81	77-86	5	5	
		LV	0.01	80	74-88	7	5	
			1.0	74	71-76	3	5	

Matrix	Analyte	Study	Fortification level, mg/kg	Recovery, %		RSD, %	N	Report
				mean	Range			
Apple sauce	Dithianon	ILV	0.01	77	70-83	7	5	DT-244-068
			1.0	78	74-84	6	5	
		LV	0.01	75	69-87	10	5	
			1.0	77	68-86	10	5	
Apple juice	Dithianon	ILV	0.01	91	81-101	8	5	DT-244-068
			1.0	94	87-99	5	5	
		LV	0.01	99	86-117	12	5	
			1.0	89	81-96	7	5	
Apple dried Pomace	Dithianon	ILV	0.01	74	71-83	7	5	DT-244-068
			1.0	71	62-76	8	5	
		LV	0.01	76	62-97	17	5	
			1.0	70	63-78	8	5	
Apples	Dithianon	LV	0.02	93	83-102	7 ^{a)}	2	DT-244-055
			0.10	99	97-100		2	
			1.0	92	91-93		2	
Apples	Dithianon	LV	0.05	80		9 ^{a)}	1	DT-244-037
			0.1	90			1	
			0.25	84			1	
			0.5	70			1	
			1.0	78			1	
Grapes	Dithianon	ILV	0.01	82	74-104	16	5	DT-244-065
			1.0	72	70-74	3	4	
		LV	0.01	73	62-82	10	5	
			1.0	78	70-86	7	5	
Grape juice	Dithianon	ILV	0.01	88	85-92	3	5	DT-244-065
			1.0	87	76-92	7	5	
		LV	0.01	79	75-82	3	5	
			1.0	86	82-93	5	5	
Wine	Dithianon	ILV	0.01	85	77-90	6	5	DT-244-065
			1.0	91	90-93	1	4	
		LV	0.01	83	78-88	4	5	
			1.0	82	79-90	6	5	
Grapes	Dithianon	LV	0.02	82	77-87	7 ^{a)}	2	DT-244-054
			0.05	82	79-85		2	
			0.10	91	87-95		2	
			1.0	90	89-90		2	
Must	Dithianon	LV	0.01	103	98-108	13 ^{a)}	2	DT-244-054
			0.10	79	75-82		2	
			1.0	95	93-97		2	
Wine	Dithianon	LV	0.01	73	69-76	7 ^{a)}	2	DT-244-054
			0.10	76	75-76		2	
			1.0	83	81-85		2	
Grapes	Dithianon	LV	0.05	66		9 ^{a)}	1	DT-244-045
			0.10	72			1	
			0.25	72			1	
			0.50	84			1	
			1.0	75			1	
Must (grape)	Dithianon	LV	0.05	82		7 ^{a)}	1	DT-244-048
			0.10	96			1	
			0.25	97			1	
			0.50	87			1	
			1.0	90			1	
White wine	Dithianon	LV	0.05	70		16 ^{a)}	1	DT-244-048
			0.10	70			1	
			0.25	99			1	
			0.50	95			1	
			1.0	84			1	
Red wine	Dithianon	LV	0.05	74		10 ^{a)}	1	DT-244-048
			0.10	73			1	
			0.25	92			1	
			0.50	75			1	
			1.0	74			1	

^{a)} Overall RSD in% within the respective matrix

Table 35 Recovery data of dithianon in apples, grapes, lettuce, whole oranges, wheat grain, rape seed and dried hops (2006/1032406)

Matrix	Fortification level (mg/kg)	N	Transition m/z 296 $\rightarrow$ m/z 264		Transition m/z 296 $\rightarrow$ m/z 238	
			mean%	RSD%	mean%	RSD%
Apple	0.01	5	81	5	79	6
	3.0	5	93	17	93	16
	0.01 + 3.0	10	87	14	86	15
Grape	0.01	5	80	12	78	11
	3.0	5	101	7	102	7
	0.01 + 3.0	10	90	15	90	16
Lettuce	0.01	5	76	4	77	4
	0.10	5	82	5	80	3
	0.01 + 0.1	10	79	6	78	4
Whole orange	0.01	5	80	6	80	6
	0.10	5	80	7	79	7
	0.01 + 0.10	10	80	6	80	6
Wheat grain	0.01	5	96	12	104	9
	0.10	5	82	6	89	5
	0.01 + 0.10	10	89	13	96	11
Rape seed	0.01	5	85	18	85	20
	0.10	5	74	9	81	9
	0.01 + 0.10	10	79	16	83	15
Hops, dried	1.0	5	106	25	Interference present	
	100.0	5	101	14	106	13

Table 36 Recovery data of dithianon in wheat, sunflower, lettuce, green apple and hops, dried, ILV of SOP-PA0281 (2007/1017102)

Matrix	Fortification level (mg/kg)	n	Transition m/z 296 $\rightarrow$ m/z 264			Transition m/z 296 $\rightarrow$ m/z 238		
			mean%	SD +/-	RSD%	mean%	SD +/-	RSD%
Wheat grain	0.01	5	108	4.5	4.1	82	4.5	5.5
	0.1	5	89	8.2	9.2	87	5.7	6.6
	0.01 + 0.1	10	99	11.8	12.0	85	5.5	6.5
Sunflower seed	0.01	5	84.0	13.4	16.0	94	11.4	12.1
	0.1	5	94.0	11.4	12.1	92	4.5	4.9
	0.01 + 0.1	10	89	12.9	14.5	93	8.2	8.9
Lettuce	0.01	5	92	8.4	9.1	96	8.9	9.3
	0.2	5	98	13.0	13.3	96	8.9	9.3
	0.01 + 0.2	10	95	10.8	11.4	96	8.4	8.8
Green apple	0.01	5	84	11.4	13.6	82	8.4	10.2
	3.0	5	105	3.6	3.5	104	4.3	4.2
	0.01 + 3.0	10	95	13.8	14.6	93	13.3	14.3
Hops, dried	1.0	5	80	9.9	12.4	100	6.6	6.6
	50	5	102	3.1	3.0	106	3.6	3.4
	1.0 + 50	10	91	13.6	14.9	103	5.9	5.8

Table 37 Recovery data for dithianon, method L0152/01 (2010/1021354)

Matrix	Fort. Level, mg/kg	Transition m/z 296 $\rightarrow$ m/z 264								Transition m/z 296 $\rightarrow$ m/z 238							
		Recoveries,%						mean %	SD +/-	RSD %	Recoveries,%				mean %	SD +/-	RSD %
Citrus	0.01	86.4	85.2	85.2	82.4	84.0	85	1.5	1.8	98.4	81.2	93.6	86.4	85.2	89	6.9	7.8
	0.1	81.6	87.6	84.0	86.4	86.4	85	2.4	2.8	86.8	86.4	88.4	86.8	85.6	87	1.0	1.2
		Overall mean:						85	1.9	2.3	Overall mean:				88	4.8	5.5
Apples	0.01	88.3	89.9	85.1	75.1	77.9	83	6.5	7.8	81.3	82.1	77.7	89.7	70.9	70	6.9	8.5
	0.1	95.6	92.4	92.4	96.4	92.8	94	1.9	2.1	94.1	92.9	95.7	96.9	94.5	95	1.5	1.6
		Overall mean:						89	7.2	8.1	Overall mean:				88	9.0	10.2

Matrix	Fort. Level, mg/kg	Transition m/z 296 $\rightarrow$ m/z 264								Transition m/z 296 $\rightarrow$ m/z 238							
		Recoveries,%						mean %	SD +/-	RSD %	Recoveries,%					mean %	SD +/-
Grapes	0.01	113.3	110.9	112.1	109.7	116.5	113	2.6	2.6	126.2	124.6	122.2	114.2	111.0	120	6.7	5.6
	0.1	105.6	103.2	107.2	104.4	104.4	105	1.5	1.4	108.7	101.1	108.3	103.9	107.1	106	3.2	3.1
		Overall mean:						109	4.5	4.1	Overall mean:					113	8.8
Wine	0.01	96.2	103.8	83.3	93.0	94.2	94	7.4	7.8	97.6	100.8	96.0	90.8	93.6	96	3.8	4.0
	0.1	77.1	97.9	80.7	80.7	81.5	84	8.2	9.8	79.1	98.7	85.5	79.9	79.9	85	8.3	9.8
		Overall mean:						89	9.2	10.4	Overall mean:					90	8.4
Plums	0.01	111.6	111.2	110.4	107.2	107.2	110	2.2	2.0	119.0	118.6	112.6	108.6	105.6	113	5.9	5.3
	0.1	102.6	103.4	100.2	103.0	101.8	102	1.3	1.2	103.4	102.2	102.2	100.2	104.2	102	1.5	1.5
		Overall mean:						106	4.2	4.0	Overall mean:					108	6.9

Table 38 Recovery data for metabolite CL 1017911 (Reg. No. 4110904), method L0152/01 (2010/1021354)

Matrix	Fort. Level, mg/kg	Transition m/z 329 $\rightarrow$ m/z 109								Transition m/z 329 $\rightarrow$ m/z 82							
		Recoveries,%						mean %	SD +/-	RSD %	Recoveries,%					mean %	SD +/-
Citrus	0.01	107.2	106.8	106.4	101.6	101.6	105	2.9	2.7	118.0	106.0	102.4	102.4	99.2	106	7.3	6.9
	0.1	97.2	94.0	96.4	93.2	94.8	95	1.7	1.7	96.0	94.0	95.2	93.6	94.4	95	1.0	1.0
		Overall mean:						100	5.5	5.5	Overall mean:					100	7.6
Apples	0.01	100.4	94.0	94.0	91.6	93.2	95	3.4	3.6	98.8	98.8	93.6	93.2	91.6	95	3.4	3.5
	0.1	102.0	99.6	100.8	101.6	100.8	101	0.9	0.9	102.0	104.4	102.4	102.0	100.0	102	1.6	1.5
		Overall mean:						98	4.1	4.2	Overall mean:					99	4.4
Grapes	0.01	124.9	123.7	112.1	119.3	114.1	119	5.7	4.8	117.8	113.1	117.1	117.9	121.1	117	2.9	2.4
	0.1	113.4	112.2	112.2	113.0	109.8	112	1.4	1.2	113.1	111.5	110.7	110.3	111.9	112	1.1	1.0
		Overall mean:						116	5.3	4.6	Overall mean:					115	3.7
Wine	0.01	119.6	113.2	118.4	118.8	116.0	117	2.6	2.2	124.4	123.2	118.8	118.4	115.2	120	3.8	3.1
	0.1	122.0	115.6	120.0	114.4	121.1	119	3.4	2.9	119.6	111.6	120.0	121.2	121.2	119	4.0	3.4
		Overall mean:						118	3.0	2.5	Overall mean:					119	3.7
Plums	0.01	104.8	97.2	97.2	96.8	97.6	99	3.4	3.5	100.8	96.0	94.0	94.4	94.0	96	2.9	3.0
	0.1	99.2	100.8	98.8	96.8	98.8	99	1.4	1.4	101.2	100.4	100.4	99.2	99.6	100	0.8	0.8
		Overall mean:						99	2.5	2.5	Overall mean:					98	3.0

Animal commodities

Bovine muscle, fat, whole milk, chicken eggs, method number M 3435 (Nejad and Connolly, 2001, DT-245-007; Nejad and Connolly, 2001, DT-245-008 amendment to DT-245-007)

Analyte: dithianon Method: HPLC-ECD LOQ: 0.01 mg/kg

Description: Residues of dithianon are extracted from chicken egg, bovine whole milk, bovine muscle and fat with acidic acetonitrile. Acid organic extracts are cleaned up by liquid-liquid partitioning followed by GPC. Residues of dithianon are determined by HPLC with an electrochemical detector operating in the reductive mode. Confirmation of dithianon residues > 0.01 mg/kg is provided by HPLC/Negative Ion Electrospray Ionization Tandem MS.

Bovine muscle, fat, whole milk, chicken eggs, method number M 3435 (Bross, 2006, 2006/1034178)

Analyte: dithianon Method: HPLC-ECD LOQ: 0.01 mg/kg

Description: Samples were extracted and cleaned up as described above (DT-245-007). Residues of dithianon are determined by HPLC with an electrochemical detector (see above) operating in the reductive mode. Confirmation of dithianon residues > 0.01 mg/kg is provided by HPLC/Negative Ion Electrospray Ionization Tandem MS.

Cow liver, kidney, fat, milk, method number L0135/01 (Schweda, 2009, 2009/1045474; 2009/1045475)

Analyte: dithianon Method: LC-MS/MS LOQ: 0.01 mg/kg
 Description: Dithianon residues are extracted with a mixture of acetonitrile/water/2 N hydrochloric acid (70:25:5, v/v/v). A portion of the extract is centrifuged and an aliquot of the supernatant is cleaned by SPE on a reversed phase column. The final determination of is performed by HPLC-MS/MS, monitoring two parent-daughter ion transitions. Matrix-matched calibration solutions are necessary

Recoveries from the internal (LV) and independent laboratory validation (ILV) testing for dithianon in animal commodities based on detection via HPLC-ECD are summarized in Tables 39 and 40.

Table 39 Recoveries for spiked dithianon in animal matrices based on detection via HPLC-ECD

Matrix	Study	Fortification level, mg/kg	Recovery rate, % mean	Range	RSD %	N	Report
Chicken eggs	ILV	0.01	97	95-102	3	5	DT-245-007
		0.1	93	83-103	8	5	
	LV	0.01	93	79-111	14	5	
		0.1	93	83-99	7	5	
Whole milk	ILV	0.01	90	85-94	4	5	DT-245-007
		0.1	88	86-91	3	5	
	LV	0.01	87	79-93	8	5	
		0.1	98	82-110	14	5	
Bovine fat	ILV	0.01	88	83-100	9	4	DT-245-007
		0.1	91	77-99	12	5	
Bovine fat	LV	0.01	97	97-98	1	5	DT-245-008
		0.1	89	80-96	9	5	
Bovine muscle	ILV	0.01	97	90-101	5	5	DT-245-008
		0.1	92	86-100	7	5	
	LV	0.01	94	83-105	9	5	
		0.1	99	94-105	5	5	
Chicken eggs	LV	0.01	91	79-105	9	5	2006/1034178
		0.1	91	82-97	7	5	
Whole milk	LV	0.01	89	84-93	4	5	2006/1034178
		0.1	94	81-104	11	5	
Muscle	LV	0.01	95	88-103	7	5	2006/1034178
		0.1	96	92-101	4	5	
Fat	LV	0.01	97	85-103	8	5	2006/1034178
		0.1	94	91-98	5	5	

Table 40 Recoveries of dithianon in cow tissues and milk, method L0135/01 (2009/1045474, 2009/1045475)

Matrix	Fortification level, mg/kg	n	Transition m/z 296 $\rightarrow$ m/z 264			Transition m/z 296 $\rightarrow$ m/z 238		
			Mean recovery, %	SD +/-	RSD, %	Mean recovery, %	SD +/-	RSD, %
Liver	0.01	5	87.8	3.9	4.4	84.2	1.4	1.7
	0.1	5	85.5	2.8	3.2	82.0	0.7	0.9
	0.01 + 0.1	10	86.6	3.4	3.9	83.1	1.6	1.9
Kidney	0.01	5	84.8	3.6	4.3	78.8	6.3	8.0
	0.1	5	98.9	2.2	2.3	99.6	1.5	1.5
	0.01 + 0.1	10	91.8	7.9	8.7	89.2	11.8	13.3
Fat	0.01	5	88.4	7.6	8.6	97.4	4.4	4.5
	0.1	5	93.2	4.3	4.6	95.8	7.4	7.7
	0.01 + 0.1	10	90.8	6.3	7.0	96.6	5.8	6.0
Milk, whole	0.01	5	74.7	2.7	3.6	81.5	8.7	10.6
	0.1	5	93.0	7.1	7.6	91.1	4.3	4.8
	0.01 + 0.1	10	83.9	10.9	13.0	86.6	8.2	9.5

Stability of residues in stored analytical samples

Information was received on the freezer storage stability of dithianon residues in plant commodities. The data are summarized in Table 41. The nominal storage interval is reported in months, if available, the actual storage interval in days is shown in brackets. In general, the values are not corrected for the procedural recovery, except study DT-326-010 (hops), where only corrected values were reported.

In study 2013/1061828, incurred residues were analysed. The samples were stored as whole fruit to exclude degradation in homogenized sample matrix during storage. The stability of the analyte in homogenized samples, the re-analysis of stored homogenized samples were performed. The variability of the results for whole apples in range of 0.15–0.36 mg/kg is caused by the fact that whole apples were stored and reflect the variability of dithianon residues in apples.

Table 41 Freezer storage stability data for dithianon residues in plant matrices

Matrix	Fortification level, mg/kg	No	Storage T, °C	Months (days)	Residues remaining, mg/kg	Mean, mg /kg	Mean, %	Report, year, method number
Apples	5	3 3 3 3 3 3 3	- 20	0 1 2 4 6 12 24	3.97, 3.79, 4.24 2.67, 3.69, 4.24 2.74, 2.37, 2.64 3.32, 3.56, 3.23 3.62, 3.72, 3.09 3.38, 3.30, 3.59 2.83, 3.08, 3.37	4.0 3.5 2.6 3.4 3.5 3.4 3.1	80 71 52 67 70 68 62	DT-326-005, 1992, HUK 460/38
Apples	0.5	3 3 3 3 2 3 3	- 5	0 1 3 6 9 12 18 24	0.45, 0.41, 0.45 0.34, 0.34, 0.36 0.33, 0.32, 0.32 0.19, 0.18, 0.19 0.16, 0.16, 0.18 0.11, 0.12 0.071, 0.082, 0.058 0.043, 0.040, 0.038	0.44 0.35 0.32 0.19 0.17 0.12 0.07 0.04	87 69 65 37 34 23 15 8.0	DT-123-019, 1994, FAMS 009.001
Apples, Whole fruit	Incurred residues	2 2 2 2 2 2 2 2	- 20	0 (14) (28) (57) (89) (182) (378) (650) (733)	0.146, 0.150 0.247, 0.286 0.205, 0.245 0.303, 0.316 0.252, 0.264 0.362, 0.330 0.249, 0.238 0.330, 0.350 0.276, 0.344	0.15 0.27 0.23 0.31 0.26 0.35 0.25 0.34 0.31		2013/1061838, 2013, L0152/01
Apples, homo-genized fruits	Incurred residues	2 2 2 2 2 2 2	- 20	0 (27) (223) (316) (348) (377) (391) (762)	0.15, 0.15 0.26, 0.27 0.35, 0.26 0.20, 0.22 0.22, 0.24 0.24, 0.19 0.27, 0.26 0.22, 0.25	0.15 0.27 0.31 0.21 0.23 0.22 0.27 0.24		2013/1061838, 2013, L0152/01
Apple sauce	5	2 2 2 2 2 2	- 20	0 1 (48) 3 (91) 6 (197) 18 (511) 24 (748)	4.59, 4.48 4.26, 4.39 4.20, 4.30 3.84, 3.94 not reported not reported	4.5 4.3 4.3 3.9	91 87 85 78 79 77	2005/1029468 (final report), 2005, 2003/1001123 (interim report), RLA 12616
Pears	5	3 3 3 3 3 3 3	- 20	0 1 2 4 6 12 24	4.05, 3.84, 4.34 3.91, 3.98, 2.62 2.65, 2.92, 2.90 2.82, 3.57, 3.50 3.09, 3.44, 2.99 3.14, 3.61, 3.09 2.45, 3.00, 2.85	4.1 3.5 2.8 3.3 3.2 3.3 2.8	82 70 56 66 63 66 55	DT-326-003, 1992, HUK 460/38
Pears	1.0	3 3 3 3	- 5	0 1 3 6	0.85, 0.82, 0.69 0.64, 0.53, 0.51 0.33, 0.23, 0.33 0.18, 0.18, 0.20	0.79 0.56 0.30 0.19	79 56 27 19	DT-123-019, 1994, FAMS 009.001

Matrix	Fortification level, mg/kg	No	Storage T, °C	Months (days)	Residues remaining, mg/kg	Mean, mg/kg	Mean, %	Report, year, method number
		3		9	0.20, 0.25, 0.19	0.21	21	
		3		12	0.10, 0.11, 0.12	0.11	11	
		3		18	0.12, 0.14, 0.13	0.13	13	
		3		24	0.091, 0.042, 0.040	0.058	5.8	
		3		30	0.037, 0.018, 0.026	0.027	2.7	
Grapes	5	3	- 20	0	5.01, 5.07, 5.69	5.3	105	DT-326-007, 1992,
		3		1	3.66, 2.94, 3.13	3.2	65	HUK 460/38
		3		2	3.21, 3.51, 3.09	3.3	65	
		2		6	6.45, 3.18	3.3	66	
		3		12	3.71, 3.51, 3.30	3.5	70	
Wine grapes	Incurred residues	3	< - 18	0	4.1, 4.3, 4.4	4.3	100	DT-326-018, 1999,
		3		4	4.4, 3.6, 4.2	4.1	95	FAMS 028-02
		3		9	4.4, 4.4, 4.6	4.5	105	
		3		14	4.8, 4.7, 4.3	4.6	107	
Wine	5	2	- 20	0	3.86, 3.71	3.8	76	2005/1029468
		2		1 (61)	0.48, 0.83	0.66	13	(final report),
		2		3 (95)	3.83, 0.81	2.3	46	2005,
		2		6 (182)	0.22, 0.20	0.21	4.2	2003/1001123 (interim report), RLA 12616
Grape must	5	2	- 20	0	4.29, 4.29	4.3	86	2005/1029468
		2		1 (63)	4.30, 4.36	4.3	86	(final report),
		2		3 (91)	4.42, 4.28	4.4	87	2005,
		2		6 (186)	4.20, 4.74	4.5	89	2003/1001123 (interim report),
		2		18 (514)	Not reported		84	RLA 12616
		2		24 (749)	Not reported		77	
Grape pomace	5	2	- 20	0	3.43, 3.43	3.4	68.6	2005/1029468
		2		1 (34)	3.47, 3.72	3.6	72.0	(final report),
		2		3 (91)	3.47, 3.26	3.4	67.4	2005,
		2		6 (195)	4.01, 4.51	4.3	85.2	2003/1001123 (interim report),
		2		18 (516)	Not reported		58.0	RLA 12616
		2		24 (783)	Not reported		42.5	
Grape juice	5	2	- 20	0	4.49, 2.77	3.6	72.6	2005/1029468
		2		1 (59)	4.28, 4.30	4.3	85.8	(final report),
		2		3 (93)	4.01, 4.13	4.1	81.4	2005,
		2		6 (182)	3.95, 3.95	4.0	79.0	2003/1001123 (interim report),
		2		18 (509)	Not reported		76.5	RLA 12616
		2		24 (748)	Not reported		69.5	
Cereal grain, not speci-fied	5	3	Not reported	0	4.19, 4.18, 3.57	4.0	79.6	DT-326-004, 1992
		3		1	2.68, 2.93, 2.56	2.7	54.4	
		3		2	2.78, 2.97, 2.86	2.9	57.4	
		3		4	2.78, 2.60, 2.79	2.7	54.4	
		3		6	2.90, 3.34, 2.74	3.0	59.8	
Cereal straw, not speci-fied	5	3	Not reported	0	3.41, 3.50, 3.85	3.6	71.8	DT-326-004, 1992
		3		1	2.26, 1.82, 1.93	2.0	40.0	
		3		2	2.24, 1.43, 1.71	1.8	35.8	
		3		4	1.57, 1.43, 1.52	1.5	30.2	
		3		6	2.03, 1.76, 1.73	1.8	36.8	
Hops, green cones	5	2	< -18	0 (1)	4.32, 3.99	4.2	83	DT-326-010, 1994,
	5	2		3 (84)	4.34, 4.38	4.4	88	P-14.005.02
	5	2		6 (180)	3.99, 3.50	3.8	75	Values corrected for procedural recovery
	50	2		0 (1)	43.00, 40.27	42	84	
	50	2		3 (84)	37.03, 41.85	39	79	
	50	2		6 (180)	38.99, 40.95	40	80	
Hops, dried cones	10	2	< - 18	0 (1)	7.99, 9.28	8.6	87	DT-326-010, 1994,
	10	2		3 (84)	7.64, 6.99	7.3	73	P-14.005.02
	10	2		6 (180)	8.63, 8.50	8.6	86	Values corrected for procedural recovery
	100	2		0 (1)	93.06, 92.41	93	93	
	100	2		3 (84)	87.11, 86.93	87	87	
	100	2		6 (180)	83.73, 83.76	84	84	
Beer	0.5	2	< - 18	0 (1)	0.37, 0.35	0.36	72	DT-326-010, 1994,
		2		0.5 (16)	0.38, 0.42	0.40	80	P-14.005.02
		2		1 (31)	0.46, 0.43	0.45	90	Values corrected for procedural recovery

Matrix	Fortification level, mg/kg	No	Storage T, °C	Months (days)	Residues remaining, mg/kg	Mean, mg /kg	Mean, %	Report, year, method number
Hops, yeast	0.5	2	< - 18	0 (1)	0.43, 0.37	0.41	81	DT-326-010, 1994, P-14.005.02 Values corrected for procedural recovery
		2		0.5 (16)	0.45, 0.47	0.46	92	
		2		1 (31)	0.43, 0.39	0.41	83	
Spent hops	0.5	2	< - 18	0 (1)	0.43, 0.39	0.41	82	DT-326-010, 1994, P-14.005.02 Values corrected for procedural recovery
		2		0.5 (16)	0.55, 0.49	0.52	105	
		2		1 (31)	0.41, 0.40	0.41	81	
		2		2 (59)	0.38, 0.45	0.42	84	

Information was received on the freezer storage stability of the metabolite Reg. No. 4110904 in plant commodities. The data are summarized in Table 42. The values reported are not corrected for the procedural recovery.

Table 42 Freezer storage stability data for the metabolite Reg. No. 4110904 in plant matrices

Matrix	Fortification level, mg/kg	No of analysis	Storage T, °C	Days	Residues remaining, mg/kg	Mean, mg/kg	Mean, %	Report, year, method number
Apples	1.0	2	- 20	0	0.956, 0.968	0.962	96.2	2013/1061837, 2013, L0152/01
		2		7	0.656, 0.684	0.670	67.0	
		2		13	not reported	-	-	
		2		43	1.07, 1.04	1.06	106	
		2		95	0.792, 0.788	0.79	79.0	
		2		368	0.769, 0.801	0.785	78.5	
		2		739	0.788, 0.872	0.83	83.0	
		2		818	0.604, 0.664	0.634	63.4	
Plums	1.0	2	- 20	0	0.904, 0.956	0.930	93.0	2013/1061837, 2013, L0152/01
		2		7	0.836, 0.860	0.844	84.4	
		2		13	0.824, 0.820	0.822	82.2	
		2		43	1.04, 1.02	1.03	103	
		2		95	0.783, 0.783	0.783	78.3	
		2		368	0.753, 0.777	0.765	76.5	
		2		739	0.800, 0.832	0.816	81.6	
		2		818	0.648, 0.660	0.654	65.4	
Grapes	1.0	2	- 20	0	0.937, 0.785	0.861	86.1	2013/1061837, 2013, L0152/01
		2		7	0.706, 0.750	0.728	72.8	
		2		13	0.660, 0.704	0.682	68.2	
		2		43	0.936, 0.908	0.922	92.2	
		2		95	0.664, 0.628	0.646	64.6	
		2		368	0.684, 0.644	0.664	66.4	
		2		739	0.676, 0.644	0.660	66.0	
		2		818	0.524, 0.584	0.554	55.4	
Wine	1.0	2	- 20	0	0.856, 0.852	0.854	85.4	2013/1061837, 2013, L0152/01
		2		7	0.634, 0.694	0.664	66.4	
		2		13	0.728, 0.724	0.726	72.6	
		2		43	1.02, 0.968	0.994	99.4	
		2		95	0.736, 0.748	0.742	74.2	
		2		368	0.842, 0.838	0.840	84.0	
		2		739	1.11, 1.07	1.09	109	
		2		818	0.688, 0.728	0.708	70.8	
Lemon	1.0	2	- 20	0	0.816, 0.820	0.818	81.8	2013/1061837, 2013, L0152/01
		2		7	0.562, 0.538	0.550	55.0	
		2		13	0.543, 0.555	0.549	54.9	
		2		43	0.652, 0.696	0.674	67.4	
		2		95	0.484, 0.512	0.498	49.8	
		2		368	0.519, 0.491	0.505	50.5	
		2		739	0.520, 0.564	0.542	54.2	
		2		818	0.408, 0.440	0.424	42.4	

USE PATTERNS

The fungicide dithianon is registered in many countries for control of diseases on a large variety of crops. Dithianon is applied either as solo product or in combinations with other active substances as cymoxanil, dimethomorph, pyraclostrobin and pyrimethanil. The information available to the Meeting on registered uses on citrus fruits, pome fruits, stone fruits, berries and other small fruits, tree nuts and hops is summarized in Table 43 and refers for application rates etc. to dithianon only. Labels were submitted by the manufacturer.

Table 43 Registered uses of dithianon

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Citrus fruits	Argentina	SC	Spraying	1–4	15	0.068	4000	2.7	14
Citrus fruits	Spain	SC	Spraying			0.038– 0.053			
Citrus fruits	Japan	SC	Spraying	1–3	10	0.012– 0.015	2000–7000	0.84–2.94	30
Citrus fruits	Taiwan	WG	Foliar spraying			0.053 - 0.093	1500–2000	1.05–1.4	
Citrus fruits	Uruguay	SC, WP				0.075–0.1			30
Mandarin	Korea	WG	Foliar spraying	5	10	0.044	4800–5200	2.11–2.29	14
Mandarin	Korea	WP	Foliar spraying	3	30	0.026	4800–5200	1.25–1.35	7
Mandarin	Korea	SC	Foliar spraying	5	14	0.043	4800–5200	2.06–2.24	21
Mandarin	Korea	WP	Foliar spraying	3	10	0.075	4800–5200	3.6–3.9	30
Mandarin	Korea	WG	Foliar spraying	5	15	0.03	4800–5200	1.44–1.56	14
Mandarin	Korea	SE	Foliar spraying	3	10	0.012	4800–5200	0.58–0.62	7
Mandarin	Korea	WP	Foliar spraying	3	14	0.03	4800–5200	1.44–1.56	30
Pome fruits	Austria	WG	Foliar spraying	12		0.035	500 (per m crown height)	0.18 (per m crown height)	21
Pome fruits	Bulgaria	WG	High volume spraying	1–12	7–12	0.035– 0.088	400–1000	0.35	20
Pome fruits	Czech Republic	WG	Spraying		8–14	0.049– 0.163	300–1000	0.49	21
Pome fruits	Estonia	WG	High volume spraying	3	7	0.035	1000	0.35	21
Pome fruits	France	WG	High volume spraying	1–7	7	0.023– 0.175	200–1500	0.35	14
Pome fruits	Germany	WG	Foliar spraying	12		0.035	500 (per m crown height)	0.18 (per m crown height)	21
Pome fruits	Germany	WG	Foliar spraying	4	10 -14	0.02	500 (per m crown height)	0.1 (per m crown height)	35
Pome fruits	Hungary	WG	High volume spraying		7–10	0.025– 0.044	800–1000	0.25–0.35	21

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Pome fruits	Slovakia	WG	High volume spraying		8–14	0.049– 0.163	300–1000	0.49	21
Pome fruits	Spain	SC	Spraying	1–5	8	0.038–0.07	800–1000	0.38–0.56	21
Apple	Argentina	SC	Spraying	1–4	15	0.053	2000	1.05	14
Apple	Belgium	WG	High volume spraying	1–18	7–10	0.03–0.263	200–1500	0.45–0.53	28
Apple	Belgium	WG	Spraying	1–4	8–10	0.023	1000	0.23	35
Apple	Belarus	WG	Foliar spraying	6	5–7	0.035– 0.049	1000	0.35–0.49	20
Apple	Belarus	WG	Foliar spraying	4	10–14	0.024–0.03	1000	0.24–0.3	35
Apple	Bulgaria	WG	High volume spraying	1–4	7	0.052	1500	0.78	28
Apple	Chile	WG	Foliar spraying	1–14	7	0.052	1500	0.78	28
Apple	Croatia	WG	Spraying	1–6		0.035– 0.053	1000	0.35–0.53	35
Apple	Croatia	WG	Spraying	1–4		0.024–0.03	1000	0.24–0.3	35
Apple	Cyprus	WG	Foliar Spraying	4		0.028– 0.112	1000–2000	0.56–1.01	21
Apple	Cyprus	WG	Foliar Spraying	4		0.018–0.07	1000–2000	0.35–0.7	21
Apple	Cyprus	WG	Foliar Spraying	4		0.026– 0.14	1000–2000	0.53–1.4	21
Apple	Cyprus	WG	Foliar Spraying	3	10–14	0.015–0.03	1000–1500	0.23–0.3	35
Apple	Czech Republic	WG	Spraying	3	7–10	0.03–0.1	300–1000	0.3	35
Apple	Denmark	WG	High volume spraying	10–15	10			0.7	21
Apple	Georgia	WG	High volume spraying	3	7–10	0.035– 0.098	500–1000	0.35–0.49	30
Apple	Georgia	WG	High volume spraying	3	7–10	0.024–0.06	500–1000	0.24–0.3	30
Apple	Greece	WG	Foliar Spraying	4		0.028– 0.112	1000–2000	0.56–1.01	21
Apple	Greece	WG	Foliar Spraying	4		0.018–0.07	1000–2000	0.35–0.7	21
Apple	Greece	WG	Foliar Spraying	4		0.026–0.14	1000–2000	0.53–1.4	21
Apple	Greece	SC	Foliar Spraying	4		0.03–0.12	1000–2000	0.6–1.2	21
Apple	Greece	SC	Foliar Spraying	4		0.019– 0.075	1000–2000	0.38–0.75	21
Apple	Greece	SC	Foliar Spraying	4		0.025–0.15	1000–2000	0.5–1.5	21
Apple	Greece	WG	Foliar Spraying	3	10–14	0.015–0.03	1000–1500	0.23–0.3	35
Apple	Ireland	SC	Foliar spraying	8	10–14	0.038– 0.638	200–1000	0.38–1.28	28

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Apple	Ireland	WG	Foliar spraying	12	7–14	0.053– 0.263	200–1000	0.53	21
Apple	Israel	SC	Foliar spraying	2–4	7–12	0.05	600–1200		
Apple	Italy	WG	High volume spraying	6–8	7–10	0.046– 0.126	1000–1500	0.7–1.26	21
Apple	Italy	WG	High volume spraying	6–8	7–10	0.037– 0.063	1000–1500	0.56–0.63	21
Apple	Italy	SC	High volume spraying	6–8	7–10	0.043–0.12	1000–1500	0.65–1.2	21
Apple	Italy	SC	High volume spraying	6–8	7–10	0.04–0.09	1000–1500	0.6–0.9	21
Apple	Italy	WP	High volume spraying	6–8	7–10	0.044– 0.119	1000–1500	0.66–1.19	21
Apple	Italy	WP	High volume spraying	6–8	7–10	0.035– 0.089	1000–1500	0.53–0.89	21
Apple	Italy	WG	Spraying	1–4	8–14	0.02	1500	0.3	35
Apple	Japan	SC	Spraying	1–3	10	0.012– 0.147	2000–7000	0.84–2.09	60
Apple	Japan	SC	Spraying	1–3	10	0.006– 0.147	2000–7000	0.42–2.94	60
Apple	Latvia	WG	High volume spraying	6	7–14	n.a.	500 (per m crown height)	0.25–0.5	21
Apple	Lithuania	WG	High volume spraying	2–6	8–14	0.035–0.1	700–1000	0.35–0.7	21
Apple	Luxem- bourg	WG	High volume spraying	1–18	7–10	0.023–0.26 (BBCH 7– 67) 0.011– 0.123 (BBCH 67– 79)	200–1500	0.35–0.52 0.16–0.25	28
Apple	Macedonia	WG	Spraying	2–3	10–14	0.035– 0.053	1000	0.35–0.53	35
Apple	Macedonia	WG	Spraying	4	10	0.024– 0.030	1000–1200	0.24–0.30	35
Apple	Moldova	WG	High volume spraying	4	7–10	0.035– 0.098	500–1000	0.35–0.49	30
Apple	Moldova	WG	High volume spraying	2–3	7–10	0.024–0.06	500–1000	0.24–0.3	35
Apple	Netherlands	WG	Spraying	1–12	7	0.019– 0.105	500–100	0.19–0.53	28
Apple	Poland	WG	Spraying	6	5	0.05–0.21	250–750	0.35–0.53	21
Apple	Poland	WG	Spraying	2	12	0.032–0.12	250–750	0.24–0.3	35
Apple	Portugal	WG	High volume spraying		8–10	0.035– 0.044	800–1000	0.35	21

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Apple	Romania	WG	Spraying	1–5	7–10	0.035	1000	0.35	21
Apple	Romania	WG	Spraying	3	12	0.027	1000	0.27	35
Apple	Russia	WG	Foliar spraying	5	7–14	0.035– 0.049	1000	0.35–0.49	28
Apple	Russia	WG	Foliar spraying	3	10–14	0.024–0.03	1000	0.35–0.49	20
Apple	Serbia	WG	Foliar spraying	1–3		0.053–0.07	1000	0.53–0.7	35
Apple	Serbia	WG	Foliar spraying	1–3		0.009– 0.012	1000	0.09–0.12	35
Apple	Slovakia	WG	Spraying	2–3	12	0.03–0.05	600–1000	0.3	35
Apple	Slovenia	WG	Spraying	1–5		0.035	1000	0.35	21
Apple	Slovenia	WG	Spraying	1–3	10	0.03	1000	0.3	35
Apple	United Kingdom	SC	Foliar spraying	8	10–14	0.056– 0.413	200–1000	0.56–0.83	28
Apple	United Kingdom	WG	Foliar spraying	12	7–14	0.053– 0.263	200–1000	0.53	28
Apple	United Kingdom	SC, WG	Foliar spraying	4	7–10	0.03–0.15	200–1000	0.3	7–10
Apple	Uruguay	SC, WP	Foliar spraying			0.05–0.08			21
Medlar	Spain	SC	Drip application	1–5	8	0.031– 0.084	800–1200	0.38–0.67	14
Medlar	Hungary	WG	Spraying	4	10–16	0.02– 0.0375	800–1200	0.24–0.3	35
Pear	Argentina	SC	Spraying	1–4	15	0.034	2000	0.67	21
Pear	Austria	WG	Foliar spraying	4		0.035 up to BBCH 65	500 (per m crown height)	0.18 (per m crown height)	F ^a Up to BBCH 65
Pear	Austria	WG	Foliar spraying	8		0.035	500 (per m crown height)	0.18 (per m crown height)	21
Pear	Belgium	WG	High volume spraying	1–18	7–10	0.03–0.263	200–1500	0.45–0.53	28
Pear	Belgium	WG	Spraying	1–4	8–10	0.023	1000	0.23	35
Pear	Belarus	WG	Foliar spraying	6	5–7	0.035– 0.049	1000	0.35–0.49	20
Pear	Croatia	WG	Spraying	1–6		0.035– 0.053	1000	0.35–0.53	35
Pear	Denmark	WG	High volume spraying	10–15	10			0.7	21
Pear	Georgia	WG	High volume spraying	3	7–10	0.035– 0.098	500–1000	0.35–0.49	30
Pear	Georgia	WG	High volume spraying	3	7–10	0.024–0.06	500–1000	0.24–0.3	30
Pear	Germany	WG	Foliar spraying	4		0.035	500 (per m crown height)	0.18 (per m crown height)	F ^a Up to BBCH 65
Pear	Germany	WG	Foliar spraying	8		0.035	500 (per m crown height)	0.18 (per m crown height)	21

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Pear	Greece	WG	Foliar Spraying	4		0.028– 0.112	1000–2000	0.56–1.01	21
Pear	Greece	WG	Foliar Spraying	4		0.018–0.07	1000–2000	0.35–0.7	21
Pear	Greece	WG	Foliar Spraying	4		0.026–0.14	1000–2000	0.53–1.4	21
Pear	Greece	SC	Foliar Spraying	4		0.03–0.12	1000–2000	0.6–1.2	21
Pear	Greece	SC	Foliar Spraying	4		0.019– 0.075	1000–2000	0.38–0.75	21
Pear	Greece	SC	Foliar Spraying	4		0.025–0.15	1000–2000	0.5–1.5	21
Pear	Greece	SC	Foliar Spraying	4		0.038– 0.075	1000–2000	0.38–0.75	21
Pear	Greece	WG	Foliar Spraying	3	10–14	0.015 – 0.03	1000–1500	0.23–0.3	35
Pear	Hungary	WG	Spraying	4	10–16	0.02– 0.0375	800–1200	0.24–0.3	35
Pear	Ireland	SC	Foliar spraying	8	10–14	0.038– 0.638	200–1000	0.38–1.28	28
Pear	Ireland	WG	Foliar spraying	12	7–14	0.053– 0.263	200–1000	0.53	21
Pear	Israel	SC	Foliar spraying	2–4	7–12	0.05	600–1200		
Pear	Italy	WG	High volume spraying	6–8	7–10	0.037– 0.084	1000–1500	0.56–0.84	21
Pear	Italy	WG	High volume spraying	3–4	7–10	0.105	1000	1.05	21
Pear	Italy	SC	High volume spraying	6–8	7–10	0.04–0.09	1000–1500	0.60–0.9	21
Pear	Italy	SC, WP	High volume spraying	3–4	7–10	0.1	1000	1.0	21
Pear	Italy	WP	High volume spraying	6–8	7–10	0.035– 0.079	1000–1500	0.53–0.79	21
Pear	Italy	WG	Spraying	1–3	8–14	0.02	1500	0.3	35
Pear	Japan	SC	Spraying	1–4		0.012– 0.147	2000–7000	0.84–2.94	60
Pear	Lithuania	WG	High volume spraying	2–6	7–14	0.0525–0.1	700–1000	0.525–0.7	21
Pear	Luxem- bourg	WG	High volume spraying	1–18	7–10	0.023–0.26	200–1500	0.35–0.52	28
Pear	Macedonia	WG	Spraying	4	10	0.032– 0.040	1000–1200	0.32–0.40	35
Pear	Nether-lands	WG	Spraying	1–12	7	0.019– 0.105	500–100	0.19–0.53	28
Pear	Portugal	WG	High volume spraying		8–10	0.035– 0.044	800–1000	0.35	21
Pear	Romania	WG	Spraying	1–5	7–10	0.035	1000	0.35	21
Pear	Slovenia	WG	Spraying	1–5		0.035	1000	0.35	21

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Pear	Slovenia	WG	Spraying	1–3	10	0.03	1000	0.3	35
Pear	United Kingdom	SC	Foliar spraying	8	10–14	0.056–0.413	200–1000	0.56–0.83	28
Pear	United Kingdom	WG	Foliar spraying	12	7–14	0.053–0.263	200–1000	0.53	28
Pear	United Kingdom	WG	Foliar spraying	4	7–10	0.03–0.012	250–1000	0.3	7–10
Pear	Uruguay	SC, WP	Foliar spraying			0.05–0.08			21
Quince	Cyprus	WG	Foliar Spraying	4		0.028–0.112	1000–2000	0.56–1.01	28
Quince	Cyprus	WG	Foliar Spraying	4		0.018–0.07	1000–2000	0.35–0.7	28
Quince	Greece	WG	Foliar Spraying	4		0.028–0.112	1000–2000	0.56–1.01	28
Quince	Greece	WG	Foliar Spraying	4		0.018–0.07	1000–2000	0.35–0.7	28
Quince	Greece	SC	Foliar Spraying	4		0.03–0.12	1000–2000	0.6–1.2	28
Quince	Greece	SC	Foliar Spraying	4		0.025–0.15	1000–2000	0.5–1.5	28
Quince	Greece	SC	Foliar Spraying	4		0.019–0.075	1000–2000	0.38–0.75	28
Quince	United Kingdom	SC	Foliar spraying	8	10–14	0.056–0.413	200–1000	0.56–0.83	28
Stone fruits	Estonia	WG	High volume spraying	3	7	0.035	1000	0.35	21
Stone fruits	Hungary	WG	High volume spraying	2–3	7–10	0.053–0.066	800–1000	0.53	21
Cherries	Austria	WG	Foliar Spraying	3		0.035	500 (per m crown height)	0.18 (per m crown height)	21
Cherries	Belgium	WG	High volume spraying	1–6	10	0.047–0.245	300–1500	0.7–0.74	28
Cherries	Bulgaria	WG	High volume spraying	1–6	7–14	0.035–0.088	400–1000	0.35	20
Cherries	Cyprus	WG	Foliar spraying	2	-	0.024	1500	0.35	28
Cherries	Denmark	WG	High volume spraying	3	10			0.7	21
Cherries	France	WG	High volume spraying	3	7–10	0.033–0.245	200–1500	0.49	14
Cherries	Germany	WG	Foliar Spraying	3		0.035	500 (per m crown height)	0.18 (per m crown height)	21
Cherries	Greece	WG	Foliar spraying	2		0.024	1500	0.35	28
Cherries	Greece	SC	Foliar spraying	2		0.025	1500	0.38	28

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Cherries	Lithuania	WG	High volume spraying	2–4	14	0.035–0.1	700–1000	0.35–0.7	21
Cherries	Luxem- bourg	WG	High volume spraying	2	10	0.032–0.23	300–1500	0.49–0.7	28
Cherries	Luxem- bourg	WG	High volume spraying	3	10–15	0.012– 0.058	300–1500	0.175	28
Cherries	Netherlands	WG	Spraying	1–3	7	0.019– 0.105	500–1000	0.19–0.53	
Cherries	Serbia	WG	Foliar spraying	1–2		0.053–0.07	1000	0.53–0.7	35
Cherries	Slovakia	WG	High volume spraying		14	0.049– 0.163	300–1000	0.49	28
Cherry sour	Belgium	WG	High volume spraying	1–6	10	0.047–0.23	300–1500	0.7 High trees: 0.15–0.74	28
Cherry sour	Czech Republic	WG	Spraying	1–5	14	0.047–0.23	300–1000	0.49	28
Cherry sweet	Czech Republic	WG	Spraying	1–5	14	0.047–0.23	300–1000	0.49	28
Cherry sweet	Lithuania	WG	High volume spraying	2–4	14	0.035–0.1	700–1000	0.35–0.7	21
Plums	Belarus	WG	Foliar Spraying	2	5–7	0.049	1000	0.49	39
Plums	Cyprus	WG	Foliar spraying	2		0.023	1500	0.35	28
Plums	Cyprus	SC	Foliar spraying	2		0.025	1500	0.38	28
Plums	France	WG	High volume spraying	3	7–10	0.023– 0.175	200–1500	0.35	14
Plums	Greece	WG	Foliar spraying	2		0.023	1500	0.35	28
Plums	Greece	SC	Foliar spraying	2		0.025	1500	0.38	28
Plums	Lithuania	WG	High volume spraying	2–4	14	0.053–0.1	700–1000	0.53–0.7	21
Plums	Luxembourg	WG	High volume spraying	2		0.007– 0.175	300–1500	0.11–0.53	28
Plums	Romania	WG	Spraying	1–5	7–10	0.024– 0.035	1000	0.24–0.35	21
Cherry plum	France	WG	High volume spraying	3	7–10	0.023– 0.175	200–1500	0.35	14
Apricot	Austria	WG	Foliar spraying	3	10–14	0.035	500 (per m crown height)	0.18 (per m crown height)	F ^a
Apricot	Belgium	WG	High volume spraying	3		0.042–0.21	300–1500	0.63	28
Apricot	Belgium	WG	High volume spraying	3		0.059– 0.294	300–1500	0.88	28

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Apricot	Bulgaria	WG	High volume spraying	1–6	7–14	0.035– 0.088	400–1000	0.35	20
Apricot	Croatia	WG	Spraying			0.053–0.07	1000	0.53–0.7	35
Apricot	Cyprus	WG	Foliar spraying	2		0.056–0.07	1500	0.84–1.05	28
Apricot	France	WG	High volume spraying	4	7–10	0.023– 0.175	200–1500	0.35	28
Apricot	France	WG	High volume spraying	4	7–10	0.033– 0.245	200–1500	0.49	
Apricot	Georgia	WG	High volume spraying	3	7–10	0.035– 0.098	500–1000	0.35–0.49	20
Apricot	Germany	WG	Foliar spraying	3	10–14	0.035	500 (per m crown height)	0.18 (per m crown height)	F ^a
Apricot	Greece	WG	Foliar spraying	2		0.056–0.07	1500	0.84–1.05	28
Apricot	Greece	SC	Foliar spraying	2		0.07	1500	1.05	28
Apricot	Greece	SC	Foliar spraying	2		0.06–0.07	1500	0.90–1.05	28
Apricot	Israel	SC		2–4	7–12		600–1200		
Apricot	Luxembourg	WG	High volume spraying	1–2	10–14	0.023–0.21	300–1500	0.35–0.63	28
Apricot	Luxembourg	WG	High volume spraying	1–2		0.032– 0.294	300–1500	0.49–0.88	28
Nectarine	Cyprus	WG	Foliar spraying	2		0.07	1500	1.05	28
Nectarine	Greece	SC, WG	Foliar spraying	2		0.056–0.07	1500	0.84–1.05	28
Nectarine	Japan	SC	Spraying	1		0.02–0.245	2000–7000	1.4–4.9	90
Nectarine	Japan	SC	Spraying	1		0.012– 0.245	2000–7000	0.84–4.9	90
Nectarine	Luxembourg	WG	High volume spraying	1–2	10–14	0.023–0.21	300–1500	0.35–0.63	28
Nectarine	Luxembourg	WG	High volume spraying	1–2		0.032– 0.294	300–1500	0.49–0.88	28
Nectarine	Luxembourg	WG	High volume spraying	1–2		0.023– 0.117	300–1500	0.35	28
Peach	Argentina	SC	Spraying	1–4	15	0.067	1500	1.01	21
Peach	Austria	WG	Foliar spraying	3	10–14	0.035	500 (per m crown height)	0.18 (per m crown height)	F ^a
Peach	Azerbaijan	WG	High volume spraying	2	7–10	0.035– 0.098	500–1000	0.35–0.49	20
Peach	Belgium	WG	High volume spraying	3		0.042–0.21	300–1500	0.63	28
Peach	Belgium	WG	High volume spraying	3		0.059– 0.294	300–1500	0.88	28

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Peach	Bulgaria	WG	High volume spraying	1–6	7–14	0.035– 0.088	400–1000	0.35	20
Peach	Croatia	WG	Spraying			0.053–0.07	1000	0.53–0.7	35
Peach	Cyprus	WG	Foliar spraying	2		0.056 - 0.07	1500	0.84–1.05	28
Peach	Czech Republic	WG	Spraying		10–14	0.07–0.233	300–1000	0.7	
Peach	France	WG	High volume spraying	4	7–10	0.023– 0.175	200–1500	0.35	28
Peach	France	WG	High volume spraying	4	7–10	0.033– 0.245	200–1500	0.49	
Peach	Georgia	WG	High volume spraying	3	7–10	0.035– 0.098	500–1000	0.35–0.49	20
Peach	Germany	WG	Foliar spraying	3	10–14	0.035	500 (per m crown height)	0.18 (per m crown height)	F ^a
Peach	Greece	SC, WG	Foliar spraying	2		0.056 - 0.07	1500	0.84–1.05	28
Peach	Israel	SC		2–4	7–12	0.05	600–1200		
Peach	Italy	WG	High volume spraying	3	7–10	0.07–0.105	1000–1500		21
Peach	Italy	SC, WP	High volume spraying	3	7–10	0.058–0.1	1000–1200	0.7–1.0	21
Peach	Luxembourg	WG	High volume spraying	1–2	10–14	0.023–0.21	300–1500	0.35–0.63	28
Peach	Luxembourg	WG	High volume spraying	1–2		0.032– 0.294	300–1500	0.49–0.88	28
Peach	Moldova	WG	High volume spraying	4	7–10	0.035– 0.098	500–1000	0.35–0.49	30
Peach	Serbia	WG	Foliar spraying	1–2		0.0525– 0.07	1000	0.53–0.7	F ^a Until BBCH 51
Peach	Slovakia	WG	High volume spraying		10–14	0.070– 0.233	300–1000	0.7	28
Peach	Taiwan	SC	Foliar spraying	3–5	7–10	0.025–0.1	1500–3000	0.75–1.5	30
Peach	Ukraine	WG	High volume spraying	3	7–10	0.07–0.14	500–1000	0.7	20
Peach	Uruguay	SC, WP				0.1			21
Berries	Netherlands	WG	Spraying	1–3	7	0.07	1000–1200	0.84	
Blueberries	Belgium	WG	High volume spraying	3	7	0.098– 0.326	300–1000	0.98	
Blueberries	Belarus	WG	Foliar spraying	2	10–14	0.06	500	0.3	50

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Blueberries	Luxembourg	WG	High volume spraying	3	7	0.098– 0.326	300–1000	0.98	
Currants	Belgium	WG	High volume spraying	3	7	0.098– 0.326	300–1000	0.98	
Currants	France	WG	High volume spraying	2	7–10	0.033– 0.245	200–1500	0.49	14
Currants	Luxembourg	WG	High volume spraying	3	7	0.098– 0.326	300–1000	0.98	
Currant, black	France	WG	High volume spraying	2	7–10	0.033– 0.245	200–1500	0.49	14
Currant, black	Lithuania	WG	High volume spraying	2–4	10–14	0.07–0.14	500	0.35–0.7	21
Currant, red	Lithuania	WG	High volume spraying	2–4	10–14	0.07–0.14	500	0.35–0.7	21
Bilberry, red	Belgium	WG	High volume spraying	3	7	0.098– 0.326	300–1000	0.98	
Bilberry, red	Luxembourg	WG	High volume spraying	3	7	0.098– 0.326	300–1000	0.98	
Blackberry	Belgium	WG	High volume spraying	3		0.098– 0.326	300–1000	0.98	14
Blackberry	Luxembourg	WG	High volume spraying	2–3		0.098– 0.326	300–1000	0.98	14
Cranberry	Belarus	WG	Foliar spraying	6	5–7	0.07–0.098	500	0.35–0.49	70
Cranberry	Belarus	WG	Foliar spraying	2	10–14	0.048–0.06	500	0.24–0.3	50
Gooseberry	Belgium	WG	High volume spraying	3	7	0.098– 0.326	300–1000	0.98	
Gooseberry	Lithuania	WG	High volume spraying	2–4	10–14	0.07–0.14	500	0.35–0.7	21
Gooseberry	Luxembourg	WG	High volume spraying	2–3	7	0.098– 0.326	300–1000	0.98	
Grapes	Argentina	SC	Spraying	1–4	15	0.053–0.14	500–1000	0.53–0.7	21
Grapes	Belgium	WG	Spraying	1		0.05	1000	0.5	48
Grapes	Belarus	WG	Foliar spraying	6	5–7	0.042– 0.053	800–1000	0.42	30
Grapes	Bulgaria	WG	High volume spraying	1–8	7–12	0.035– 0.088	400–1000	0.35	20
Grapes	Croatia	WG	Spraying	1–6		0.026	1000	0.26	49
Grapes	Cyprus	WG	Foliar spraying	4		0.028–0.14	500–1000	0.28–0.7	28

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Grapes	France	WG	High volume spraying	2		0.041– 0.123	4000–1200	0.49	42
Grapes	Georgia	WG	High volume spraying	3	7–10	0.035– 0.098	500–1000	0.35–0.49	30
Grapes	Georgia	WG	High volume spraying	3	7–10	0.053–0.14	500–1000	0.53–0.7	30
Grapes	Greece	WG	Foliar spraying	4		0.028–0.14	500–1000	0.28–0.7	28
Grapes	Greece	SC	Foliar spraying	4		0.03–0.15	500–1000	0.3–0.75	28
Grapes	Greece	WG	Foliar spraying	3	10–12	0.021– 0.084	500–1000	0.21–0.42	28
Grapes	Hungary	WG	High volume spraying		7–10	0.025– 0.058	600–1000	0.25–0.35	28
Grapes	Italy	WG, WP	High volume spraying	3–5	7–10	0.046– 0.126	800–1200	0.56–1.01	40
Grapes	Japan	SC	Spraying	1–2		0.014– 0.175	2000–7000	1.00–3.5	75
Grapes	Japan	SC	Spraying	1		0.071– 0.875	2000–7000	5.0–17.5	Dormancy application
Grapes	Moldavia	WG	High volume spraying	3–4	7–10	0.053–0.14	500–1000	0.525–0.7	30
Grapes	Morocco	WG		3	7–12			0.53	
Grapes	Romania	WG	Spraying	1–5	7–10	0.035	1000	0.35	21
Grapes	Russia	WG	Foliar spraying	6	7–14	0.035– 0.061	800–1000	0.35–0.49	28
Grapes	Russia	WG	Foliar spraying	3	10–12	0.042– 0.053	1000	0.42–0.53	30
Grapes	Serbia	WG	Foliar spraying	1–3		0.026– 0.035	1000	0.26–0.35	35
Grapes	Slovakia	WG	High volume spraying		8–14	0.035	1000	0.35	21
Grapes	Slovenia	WG	Spraying	1–8		0.035	1000	0.35	42
Grapes	Slovenia	WG	Spraying	1–8		0.053	1000	0.53	42
Grapes	Ukraine	WG	High volume spraying	3	7–10	0.035–0.14	500–1000	0.35–0.7	30
Grapes	Uruguay	SC, WP				0.05–0.1			21
Table grapes	Macedonia	WG	Foliar spraying	3		Basic: 0.021–0.17 GS 61: 0.042 – 0.34 GS 71: 0.063–0.5 GS 73: 0.068–0.5	100–800	Basic: 0.17 GS 61: 0.34 GS 71: 0.5 GS 73: 0.55	35

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Wine grapes	Austria	WG	Foliar spraying	8 (per crop and year)		0.053	Basic: 400 GS 61: 800	Basic: 0.21 GS 61: 0.42	49
Wine grapes	Austria	WG	Foliar spraying	3		0.042	Basic: 400 GS 61: 800 GS 71: 1200 GS 73: 1300	Basic: 0.17 GS 61: 0.34 GS 71: 0.5 GS 73: 0.55	35
Wine grapes	Austria	WP	Spraying	5	8–14	0.025	1000	0.25	42
Wine grapes	Austria	WP	Spraying	3	8–14	0.0313	1000	0.313	42
Wine grapes	France	WG	Spraying	3		0.21–0.525	100–250	0.53	35
Wine grapes	Germany	WG	Foliar spraying	8 (per crop and year)		0.053	Basic: 400 GS 61: 800	Basic: 0.21 GS 61: 0.42	49
Wine grapes	Germany	WG	Foliar spraying	3		0.042	Basic: 400 GS 61: 800 GS 71: 1200 GS 73: 1300	Basic: 0.17 GS 61: 0.34 GS 71: 0.5 GS 73: 0.55	35
Wine grapes	Italy	WG	Spraying	1–3	10–12	0.043– 0.053	1000	0.44–0.53	40
Wine grapes	Luxembourg	WG	High volume spraying	1		0.049	1000	0.49	48
Wine grapes	Macedonia	WG	Foliar spraying	3		Basic: 0.021–0.17 GS 61: 0.042 – 0.34 GS 71: 0.063–0.5 GS 73: 0.068–0.55	100–800	Basic: 0.17 GS 61: 0.34 GS 71: 0.5 GS 73: 0.55	35
Wine grapes	Netherlands	WG	Foliar spraying	3	7–10	0.14	150	0.21	42 BBCH 19–59
Raspberries	Belgium	WG	High volume spraying	3	14	0.098– 0.326	300–1000	0.98	
Raspberries	France	WG	High volume spraying	2	7–10	0.033– 0.245	200–1500	0.49	14
Raspberries	Lithuania	WG	High volume spraying	2–4	10–14	0.105–0.14	500	0.525–0.7	21
Raspberries	Luxembourg	WG	High volume spraying	2–3		0.098– 0.326	300–1000	0.98	14
Strawberry	Japan	SC	Spraying	1–2		0.014– 0.126	1000–3000	0.42–1.26	
Strawberry	Uruguay	SC, WP	Spraying			0.1			21
Tree nuts	Luxembourg	WG	High volume spraying	1		0.049	1000	0.49	
Almonds	France	WG	High volume spraying	2	7–10	0.023– 0.175	200–1500	0.35	58

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Almonds	France	WG	High volume spraying	2	7–10	0.033– 0.245	200–1500	0.49	
Almonds	Israel	SC		2–4	7–12	0.05	600–1200		
Almonds	Luxembourg	WG	High volume spraying	2		0.35	1000	0.35	
Walnut	France	SC	High volume spraying	1	7–10	0.35–0.263	200–1500	0.53	42
Walnut	France	WG	High volume spraying	1	7–10	0.033– 0.245	200–1500	0.35	42
Hops	Austria	WG	Foliar spraying	10				until GS 37: 0.63 until GS 55: 0.98 at GS 55: 1.4	14
Hops	Austria	WP	Spraying	2	10–14	0.007– 0.094	400–1500	0.1–0.375	14
Hops	Belgium	WG	Spraying	1–8	7–10	0.035	1000	0.35	28
Hops	Cyprus	WG	Foliar spraying	4		0.046–0.07	2500	1.12–1.75	28
Hops	Germany	WG	Foliar spraying	10				until GS 37: 0.63 until GS 55: 0.98 at GS 55: 1.4	14
Hops	Greece	SC, WG	Foliar spraying	4		0.045– 0.075	2500	1.13–1.88	28
Hops	Luxembourg	WG	High volume spraying	1–8	7–10	0.035	1000	0.35	28
Hops	Slovenia	WG	Spraying	1–8		0.035	1000	0.35	14

^a F: PHI is fixed by the approved use

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised field trials for dithianon uses that produced residues on the following commodities:

Crop Group	Commodity	Tables
Citrus fruits	Citrus fruits	44
Pome fruits	Apple	45, 46
	Pear	47
Stone fruits	Cherries	48, 49
	Peaches	50, 51
		52, 53
Berries and other small fruits	Grapes	54, 55
	Currants, black	56

Crop Group	Commodity	Tables
Tree nuts	Almonds	57
Dried herbs	Hops, dry	58

Conditions of the supervised residue trials were generally well reported in detailed field reports. However, some trials conducted in the 1970s and 1980s were reported in summary tables only. Laboratory reports generally included method validation with procedural recoveries from spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analysis or duration of residue sample storage were provided in most cases, if not, it is indicated in the relevant table.

Because of the age of many trials, the analytical methods used are described in the text and are listed in the tables below. Residue data are recorded unadjusted for recovery. Undetected residues were generally reported lower than the LOQ. Residues and application rates have generally been rounded to two significant figures. Residue values from the trials conducted according to maximum GAP, or, in case of exceeding the ARfD, according to an alternative GAP, have been used for the estimation of maximum residue levels. Those results included in the evaluation are underlined.

In some supervised trials on apples, cherries, peaches, plums and grapes, residues of the parent dithianon and the metabolite 5,6-dicyano-3-(2-hydroxybenzoyl)-1,4-dithiine-2-carboxylic acid (Reg. No. 411094) were analysed.

Citrus fruits

The reports for dithianon residues in citrus fruits conducted in Japan were submitted in the Japanese language but only with a short English explanation. Trials were carried out on mandarins (varieties unshiu, mikan, satsuma), pomelos (natsudaikai, variety amanatsu), citrus sudachi and citrus sphaerocarpa (variety kabosu). Trials were carried out either indoors “G” or outdoors “F”. Peel and pulp samples were analysed separately. The residues in whole fruits were calculated from the weight ratio of peel and pulp.

Samples were analysed using HPLC with UV-detection in parallel in different analytical laboratories: Japan Food Research Laboratories (JFRL), Institute of Environmental Toxicology (IET), Tahara Laboratories, Dainihon Jochugiku or in the Japanese Food Analysis Center (JFAC). Average recoveries in pulp and peel as reported in the English summary, ranged between 77% and 93%; LODs were reported as 0.01–0.02 mg/kg for pulp and 0.02–0.05 mg/kg for peel. The residue trials data are presented in Table 44.

Table 44 Dithianon residues in citrus fruits, scaled residue values are shown in brackets

Country, year, location, F/G ^{a)} (variety)	Application				PHI, days	Commodity	Residue, mg/kg	Doc ID-No, analysis facility
	Form	kg ai/hL	Water L/ha	No				
Japan, 1990, Kagawa, G Mandarin (Unshiu Mikan)	SC	0.5	5000	3	21	Pulp	0.23	2012/1278420, analysis by JFRL, LOQ 0.02 mg/kg
					30	Pulp	0.05	
					21	Peel	16	
					30	Peel	12	
					21	Whole fruit	2.9	
					30	Whole fruit	2.2	
					21	Pulp	0.20	2012/1278420, analysis by IET, LOQ 0.01 mg/kg
					30	Pulp	0.09	
					21	Peel	13	
					30	Peel	12	
					21	Whole fruit	2.3	
					30	Whole fruit	2.2	
					30	Mean fruit	2.2	
					30	Mean pulp	0.07	

Country, year, location, F/G ^{a)} (variety)	Application				PHI, days	Commodity	Residue, mg/kg	Doc ID-No, analysis facility
	Form	kg ai/hL	Water L/ha	No				
Japan, 1990, Kagoshima, G Mandarin (Unshiu Mikan)	SC	0.5	5000	3	20	Pulp	0.08	2012/1278420, analysis by JFRL, LOQ 0.02 mg/kg
					29	Pulp	0.06	
					20	Peel	1.5	
					29	Peel	2.6	
					20	Whole fruit	0.45	
					29	Whole fruit	0.68	
					20	Pulp	0.11	2012/1278420, analysis by IET, LOQ 0.01 mg/kg
					29	Pulp	0.04	
					20	Peel	2.1	
					29	Peel	2.6	
					20	Whole fruit	0.62	
					29	Whole fruit	0.72	
					29	Mean fruit	0.7	
					29	Mean pulp	0.05	
Japan, 1990, Shizuoka, F Pomelo (Natsudaidai)	SC	0.5	5000	3	23	Pulp	< 0.02	2012/1278421, analysis by JFRL, LOQ 0.02 mg/kg
					32	Pulp	< 0.02	
					45	Pulp	< 0.02	
					60	Pulp	< 0.02	
					23	Peel	3.8	
					32	Peel	3.4	
					45	Peel	1.1	
					60	Peel	3.1	
					23	Whole fruit	1.1	
					32	Whole fruit	1.0	
					45	Whole fruit	0.36	2012/1278421, analysis by IET, LOQ 0.01 mg/kg
					60	Whole fruit	0.86	
					22	Pulp	0.01	
					32	Pulp	0.01	
					50	Pulp	0.02	
					60	Pulp	0.01	
					22	Peel	4.1	
					32	Peel	3.7	
					50	Peel	2.7	
					60	Peel	4.1	
					22	Whole fruit	1.2	
					32	Whole fruit	1.1	
					50	Whole fruit	0.76	
					60	Whole fruit	1.2	
					32	Mean fruit	1.05	
					50	Pulp	0.02	
Japan, 1990, Ehime, F Pomelo (Natsudaidai)	SC	0.5	5000	3	20	Pulp	< 0.02	2012/1278421, analysis by JFRL, LOQ 0.02 mg/kg
					30	Pulp	< 0.02	
					46	Pulp	< 0.02	
					60	Pulp	< 0.02	
					20	Peel	4.7	
					30	Peel	4.2	
					46	Peel	3.5	
					60	Peel	3.4	
					20	Whole fruit	1.5	
					30	Whole fruit	1.4	
					46	Whole fruit	0.92	
					60	Whole fruit	1.2	

Country, year, location, F/G ^{a)} (variety)	Application				PHI, days	Commodity	Residue, mg/kg	Doc ID-No, analysis facility
	Form	kg ai/hL	Water L/ha	No				
					20	Pulp	0.02	2012/1278421, analysis by IET, LOQ 0.01 mg/kg
					30	Pulp	< 0.01	
					46	Pulp	0.08	
					60	Pulp	< 0.01	
					20	Peel	3.4	
					30	Peel	4.6	
					46	Peel	3.8	
					60	Peel	4.3	
					20	Whole fruit	1.1	
					30	Whole fruit	1.5	
					46	Whole fruit	1.3	
					60	Whole fruit	1.4	
					30	Mean fruit	1.45	
					46	Mean pulp	0.05	
Japan, 1984, Mie, F Mandarin (Unshiu)	WP	0.7	6000	3	14	Pulp	< 0.01	2012/1278423, analysis by Dainihon Jochugiku, LOQ 0.01 mg/kg
					30	Pulp	< 0.01	
					45	Pulp	0.01	
					14	Peel	9.4	
					30	Peel	3.5	
					45	Peel	2.6	
					14	Whole fruit	2.0	
					30	Whole fruit	0.78	
					45	Whole fruit	0.65	
					14	Pulp	< 0.04	2012/1278423, analysis by JFAC, LOQ 0.04 mg/kg
					30	Pulp	< 0.04	
					45	Pulp	< 0.04	
					14	Peel	7.9	
					30	Peel	2.1	
					45	Peel	2.2	
					14	Whole fruit	1.68	
					30	Whole fruit	0.49	
					45	Whole fruit	0.56	
					30	Mean fruit	0.64 (0.46)	
					45	Mean pulp	< 0.025 (< 0.018)	
Japan, 1984, Mie, F Mandarin (Unshiu)	WP	0.7	6000	5	14	Pulp	< 0.01	2012/1278423, analysis by Dainihon Jochugiku, residue in whole fruit were not calculated
					30	Pulp	< 0.01	
					45	Pulp	< 0.01	
					14	Peel	5.6	
					30	Peel	5.4	
					45	Peel	4.5	
					14	Pulp	< 0.04	2012/1278423, analysis JFAC, residues for whole fruit not calculated
					30	Pulp	< 0.04	
					45	Pulp	< 0.04	
					14	Peel	3.4	
					30	Peel	4.9	
					45	Peel	5.4	
Japan, 1984, Saga, F Mandarin (Unshiu)	WP	0.7	5000	3	30	Mean pulp	< 0.025 (< 0.018)	2012/1278423, analysis by Dainihon Jochugiku, LOQ 0.01 mg/kg
					16	Pulp	< 0.01	
					32	Pulp	< 0.01	
					46	Pulp	0.01	
					16	Peel	13	
					32	Peel	4.7	
					46	Peel	1.7	
					16	Whole fruit	2.8	
					32	Whole fruit	1.0	
					46	Whole fruit	0.43	

Country, year, location, F/G ^{a)} (variety)	Application				PHI, days	Commodity	Residue, mg/kg	Doc ID-No, analysis facility
	Form	kg ai/hL	Water L/ha	No				
					16	Pulp	< 0.04	2012/1278423, analysis by JFAC, LOQ 0.04 mg/kg
					32	Pulp	< 0.04	
					46	Pulp	< 0.04	
					16	Peel	10	
					32	Peel	6.0	
					46	Peel	2.6	
					16	Whole fruit	2.2	
					32	Whole fruit	1.3	
					46	Whole fruit	0.65	
					32	Mean fruit	1.15 (0.82)	
Japan, 1984, Saga, F Mandarin (Unshiu)	WP	0.58	6000	5	46	Mean pulp	< 0.025 (< 0.018)	2012/1278423, analysis by Dainihon Jochugiku, residues in whole fruit not calculated
					16	Pulp	0.03	
					32	Pulp	< 0.01	
					46	Pulp	< 0.01	
					16	Peel	9.1	
					32	Peel	1.2	
					46	Peel	2.9	
					16	Pulp	< 0.04	
					32	Pulp	< 0.04	
					46	Pulp	< 0.04	
					16	Peel	6.6	
					32	Peel	3.3	
					46	Peel	1.8	
					32	Mean pulp	< 0.025 (< 0.021)	
Japan, 2001, Tokushima, F (Sudachi)	SC	0.5	4000	3	21	Whole fruit	1.2	2012/1278422, analysis by Tahara Lab.
					28		0.84 (1.2)	
					42		0.66	
Japan, 2001, Ohita, F (Kabosu)	SC	0.5	6400	3	21	Whole fruit	2.2	2012/1278422, analysis by Tahara Lab.
					28		2.5 (2.3)	
					42		0.94	

^{a)} G indoor, F outdoor

Apple

During the years 1975–2003, trials were conducted in Northern and Southern Europe. In 2003, different products were tested in three plots side-by-side (Doc ID-No. 2004/1000752). The summary of the residue trials data for apple, whole fruit, is presented in Table 45. The samples were analysed as follows:

Apples from trials conducted during 1975–1985 were analysed by similar methods using HPLC-UV (e.g. RU 107/34/10) or by colorimetry (Merck-Method M 101/67; only for two trials in 1975), all of which were validated at 0.03–0.05 mg/kg and for which procedural recoveries of dithianon were 70–110%.

For trials conducted from 1990–1995, samples were analysed using method FAMS 028-02 for which procedural recoveries of dithianon fortified in fruit at 0.02–1.0 mg/kg were 91–103%; or the samples were analysed using methods similar to FAMS 028-02, such as method FAMS 009-01 and HUK 460/38. Using the latter methods, recoveries of parent obtained from apple fruit fortified at 0.05–1.9 mg/kg were 74–95%.

Most of the samples from the trials conducted in the years 2000 were analysed with method RLA 12616 or further versions, which quantifies dithianon using HPLC with UV detection and an LOQ of 0.01 mg/kg in apple fruit. Procedural recoveries of dithianon fortified in whole fruit at 0.01 mg/kg were 70–110%. HPLC-UV methods similar to RLA 12616 were employed to analyse samples from the remaining trials.

Table 45 Dithianon residues in apples

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1975, Oberraderach, (Golden Delicious), F 75-01-06-01	SC	Foliar spray	0.63	420	14	0 2 7 15 22	1.0 0.5 0.03 <0.03 <0.03	DT-711-005, Colorimetric method Merck M 101/67, not further specified, LOQ 0.03 mg/kg
Germany, 1975 Kippenhausen (Golden Delicious) F 75-01-06-02	SC	Foliar spray	0.63	1800	13	0 3 7 15 22	0.4 0.2 < 0.05 < 0.05 < 0.05	DT-711-006, Colorimetric method Merck M 101/67, not further specified, LOQ 0.03 mg/kg
Germany, 1985 Hagnau (Boskop) C 85 11 06b	SC	Foliar spray	0.6	400	13	0 7 14 21	0.85 0.31 0.48 0.48	DT-711-009, Method not specified, HPLC-UV, LOQ 0.05 mg/kg
Germany, 1985 Ingelheim (Golden Delicious) C 85 11 72 01d	SC	Foliar spray	0.56	500	12	0 7 14 21 28 35	2.6 2.1 2.1 1.9 1.0 0.95	DT-711-013, Method not specified, HPLC-UV, LOQ 0.05 mg/kg
Germany, 1985 Hagnau (Boskop) C 85 11 06a	SC	Foliar Spray	4 × 0.81 9 × 0.61	400	13	0 7 14 21	0.72 0.46 0.41 0.38	DT-711-019, Method not specified, HPLC-UV, LOQ 0.05 mg/kg
Germany, 1985 Ingelheim (Golden Delicious) C 85 11 72 02b	SC	Foliar Spray	3 × 0.76 9 × 0.6	500	12	0 7 14 21 28 35	1.8 2.1 1.5 1.0 1.3 0.82	DT-711-020, Method not specified, HPLC-UV, LOQ 0.05 mg/kg
France South, 1990 not reported (Red Delicious) FRA-90-01	SC	Foliar Spray	0.53	393 - 536	14	0 3 7 14 21 80	4.4 3.8 1.7 1.9 1.7 0.39	DT-711-085, HUK 460/38
Germany, 1993 Bornheim- Breuig (Jonica) SKG-9302-01	SC	Foliar Spray	0.55 - 0.64 last treatment0.56	737 - 833	12	0 21	2.5 1.7	DT-711-094, FAMS 028-02
Germany, 1993 Mühlheim-Klärlich (Gloster) SKG-9302-02	SC	Foliar Spray	0.55 - 0.57	735 - 754	12	0 21	1.6 1.5	DT-711-095, FAMS 028-02
Germany, 1995 Bornheim-Breuig (Berlepesch) 95-082-01	WG	Foliar spray	0.53 - 0.55	1510 - 1576	12	-0 0 5 11 17 21	0.47 0.92 0.93 0.68 0.32 0.36	DT-711-098, FAMS 028-02
Germany, 1995 Euskirchen-Dorn Esch (Gloster) 95-082-02	WG	Foliar spray	0.53 - 0.54	1501 - 1528	12	-0 0 7 11 16 21	0.84 1.3 0.86 0.89 1.1 0.48	DT-711-098 FAMS 028-02
Germany, 1995 Meckenheim- Altendorf (Elstar)	WG	Foliar spray	0.51 - 0.54	721 - 773	12	-0 0 7 11	1.1 2.3 1.3 1.0	DT-711-098, FAMS 028-02

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
95-082-03						16 21	1.2 0.76	
Germany, 1995 Koblenz-Gülz (Jonagold) 95-082-04	WG	Foliar spray	0.51 - 0.55	730 - 792	12	-0 0 6 11 17 21	0.96 1.5 1.0 0.94 0.77 0.62	DT-711-098, FAMS 028-02
France South, 2000 Saint Andiol (Golden Delicious) 00-981-640	WG	Foliar spray	0.48–0.55 last treatment 0.51	922 - 1044	12	21	0.13	DT-711-104, RLA 12616
France South, 2000 Saint Andiol (Golden Delicious) 00-981-640	WG	Foliar spray	0.67–0.73 last treatment 0.69	958 - 1044	8	21	0.18	DT-711-104, RLA 12616
France South, 2000 Noves (Golden Delicious) 00-981-641	WG	Foliar spray	0.5–0.57 last treatment 0.54	943 - 1083	12	-0 +0 3 7 14 21	0.14 0.53 0.50 0.40 0.34 0.24	DT-711-105, RLA 12616
France South, 2000 Noves (Golden Delicious) 00-981-641	WG	Foliar spray	0.68–0.73 last treatment 0.72	971 - 1048	8	-0 +0 3 7 14 21	0.03 0.57 0.47 0.27 0.12 0.18	DT-711-105, RLA 12616
Italy, 2000 Fossanova, San Marco (Golden) 00-801-01	WG	Foliar spray	0.53	1250	12	21	0.20	2002/1011502, RLA 12620.00V
Italy, 2000 Fossanova, San Marco (Golden) 00-801-01	WG	Foliar spray	0.7	1250	8	21	0.13	2002/1011502, RLA 12620.00V
Italy, 2000 Fossanova, San Marco (Red Chief) 00-802-01	WG	Foliar spray	0.53	1250	12	0- 0+ 3 7 14 21	0.13 0.39 0.28 0.18 0.21 0.12	2002/1011501, RLA 12620.00V
Italy, 2000 Fossanova, San Marco (Red Chief) 00-802-01	WG	Foliar spray	0.7	1250	8	0- 0+ 3 7 14 21	0.06 0.35 0.26 0.16 0.12 0.10	2002/1011501, RLA 12620.00V
Spain, 2001 Calatorao, Zaragoza (Golden Smooth) ALO/45/01	WG	Foliar spray	0.53	1000	12	0 7 15 21 28	0.70 0.74 0.47 0.37 0.43	2002/1011505, RLA 12616
Spain, 2001 Calatorao, Zaragoza (Golden Smooth) ALO/45/01	WG	Foliar spray	0.7	1000	8	0 7 15 21 28	0.81 0.60 0.61 0.39 0.43	2002/1011505, RLA 12616
Spain, 2001 Calatorao, Zaragoza (Red Chief)	WG	Foliar spray	0.53	1000	12	0 7 15	1.4 1.0 0.82	2002/1011505, RLA 12616

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
ALO/46/01						21 28	0.85 0.86	
Spain, 2001 Calatorao, Zaragoza (Red Chief) ALO/46/01	WG	Foliar spray	0.7	1000	8	0 7 15 21 28	1.6 1.7 0.72 1.0 0.98	2002/1011505, RLA 12616
Greece, 2001 Arnissa, Macedonia (Granny Smith) HEL/06/01	WG	Foliar spray	0.53	1000	12	0 7 14 21 28	2.1 0.79 0.89 0.04 0.59	2002/1011505, Method RLA 12616
Greece, 2001 Arnissa, Macedonia (Granny Smith) HEL/06/01	WG	Foliar spray	0.7	1000	8	0 7 14 21 28	1.3 1.3 0.92 0.19 0.07	2002/1011505, RLA 12616
Italy, 2001 Piemonte (Golden Delicious) ITA/24/01	WG	Foliar spray	0.53	1000	12	0 7 14 21 29	1.9 1.5 2.2 1.7 1.5	2002/1011505, RLA 12616
Italy, 2001 Piemonte (Golden Delicious) ITA/24/01	WG	Foliar spray	0.7	1000	8	0 7 14 21 29	2.9 2.1 2.5 1.4 1.2	2002/1011505, RLA 12616
Belgium, 2003 Limburg (Decofta) AGR/09/03	WG	Foliar spray	0.35	1000	4	0 21 28 35 42	0.19 0.09 0.05 0.10 0.04	2004/1000752, RLA 12616.05V
	WG	Foliar spray	0.35	1000	4	0 21 28 35 42	0.33 0.11 0.10 0.09 0.08	
	WG	Foliar spray	0.3	1000	4	0 21 28 35 42	0.26 0.13 0.11 0.11 0.04	
	WG	Foliar Spray	0.35	1000	4	0 20 27 34 41	0.64 0.34 0.15 0.30 0.25	
	WG	Foliar Spray	0.35	1000	4	0 20 27 34 41	0.49 0.48 0.12 0.39 0.34	
	WG	Foliar spray	0.3	1000	4	0 20 27 34 41	0.46 0.30 0.30 0.29 0.32	
	WG	Foliar spray	0.35	1000	4	0 20 28 35 42	0.14 0.09 0.11 0.05 0.04	
	WG	Foliar spray	0.35	1000	4	0 20 28 35 42	0.14 0.09 0.11 0.05 0.04	
	WG	Foliar spray	0.35	1000	4	0 20 28 35 42	0.14 0.09 0.11 0.05 0.04	
France North, 2003 Alsace (Golden) FAN/09/03	WG	Foliar spray	0.35	1000	4	0 20 28 35 42	0.14 0.09 0.11 0.05 0.04	2004/1000752, RLA 12616.05V

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha					
	WG	Foliar spray	0.35	1000	4	0	0.50		
						20	0.15		
						28	0.21		
						35	0.13		
						42	0.11		
	WG	Foliar spray Foliar spray	0.3	1000	4	0	0.33		
						20	0.15		
						28	0.11		
						35	0.14		
						42	0.08		
France South, 2003 Midi-Pyrenees (Star Kimson) FTL/05/03	WG	Foliar spray	0.35	1000	4	0	0.70	2004/1000752, RLA 12616.05V	
						21	0.33		
						28	0.15		
						35	0.20		
						42	0.16		
	WG	Foliar spray	0.35	1000	4	0	0.98		
						21	0.31		
						28	0.36		
						35	0.34		
	WG	Foliar spray	0.3	1000	4	0	1.1		
						21	0.52		
						28	0.37		
						35	0.42		
						42	0.43		
Italy, 2003 Piemonte (Cooper) ITA/07/03	WG	Foliar spray	0.35	1000	4	0	0.58	2004/1000752, RLA 12616.05V	
						21	0.50		
						29	0.26		
						35	0.20		
						42	0.13		
	WG	Foliar spray	0.35	1000	4	0	0.85		
						21	0.70		
						29	0.39		
	WG	Foliar spray	0.3	1000	4	0	0.86		
						21	0.44		
						29	0.27		
						35	0.29		
						42	0.22		

During the 2010 growing season, a total of 11 field trials were conducted in Germany, the United Kingdom, Belgium, the Netherlands, France, Greece, Italy and Spain. Specimens were analysed for dithianon and its metabolite Reg. No. 4110904 using method No. L0152/01 with a LOQ of 0.01 mg/kg. The results for apple, whole fruit are summarized in Table 46.

Table 46 Residues of dithianon and metabolite Reg. No. 4110904 in apples

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			Dithianon	4110904	
Germany, 2010 Werneuchen (Jonagold) L100477	WG	Foliar spray	0.36	1000	4	0	0.39	< 0.01	2011/1059016, L0152/01
						28	0.05	< 0.01	
						35	0.06	0.01	
						42	0.05	0.01	
UK, 2010 Cottenham (Discovery) L100478	WG	Foliar Spray	0.36	1000	4	0	0.08	< 0.01	2011/1059016, L0152/01
						29	< 0.01	< 0.01	
						36	< 0.01	0.01	
						43	< 0.01	0.01	

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			Dithianon	4110904	
Belgium, 2010 Fleurus (Cabarette) L100479	WG	Foliar Spray	0.36	1000	4	0 28 35 42	0.30 0.17 0.16 0.07	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
The Netherlands, 2010 LC Homoet (Elstar) L100480	WG	Foliar Spray	0.36	1000	4	0 28 35 42	0.31 0.04 0.02 0.02	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
France North, 2010 Saint Hilaire-saint-Mesmin (Golden) L100481	WG	Foliar Spray	0.36	1000	4	0 28 35 42	0.33 0.16 0.10 0.08	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
Spain, 2010 Bellvis (Golden Delicious) L100482	WG	Foliar Spray	0.36	1000	4	0 28 35 42	0.55 0.21 0.14 0.14	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
Greece, 2010 Nea-Trapezounda (Fuji) L100483	WG	Foliar Spray	0.36	1000	4	0 29 36 42	0.77 0.40 0.22 0.27	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
France South, 2010 Orange (Smothie) L100484	WG	Foliar Spray	0.36	1000	4	0 28 36 42	0.50 0.16 0.21 0.12	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016,L0152/01
Italy, 2010 Arcagna Montanaso L.do (Top Red) L100485	WG	Foliar Spray	0.36	1000	4	0 28 35 42	1.8 0.32 0.48 0.65	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016,L0152/01
Spain, 2010 Bellvis (Granny Smith) L100486	WG	Foliar Spray	0.36	1000	4	0 28 35 42	0.15 0.08 0.02 0.02	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
Italy, 2010 Faedo Valtellino (Stark) L100487	WG	Foliar Spray	0.36	1000	4	0 28 36 42	0.35 0.27 0.34 0.12	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016,L0152/01

Pear

Four field trials with pears were conducted in 2004 in Northern France, Denmark, Germany and the Netherlands. The specimens were analysed for residues of dithianon according to method M 3442 (= RLA 12616) with an LOQ of 0.01 mg/kg. The residue trials data for pear, whole fruit are presented in Table 47.

Table 47 Residues of dithianon in pears

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
Germany, 2004 Werder, Brandenburg (Conference) ACK/04/04	WG	Foliar spray	0.53	1000	12	0 7 14 22 29	0.85 0.61 0.19 0.19 0.18	2005/1014012, RLA 12616

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
The Netherlands, 2004 Limburg (Doyenné du Comice) AGR/05/04	WG	Foliar spray	0.53	1000	12	0 8 15 21 28	1.9 0.82 0.79 0.37 0.30	2005/1014012, RLA 12616
Denmark, 2004 Fuenen (Clara Friis) ALB/01/04	WG	Foliar spray	0.53	1000	12	0 7 14 21 28	1.7 0.86 0.82 0.69 0.87	2005/1014012, RLA 12616
France North, 2004 Alsace (Williams) FAN/04/04	WG	Foliar spray	0.53	1000	12	0 7 14 21 28	2.0 0.74 0.52 0.39 0.33	2005/1014012, RLA 12616

Cherries

Trials on cherries were conducted in Germany in the years 1985, 1986 and 1995. The residue data (whole fruit) are summarized in Table 48. Samples from 1985 and 1986 were analysed for dithianon residues by method CM-RU 107/34/10 (HPLC-UV) with an LOQ of 0.05 mg/kg and a recovery of about 75%. The samples from the trials conducted in the year 1995 were analysed by method FAMS 028-01 (HPLC-UV). The LOQ for dithianon was 0.02 mg/kg in cherry fruit with recoveries at 89%.

Table 48 Residues of dithianon in cherries, sour

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1985 Schwabenheim (Schattenmorellen) C 85 12 72 B	SC	Foliar spray	0.53	500	3	0 14 21 28	1.9 1.3 0.80 0.41	DT-712-006, CM-RU 107/34/10
Germany, 1986 Schwabenheim (Schattenmorellen) C 86 02 72 D	SC	Foliar spray	0.53	390	3	0 14 21 28 35	2.5 0.92 0.49 0.26 0.20	DT-712-007, CM-RU 107/34/10
Germany, 1986 Schwabenheim (Schattenmorellen) C 86 02 72 S	SC	Foliar spray	0.53	390	3	0 14 21 28 35	2.2 0.86 0.28 0.22 0.12	DT-712-008, CM-RU 107/34/10
Germany, 1995 Bornheim-Brenig (Schattenmorellen) 95-078-01	WG	Foliar spray	0.53	1500	3	-0 +0 9 15 22 28	0.48 2.9 0.86 0.34 0.17 0.12	DT-712-028, FAMS 028-01
Germany, 1995 Meckenheim Altendorf (Schattenmorellen) 95-078-02	WG	Foliar spray	0.53	1500	3	-0 +0 8 14 21 28	0.77 1.6 1.1 1.3 0.34 0.23	DT-712-028, FAMS 028-01

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha					
Germany, 1995 Grafschaft Gelsdorf (Schattenmorellen) 95-078-03	WG	Foliar spray	0.53	750	3	-0 +0 8 14 21 28	1.5 3.5 1.2 0.97 0.41 0.26		DT-712-028, FAMS 028-01
Germany, 1995 Winningen, Mosel (Schattenmorellen) 95-078-04	WG	Foliar spray	0.53	750	3	-0 +0 8 15 22 28	2.0 2.0 1.1 0.63 0.20 0.26		DT-712-028, FAMS 028-01

In 2009 and 2010, trials with sweet and sour cherries were conducted in France, Germany, Italy, Greece, the Netherlands, the United Kingdom and Spain in order to determine the residues of dithianon and its metabolite Reg. No. 4110904. The results for whole fruits are summarized in Table 49. Samples were analysed with method L0152/01 for dithianon (LOQ 0.01 mg/kg) and its metabolite Reg. No. 4110904 (LOQ 0.01 mg/kg). The recoveries were 93–94% for dithianon and 89–111% for the metabolite Reg. No. 4110904 at fortification levels of 0.01 and 0.1 mg/kg.

Table 49 Residues of dithianon and metabolite Reg. No. 4110904 in cherries, sweet and sour

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			Dithianon	4110904	
United Kingdom, 2010, Essex (Stella) Cherries, sweet, L100277	WG	Foliar spray	0.53	1000	3	0 13 20 26	2.4 1.0 0.59 0.34	0.05 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
France (S), 2010 Goult, (Folfer) Cherries, sweet L100281	WG	Foliar spray	0.53	1000	3	0 14 21 26	1.4 0.27 0.15 0.19	0.3 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
Greece, 2010 Pella, (Bourla) Cherries, sweet L100282	WG	Foliar spray	0.53	1000	3	0 14 21 26	1.3 0.20 0.04 0.03	0.02 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
The Netherlands, 2010, Ressen, (Morellenfeuer) Cherries, sour L100279	WG	Foliar spray	0.53	1000	3	0 13 20 26	3.0 0.95 0.21 0.82	0.05 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
Germany, 2010, Gau Algesheim (Schattenmorellen) Cherries, sour L100280	WG	Foliar spray	0.53	1000	3	0 13 20 26	3.0 1.2 0.89 1.0	0.04 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
Italy, 2010, Castellfranco, (Marasca di Vigo) Cherries, sour L100283	WG	Foliar spray	0.53	1000	3	0 14 20 26	3.7 0.33 0.19 0.17	0.02 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
Italy, 2010, Modena, (Montmoreny) Cherries, sour L100284	WG	Foliar spray	0.53	1000	3	0 14 20 25	3.2 1.5 0.90 0.63	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			Dithianon	4110904	
Germany, 2009 Gau Algesheim (Sweet heart) CFL0008-01	WG	Foliar spray	0.53	1000	3	0 13 20 27	0.99 0.74 0.50 0.19	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
France North, 2009/2010 Coulanges la Vineuse (Hedelfinger) CFL0008-02	WG	Foliar spray	0.53	1000	3	0 14 21 28	1.4 0.33 0.09 0.08	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
The Netherlands, 2009, Ressen (Kelleriis 16) CFL0008-03	WG	Foliar spray	0.53	1000	3	0 14 21 28	1.3 0.58 0.38 0.20	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
UK, 2009 Boxford, (Morello) CFL0008-04	WG	Foliar spray	0.53	1000	3	0 13 20 27	2.0 0.89 0.69 0.08	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
Spain, 2010 Beniaia (Sweet heart) CFL0008-05	WG	Foliar spray	0.53	1000	3	0 14 21 28	2.6 0.72 0.43 0.13	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
Greece, 2010 Platani, Pella (Lapin) CFL0008-06	WG	Foliar spray	0.53	1000	3	0 14 21 28	1.4 0.81 0.45 0.33	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
France South, 2010 Apt, (Montmorency) CFL0008-07	WG	Foliar spray	0.53	1000	3	0 14 21 28	2.5 0.59 0.57 0.52	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
Italy, 2010 Rivoli Veronese (Stevemberg) CFL0008-08	WG	Foliar spray	0.53	1000	3	0 14 21 28	1.1 0.28 0.21 0.17	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01

Peach

Trials with dithianon on peaches were conducted in 2001 in Southern France. Fruits were analysed with a “GRAPPA in-house” HPLC-method (UV-detection) for dithianon (LOQ 0.05 mg/kg) using extraction with 2N hydrochloric acid and dichloromethane. After some purification steps the extract is further purified by using SPE (Sep-Pak Florisil Plus). The recovery of dithianon in peaches ranged from 78 to 85%. The data are summarized in Table 50.

Table 50 Residues of dithianon in peaches

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No
	Form	Method	kg ai/ha	Water L/ha					
France South, 2001 Montfavet (Flavorcrest) RE01029	WG		0.45	960 - 980	2	25 25	Whole fruit Pulp	0.24 0.25	2002/1025517
France South, 2001 Grabeson (Fantasia) RE01030	WG		0.46	580 - 600	2	28 28	Whole fruit Pulp	0.05 0.05	2002/1025517
France South, 2001 Montans (Red Top) RE01031	WG		0.47	790 - 830	2	27 27	Whole fruit Pulp	0.14 0.15	2002/1025517

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No
	Form	Method	kg ai/ha	Water L/ha					
France South, 2001 Montans (Dixired) RE01032	WG		0.46	800 - 805	2	28 28	Whole fruit Pulp	0.13 0.14	2002/1025517

Trials on peaches were conducted in 2009 and 2010 in Germany, France, Greece, Italy and Spain. Specimens were analysed by method L0152/01 for dithianon and its metabolite Reg. No. 4110904 (LOQ each 0.01 mg/kg). The recoveries were about 81% for dithianon and about 102% for the metabolite Reg. No. 4110904 at fortification levels of 0.01 and 0.1 mg/kg. The results for peaches, whole fruit are summarized in Table 51.

Table 51 Residues of dithianon and metabolite Reg. No. 4110904 in peaches

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Germany, 2009 Windischenbach (Red Heaven) CFL0006-01	WG	Foliar spray	0.53	1000	3	0 20 27 34	4.2 1.6 0.66 0.60	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
France (N), 2009 Mont Villers (Sanguine) CFL0006-02	WG	Foliar spray	0.53	1000	3	0 22 29 36	1.4 0.24 0.36 0.38	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
France South (S), 2009, Mirmande (September Star) CFL0006-03	WG	Foliar spray	0.53	1000	3	0 21 28 35	0.56 0.24 0.11 0.11	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
Greece, 2009 Galatades (A37) CFL0006-04	WG	Foliar spray	0.53	1000	3	0 21 27 35	0.76 0.17 0.08 0.07	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
Italy, 2009 San Giovanni Lupatoto (Roberta Barolo) CFL0006-05	WG	Foliar spray	0.53	1000	3	0 20 28 35	1.3 0.32 0.43 0.15	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
Spain, 2009 Turis, (Federica) CFL0006-06	WG	Foliar spray	0.53	1000	3	0 21 28 35	1.3 0.56 0.19 0.13	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
Germany, 2010 Coswig, (Redhaven) L100368	WG	Foliar spray	0.53	1000	3	0 21 28 35	2.6 1.0 0.60 0.24	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01
France (N), 2010 Loromontzey (Sanguine chanas) L100369	WG	Foliar spray	0.53	1000	3	0 21 29 36	1.9 0.60 0.33 0.30	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01
Fance (S), 2010 Garons, (Orion) L100370	WG	Foliar spray	0.53	1000	3	0 21 28 35	0.40 0.13 0.18 0.15	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01
Greece, 2010 Galatades (Katerina) L100371	WG	Foliar spray	0.53	1000	3	0 21 28 34	4.6 0.36 0.44 0.24	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Italy, 2010 Ceolara Caselle di Sommacampagna (Royal Glory) L100372	WG	Foliar spray	0.53	1000	3	0 21 28 35	4.1 0.36 0.07 0.15	0.02 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01
Spain, 2010 Turis (Spring crest) L100373	WG	Foliar spray	0.53	1000	3	0 21 28 35	2.2 0.45 0.16 0.10	0.02 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01

Plums

During the 1996 growing season, three field trials with plums were conducted in France. Dithianon residues in plums were analysed after acetonitrile extraction with an HPLC-UV (LOQ 0.03 mg/kg, recovery 77%, GRAPPA in-house method). Further trials on plums were conducted in 1998 in France. Dithianon residues were analysed with method FAMS 028-02. The results are summarized in Table 52.

Table 52 Residues of dithianon in plums

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha					
France (S), 1996 Riocaud Aquitaine (Ente 707), 54102	WG	Foliar Spray	0.35	500	2	15 30 15 30	Flesh Flesh Whole fruit ^{a)} Whole fruit	0.06 0.07 0.06 0.06	DT-712-031, GRAPPA in-house method HPLC-UV
France (S), 1996 Labastide St Pierre (Reine-Claude), 54103	WG	Foliar spray	0.35	600	2	15 30 15 30	Flesh Flesh Whole fruit Whole fruit	0.03 <0.03 0.03 <0.03	DT-712-031, GRAPPA in-house method HPLC-UV
France (S), 1996 Malaucène (Golden Japan), 54104	WG	Foliar Spray	0.35	500	2	15 24 15 24	Flesh Flesh Whole fruit Whole fruit	0.12 0.17 0.11 0.15	DT-712-031, GRAPPA in-house method HPLC-UV
France (N), 1998 80400 Douilly (Mirabelle de Nancy) 98-116-001	WG	Foliar Spray	0.35	1000	2	-0 -0 +0 +0 3 3 7 7 14 14	Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit	0.11 0.10 0.17 0.16 0.20 0.18 0.14 0.13 0.14 0.13	DT-712-032, FAMS 028-02
France (N), 1998 55210 Vieville sous les cotes, (Mirabelle de Nancy) 98-116-002	WG	Foliar Spray	0.35	1000	2	-0 -0 +0 +0 3 3 7 7 14 14	Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit	0.07 0.07 0.17 0.16 0.21 0.19 0.11 0.10 0.13 0.12	DT-712-032, FAMS 028-02

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha					
France (N), 1998 08130 Suzanne (Quetsche), 98-116-003	WG	Foliar Spray	0.35	1000	2	-0	Flesh	< 0.02	DT-712-032, FAMS 028-02
						-0	Whole fruit	< 0.02	
						+0	Flesh	0.03	
						+0	Whole fruit	0.03	
						3	Flesh	0.03	
						3	Whole fruit	0.03	
						7	Flesh	0.02	
						7	Whole fruit	< 0.02	
						14	Flesh	< 0.02	
						14	Whole fruit	< 0.02	
France (N), 1998 80400 Douilly (Quetsche d'Alsace) 98-116-004	WG	Foliar Spray	0.35	1000	2	-0	Flesh	0.03	DT-712-032, FAMS 028-02
						-0	Whole fruit	0.03	
						+0	Flesh	0.06	
						+0	Whole fruit	0.06	
						3	Flesh	0.06	
						3	Whole fruit	0.06	
						7	Flesh	0.05	
						7	Whole fruit	0.05	
						15	Flesh	0.04	
						15	Whole fruit	0.04	

^a Residue concentrations calculated for whole fruit including stones.

During the 2009/2010 growing seasons, trials in plums were conducted in Northern France, Italy, Spain and Germany. The results are summarized in Table 53. Shortly before analyses the plum fruits were pitted and the weight ratio of the stones and flesh was determined. Only the flesh was analysed. The residues were calculated for the whole fruit based on the individual ratio stone to flesh. All specimens were analysed for dithianon and its metabolite Reg. No. 4110904 using BASF method number L0152/01 which has a limit of quantitation of 0.01 mg/kg for each of the two analytes.

Table 53 Residues of dithianon and metabolite Reg. No. 4110904 in plums, residues calculated for whole fruit

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Germany, 2009 Gau Algesheim (Elena), L090435	WG	Foliar spray	0.53	1000	3	0	0.17	< 0.01	2010/1006343, L0152/01
						14	0.09	< 0.01	
						21	0.10	< 0.01	
						27	0.10	< 0.01	
Germany, 2009 Werder (Cacaks Fruchtbare) L090436	WG	Foliar spray	0.53	1000	3	0	0.12	< 0.01	2010/1006343, L0152/01
						14	0.04	< 0.01	
						20	0.04	< 0.01	
						27	0.03	< 0.01	
France North, 2009 Billy sous les Cotes Lorrains (Mirabelle), L090437	WG	Foliar spray	0.53	1000	3	0	0.33	< 0.01	2010/1006343, L0152/01
						14	0.32	< 0.01	
						22	0.27	< 0.01	
						28	0.24	< 0.01	
France North, 2009 Vigneulles les Hattochatel Lorrains (Quetsche d'Alsace) L090438	WG	Foliar spray	0.53	1000	3	0	0.27	< 0.01	2010/1006343, L0152/01
						14	0.10	< 0.01	
						21	0.10	< 0.01	
						28	0.07	< 0.01	
Spain, 2009 El Coronil Andalucia/Sevilla (Friar), L090439	WG	Foliar spray	0.53	1000	3	0	0.09	< 0.01	2010/1006343, L0152/01
						13	0.03	< 0.01	
						20	0.05	< 0.01	
						28	0.06	< 0.01	

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Italy, 2009 Barbiano di Cotignola Ravenna (Bella die Barbiano) L090440	WG	Foliar spray	0.53	1000	3	0 14 21 28	0.08 0.04 0.05 0.04	< 0.01 < 0.01 < 0.01 < 0.01	2010/1006343, L0152/01
Germany, 2010 Gau Algesheim (Hauszwetsche) L100212	WG	Foliar spray	0.53	1000	3	0 15 22 29	0.19 0.22 0.18 0.06	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01
Germany, 2010 Werder (Elena), L200213	WG	Foliar spray	0.53	1000	3	0 15 22 29	0.26 0.34 0.32 0.13	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01
Belgium, 2010 Gelrod (Valor), L100214	WG	Foliar spray	0.53	1000	3	0 14 21 29	0.20 0.22 0.25 0.13	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01
France North, 2010 Vigneulies les Hattonchâtel (Mirabelle de Nancy) L100215	WG	Foliar spray	0.53	1000	3	0 15 21 29	0.59 0.55 0.40 0.21	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01
Spain, 2010 Utrera (Fortune), L100216	WG	Foliar spray	0.53	1000	3	0 14 21 27	0.32 0.73 0.45 0.23	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01
Italy, 2010 Barbiano di Cotignola (T.C. Sun), L100217	WG	Foliar spray	0.53	1000	3	0 14 21 28	0.10 0.21 0.21 0.10	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01

Grapes

Trials on grapes were conducted in Northern Europe in the 1970s, 1980s and early 1990s. The samples were either analysed for dithianon by HPLC-UV (methods RU 501/02/10, RU 107/34/10, SFS AMS 003-02 and FAMS 028-02), GC-ECD (methods P-14.078.01 and P-14.013.02) or, in one case, by a colorimetric method. The LOQs of all methods applied vary between 0.01 mg/kg and 0.05 mg/kg and the recoveries from 71 to 100%.

Further trials were conducted from 2001 to 2004 in France (North and South), Germany, Greece, Spain and Italy. The fruits were analysed for residues of dithianon using methods M 3442 (RLA 12616) or version RLA 12616.05V with an LOQ of 0.01 mg/kg and mean recovery rates of 70–110%. In the trial FTL/17/03 conducted in Southern France, the harvest was very poor due to extremely dry weather conditions in this area. Because of this, the last sampling was not possible anymore as no more grape samples were left at that time. These extreme conditions also caused considerably higher residues found in this trial compared to all other ones. A summary of the residue trials data is presented in Table 54. The scaled residues according to Slovenian GAP (8×0.35 kg ai/ha) and to Serbian GAP (3×0.35 kg ai/ha) are shown in brackets.

Table 54 Residues of dithianon in grapes, scaled values in brackets

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1979 Hagnau (Müller-Thurgau) C 79 09 06 01	WP	Foliar spray	0.47	1500	8	0 14 21 28 35	1.4 0.92 0.79 0.87 0.60	DT-713-006, colorimetric determination, LOQ 0.05 mg/kg, method not further described

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1986 Bockenheim (Müller-Thurgau) C 86 04 34	SC	Foliar spray	0.23 - 0.6	200 - 533	8	0 14 28 35 42	1.2 0.88 0.49 0.64 0.62 (0.36)	DT-713-031, RU 107/34/10
Germany, 1986 Schwabenheim (Müller-Thurgau) C 86 04 72	SC	Foliar spray	0.23 - 0.44	200 - 350	8	0 14 28 35 42	0.96 0.70 0.47 1.2 1.0 (0.80)	DT-713-039, RU 107/34/10
Germany, 1987 Bockenheim (Müller-Thurgau) C 87 14 34	SC	Foliar spray	0.3 - 0.6	266 - 533	8	0 14 28 35 42	0.98 0.97 0.63 0.73 0.25 (0.15)	DT-713-034, RU 107/34/10
Germany, 1987 Gleiszellen (Müller-Thurgau) C 87 14 03	SC	Foliar spray	0.23 - 0.68	600 - 1800	8	0 14 28 35 42	6.5 3.7 2.1 1.8 2.7 (1.4)	DT-713-035, RU 107/34/10
Germany, 1987 Schwabenheim (Müller-Thurgau) C 87 14 72	SC	Foliar spray	0.38 - 0.56	1000 - 1500	8	0 14 28 35 42	1.7 1.4 0.86 1.6 1.2 (0.75)	DT-713-037, RU 107/34/10
Germany, 1987 Deidesheim (Portugieser) CU 88-501	SC	Foliar spray	0.19 - 0.68	170 - 600	7	0 14 28 35 42	4.5 9.4 3.0 4.5 1.9 (1.0)	DT-713-038, RU 107/34/10
Germany, 1988 Geisenheim (Riesling) R 117-88	SC	Foliar spray	0.25 - 0.56	800 - 1800	8	0 14 28 35 42	2.2 1.5 1.0 0.94 0.97 (0.61)	DT-713-029, SFS AMS 003-02
Germany, 1988 Geisenheim (Riesling) R 117-88 / 05393	WP	Foliar spray	0.25 - 0.56	800 - 1800	8	0 14 28 35 42	1.9 1.8 0.68 0.56 0.30 (0.19)	DT-713-030, SFS AMS 003-02
Germany, 1989 Veitshöchheim (Müller-Thurgau) R 79/89	EC	Foliar spray	0.4 - 0.47	300 - 350	8	0 14 28 35 42 49	3.3 2.2 3.6 3.1 3.4 (2.5) 3.0	DT-713-043, P-14-013.02
Germany, 1989 Geisenheim (Riesling) R 80/89	EC	Foliar spray	0.33 - 0.5	1000 - 1500	8	0 14 28 35 42 49	0.26 0.25 0.25 0.41 0.40 0.69 (0.48)	DT-713-043, P-14-013.02
Germany, 1989 Neustadt (Portugieser) R 81/89	EC	Foliar spray	0.17 - 0.6	170 - 600	8	0 14 28 35 42 49	3.5 1.7 1.8 1.3 1.2 1.3 (0.76)	DT-713-043, P-14-013.02

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1989 Ingelheim (Spätburgunder) R 82/89	EC	Foliar spray	0.33 - 0.5	1000 - 1500	8	0 14 28 35 42 49	1.4 1.3 1.3 0.69 0.61 (0.43) 0.54	DT-713-043, P-14-013.02
Germany, 1990 Veitshöchheim (Müller Thurgau) R 166-90	EC	Foliar spray	0.4 - 0.53	300 - 400	8	0 14 29 35 42 47 49	4.6 2.6 2.3 2.2 1.6 1.8 (1.2) 1.6	DT-713-045, P-14-013.02
Germany, 1993 Partenheim (Dornfelder) SKG-9307-01	WP	Foliar spray	0.25 - 0.48	199 - 386	8	0 14 28 42 49	1.2 1.4 0.58 0.61 (0.44) 0.45	DT-790-065, P-14.078.01
Germany, 1994 Weisenheim am Sand (Portugieser) 9402-01	WP	Foliar spray	0.27 - 0.48	217 - 385	8	43	0.69 (0.50)	DT-713-114, FAMS 028-01
Germany, 1994 Weisenheim am Sand (Riesling) 9402-02	WP	Foliar spray	0.27 - 0.5	214 - 391	8	42	1.5 (1.05)	DT-713-114, FAMS 028-01
Germany, 1995 Weisenheim am Sand (Müller Thurgau) 95-085-01	WG	Foliar spray	0.24 - 0.64	688 - 1817	8	+0 -0 14 28 35 43 49	1.8 2.4 1.4 1.5 1.2 0.98 (0.54) 0.57	DT-713-058 FAMS 028-02
Germany, 1995 Bockenheim (Spätburgunder) 95-085-02	WG	Foliar spray	0.25 - 0.63	704 - 1802	8	+0 -0 14 28 35 42 49	2.8 3.6 1.5 2.6 2.2 2.2 (1.2) 0.91	DT-713-058 FAMS 028-02
Germany, 1995 Gau Algesheim (Dornfelder) 95-085-03	WG	Foliar spray	0.28 - 0.68	197 - 486	8	+0 -0 14 28 35 41 49	2.3 4.5 2.0 2.0 1.9 0.57 (0.29) 0.56	DT-713-058 FAMS 028-02
Germany, 1995 Gau Algesheim (Silvaner) 95-085-04	WG	Foliar spray	0.25 - 0.64	182 - 456	8	+0 -0 13 27 34 42 48	1.3 1.8 1.0 0.66 0.64 0.58 0.62 (0.34)	DT-713-058 FAMS 028-02
Germany, 1995 Weisenheim am Sand (Portugieser) 95-115-01	WG	Foliar spray	0.25 - 0.64	701 - 1827	8	+0 -0 7 14 28 35 42	2.4 2.4 1.9 1.1 1.4 1.4 1.1 (0.60)	DK-713-032, FAMS 002-04

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1995 Bockenheim (Scheurebe) 95-155-02	WG	Foliar spray	0.25 - 0.63	703 - 1812	8	+0 -0 7 14 28 35 42	2.2 3.5 2.7 2.1 2.3 1.1 1.3 (0.72)	DK-713-032, FAMS 002-04
Germany, 1995 Heidesheim (Portgieser) 95-115-03	WG	Foliar spray	0.25 - 0.65	178 - 465	8	+0 -0 8 15 29 35 43	2.5 3.0 1.3 1.6 1.3 0.72 1.7 (0.92)	DK-713-032, FAMS 002-04
Germany, 1995 Gau-Algesheim (Silvaner) 95-115-04	WG	Foliar spray	0.25 - 0.64	177 - 456	8	+0 -0 6 13 27 35 41	1.4 1.8 1.2 1.6 0.8 0.59 0.80 (0.44)	DK-713-032, FAMS 002-04
Spain, 2001 Sevilla, Andalucia (Cardenal) ALO/1901	WG	Foliar spray	0.56	1000	8	0 27 34 41 48	0.87 0.38 0.43 0.34 (0.21) 0.26	2002/1008746, 2003/1018259, RLA 12616
Germany, 2001 Wachenheim (Portugieser) DU4/04/01	WG	Foliar spray	0.56	1000	8	0 28 35 42 48	1.7 2.4 1.5 1.3 (0.81) 1.2	2002/1008746, 2003/1018259, RLA 12616
France North, 2001 Handschuheim (Pinot noir) FAN/14/01	WG	Foliar spray	0.56	1000	8	0 27 34 41 48	2.5 0.96 0.85 1.4 (0.88) 0.90	2002/1008746, 2003/1018259, RLA 12616
Greece, 2001 Edessa, Nisi (Mochato) HEL/12/01	WG	Foliar spray	0.56	1000	8	0 28 35 42 49	5.6 4.7 3.2 2.7 3.4 (2.1)	2002/1008746, 2003/1018259, RLA 12616
Italy, 2001 Monleale (Croatina) ITA/25/01	WG	Foliar spray	0.56	1000	8	0 28 35 42 49	1.7 2.4 1.5 1.3 (0.81) 1.2	2002/1008746, 2003/1018259, RLA 12616
Italy, 2001 Monleale (Timorasso) ITA/26/01	WG	Foliar spray	0.56	1000	8	0 29 35 42 49	2.1 0.98 1.0 1.1 (0.69) 0.79	2002/1008746, 2003/1018259, RLA 12616
Spain, 2002 Utrera (Cardenal) ALO/16/02	WG	Foliar spray	0.56	1000	8	0 28 35 42 49	0.98 0.53 0.36 0.52 (0.33) 0.25	2003/1004349, RLA 12616
Spain, 2002 La Frontera (Palomino) AYE/12/02	WG	Foliar spray	0.56	1000	8	0 27 34 41 48	1.0 0.85 1.1 0.59 (0.37) 0.53	2003/1004349, RLA 12616

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
France South, 2002 Pont de L'isère (Syrah) FBD/10/02	WG	Foliar spray	0.56	1000	8	0 28 34 41 49	8.5 6.8 5.5 7.4 (4.6) 4.7	2003/1004349, RLA 12616
France South, 2002 Fronton (Negrette) FTL/11/02	WG	Foliar spray	0.56	1000	8	0 29 36 43 50	2.1 1.1 1.2 1.5 (0.94) 1.1	2003/1004349, RLA 12616
Italy, 2002 Monleale (Croatina) ITA/18/02	WG	Foliar spray	0.56	1000	8	0 29 36 42 50	1.1 0.34 0.33 0.38 0.44 (0.28)	2003/1004349, RLA 12616
Spain, 2003 Andalucia, Sevilla (Cardenal) ALO/18/03	WG	Foliar spray	0.56	1000	8	0 28 35 42 49	5.1 1.5 0.72 1.1 (0.69) 0.69	2003/1001125, RLA 12616.05V
Italy, 2003 Monleale, Piemonte (Croatina) ITA/12/03	WG	Foliar spray	0.56	1000	8	0 28 35 41 49	2.8 1.4 1.6 1.0 (0.63) 0.93	2003/1001125, RLA 12616.05V
Germany, 2003 Kesten (Müller Thurgau) AGR/23/03	WG	Foliar Spray	0.53	800	3	0 21 27 35 42	2.8 1.8 1.5 0.87 (0.57) 0.10	2004/1000746, RLA 12616
Germany, 2003 Kesten (Dornfelder) AGR/24/03	WG	Foliar Spray	0.53	800	3	0 21 27 35 42	3.5 2.5 1.4 1.5 (0.99) 1.3	2004/1000746, RLA 12616
Spain, 2003 Utrera, Andalucia (Cardenal) ALO/19/03	WG	Foliar Spray	0.53	800	3	0 21 28 35 42	1.8 0.65 0.93 0.41 0.44 (0.29)	2004/1000746, RLA 12616
France North, 2003 Handschuheim (Pinot noir) FAN/22/03	WG	Foliar Spray	0.53	800	3	0 21 28 35 42	2.6 1.7 1.7 1.6 (1.1) 1.3	2004/1000746, RLA 12616
France South, 2003 Pont de L'isère (Syrah) FBD/14/03	WG	Foliar Spray	0.53	800	3	0 21 27 35 41	4.6 3.9 1.9 1.8 (1.2) 1.5	2004/1000746, RLA 12616
France North, 2003 Martigné-Biand (Cabernet Sauvignon) FBM/16/03	WG	Foliar Spray	0.53	800	3	0 21 29 35 43	1.3 1.8 1.6 1.0 1.1 (0.73)	2004/1000746, RLA 12616
France South, 2003 Fronton, Midi-Pyrenees (Negrette) FTL/17/03	WG	Foliar Spray	0.53	800	3	0 21 28 35	7.5 8.4 6.6 4.9	2004/1000746, RLA 12616 Extreme weather conditions, high temperature and dryness

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
Italy, 2003 Monleale, Piemonte (Dolcetto) ITA/13/03	WG	Foliar Spray	0.53	800	3	0 21 29	2.3 2.0 1.6	2004/1000746, RLA 12616
Spain, 2004 Utrera, Andalucia (Alren) ALO/29/04	WG	Foliar Spray	0.53	800	3	0 21 28 35 42	1.4 0.70 0.70 0.60 0.72 (0.48)	2005/1004963, RLA 12616
Germany, 2004 Wiesloch (Riesling) DU2/11/04	WG	Foliar Spray	0.53	800	3	0 20 28 35 42	1.6 1.5 1.1 0.95 (0.63) 0.70	2005/1004963, RLA 12616
Germany, 2004 Eschbach (Portugieser) DU4/11/04	WG	Foliar Spray	0.53	800	3	0 21 28 35 42	1.1 0.69 0.42 0.48 0.76 (0.50)	2005/1004963, RLA 12616
France North, 2004 Handschuheim (Auxerols) FAN/18/04	WG	Foliar Spray	0.53	800	3	0 21 28 35 42	1.7 1.3 1.4 0.79 0.89 (0.59)	2005/1004963, RLA 12616
France South, 2004 Pont de L'isère (Syrah) FBD/19/04	WG	Foliar Spray	0.53	800	3	0 21 29 35 42	3.2 0.73 0.53 0.59 (0.39) 0.51	2005/1004963, RLA 12616
France North, 2004 Martigné-Brand (Chenin) FBM/11/04	WG	Foliar Spray	0.53	800	3	0 20 28 35 42	1.7 1.9 2.4 1.3 (0.86) 1.3	2005/1004963, RLA 12616
France South, 2004 Fronton, Midi-Pyrenees (Negrette) FTL/18/04	WG	Foliar Spray	0.53	800	3	0 21 29 35 42	0.67 1.1 0.74 0.75 0.97 (0.64)	2005/1004963, RLA 12616
Greece, 2004 Naousa, Macedonia (Xinomavro) GRE/20/04	WG	Foliar Spray	0.53	800	3	0 21 29 35 42	2.6 2.1 1.6 1.9 (1.3) < 0.01	2005/1004963, RLA 12616
Italy, 2004 Monleale, Piemont (Croatina) ITA/19/04	WG	Foliar Spray	0.53	800	3	0 20 28 34 42	1.3 0.61 0.75 0.85 (0.56) 0.57	2005/1004963, RLA 12616

During the growing season of 2010, four trials with grapes were conducted in Greece, Italy and Spain in order to determine the influence of different water volumes on the residue situation. Each field trial consisted of five plots and a control plot. All treated grape specimens were analysed for dithianon and its metabolite Reg. No. 4110904 according to analytical method L0152 (LC-MS/MS, LOQ for each analyte 0.01 mg/kg). The results are summarized in Table 55.

Table 55 Residues of dithianon and metabolite Reg. No. 4110904 in grapes

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Spain, 2010 Seville (Cardinal) L100541	WG	Foliar spray	0.53	1000	1	0 28 35 42	0.85 0.17 0.11 0.07	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	1000	2	0 28 35 42	2.0 0.22 0.13 0.27	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	800	2	0 28 35 42	2.1 0.40 0.38 0.46	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	400	2	0 28 35 42	2.0 0.38 0.86 0.42	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	200	2	0 28 35 42	1.8 0.88 0.80 0.50	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
Spain, 2010 Seville (Matilde) L100542	WG	Foliar spray	0.53	1000	1	0 28 35 42	2.2 0.28 0.18 0.27	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	1000	2	0 28 35 42	2.2 0.26 0.24 0.31	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	800	2	0 28 35 42	3.2 0.32 0.32 0.47	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	400	2	0 28 35 42	2.4 0.38 0.31 0.44	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
Italy, 2010 Taranto (Victoria) L100543	WG	Foliar spray	0.53	1000	1	0 28 35 42	1.1 0.27 0.27 0.11	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	1000	2	0 28 35 42	3.4 0.74 0.84 0.91	0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	800	2	0 28 35 42	1.6 1.2 0.71 0.41	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	400	2	0 28 35 42	1.8 0.50 0.65 0.63	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	200	2	0 28 35 42	2.8 0.57 0.72 0.93	0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Greece, 2010 Aggelochori (Victoria) L100544	WG	Foliar spray	0.53	1000	1	0 29 35 42	2.1 0.38 0.26 0.15	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	1000	2	0 29 35 42	2.2 0.34 0.16 0.11	< 0.01 < 0.01 < 0.01 < 0.01	
	WG	Foliar spray	0.53	800	2	0 29 35 42	2.6 0.30 0.23 0.18	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	400	2	0 29 35 42	2.7 0.34 0.26 0.20	< 0.01 < 0.01 < 0.01 < 0.01	
	WG	Foliar spray	0.53	200	2	0 29 35 42	1.2 0.34 0.25 0.22	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152

Currants, black

Six field trials with black currants were conducted in 1993/1994 in France (see Table 56). Specimens were analysed after extraction with acetonitrile and liquid-liquid partition with dichloromethane by HPLC-UV with LOQs of 0.05 mg/kg (SICACRO Laboratoire in-house method) or 0.1 mg/kg (no method number, recovery levels were 77% and 85% at 0.1 mg/kg fortification level).

Table 56 Residues of dithianon in black currants

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
France North, 1993 Marchenoir (Black Down) RCAS 93.03/41.01	SC	Foliar spray	0.53	600	2	7 14	< 0.05 < 0.05	DT-713-063, SICACRO Laboratoire in-house method, HPLC-UV
France South, 1993 Anneyron (Andega) RCAS 93.03/26.01	SC	Foliar spray	0.53	1150	2	7 14	< 0.05 0.61	DT-713-063, SICACRO Laboratoire in-house method, HPLC-UV
France South, 1993 St. Didier sous Riverie (Black Down) RCAS 93.03/69.01	SC	Foliar spray	0.53	400 - 500	2	7 14	2.7 0.89	DT-713-063, SICACRO Laboratoire in-house method, HPLC-UV
France North, 1993 Bagny sur Saône (Noir de Bourgogne) RCAS 93.03/71.01	SC	Foliar spray	0.53	300	2	7 14	< 0.05 < 0.05	DT-713-063, SICACRO Laboratoire in-house method, HPLC-UV
France North, 1994 Marey les Fussey (Noir de Bourgogne) 02101	SC	Foliar spray	0.53	600	2	14	< 0.1	DT-713-127, No method no., HPLC-UV
France North, 1994 Marchenoir (Black Down) 04101	SC	Foliar spray	0.53	600	2	14	0.11	DT-713-127, No method no., HPLC-UV

Almonds

Four trials were laid down in France in 1996. The crop growth stage at the final application was “young fruit” in all trials. Almonds without shell were analysed with a “GRAPPA in-house” HPLC-method (UV-detection) for dithianon (LOQ 0.05 mg/kg) using extraction with dichloromethane. Recoveries were in the range of 62% to 92%. The results are summarized in Table 57.

Table 57 Residues of dithianon in almonds, whole fruit without shell

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
France, 1996 Saint Marcel D'ardeche (Al), 53/100	WG	Foliar spray	0.35	683	2	63 140	< 0.05 < 0.05	DT-740-002, GRAPPA in-house method, HPLC-UV
France, 1996 Saint Marcel D'ardeche (Ferragnes), 53/101	WG	Foliar spray	0.35	683	2	63 140	< 0.05 < 0.05	DT-740-002, GRAPPA in-house method, HPLC-UV
France, 1996 Fontvieille (Ferra Star), 53/98	WG	Foliar spray	0.35	500	2	58 119	< 0.05 < 0.05	DT-740-002, GRAPPA in-house method, HPLC-UV
France, 1996 St. Martin de Crau (Laurane), 53/99	WG	Foliar spray	0.35	500	2	58 119	< 0.05 < 0.05	DT-740-002, GRAPPA in-house method, HPLC-UV

Hops

Trials were conducted in representative hops growing areas in Germany in the growing seasons 1987, 1989–1991 and 1995. The samples from the trials conducted between 1987 and 1991 were either analysed with a GC-ECD method (P-14.005.01 and P-14.005.02). The samples from the trials conducted in 1995 were analysed with method P-14.078 of Dr. Specht & Partner Laboratories. The LOQ for dithianon of all methods is 0.05 mg/kg in hop cones. The recoveries were in the range of 71 to 100% at varying fortification levels. A summary of the residue trials data is presented in Table 58.

Table 58 Residues of dithianon in hops

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water lL/ha					
Germany, 1987 Forchheim (Perle) C 87 08 05 01	WP	Foliar spray	0.45 - 1.13	1200 - 3000	8	0 7 10 14	Green cones	12 10 9.7 8.0	DT-790-022, 14.005.01
Germany, 1987 Forchheim (Hersbrucker) C 87 08 05 02	WP	Foliar spray	0.45 - 1.13	1200 - 3000	8	0 7 10 14	Green cones	12 13 11 7.6	DT-790-023, 14.005.01
Germany, 1989 Au, Hallertau (Brewers Gold) R 95-89	SC	Foliar spray	0.3 - 1.13	800 - 3000	12	0 7 10 10 14 14	Green cones Green cones Dried cones Green cones Dried cones Green cones	10 9.2 13 7.4 4.1 5.4	DT-790-035, 14.005.02

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water lL/ha					
Germany, 1989 Tett nang (Tett nanger Landsorte) R 96-89	SC	Foliar spray	0.38 - 1.13	1000 - 3000	10	0 7 10 10 14 14	Green cones Green cones Dried cones Green cones Dried cones Green cones	4.3 2.6 2.5 3.2 16 9.7	DT-790-036, 14.005.02
Germany, 1989 Au, Hallertau (Brewers Gold) R 97-89	SC	Foliar spray	0.3 - 1.13	800 - 3000	12	0 7 10 10 14 14	Green cones Green cones Dried cones Green cones Dried cones Green cones	94 78 29 22 21 12	DT-790-037, 14.005.02
Germany, 1989 Tett nang (Tett nanger Landsorte) R 98-89	SC	Foliar spray	0.38 - 1.13	1000 - 3000	10	0 7 10 10 14 14	Green cones Green cones Dried cones Green cones Dried cones Green cones	8.6 4.4 21 4.2 17 8.4	DT-790-038, 14.005.02
Germany, 1990 Forchheim (Perle) 14429	SC	Foliar spray	0.42 - 1.11	753 - 2064	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	35 35 30 92 24 94	DT-790-031, 14.005.02
Germany, 1990 Meckenbeuren (Hallertauer) 14425	SC	Foliar spray	0.45 - 1.5	1200 - 4000	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	41 22 30 85 27 96	DT-790-041, 14.005.02
Germany, 1990 Forchheim (Hersbrucker) 14428	SC	Foliar spray	0.52 - 1.24	920 - 2206	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	26 32 30 74 42 88	DT-790-042, 14.005.02
Germany, 1990 Meckenbeuren (Tett nanger) 14424	SC	Foliar spray	0.45 - 1.5	1200 - 4000	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	67 61 38 91 17 58	DT-790-043, 14.005.02
Germany, 1991 Heißmanning (Hersbrucker) 9142-01	SC	Foliar spray	0.59 - 1.49	1578 - 3975	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	76 63 57 187 56 89	DT-790-044, 14.005.02
Germany, 1991 Rohr (Northern Brewer) 9142-02	SC	Foliar spray	0.6 - 1.5	1603 - 3971	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	155 143 92 193 123 242	DT-790-045, P-14.005.02
Germany, 1991 Holstum (Tett nanger) 9142-03	WG	Foliar spray	0.53 - 0.84	2000	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	17 94 12 81 36 84	DT-790-046, 14.005.02

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water lL/ha					
Germany, 1995 Prünzurlay (Northern Brewer) 95-079-01	WG	Foliar spray	0.52 - 1.4	1498 - 4010		-0	Green cones	7.0	DT-790-049, P-14.078
						+0	Green cones	20	
						7	Green cones	11	
						14	Green cones	6.4	
						14	Dried cones	13	
						21	Green cones	9.7	
						21	Dried cones	32	
Germany, 1995 Holsthum (Brewers Gold) 95-079-02	WG	Foliar spray	0.52 - 1.43	1498 - 4089	10	-0	Green cones	2.4	DT-790-049, P-14.078
						+0	Green cones	11	
						8	Green cones	6.2	
						14	Green cones	4.2	
						14	Dried cones	22	
						21	Green cones	2.7	
						21	Dried cones	8.9	
Germany, 1995 Pfaffenhofen- Heißmannig (Brewers Gold) 95-079-03	WG	Foliar spray	0.55 - 1.43	1567 - 4073	10	-0	Green cones	13	DT-790-049, P-14.078
						+0	Green cones	24	
						7	Green cones	13	
						15	Green cones	6.4	
						15	Dried cones	82	
						21	Green cones	14	
						21	Dried cones	16	
Germany, 1995 Oberempfenbach (Brewers Nugget) 95-079-04	WG	Foliar spray	0.55 - 1.43	1582 - 4094	10	-0	Green cones	14	DT-790-049, P-14.078
						+0	Green cones	40	
						7	Green cones	24	
						15	Green cones	18	
						15	Dried cones	70	
						21	Green cones	4.3	
						21	Dried cones	59	

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing - nature of residues

Three studies were provided on hydrolysis of dithianon to assist with identification of the nature of the residues during processing. To estimate the degradation behaviour of dithianon during industrial processing or household preparation, the process of pasteurization (90 °C, 20 min), the process of baking, boiling, brewing (100 °C, 60 min) and the process of sterilization (120 °C, 20 min) was simulated.

Study DT-790-060 (Tsalta, 2001)

The hydrolysis of dithianon was performed using ¹⁴C-dithianon labelled at positions 5, 6, 9 and 10 of the molecule. The test substance had a radiochemical purity of 98.7% (by HPLC) and a specific activity of 42.4 µCi/mg. The experiments were carried out in a closed system under the simulated processing conditions. The hydrolysis of ¹⁴C-dithianon was studied at 90, 100, and 120 °C in sterile buffers at pH 4, 5, and 6, respectively. Radio-labelled test compound was applied at an application rate of 0.13 mg/L. The samples were incubated for 20 to 60 minutes at 90, 100, and 120 °C in the dark. Samples from the test solutions were assayed by liquid scintillation counting at 0-time (immediately after dosing) and after incubation to determine the concentration and recovery. Aliquots of the samples were analysed by reversed phase HPLC directly without sample work-up.

The results for the hydrolysis experiment conducted at pH 4 showed that dithianon was stable under simulated processing conditions of pasteurization. ¹⁴C-dithianon accounted for 94.7% to 97.1% and 90.2% to 94.2% of the recovered radioactivity at 0-time and after 90 °C, 20 minutes incubation, respectively.

The results for the hydrolysis experiment conducted at **pH 5** showed that dithianon was significantly degraded under simulated processing conditions of baking, brewing, and boiling (100 °C, 60 min). ¹⁴C-dithianon accounted for 93.4% to 94.4% of the recovered radioactivity at 0-time.

After incubation at 100 °C for 60 minutes at pH 5, ¹⁴C-dithianon had degraded to a large extent (> 90%) to many mostly polar substances. One major and four minor degradation products were detected. The major degradation product, accounting for 46% to 57% of the recovered radioactivity, was identified by MS and ¹H-NMR as compound Reg. No. 4110904 (CL 1017911) [(1,4-dithiin-2-carboxylic acid, 5,6-dicyano-3-(2-hydroxy-benzoyl)]. The minor degradates formed each accounted for 3.5% to 8.5% of the recovered radioactivity. The MS and ¹H-NMR data revealed that compound Reg. No. 4110904 was formed by cleavage of the quinone ring (under high temperature hydrolytic conditions) resulting in a carboxylic acid. The ¹H-NMR data also showed that the isolated product contained a minor component postulated as CL 1017912 {benzoic acid, 2-[(5,6-dicyano-3-hydroxy-1,4-dithiin-2-yl)carbonyl]} which is probably the positional isomer with the carboxyl and the hydroxy groups in reversed positions.

The results for the hydrolysis experiment conducted at pH 6 showed that dithianon was significantly degraded under simulated processing conditions of sterilization (120 °C, 20 minutes).

The HPLC analysis of the 0-time solutions showed that ¹⁴C-dithianon was degrading rapidly even at room temperature conditions. Dithianon accounted for 75.1% to 77.1% of the recovered radioactivity and compound Reg. No. 4110904 had already started forming at 6.5% to 6.9% of the recovered radioactivity at 0-time. The HPLC analysis of the incubated solutions (20 min) showed no detectable peak corresponding to parent. The major degradation product formed at pH 6, compound Reg. No. 4110904, accounted for 19.8% to 21.2% of the recovered radioactivity. The chromatographic profile of the degradation products was qualitatively very similar to the profile at pH 5. As at pH 5, an additional four degradation products formed, each accounting for an average 6% to 9.5% of recovered radioactivity.

Study 2009/1065632 (Hassink, 2009)

To estimate the degradation behaviour of the test item during industrial processing or household preparation of apple juice, the process of pasteurization was simulated. The test solution containing 0.01 mg dithianon suspended in natural turbid apple juice at pH 3.8 was heated to 90 °C in a round-bottom flask under backflow. The test was performed in duplicate (test A and B). The samples were measured for radioactivity (LSC) and were analysed by HPLC to determine an eventual metabolite pattern. Comparing the overall radioactivity measured by LSC before and after each test it can be seen that no loss of radioactive material occurred.

Test	% Total applied radioactivity (TAR)	
	pH 4, 90 °C, test A	pH 4, 90 °C, test B
Before test (% TAR)	100	100
After test (% TAR)	94.82	98.99

The distribution of radioactivity was determined by HPLC-analysis. Dithianon degraded in both experiments (test A: 24.4% TAR, test B: 31.7% TAR) to a high number of unknown degradation products. In test A about 44 HPLC-peaks could be separated, three of them above 5% TAR (4.9 min: 8.3%; 13.8 min: 6.3%; 46.4 min: 5.9%). In test B 39 peaks occurred, only one of them was quantified above 5% TAR (5.1 min: 5.1%). The quantified peaks consist of several compounds and could not be separated.

Study 2013/1078029 (Class, 2013)

To estimate the degradation behaviour of the test item during industrial processing or household preparation of fruits, the process of pasteurization (90 °C, 20 min), the process of baking, boiling,

brewing (100 °C, 60 min) and the process of sterilization (120 °C, 20 min) was simulated. Apple juice was used as example. ^{14}C -dithianon was diluted with ^{12}C -dithianon in a ratio of about 1:1, in acetonitrile + 1% formic acid as solvent. This dose solution was then added to a commercial naturally turbid apple juice (containing 10% of a pH 4 buffer) to prepare the test solutions. The test solutions were examined by direct LSC for total applied radioactivity (TAR) prior to hydrolysis and after hydrolysis for total radioactive residue (TRR), indicating complete mass balance during hydrolysis. The culture tubes were heated in an oil bath to 90 °C for 20 minutes, 100 °C for 60 minutes or 120 °C for 20 minutes. After hydrolysis the culture tubes were cooled in an ice/water bath, subsequently stored refrigerated (approximately 5 °C). An aliquot of the hydrolysed juice was used for radio-chromatography by RP-HPLC analysis. Additionally, aliquots of the hydrolysed test solutions were dosed with solutions of selected reference compounds for identification by co-chromatography. Selected hydrolysis solutions were re-injected after various storage intervals to establish stable radio-chromatographic patterns. Almost all degradation products identified by RP-HPLC-UV/LSC and found to be $\geq 5\%$ of the TAR was confirmed by HPLC-MS/MS.

Based on the results of the initial high temperature hydrolysis of apple juice at 120 °C for 20 minutes and subsequent refrigerated storage, an additional hydrolysis test was conducted to confirm the presence of component Reg. No. 4107273 (D2) only found immediately after hydrolysis. This sample was dosed with ^{14}C -dithianon, hydrolysed as described above, characterised using HPLC-UV/LSC immediately after hydrolysis and the structure of component Reg. No. 4107273 (D2) confirmed by HPLC-MS/MS immediately following characterisation.

Further hydrolysis tests were conducted with un-buffered apple juice, in order to demonstrate that apple juice available to the consumer would have a similar degradation pattern as that determined in the presence of buffer. In this case, an apple juice sample was dosed with ^{14}C -dithianon, hydrolysed at 120 °C for 20 minutes as described initially, but without buffer, and examined by HPLC-UV/LSC immediately after hydrolysis. Samples were then analysed after 6, 24 and 48 hours, and 7, 14/15, 21 days of room temperature storage until a stable radio-chromatographic pattern was obtained.

All samples of the test solutions were analysed directly without further work-up. Samples were measured for radioactivity (LSC) and were analysed by HPLC-UV/LSC to determine an eventual degradation pattern. Confirmation of almost all degradation products identified in excess of 5% of the TAR was accomplished using HPLC-MS/MS.

The results of initial high temperature hydrolysis tests with ^{14}C -dithianon in buffered apple juice are shown in Table 59.

Table 59 Degradation products observed direct after hydrolysis

Hydrolysis / Degradation Product	Hydrolysis conditions		
	90 °C, 20 min % TAR	100 °C, 60 min % TAR	120 °C, 20 min % TAR
Compound identified			
Dithianon	44.4–47.3	0.9–1.0	0.2–0.5
Naphthoquinone, Reg. No. 4107273 ^{a)} (D2)	na	na	12.0–12.7
Reg. No. 4110904	5.5–6.2	7.3–9.4	5.5–5.8
Reg. No. 31062 (D4)	1.1–2.0	8.8–10.5	8.8–10.0
Phthalic acid, Reg. No. 4005234	na	1.8–2.2	1.3–2.0
Reg. No. 4110933 (D8)	2.1–2.2	3.5–4.0	4.0–4.1
Characterized			
UK1 (polar)	na	4.3–4.8	3.8–4.7
UK2 (polar)	na	4.3–4.5	na
UK3 (less polar) ^{a b}	2.8–3.6	3.2–4.5	6.1–7.4
UK4 (less polar)	1.6–1.7	na	na
UK5 (non-polar)	na	1.6–2.7	na

na = not assignable;

^a is not assignable after 21 days of storage

^b less polar, co-elutes with Reg. No. 4110934 (D15)

A stable radio-chromatographic pattern was achieved, as confirmed by the percentage of the TAR assigned, between hydrolysed apple juice samples stored refrigerated for 18/21 days and the sample stored refrigerated for 30/33 days. These results are shown in Tables 60 to 62.

Table 60 Degradation products after hydrolysis at 90 °C and 21 or 33 days refrigerated storage

Identified Degradation Product	Hydrolysis conditions / storage	
	90 °C, 20 min / 21 days,% TAR	90°C, 20 min / 33 days,% TAR
Phthalic acid, Reg. No. 4005234	1.6	2.1
Reg. No. 4110904	5.5	6.1
Reg. No. 4110933 (D8)	2.3	2.2
Dithianon	50.8	52.7
Reg. No. 31062 (D4)	1.7	1.3

Table 61 Degradation products after hydrolysis at 100 °C and 18 or 30 days refrigerated storage

Identified Degradation Product	Hydrolysis conditions / storage	
	100 °C, 60 min / 18 days,% TAR	100 °C, 60 min / 30 days,% TAR
Phthalic acid, Reg. No. 4005234	2.5	2.6
Reg. No. 4110904	7.9	8.2
Reg. No. 4110933 (D8)	3.4	3.5
Dithianon	0.6	0.6
Reg. No. 31062 (D4)	9.8	8.9

Table 62 Degradation products after hydrolysis at 120 °C and 21 or 33 days refrigerated storage

Identified Degradation Product	Hydrolysis conditions / storage	
	120 °C, 20 min / 21 days,% TAR	120 °C, 20 min / 33 days,% TAR
Phthalic acid, Reg. No. 4005234	3.1	3.8
Reg. No. 4110904	5.3	5.7
Reg. No. 4110933 (D8)	4.2	4.8
Dithianon	0.0	0.0
Reg. No. 31062 (D4)	10.9	11.2

The room temperature storage of apple juice samples hydrolysed at 120 °C for 20 minutes showed that the radio-chromatographic pattern/composition of the ¹⁴C-dithianon degradates remained stable from 7 days through 21 days (see Table 63). The degradation pattern is essentially the same with buffer (stored refrigerated for 33 days) and without buffer (stored at room temperature).

Table 63 Degradation products after hydrolysis at 120 °C and storage at room temperature

Degradation Product	Average% TAR						
	Storage interval						
	0 hours	6 hours	24 hours	48 hours	7 days	14/15 days	21 days
Phthalic acid, 4005234	2.1	2.6	3.1	2.8	4.1	3.2	3.4
UK1	5.3	4.7	5.4	7.0	5.5	4.3	5.8
UK3 ^a	8.7	na	na	na	na	na	na
Reg. No. 4107273 (D2)	13.7	11.7	5.9	4.4	na	na	na
Reg. No. 4110904	5.7	4.9	5.4	5.7	4.0	4.8	4.9
Reg. No. 4110933(D8)	4.1	3.8	3.1	4.3	3.9	3.9	3.9
Dithianon	na	na	na	na	na	na	na
Reg. No. 31062 (D4)	7.4	7.0	2.8	8.0	7.8	7.2	8.5

na = not assignable;

^a less polar, co-elutes with Reg. No. 4110934 (D15)

In processing – effect on the residue level

The Meeting received information on the fate of dithianon residues during the processing of oranges to juice and pulp, of apple to juice, sauce, pomace and dried fruits, of grapes to juice, must, wine and pomace and of hops to beer. Further studies conducted in 2009/2010 on apples, cherries, plums and

grapes investigated the fate of parent dithianon and of the metabolite Reg. No. 4110904 after processing. The information submitted on processing procedures is summarized below.

RAC, Country, year	Procedure description, remarks	Doc Id-No
Oranges, USA, 1991	No detailed information on the processing procedures of oranges to peel, juice, dry and wet pulp, oil and molasses was submitted.	DT-710-008
Apple, Germany, 1993	A description of processing methods used was not provided.	DT-711-094 DT-711-095
Apple, Italy, 2000	Apples were crushed and pressed to produce <u>juice</u> and <u>wet pomace</u> . Pectolytic enzymes were added to the juice and it was left to settle at least for 12 hours. The juice was filtered, pasteurised by heating to approximately 85 °C for at least one minute, and was then placed in sterilized glass bottles with screw caps. For dried pomace, the wet pomace was placed into an oven and dried at 60 °C for one day. To produce <u>puree</u> , the apples were blanched in hot water (80 °C for 5 minutes) and crushed and sieved to obtain puree. After addition of sugar, heating until a degree Brix of about 24%. The puree was then sterilised at 115-120 °C for 10 minutes and frozen. To produce <u>canned apples</u> the apples were peeled, blanched in hot water (80 °C, for 5 min), core was removed and the apples were cut into pieces.	2002/1011501 2002/1011502
Apple, Italy, Spain, 2001	Apples were processed into apple <u>juice</u> by crushing with a crushing machine. Ascorbic acid (300 mg/kg) was added to prevent oxidation. The crushed apples were immediately pressed in a mechanical wine press. The juice was then poured into a stainless steel vat. Pectolytic enzymes (at a concentration of 5 g/hl) were added to the juice to accelerate the clarification process. A subsample of pomace was taken from each specimen and frozen. After a clarification period of at least 12 hours, the dregs were discarded and only clear juice was bottled, and samples of juice were taken.	2002/1011555
Apple, Germany, 2003	In a first step the apples were filled in a stainless steel tank and washed by hand. The washed apples were transferred into a shredder and subsequently ground. The resulting pulp samples were divided into two parts - the major part was used for juice production; the other part was processed to apple sauce. For the production of <u>juice</u> , an aliquot of the pulp sample was transferred into a tube press. The pressure was increased. The resulting juice was passed through a cloth and a metal sieve. The juice and the <u>fresh pomace</u> were collected separately in tubs. Parts of the fresh pomace were dried at an oven at 90 °C until constant weights were achieved. The other part was used as specimen for analysis. For clarification of the fresh juice, pectinase was added first; in a second step and prior to a filtration step gelatine and Kieselsol were added. The clear juice resulting from the filtration step was subjected to pasteurization (90 °C, 5 min). For the preparation of <u>apple sauce</u> , an aliquot of pulp was filled into a sauce pan and heated up to 85 °C. As soon as the 85 °C was reached (which is sufficient to turn the pulp into mash, duration between 30 and 70 min), the mash was strained using a puree apparatus and filled into sample containers while still hot. Cooling down.	2003/1001126
Apple, Germany, 2010	Preparation of <u>canned apple</u> : Peeling, cutting in small pieces, removal of core and stalk. Addition of water, ascorbic acid, citric acid and glucose syrup. Boiling. Regulation of pH and dry substance. Pasteurisation in jars. Cooling down. Preparation of <u>apple sauce</u> : Cutting in half pieces, removal of stalks. Soft boiling of apple pieces in water. Sieving of cooked apples. Addition of sugar and ascorbic acid. Regulation of pH and dry substance. Pasteurisation in jars. Cooling down. <u>Dried apple</u> preparation: Removal of core and stalks, cutting into rings. Drying in an oven. <u>Juice</u> preparation: Apples were mashed. Pressing to extract the raw juice → wet pomace. The raw juice was pasteurized. Cooling down. Wet pomace dried in an oven → dried pomace.	2011/1135917
Cherries, Germany, 2009	<u>Jam preparation</u> : Washed fruits will be stoned, addition of sugar and glucose syrup to the fruits. Cooking until a dry substance of 63 – 65%. Adding of pectine and citric acid. Cooking until a dry substance of 60 – 62%. Cooling down. Preparation of <u>canned cherries</u> : Addition of water, ascorbic acid, citric acid and sugar to the	2010/1093253

RAC, Country, year	Procedure description, remarks	Doc Id-No
	fruits. Cooking, filling product into cans. Cooling down. Preparation of <u>juice</u> : Washed cherries were mashed in a masher. Pressing to extract the raw juice → wet pomace. The raw juice was pasteurized. Cooling down.	
Plums, Germany, 2009	Preparation of <u>puree</u> : Plums washed, stalks were removed. Fruits will be stoned, cut into small pieces. Addition of sugar, gingerbread, spice, citric acid and glucose syrup to the fruits. Cooking until dry substance > 53%. Cooling down. Preparation of <u>dried prunes</u> : Fruits will be stoned. Dipping in 0.5% ascorbic acid solution. Drying in an oven (65 °C) until a maximal moisture content of 25%.	2011/1031148
Grapes, Germany, 2010	<u>Rose grape variety</u> : The unwashed grapes were crushed. The mesh (stalks, flesh, skin, seed, juice) was pressed to extract the liquid. Before the must was clarified, K ₂ S ₂ O ₅ was added. After the clarification, <u>raw juice</u> was pasteurized (83–87 °C, 2 min). Raw juice was poured into glass vessels, yeast and nutrient salt was added for fermentation. After fermentation, K ₂ S ₂ O ₅ was added. Clarification of the fermentation product. First transfer of wine between vessels. Bentonite was added to absorb proteins. Second transfer of wine and K ₂ S ₂ O ₅ was added. The young <u>wine</u> was filtered after clarification, bottled for maturation and stored at 5–8 °C. <u>Red grape variety</u> : The unwashed grape bunches were crushed. The stalks were removed. K ₂ S ₂ O ₅ was added. The mesh (flesh, skin, seed, juice) was heated up to 60 °C. During heating, mesh was stirred. Subsequent to the cooling down phase, the mesh was pressed to extract the liquid. After the clarification, <u>raw juice</u> was pasteurized (83–87 °C, 2 min.). Raw juice was poured into glass vessels, yeast and nutrient salt was added for fermentation. After fermentation, K ₂ S ₂ O ₅ was added. Clarification of the fermentation product. First transfer of wine between vessels. Bentonite was added to absorb proteins. Second transfer of wine and K ₂ S ₂ O ₅ was added. The young <u>wine</u> was filtered after clarification, bottled for maturation and stored at 5–8 °C. <u>Raisin production</u> : washed grape bunches were put in boiling water for 8–10 sec and afterwards they were manually washed (3 min) with cold tap water. The bunches were dried in a oven (66–74 °C) for 24 hours until a moisture content of 10–14% was achieved. After drying, raisins were removed from the stalks.	2011/1248836
Grapes, Germany, 1986/87	Trials on red grapes (variety Portugieser) and white grapes (variety Müller-Thurgau). A description of processing methods used in the trials was not provided.	DT-713-031
Grapes, Germany, Spain, France, Italy, 2001	<u>White wine production (Germany, Italy)</u> : The grapes were placed directly into the wine press in order to be pressed. Wet pomace and must were separated immediately after the pressing step. Aliquots of the wet pomace sample were dried at about 60 °C in an oven. The resulting must was allowed to settle. After decantation from the must deposits, the alcoholic fermentation took place; it is considered as complete when fermentation has slowed down or stopped (indicated by a density below 1000). For stabilizing and after addition of gelatine / potassium metabisulphite, the young wine was kept under cold storage conditions for at least two weeks. After filtration, the wine was bottled. <u>Red wine production (Spain, France)</u> : The grapes used for red wine processing were crushed and stemmed with an electric crusher/stemmer. The crushed grapes were recovered in a stainless steel tank. The stems were weighed and discarded. Potassium metabisulphite was added to the remaining crushed grapes. Dry active yeasts (0.1 g/L) were added to the must. The progress of the alcoholic fermentation was followed each day by measuring the density, temperature and pH of the must. In case of the French trial, sugar was added to increase the alcohol concentration. The alcoholic fermentation was considered as complete when the density of the must fell below the value 1000 (duration: about one week). The wine was run off to the tank (free-run wine) and the solid part was pressed with a water press in such a manner as to recover the maximum quantity of wine. The pressed wine was added to the free-run wine; wet pomace and young wine sample were taken. Aliquots of the wet pomace sample were dried at about 60 °C in an oven. The malolactic fermentation was carried out in absence of air, at ambient temperatures with a direct inoculation of lactic bacteria. The progress of the malolactic fermentation was followed-up one time each week. After the completion of the malolactic fermentation, potassium metabisulphite was added for natural clarification. After the first clarification step, sediment samples (designated as lees) were taken; subsequently, dry gelatine and further potassium metabisulphite were added to the wine. As for white wine, the young wine was stored in the cold room for stabilization. In order to remove impurities (solid material), the wine was finally filtered and bottled.	2003/1014014

RAC, Country, year	Procedure description, remarks	Doc Id-No
	<u>Juice production:</u> The grapes kept for grape juice processing were crushed and stemmed. The crushed grapes were weighed and, after addition of pectolytic enzymes, placed in plastic jars. The depectinisation of juice took place for two hours at a temperature between 45°C and 60°C (measured by a thermometric probe inside the jar). The glass jars were then removed from the saucepan and their content was pressed in a water press. The wet pomace was then weighed and discarded. The recovered juice was analysed (degree Brix, total acidity, and pH) and then put back in glass jars for clarification. The clarification took place for 5 minutes at a temperature of about 85 °C. This clarification phase was followed by a cold storage of at least 12 hours. After cold storage and racking, only the clear juice (without sediment) was filtered, pasteurized for 1 minute at 85 °C and bottled.	
Hops, Germany, 2001	Besides the hops, malt, yeast and drinking water were used. The brewing process was done at a laboratory scale, but fully comparable to industrial brewing process, including the steps brewing, lautering (→ brewer's grain), wort cooking (→ spent hops), primary fermentation (→ brewer's yeast) and secondary fermentation (→ beer).	2002/1006301

The results of the processing studies on oranges, apples, cherries, plums, grapes and hops for parent dithianon and of the degradation product Reg. No. 4110904 on apples, cherries, plums and grapes are presented in Table 64.

Table 64 Dithianon residues after processing (concentration of Reg. No. 4110904 in brackets)

RAC, country, year	Application			PHI, Days	Commodity	Residues, mg/kg	Doc Id-No, Analytical Method
	Form	kg ai/ha	No				
Oranges, USA, FL 1991	SC	5.6	2	0	Whole fruit Peel Dry pulp Wet pulp Juice Molasses Oil	0.59 0.11 < 0.05 < 0.05 < 0.05 < 0.05 0.30	DT-710-008, HUK 460/62-01R
Oranges, USA, FL 1991	SC	7.5	3	30	Whole fruit Peel Dry pulp Wet pulp Juice Molasses Oil	3.48 0.42 0.10 0.10 < 0.05 < 0.05 1.59	DT-710-008, HUK 460/62-01R
Apple, Germany, 1993	SC	0.55-0.64	12	21	Whole fruit Washed apple Juice Wet pomace Sauce Dried apple	1.7 1.5 < 0.05 2.1 < 0.05 < 0.05	DT-711-094, FAMS 009-01
Apple, Germany, 1993	SC	0.55-0.57	12	21	Whole fruit Washed apple Juice Wet pomace Sauce Dried apple	1.5 1.4 0.06 1.6 < 0.05 < 0.05	DT-711-095, FAMS 009-01
Apple, Germany, 2003	WG	1.05	8	21	Whole fruit Washed apple Juice Wet pomace Dry pomace Sauce	0.95 0.62 < 0.01 1.4 0.57 < 0.01	2003/1001126, RLA 12616.05V
Apple, Germany, 2003	WG	1.05	8	21	Whole fruit Washed apple Juice Wet pomace Dry pomace Sauce	1.8 1.4 < 0.01 5.5 0.91 < 0.01	2003/1001126, RLA 12616.05V
Apple, Italy,	WG	0.51-0.53	12	21	Whole fruit	0.13	2002/1011501,

RAC, country, year	Application			PHI, Days	Commodity	Residues, mg/kg	Doc Id-No, Analytical Method
	Form	kg ai/ha	No				
2000					Washed apple Juice Wet pomace Dry pomace Sauce Canned apple	0.23 < 0.01 0.36 0.10 < 0.01 < 0.01	RLA 12616.03V RLA 12620.00V
Apple, Italy, 2000	WG	0.69-0.71	8	21	Whole fruit Washed apple Juice Wet pomace Dry pomace Sauce Canned apple	0.10 0.10 < 0.01 0.34 0.07 < 0.01 < 0.01	2002/1011501, RLA 12616.03V RLA 12620.00V
Apple, Italy, 2000	WG	0.51-0.54	12	21	Whole fruit Washed apple Juice Wet pomace Dry pomace Sauce Canned apple	0.30 0.07 < 0.01 0.32 0.13 < 0.01 < 0.01	2002/1011502, RLA 12616.03V RLA 12620.00V
Apple, Italy, 2000	WG	0.68-0.71	8	21	Whole fruit Washed apple Juice Wet pomace Dry pomace Sauce Canned apple	0.08 0.06 < 0.01 0.28 0.04 < 0.01 < 0.01	2002/1011502, RLA 12616.03V RLA 12620.00V
Apple, Italy, 2001	WG	1.05	8	22	Whole fruit Whole fruit ^{a)} Washed apple Juice Wet pomace	2.21 2.92 0.02 < 0.01 4.98	2002/1011555, RLA 12616
Apple, Spain, 2001	WG	1.05	8	21	Whole fruit Whole fruit ^{a)} Juice Wet pomace	1.85 0.58 0.91 < 0.01	2002/1011555, RLA 12616
Apple, Germany, 2010	WG	0.7	4	35	Whole fruit Washed apple Sauce Canned apples Wet pomace Juice Dried apples Dried pomace Fruit syrup	0.14 (< 0.01) 0.10 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.52 (< 0.01) < 0.01 (< 0.01) 0.03 (< 0.01) 1.72 (< 0.01) < 0.01 (< 0.01)	2011/1135917, Trial L100471, L0152/01
Apple, Germany, 2010	WG	0.7	4	35	Whole fruit Washed apple Sauce Canned apples Wet pomace Juice Dried apples Dried pomace Fruit syrup	0.32 (< 0.01) 0.14 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.71 (< 0.01) < 0.01 (< 0.01) 0.02 (< 0.01) 1.81 (< 0.01) < 0.01 (< 0.01)	2011/1135917, Trial L100472, L0152/01
Apple, Germany, 2010	WG	0.7	4	35	Whole fruit Washed apple Sauce Canned apples Wet pomace Juice Dried apples Dried pomace Fruit syrup	0.21 (< 0.01) 0.12 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.48 (< 0.01) < 0.01 (< 0.01) 0.03 (< 0.01) 1.24 (< 0.01) < 0.01 (< 0.01)	2011/1135917, Trial L100473, L0152/01
Apple,	WG	0.7	4	35	Whole fruit	0.40 (< 0.01)	2011/1135917,

RAC, country, year	Application			PHI, Days	Commodity	Residues, mg/kg	Doc Id-No, Analytical Method
	Form	kg ai/ha	No				
Germany, 2010					Washed apple Sauce Canned apples Wet pomace Juice Dried apples Dried pomace Fruit syrup	0.24 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 1.64 (< 0.01) 0.01 (< 0.01) 0.10 (< 0.01) 5.20 (0.02) < 0.01 (< 0.01)	Trial L100474, L0152/01
Cherries, 2009	WG	1.6	3	21	Cherries Washed cherries Canned cherries Jam Juice Wet pomace	0.08 (< 0.01) 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.04 (< 0.01)	2010/1093253, Trial L090416, L0152/01
Cherries, 2009	WG	1.6	3	21	Cherries Washed cherries Canned cherries Jam Juice Wet pomace	0.27 (< 0.01) 0.03 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.10 (< 0.01)	2010/1093253, Trial L090417, L0152/01
Cherries, 2009	WG	1.6	3	21	Cherries Washed cherries Canned cherries Jam Juice Wet pomace	0.14 (< 0.01) 0.02 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.05 (< 0.01)	2010/1093253, Trial L090418, L0152/01
Cherries, 2009	WG	1.6	3	21	Cherries Washed cherries Canned cherries Jam Juice Wet pomace	0.39 (< 0.01) 0.03 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.08 (< 0.01)	2010/1093253, Trial L090419, L0152/01
Plums, Germany, 2009	WG	1.6	3	21	Whole fruit Washed plums Puree Dried prunes	0.19 (< 0.01) 0.12 (< 0.01) < 0.01 (< 0.01) 0.11 (< 0.01)	2011/1031148, Trial L090412, L0152/01
Plums, Germany, 2009	WG	1.6	3	21	Whole fruit Washed plums Puree Dried prunes	0.25 (< 0.01) 0.12 (< 0.01) < 0.01 (< 0.01) 0.17 (< 0.01)	2011/1031148, Trial L090413, L0152/01
Plums, Germany, 2009	WG	1.6	3	21	Whole fruit Washed plums Puree Dried prunes	0.30 (< 0.01) 0.16 (< 0.01) < 0.01 (< 0.01) 0.07 (< 0.01)	2011/1031148, Trial L090414, L0152/01
Plums, Germany, 2009	WG	1.6	3	21	Whole fruit Washed plums Puree Dried prunes	0.95 (< 0.01) 0.51 (< 0.01) 0.03 (< 0.01) 0.43 (< 0.01)	2011/1031148, Trial L090415, L0152/01
Grapes, Germany, 2010	WG	1.05	4	35	Fruit Rose wine: - Pomace, wet - Must - Juice - Wine Red wine: - Pomace, wet - Must - Juice - Wine Raisins	6.84 (0.01) 8.92 (0.04) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 3.01 (< 0.01) 0.02 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 21.28 (0.11)	2011/1248836, Trial L100595, L0152/01
Grapes, Germany, 2010	WG	1.05	4	35	Fruit Rose wine: - Pomace, wet - Must	2.96 (< 0.01) 8.40 (0.02) < 0.01 (< 0.01)	2011/1248836, Trial L100596, L0152/01

RAC, country, year	Application			PHI, Days	Commodity	Residues, mg/kg	Doc Id-No, Analytical Method
	Form	kg ai/ha	No				
					- Juice - Wine Red wine: - Pomace, wet - Must - Juice - Wine Raisins	< 0.01 (< 0.01) < 0.01 (< 0.01) 1.66 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 6.16 (0.02)	
Grapes, Germany, 2010	WG	1.05	4	35	Fruit Rose wine: - Pomace, wet - Must - Juice - Wine Red wine: - Pomace, wet - Must - Juice - Wine Raisins	3.43 (< 0.01) 4.52 (< 0.01) 0.02 (< 0.01) 0.01 (< 0.01) < 0.01 (< 0.01) 1.88 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 4.08 (0.02)	2011/1248836, Trial L100597, L0152/01
Grapes, Germany, 2010	WG	1.05	4	35	Fruit Rose wine: - Pomace, wet - Must - Juice - Wine Red wine: - Pomace, wet - Must - Juice - Wine Raisins	7.96 (< 0.01) 10.96 (0.02) 0.02 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 2.85 (< 0.01) 0.02 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 5.04 (0.02)	2011/1248836, Trial L100598, L0152/01
Grapes, Germany, 1986	SC	0.3–0.8	8	35	Grapes Must Wine	0.64 < 0.05 < 0.05	DT-713-031, RU 107/34/10
Grapes, Germany, 1986	SC	0.38	8	35	Grapes Must Wine	1.11 0.11 < 0.05	DT-713-032, RU 107/34/10
Grapes, Germany, 1986	SC	0.23	8	35	Grapes Must Wine	4.16 0.10 < 0.05	DT-713-033, RU 107/34/10
Grapes, Germany, 1987	SC	0.3-0.6	8	35	Grapes Must Wine	0.73 0.02 0.03	DT-713-034, RU 107/34/10
Grapes, Germany, 1987	SC	0.23-0.68	8	35	Grapes Must Wine	1.83 0.04 0.03	DT-713-035, RU 107/34/10
Grapes, Germany, 1987	SC	0.3-0.45	7	35	Grapes Must Wine	2.9 0.24 < 0.02	DT-713-036, RU 107/34/10
Grapes, Germany, 1987	SC	0.38-0.56	8	35	Grapes Must Wine	1.61 < 0.02 < 0.02	DT-713-037, RU 107/34/10
Grapes, Germany, 1987	SC	0.19-0.68	7	35	Grapes Must Wine	4.5 0.11 < 0.02	DT-713-038, RU 107/34/10
Grapes, Germany, 1987	SC	0.23-0.44	8	35	Grapes Must Wine	1.21 < 0.05 < 0.05	DT-713-039, RU 107/34/10
Grapes, Germany, 2001	WG	1.1	8	41	Grapes Grapes ^{a)} Must Wet pomace Dry pomace	4.17 3.45 0.72 6.79 1.18	2003/1014014, 2003/1014345, RLA 12616V RLA 12620V

RAC, country, year	Application			PHI, Days	Commodity	Residues, mg/kg	Doc Id-No, Analytical Method
	Form	kg ai/ha	No				
					Young wine Wine Juice	< 0.01 < 0.01 < 0.01	
Grapes, Italy, 2001	WG	1.1	8	42	Grapes Grapes ^{a)} Must Wet pomace Dry pomace Young wine Wine Juice	4.68 4.77 1.55 10.22 0.72 < 0.01 < 0.01 < 0.01	2003/1014014, 2003/1014345, RLA 12616V RLA 12620V
Grapes, Spain, 2001	WG	1.1	8	41	Grapes Grapes ^{a)} Must Wet pomace Dry pomace Young wine Wine Juice	3.27 2.03 0.85 0.61 0.25 < 0.01 < 0.01 < 0.01	2003/1014014, 2003/1014345, RLA 12616V RLA 12620V
Grapes, France, 2001	WG	1.1	8	41	Grapes Grapes ^{a)} Must Wet pomace Dry pomace Young wine Wine Juice	4.85 4.60 0.20 1.65 1.03 < 0.01 < 0.01 < 0.01	2003/1014014, 2003/1014345, RLA 12616V RLA 12620V
Hops, Germany, 2001, Trial 11- G01N059R	WG	0.7-2.8	10	13	Dried hops Brewer's grain Spent hops Brewer's yeast Beer	140 < 0.02 ^{b)} < 0.1 ^{c)} < 0.02 < 0.02	2002/1006301, M 3442
Hops, Germany, 2001, Trial 5- G01N060R	WG	0.7-2.8	10	13	Dried hops Brewer's grain Spent hops Brewer's yeast Beer	94 < 0.02 < 0.1 < 0.02 < 0.02	2002/1006301, M 3442
Hops, Germany, 2001, Trial 11- G01N061R	WG	0.7-2.8	10	13	Dried hops Brewer's grain Spent hops Brewer's yeast Beer	69 < 0.02 < 0.02 < 0.02 < 0.02	2002/1006301, M 3442
Hops, Germany, 2001, Trial 11- G01N062R	WG	0.7-2.8	10	13	Dried hops Brewer's grain Spent hops Brewer's yeast Beer	51 < 0.02 < 0.02 < 0.02 < 0.02	2002/1006301, M 3442

^a Whole fruit, starting material: RAC just before processing

^b LOD 0.02 mg/kg

^c LOQ 0.1 mg/kg

The processing factors for dithianon residues were calculated from the data recorded in Table 64 and reflect commercial and household processing. The factors and the best estimate are summarized in Table 65.

Table 65 Summary of processing factors for dithianon residues

RAC	Processed commodity	Calculated processing factors	Best estimate
Oranges	Juice	< 0.014, <0.085	< 0.05 (mean)
	Oil	0.46, 0.51	0.49 (mean)
	Wet pulp	0.029, <0.085	<0.06 (mean)
	Dry pulp	0.029, <0.084	<0.06 (mean)
Apple	Juice	<0.005, <0.005, <0.006, < 0.01, <0.03, <0.03, <u><0.03</u> , <u><0.03</u> , 0.04, < 0.05, <0.07, <0.08, <0.1, <0.13	<0.03 (median)
	Sauce	<0.006, <0.08, < 0.01, <0.03, <0.03, <u><0.03</u> , <u><0.03</u> , <0.03, < 0.05, <0.07, <0.1, <0.13	<0.03 (median)
	Fruit syrup	<0.03, <u><0.03</u> , <u>< 0.05</u> , <0.07	< 0.04 (median)
	Canned apple	<0.03, <0.03, < 0.04, <u>< 0.05</u> , <u><0.07</u> , <0.08, <0.1, <0.13	<0.06 (median)
	Dried apple	<0.03, <0.03, <u>0.06</u> , <u>0.14</u> , 0.21, 0.25	0.1 (mean)
	Wet pomace	0.49, 1.07, 1.07, 1.2, 1.47, <u>2.22</u> , <u>2.25</u> , 2.29, 2.77, 3.06, 3.4, 3.5, 3.71, 4.10	2.2 (median)
Cherries	Juice	<0.03, <u>< 0.04</u> , <u><0.07</u> , <0.13	< 0.055 (median)
	Canned cherry	<0.03, <u>< 0.04</u> , <u><0.07</u> , <0.13	< 0.055 (median)
	Jam	<0.03, <u>< 0.04</u> , <u><0.07</u> , <0.13	< 0.055 (median)
Plums	Puree	<0.03, 0.03, < 0.04, < 0.05,	0.035 (median)
	Dried prunes	0.23, <u>0.45</u> , <u>0.58</u> , 0.68	0.515 (median)
Grapes	Juice	<0.001, <0.001, <0.001, <0.001, <0.002, <u><0.002</u> , <u><0.003</u> , <0.003, <0.003, <0.003, 0.003, <0.005	<0.0025 (median)
	Must	<0.001, <0.003, <0.003, <0.003, 0.003, 0.003, 0.003, 0.01, < 0.012, 0.022, <u>0.024</u> , 0.024, 0.027, < 0.041, 0.043, <0.078, 0.083, 0.099, 0.21, 0.32, 0.42	0.024 (median)
	Wine	<0.001, <0.001, <0.001, <0.001, <0.002, <0.002, <0.003, <0.003, <0.003, <0.003, <u><0.003</u> , <0.004, <0.005, <0.007, < 0.012, < 0.012, 0.016, < 0.041, 0.041, < 0.045, <0.078	<0.003 (median)
	Wet pomace	0.30, 0.36, 0.36, 0.44, 0.55, <u>0.56</u> , <u>1.3</u> , 1.32, 1.38, 1.97, 2.14, 2.84	0.93 (median)
	Dry pomace	0.12, <u>0.15</u> , <u>0.22</u> , 0.34	0.19 (median)
	Raisins	0.63, <u>1.19</u> , <u>2.08</u> , 3.11	1.64 (median)
Hops	Beer	<0.0001, <u><0.0002</u> , <u><0.0003</u> , <0.0004	<0.0003 (median)
	Brewer's grain	<0.0001, <u><0.0002</u> , <u><0.0003</u> , <0.0004	<0.0003 (median)

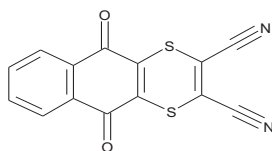
RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

No data were received.

APPRAISAL

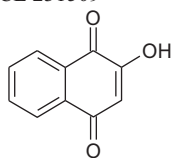
The fungicide dithianon (5,10-dihydro-5,10-dioxonaphtho-[2,3-beta]-1,4-dithiine-2,3-dicarbonitrile) has been evaluated by the JMPR for the first time in 1992 (T, R). The compound was evaluated for toxicology by the 2010 JMPR where an ADI of 0.01 mg/kg bw and an ARfD of 0.1 mg/kg was allocated. The periodic review for residues was scheduled at the 39th session of the CCPR for the 2012 JMPR but postponed to evaluate in 2013.



The Meeting received information from the manufacturer on physical and chemical properties, metabolism studies on plants and animals, analytical methods, supervised residue trials data, processing studies as well as use pattern.

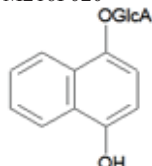
The metabolism and distribution of dithianon in plants and animals as well as the nature of the residue under simulated processing conditions, was investigated using the [5,6,9,10-]¹⁴C-labelled compound or, in some studies, a [5,6,9,10-]¹³C/¹⁴C-labelled compound. The following abbreviations are used for the metabolites or degradation products discussed below.

CL 231509

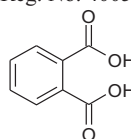


2-Hydroxy-1,4-naphthoquinone

M216F020

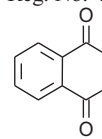
Glucuronic acid conjugate of 1,4-dihydroxy-naphthalene
Reg. No. 4110904

Reg. No. 4005234



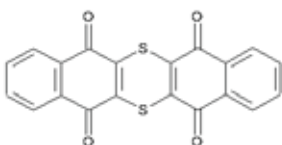
Phthalic acid

Reg. No. 4107273

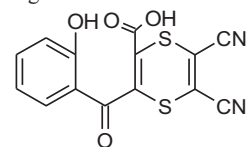


1,4-Naphthoquinone

Reg. No. 31062

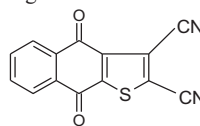
Dibenzo-[*b,i*]-thianthrene-5,7,12,14-tetrone

Reg. No. 4110904

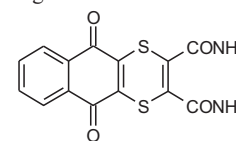


5,6-Dicyano-3-(2-hydroxybenzoyl)-1,4-dithiine-2-carboxylic acid

Reg. No- 4110933

4,9-Dihydro-4,9-dioxonaphtho[2,3-*b*]-thiophene-2,3-dicarbonitrile

Reg. No. 4110934

5,10-Dihydro-5,10-dioxo-naphtho[2,3-*b*]-1,4-dithiin-2,3-dicarboxylic acid diamide

Animal metabolism

Metabolism studies on rats reviewed by the 2010 JMPR show that at tested doses of 10 and 50 mg/kg bw orally administered dithianon was about 40–50% absorbed in rats. The majority of the administered dose was recovered in faeces (64–72%) and in urine (27–31%). Dithianon was extensively metabolized according to the following key transformation steps: oxidation of the sulphur atoms, cleavage of the dithiine ring, reduction of the 1,4-naphthoquinone moiety and further glucuronidation, as well as substitution of the carbonitrile moieties by amino and carboxy groups. The only metabolite in rat urine at a level greater than 2% was M216F020.

Two studies were submitted on the metabolism of dithianon in lactating goats. In the first study, one lactating goat each was dosed by capsule at a daily nominal rate of 6 mg (equiv. to 2.5 ppm in the feed) and 60 mg [¹⁴C] dithianon (equiv. to 28 ppm) for five days. The highest radioactive residues (TRR) of the high dose group were detected in kidney (0.49 mg/kg as dithianon equivalents) and in liver (0.17 mg/kg equiv.). Lowest TRR were found in fat (0.013 mg/kg equiv.), in milk (0.018 mg/kg equiv.) and muscle (0.013 mg/kg equiv.). Most of the [¹⁴C] residue was rapidly and constantly excreted via faeces and urine - almost 80% of the applied dose was eliminated at the end of the study.

Further investigation on the nature of radioactive residues was carried out with the high dose (60 mg/day) samples. The TRR (calculated as dithianon equivalents) in muscle and fat were very low

(0.013–0.014 mg/kg equiv.), and no further characterization was possible. For milk and edible tissues, the extracted radioactive residues ranged from 49% of TRR (0.08 mg/kg equiv.) in liver to 77% (0.018 mg/kg equiv.) in milk. The radioactivity in post extraction solids (PES) ranged from 20% (0.005 mg/kg equiv.) in milk to 74% (0.36 mg/kg equiv.) in kidney. Several radioactive components were detected in the extracts but not further identified. Parent dithianon was identified in liver (0.96% of TRR), kidney (2.3% of TRR) and milk (8.2% of TRR).

In the second goat study, after five consecutive daily administrations of [$^{13}\text{C}/^{14}\text{C}$] dithianon at a dose of 60 mg/animal and day (equivalent to 25 ppm in the feed), the highest TRR were detected in kidney (0.48 mg/kg equiv.) and in liver (0.16 mg/kg equiv.). Lower radioactive residues were found in muscle (0.013 mg/kg), in milk (0.018 mg/kg) and fat (subcutaneous 0.074 mg/kg equiv., renal 0.009 mg/kg equiv.). The major route of excretion of radioactivity was via faeces, accounting for 47% of the total administered dose. A further 18% of the total administered radioactivity was excreted via urine.

With the exception of milk, most of the radioactive residues could not be extracted. The PES in liver, kidney, muscle and fat ranged from 59.4% in kidney to 80% in muscle. Neither parent nor any corresponding metabolite was identified. However, in liver, kidney, urine and bile a very complex metabolite profile was noted. More than 20 components were found in the organic phase and at least six components were detected in the aqueous phase at low absolute residue levels (< 0.05 mg/kg) in tissues. In milk, the extracted radioactivity accounted for 78.3% of TRR (0.012 mg/kg equiv.).

The reactivity of dithianon with nucleophiles (commonly thiols in the form of proteins and peptides such as glutathione) was demonstrated *in vitro*. Glutathione and N-acetylcysteine react very quickly with dithianon when incubated in pH 6.5 buffers at 37 °C. It was indicated that the reaction of dithianon with glutathione and protein thiol groups *in vivo* should be virtually instantaneous.

Two groups of laying hens, five hens per group, were treated orally once daily for 5 consecutive days with gelatin capsules containing dithianon. The actual doses of dithianon administered were 0.4 mg/day and 4 mg/day, equivalent to 3.6 ppm and 39 ppm in the feed, respectively.

Over the dosing period, a rapid absorption and excretion of radioactivity occurred. About 90% of the total radioactivity administered was eliminated in excreta by 6 hours after the last dose. There was no indication of accumulation of [^{14}C] dithianon in poultry tissues and eggs.

The highest TRR (in mg/kg as dithianon equiv.) were found in the kidney (0.042 and 0.34–0.38 mg/kg low and high dose, respectively), liver (0.017 and 0.17–0.19 mg/kg), skin with fat (0.005 and 0.039–0.041 mg/kg) and GI Tract (0.14 and 1.5 mg/kg). The lowest concentrations were found in muscle (0.002 and 0.022 mg/kg) and abdominal fat (< 0.002 and 0.014 mg/kg). The highest TRR in egg yolks were 0.005 and 0.075 mg/kg at the end of the study.

Solvent extraction was performed on the high dose group samples and released about of 68% of TRR in muscle (0.008 mg/kg equiv.), 76% of TRR in skin with fat (0.031 mg/kg equiv.), 72% of TRR in liver (0.13 mg/kg equiv.), 74% of TRR in kidney (0.28 mg/kg equiv.) and 47% of the TRR egg yolks (0.037 mg/kg equiv.). The majority of the extracted radioactivity was aqueous/methanol-soluble (35% in egg yolk to 67% of TRR in kidney). The chloroform-soluble radioactivity, containing less polar components, accounted for 6.6% in kidney to 16% of the TRR in liver. Radioactivity in the PES accounted for 25% in liver to 54% of the TRR in egg yolk.

Parent dithianon, detected in minor amounts in the excreta only (1.5% of TRR), was extensively metabolized to yield numerous minor metabolites. The metabolites were profiled by HPLC but were not identified as low concentrations prevented isolation. The organo-soluble metabolites accounted for ≤ 0.003 mg/kg equiv. each in the kidney and liver. One major polar component found in the aqueous/methanol extract accounted for 19% TRR (0.035 mg/kg equiv.) in liver, 11% TRR (0.042 mg/kg equiv.) in kidney, 36% TRR (0.015 mg/kg equiv.) in skin and fat, and 5.7% TRR (0.004 mg/kg equiv.) in egg yolk.

Metabolism studies performed on rats, goats and hens have shown that dithianon is rapidly and intensively metabolized by a number of degradation processes; it was only detected in trace amounts in tissues and/or excreta. As key degradation steps oxidation/reduction and reaction with nucleophiles, commonly R-SH in the form of proteins and peptides such as glutathione are assumed. These reactions result in a huge number of individual metabolites, but also incorporation into natural products. No individual metabolites had been identified; all of them were present in very minor amounts.

Plant metabolism

The metabolism of dithianon has been studied with [^{14}C] dithianon on citrus trees, apple trees, spinach and wheat. The study designs of the plant up-take parts reflect the intended use pattern with several foliar post emergence applications.

Following foliar applications, there was no translocation from the part being directly treated to other parts of the plant. When applied to fruit crops, the dithianon residues remained predominantly associated with the peel. Most of the radioactivity present (> 50% TRR) could be washed off by a surface rinse using acetonitrile/HCl. Neither parent nor any metabolite was translocated to a significant degree into flesh or pulp. Dithianon was identified as the major component of the TRR and ranged from 50.9% in wheat grain up to 96% in spinach leaves.

The parent compound is further metabolized to a large number of polar components. With the exception of spinach, these components could not be identified. None of these metabolites was found in amounts exceeding 5% of the TRR. In spinach, metabolite 4110934, a dicarboxylic acid diamide derivative, 2-hydroxynaphthoquinone (CL 231509) and phthalic acid were found, indicating that the absorbed dithianon was completely metabolised by the plants. All of the individual components of the extracted residues in spinach were between 0.1 and 0.5% of the TRR (0.13–0.8 mg/kg equiv.).

The different functional groups on the dithianon molecule provide multiple sites for chemical and enzymatic attacks resulting in cleavage of the dithiine as well as the quinone ring. The primary products formed are very reactive and could be the target of quite a number of further metabolism and conjugation reactions (e.g. hydroxylation, sulphur oxidation, and reactions with naturally occurring plant constituents), but also incorporation into plant constituents. The Meeting considered parent as the only relevant residue occurring after foliar treatment of plants with dithianon.

Environmental fate

For dithianon, supervised residue trials data were received for foliar spray on permanent crops such as citrus fruits, tree nuts, pome fruits, stone fruits, grapes and hops. Therefore, neither environmental fate nor rotational crops studies are necessary.

Dithianon is not stable in aqueous media. A hydrolysis study showed DT_{50} values of 10.7 days at pH 5, 0.6 days at pH 7 and ca. 10 minutes at pH 9. The photochemical degradation at 20 °C in sterile pH 4 buffer resulted in a DT_{50} value lower than 0.05 days.

Methods of analysis

The Meeting received descriptions and validation data for analytical methods for residues of dithianon in plant and animal commodities. Residue analytical methods for dithianon rely on HPLC with UV-detection or LC-MS/MS for plants and HPLC with electrochemical detection or LC-MS/MS for animal matrices. Typical LOQs achieved for plant and animal commodities fall in the range of 0.01–0.05 mg/kg (except hops, dried, 1 mg/kg). Methods have been subjected to independent laboratory validation.

Descriptions and validation data for analytical methods for residues of the degradation product 4110904 in citrus fruit, apples, grapes, plums and grape wine were received. The analytical methods rely on LC-MS/MS. Typical LOQs achieved for plant commodities were 0.01 mg/kg.

Stability of residues in stored analytical samples

Information was received on the freezer storage stability of dithianon and 4110904 residues in plant commodities.

Older studies from 1992–1994 show that dithianon residues were not stable in spiked samples for a period longer than two months. Newer studies with incurred residues in apples (testing period 2 years) and wine grapes (testing period 14 months) show that dithianon residues were apparently stable at freezer temperature for the intervals tested. Residues of dithianon were not stable in wine, declining on average by 86% of the original fortification after 26 weeks of frozen storage.

The storage stability studies with 4110904 demonstrate that the compound is stable under freezer conditions in plant matrices for about two years in apples, plums and wine. Residues of 4110904 were not stable in grapes, declining by ca. 65% of the fortification level after 3 months, and in lemons, declining by ca. 55% after a week.

Definition of the residue

Animal metabolism studies were performed in lactating goats and laying hens. The parent compound dithianon is rapidly and intensively metabolized and was only detected in trace amounts in tissues and excreta. There was no bioaccumulation in tissues, milk and eggs. No individual metabolites had been identified; all of them were present in very minor amounts (< 0.05 mg/kg and also $< 10\%$ TRR).

Dithianon has a log P_{OW} of 3.2. In animal metabolism studies, the TRR in muscle and fat were comparable (dithianon *per se* could not be detected). The Meeting decided that the residue of dithianon is not fat-soluble.

In plant metabolism studies performed on fruits (oranges, apples), leafy crops (spinach) and cereals (wheat) the same metabolic behaviour was observed. The parent compound dithianon is the dominant component of the residue in plant commodities and ranged from 50.9% of the TRR in wheat grain up to 96% of the TRR in spinach leaves. No individual metabolite occur at relative amounts $> 10\%$ of TRR and of absolute concentrations of > 0.05 mg/kg in the same matrix.

Therefore, from the metabolism studies on plants and animals presented, the proposed definition of the residue is parent dithianon only.

The Meeting took into account the possibility of the formation of two hydrolysis products (Reg. No. 31062 and 4110904) in significant concentrations during industrial or household processing of dithianon treated fruits. Based on their dietary risk assessment, the Meeting concluded that there is no need to include both degradates in the residue definition for estimation of the dietary intake.

Definition of the residue (for compliance with the MRL and for estimation of dietary intake) for plant and animal commodities: *Dithianon*.

The residue is not fat-soluble.

Results of supervised residue trials on crops

The Meeting received supervised residue trials data for citrus fruits, apple, pear, cherries, peaches, plums, grapes, currants, almonds and hops. If two field samples were taken or results of two replicate plots were submitted, the mean value was calculated. For HR estimation, the highest single value of the trials according to GAP was used. From two or more trials carried out side-by-side the higher residue was chosen.

Citrus fruits

In Japan, dithianon is registered for foliar spray use on citrus fruits at a maximum application rate of 3×0.5 kg ai/hL with a PHI of 30 days. Supervised trials with 3×0.5 – 0.7 kg ai/hL with a PHI of 28–30 days were available from Japan: four on mandarins (four for whole fruit, six for pulp), two on pomelo, as well as one each on the small citrus fruits sudachi and kabosu (citrus sphaerocarpa).

The Meeting agreed to use the proportionality approach and scaled the residue data of the overdosed trials according to an application rate of 0.5 kg ai/hL.

The scaled dithianon residue values were in:

mandarins 0.46, 0.7, 0.82, 2.2 mg/kg (whole fruit) and < 0.018, < 0.018, < 0.018, < 0.021, 0.05, 0.07 mg/kg (pulp). The highest single value in pulp was 0.09 mg/kg.

pomelos 1.05, 1.45 mg/kg (whole fruit) and 0.02, 0.05 mg/kg (pulp)

sudachi and kabosu 0.84, 2.5 mg/kg (whole fruit).

The Meeting noted that only four residue trials on mandarin, two on pomelo and two on the small citrus varieties (sudachi/kabosu) are insufficient to estimate a maximum residue level for the whole group of citrus fruits.

The Meeting considered that six residue trials were available for mandarin. It was noted that in four trials data for whole fruit and in six trials pulp data were submitted. The Meeting agreed that only four trials on mandarin (whole fruit) are insufficient to estimate a maximum residue level for the subgroup mandarins. The previous recommendations of 3 mg/kg for mandarin, shaddocks or pomelos should be withdrawn.

Pome fruits

Dithianon is registered for foliar spray treatment on pome fruit in Germany with 12 treatments per season of 0.035 kg ai/hL and 0.18 kg ai/ha per m crown height (equivalent to 0.54 kg ai/ha for 3 m crown height) and a PHI of 21 days.

During the years 1975–2000, 21 trials on apples were conducted in Germany (12), France (3), Greece (1), Italy (3) and Spain (2). Foliar applications were made from 12 to 14 times to apple trees at application rates of 0.51–0.63 kg ai/ha. At a PHI of 21 days, the residues were < 0.03, < 0.05, 0.12, 0.13, 0.20, 0.24, 0.36, 0.38, 0.43, 0.48, 0.48, 0.59, 0.62, 0.76, 0.86, 1.0, 1.3, 1.5, 1.7, 1.7 and 1.7 mg/kg.

Four trials on pears were conducted in 2004 in Germany, The Netherlands, Northern France and Denmark with foliar spray by 12×0.53 kg ai/ha. The dithianon residues were at a PHI of 21–22 days 0.19, 0.37, 0.39 and 0.87 mg/kg.

The rank order of the combined dithianon residues on apple and pear were ($n = 25$): < 0.03, < 0.05, 0.12, 0.13, 0.19, 0.20, 0.24, 0.36, 0.37, 0.38, 0.39, 0.43, 0.48, 0.48, 0.59, 0.62, 0.76, 0.86, 0.87, 1.0, 1.3, 1.5, 1.7, 1.7 and 1.7 mg/kg.

The Meeting noted that the ARfD of 0.1 mg/kg bw is exceeded for apple by the IESTI for children (120% of ARfD) using 1.7 mg/kg as HR and decided that the dataset is not appropriate to estimate a maximum residue level for pome fruit.

An alternative GAP is an Italian use of 4×0.3 kg ai/ha on apple and of 3×0.3 kg ai/ha on pear with a PHI of 35 days. In Macedonia, dithianon is registered in apples with 4×0.24 –0.30 kg ai/ha and in pear with 4×0.32 –0.4 kg ai/ha. The PHI is 35 days also.

Five apple trials were conducted in 2003 with 4×0.3 –0.35 kg ai/ha. The dithianon residues were 34–35 days after treatment 0.11, 0.14, 0.35, 0.39 and 0.43 mg/kg.

Eleven apples trials were carried out in 2010 in Germany (1), the UK (1), Belgium (1), the Netherlands (1), France (2), Greece (1), Italy (2) and Spain (2) with 4×0.36 kg ai/ha. The dithianon residues were after a PHI of 35 days < 0.01, 0.02, 0.02, 0.06, 0.10, 0.14, 0.16, 0.21, 0.27, 0.34 and 0.65 mg/kg.

The combined dithianon residue data after application of 4×0.3 –0.36 kg ai/ha from 2003 and 2010 were ($n = 16$): < 0.01, 0.02, 0.02, 0.06, 0.10, 0.11, 0.14, 0.14, 0.16, 0.21, 0.27, 0.34, 0.35, 0.39, 0.43 and 0.65 mg/kg.

The Meeting agreed to extrapolate from apple to the whole group and estimated a maximum residue level of 1 mg/kg for dithianon residues in pome fruits to replace the previous recommendation (5 mg/kg). An STMR and an HR value of 0.15 mg/kg and 0.65 mg/kg were estimated.

Stone fruits

The GAP for stone fruits in Hungary is 2–3 times foliar spray treatment of 0.053–0.066 kg ai/hL, 0.53 kg ai/ha and a PHI of 21 days. Supervised trials were available for cherries, peaches and plums.

On cherries, sour, seven trials were carried out in Germany from 1985 to 1995 by an application of 3×0.53 kg ai/ha and a PHI of 21 days. The dithianon residues were 0.17, 0.26, 0.28, 0.34, 0.41, 0.49 and 0.80 mg/kg.

Further trials on cherries (sweet and sour) were conducted in 2009/2010 in the UK (2), France (3), Germany (2), Greece (2), Italy (3), The Netherlands (2) and Spain (1) with 3×0.53 kg ai/ha and a PHI of 20–21 days. The dithianon residues were 0.04, 0.09, 0.19, 0.19, 0.21, 0.38, 0.43, 0.45, 0.50, 0.57, 0.59, 0.69, 0.82, 0.90 and 1.0 mg/kg.

The Meeting concluded to combine the dithianon residues on cherries from both datasets. The dithianon residues on cherries were in rank order ($n = 22$): 0.04, 0.09, 0.17, 0.19, 0.19, 0.21, 0.26, 0.28, 0.34, 0.38, 0.41, 0.43, 0.45, 0.49, 0.50, 0.57, 0.59, 0.69, 0.80, 0.82, 0.90 and 1.0 mg/kg.

On plums, twelve trials were conducted in 2009/2010 in France (3), Belgium (1), Germany (4), Italy (2) and Spain (2) with 3×0.53 kg ai/ha and a PHI of 20–22 days. The dithianon residues were 0.04, 0.05, 0.06, 0.10, 0.10, 0.18, 0.21, 0.25, 0.27, 0.32, 0.40 and 0.45 mg/kg.

On peaches, twelve trials were conducted in 2009/2010 in France (4), Germany (2), Greece (2), Italy (2) and Spain (2) with 3×0.53 kg ai/ha and a PHI of 20–21 days. The dithianon residues were 0.17, 0.18, 0.24, 0.36, 0.38, 0.43, 0.44, 0.45, 0.56, 0.60, 1.0 and 1.6 mg/kg.

The Meeting noted that the Hungarian GAP is for the stone fruit group, and considered a group maximum residue level. To consider a group maximum residue level, residues in individual commodities should be similar (e.g. medians should not differ by more than five times). The Meeting agreed to estimate a maximum residue level for the group stone fruit.

In deciding whether to combine the datasets for the different crops for use in the statistical calculator or to only utilise the data from the commodity with the highest residues, the Meeting recognised the similarity of the datasets of cherries and peaches (confirmed by the Mann-Whitney U-test). The Meeting agreed to combine these datasets for the purposes of determining a group maximum residue level for stone fruit.

The rank order of the combined dataset of cherries and peaches is ($n = 34$): 0.04, 0.09, 0.17, 0.17, 0.18, 0.19, 0.19, 0.21, 0.24, 0.26, 0.28, 0.34, 0.36, 0.38, 0.38, 0.41, 0.43, 0.43, 0.44, 0.45, 0.45, 0.49, 0.50, 0.56, 0.57, 0.59, 0.60, 0.69, 0.80, 0.82, 0.90, 1.0, 1.0 and 1.6 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg, an STMR of 0.43 mg/kg and an HR of 1.6 mg/kg for dithianon residues in stone fruits. The previous recommendation of 5 mg/kg for dithianon in cherries was withdrawn.

Grapes

Dithianon is registered for foliar spray treatment on grapes in Slovenia with $1\text{--}8 \times 0.35$ kg ai/ha and a PHI of 42 days.

Trials on grapes were available from Germany (24). The plants were treated eight times during the growing season with 0.23–0.68 kg ai/ha; the last applications were in a range of 0.44–0.68 kg ai/ha. The Meeting agreed to use the proportionality approach to scale the residues of a PHI of 41–43 days according an application rate of 0.35 kg ai/ha. The rank order of scaled residues was ($n = 24$): 0.15, 0.19, 0.29, 0.34, 0.36, 0.43, 0.44, 0.44, 0.48, 0.50, 0.54, 0.60, 0.61, 0.72, 0.75, 0.76, 0.80, 0.92, 1.0, 1.05, 1.2, 1.2, 1.4 and 2.5 mg/kg.

Further trials were conducted in France (3), Germany (1), Greece (1), Italy (4) and Spain (4). Grapes were treated with 8×0.56 kg ai/ha. The PHI was 41–42 days. The rank order of the scaled dithianon residues on the application rate of 0.35 kg ai/ha were ($n = 13$): 0.21, 0.28, 0.33, 0.37, 0.63, 0.69, 0.69, 0.81, 0.81, 0.88, 0.94, 2.1 and 4.6 mg/kg.

The rank order of the combined scaled residue data was ($n = 37$): 0.15, 0.19, 0.21, 0.28, 0.29, 0.33, 0.34, 0.36, 0.37, 0.43, 0.44, 0.44, 0.48, 0.50, 0.54, 0.60, 0.61, 0.63, 0.69, 0.69, 0.72, 0.75, 0.76, 0.80, 0.81, 0.81, 0.88, 0.92, 0.94, 1.0, 1.05, 1.2, 1.2, 1.4, 2.1, 2.5 and 4.6 mg/kg.

The Meeting estimated a maximum residue level of 5 mg/kg for dithianon residues in grapes. Because the ARfD of 0.1 mg/kg bw is exceeded by the IESTI of dithianon for grapes using 4.6 mg/kg as HR (310% for children, 150% for general population), the Meeting decided that the maximum residue level of 5 mg/kg is not suitable for table grapes and should be apply to wine grapes only. For calculation of residues in processed commodities (juice, wine), a median residue level of 0.69 mg/kg was estimated.

The Meeting agreed to search for an alternative GAP to estimate a maximum residue level, an STMR and an HR for table grapes.

Another registration exists in Serbia of 3×0.35 kg ai/ha and a PHI of 35 days for grapes. Trials on grapes treated with 3×0.53 kg ai/ha and a PHI of 35 days from Germany (4), France (7), Spain (2), Italy (1) and Greece (1) were submitted. The Meeting agreed to use the proportionality approach to estimate a separate maximum residue level, an STMR and HR for table grapes. The scaled residue values according to Serbian application rate were ($n = 15$): 0.29, 0.39, 0.48, 0.50, 0.56, 0.57, 0.59, 0.63, 0.64, 0.73, 0.86, 0.99, 1.1, 1.2 and 1.3 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg for dithianon residues in table grapes. The previous recommendation for grapes of 3 mg/kg was withdrawn. An STMR of 0.63 mg/kg and an HR of 1.3 mg/kg were estimated.

Currants

In France, dithianon may be used as foliar spray on currants with an application rate of 2×0.49 kg ai/ha and a PHI of 14 days.

Six trials on black currants according to the French GAP (2×0.53 kg ai/ha, PHI 14 days) were submitted. The dithianon residues were < 0.05 , < 0.05 , ≤ 0.1 , 0.11, 0.61 and 0.89 mg/kg.

The Meeting agreed to extrapolate from black currants to currants, black, red, white and estimated a maximum residue level of 2 mg/kg, an STMR of 0.105 mg/kg and an HR of 0.89 mg/kg for dithianon residues in currants.

Almonds

The registered use of dithianon in almonds in France is foliar spray treatment of 2×0.35 kg ai/ha and a PHI of 58 days. Four French trials in line with French GAP were available. The dithianon residues were in almonds (without shell) < 0.05 mg/kg (4).

The Meeting considered four trials as sufficient for the estimation of a maximum residue level in almonds because dithianon is located on the surface of the shell and no residues are to be expected in the nutmeat and estimated a maximum residue level of 0.05* mg/kg, and an STMR and an HR of 0 mg/kg.

Hops, dry

In Austria and Germany, dithianon is registered for use on hops at 10×0.63 –1.4 kg ai/ha (depending from growth stage) and a PHI of 14 days. German trials in line with GAP (10 – 12×0.3 –1.5 kg ai/ha, PHI 14 days) were submitted. The residues were in dried cones 4.1, 16, 17, 21, 22, 32, 58, 70, 82, 88, 89, 94, 96 and 242 mg/kg.

The Meeting estimated for dithianon residues in hops, dry a maximum residue level of 300 mg/kg and an STMR of 64 mg/kg. The previous recommendation of 100 mg/kg should be replaced.

Fate of residues during processing

Nature of residues

Three studies on the nature of the residue under simulated processing conditions, performed with [¹⁴C] dithianon at higher temperatures, were received.

In the first study, hydrolysis was conducted in buffers solutions whereas in the second study, [¹⁴C] dithianon was incubated in apple juice under the conditions of pasteurization (pH 4, incubation for 20 minutes at 90 °C). In both studies, at pH 4, the parent molecule formed the major part of the radioactivity. In addition, a multiple number of unknown degradation products was formed; each of them < 10% of the total applied radioactivity (TAR). At high temperature conditions and pH 5 (simulated processing conditions of baking, brewing and boiling) or pH 6 (simulated processing conditions of sterilization) the hydrolytic degradation of dithianon was fast and resulted in many degradation products. The degradation product 4110904 was found at pH 5 and pH 6 in concentrations exceeding the level of 10% the total applied radioactivity (TAR) accounting for 46–57% of TRR at pH 5 and for about 20% of TRR at pH 6.

A third hydrolysis study on the degradation of dithianon in apple juice at 90 °C, 100 °C and 120 °C was conducted for further characterization of the components formed. The initial high temperature hydrolysis tests with [¹⁴C] dithianon in apple juice resulted in the rapid disappearance of dithianon. Between 44 and 47% of the TAR remained as dithianon after hydrolysis at 90 °C for 20 minutes, 0.9–1% of the TAR remained as dithianon after hydrolysis at 100 °C for 60 minutes and less than 1% of the TAR remained as parent after hydrolysis at 120 °C for 20 minutes. The results of the identification of the degradation products are as follows:

The initial high temperature hydrolysis tests resulted in the formation of naphthoquinone (4107273) at greater than 10% of the TAR upon 20 minutes of hydrolysis at 120 °C. Formation of 4107273 was not observed in the lower temperature hydrolysis samples. 4107273 was also no longer found after refrigerated storage (21 days/33 days) of the apple juice sample hydrolysed at 120 °C. The compound was only found immediately after hydrolysis.

Phthalic acid (4005234) and compound 4110933 were both observed in hydrolysed apple juice, but always at less than 5% of the TAR.

Compounds 4110904 and 31062 were formed at 9.4% and 10.5% of TAR, respectively, upon 60 minutes of hydrolysis at 100 °C. At 20 minutes of hydrolysis at 120 °C, 4110904 was formed at 5.8% and 31062 at 10% of TAR. Both compounds appear to be stable in hydrolysed apple juice stored refrigerated.

Level of residues

The Meeting received information on the fate of dithianon residues during the processing of oranges to juice, oil and dry pulp, of apples to juice, sauce, dried apple and wet pomace, of cherries to juice, canned cherries and jam, of plums to puree and dried prunes, of grapes to juice, must, wine, raisins and wet pomace and of hops to beer.

The processing factors obtained in the processing studies and estimated STMR-P and HR-P values are summarized below.

Raw agricultural commodity (RAC)			Processed commodity			
Name	STMR (mg/kg)	HR (mg/kg)	Name	Processing factor (median or best estimate)	STMR-P (mg/kg)	HR-P (mg/kg)
Apples	0.15		Juice	< 0.03 (median)	0.0045	
			Sauce	< 0.03 (median)	0.0045	

Raw agricultural commodity (RAC)			Processed commodity			
Name	STMR (mg/kg)	HR (mg/kg)	Name	Processing factor (median or best estimate)	STMR-P (mg/kg)	HR-P (mg/kg)
			Syrup	< 0.04 (median)	0.006	
			Canned apple	< 0.06 (median)	0.009	
			Dried apple	0.1 (median)	0.015	
			Wet pomace	2.2 (median)	0.33	
Cherries	0.43		Juice	< 0.055 (median)	0.024	
			Canned cherries	< 0.055 (median)	0.024	
			Jam	< 0.055 (median)	0.024	
Plums	0.43		Puree	0.035 (median)	0.015	
			Dried prunes	0.515 (median)	0.22	
Wine-grapes	0.69		Juice	< 0.0025 (median)	0.002	
			Must	0.024 (median)	0.017	
			Wine	< 0.003 (median)	0.002	
			Wet pomace	0.93 (median)	0.64	
Table-grapes	0.63	1.3	Raisins	1.64 (median)	1.03	2.13
Hops	64		Beer	< 0.0003 (median)	0.019	

The Meeting noted that dithianon concentrated during processing in apple pomace, wet and in raisins. Because apple pomace is not a commodity in trade, no maximum residue level is estimated.

Based on the recommended MRL of 2 mg/kg for dithianon residues in table grapes and the processing factor of 1.64, the Meeting estimated a maximum residue level of 3.5 mg/kg for dried grapes ($2 \times 1.64 = 3.28$). An STMR-P of 1.03 mg/kg and an HR-P of 2.13 mg/kg were estimated for raisins.

The Meeting discussed the relevance of the hydrolysis products 411094 and 31062 for the residue definition for industrial or household preparations of dithianon treated fruits and made the following assumptions to estimate their dietary intake:

According to the results of the hydrolysis studies, both degradation products accounted for about 10% of the TAR.

In addition to dithianon, the degradation product 4110904 was investigated in the processing studies for dithianon on apples, cherries, plums and grapes. No residues of 4110904 above the LOQ of 0.01 mg/kg were detected in the RAC. The degradate was not detected in must, wine and juice, but in raisins where the residues were lower than 1% of the dithianon residue. The Meeting agreed to use the LOQ for must, wine and juice or the highest real measured value for raisins to estimate the dietary intake of 4110904. For hops, because no data for 4110904 were available, 10% of the STMR for dithianon in hops adjusted by the molecular weight of 4110904 (330.3) was used.

Because no residue data for the degradate 31062 in RAC and the related processed products were submitted, the estimated dietary intake is based on 10% of the STMR of parent dithianon. The Meeting noted that 31062 was formed by dimerization, resulting in the doubling of the radioactivity per molecule. Therefore the stoichiometric factor to extrapolate from dithianon to 31062 residues is 0.635 [$376.1 \div (2 \times 296.3)$]. The 31062 concentrations are calculated as follows:

$$\text{RESIDUE}_{31062} = \text{STMR}_{\text{Dithianon}} \times 0.635 \div 10.$$

The following concentrations of the degradates 4110904 and 31062 were estimated for chronic and acute dietary intake purposes:

Name	Name	4110904, mg/kg	Basis	31062, mg/kg	Basis
Apples,	Juice	0.01	LOQ ₄₁₁₀₉₀₄	0.0095	STMR _{Dithianon}
Pears	Sauce	0.01	LOQ ₄₁₁₀₉₀₄	0.0095	STMR _{Dithianon}
	Canned	0.01	LOQ ₄₁₁₀₉₀₄	0.0095	STMR _{Dithianon}
	Dried	0.01	LOQ ₄₁₁₀₉₀₄	0.0095	STMR _{Dithianon}
Currants	Juice	0.012	STMR _{Dithianon}	0.007	STMR _{Dithianon}
Stone fruits	Juice	0.01	LOQ ₄₁₁₀₉₀₄	0.0273	STMR _{Dithianon}
	Canned	0.01	LOQ ₄₁₁₀₉₀₄	0.0273	STMR _{Dithianon}

Name	Name	4110904, mg/kg	Basis	31062, mg/kg	Basis
	Jam	0.01	LOQ ₄₁₁₀₉₀₄	0.0273	STMR _{Dithianon}
	Plum puree	0.01	LOQ ₄₁₁₀₉₀₄	0.0273	STMR _{Dithianon}
	Dried prunes	0.01	LOQ ₄₁₁₀₉₀₄	0.052	HR _{Dithianon}
Wine-grapes	Juice	0.01	LOQ ₄₁₁₀₉₀₄	0.044	STMR _{Dithianon}
	Must	0.01	LOQ ₄₁₁₀₉₀₄	0.044	STMR _{Dithianon}
	Wine	0.01	LOQ ₄₁₁₀₉₀₄	0.044	STMR _{Dithianon}
Table-grapes	Raisins	0.11	4110904 measured value	0.135	HR _{Dithianon}
Hops	Beer	7.1	STMR _{Dithianon}	4.06	STMR _{Dithianon}

Conservative estimates of long-term exposure of the degradation products Reg. No. 31062 and Reg. No. 4110904 after industrial or household processing were calculated for the 13 GEMS/Food cluster diets using residue concentrations estimated above. The maximum long-term daily intake was 4.7 µg per person (0.00008 mg/kg bw). Applying this intake to the TTC approach (threshold value 0.0015 mg/kg bw, Cramer Class III), the calculated exposures were up to 5% of the TTC.

Conservative estimates of short-term exposure of the degradation products Reg. No. 31062 and Reg. No. 4110904 were calculated using the residue concentrations estimated above. The maximum short-term daily intake was 115 µg per person (0.00192 mg/kg bw). Applying this intake to the TTC approach (threshold value 0.005 mg/kg bw, Cramer Class III), the maximum calculated exposure was 40% of the TTC.

The Meeting concluded that the long-term and short-term intake of residues of Reg. No. 31062 and Reg. No. 4110904 arising of dithianon, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

Farm animal dietary burden

The 2013 JMPR evaluated residues of dithianon in apple pomace wet and grape pomace wet which are listed under by-products in the OECD feeding table for beef and dairy cattle but not for poultry.

Estimated maximum and mean dietary burdens of farm animals

Dietary burden calculations based on the feed items evaluated for beef cattle and dairy cattle as presented in Annex 6. The calculations were made according to the livestock diets from Australia, the EU, Japan and US-Canada in the OECD Table. Because the calculation based on the STMR-P values of the processed by-products, the maximum and mean burden is identical. The table below shows the values calculated.

Because apple pomace wet and grape pomace wet are no feed items for poultry, the livestock dietary burden for broiler and layer is zero.

	Livestock dietary burden, dithianon, ppm of dry matter diet							
	US-Canada		EU		Australia		Japan	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	0	0	0.165	0.165	0.853 ^a	0.853 ^a	0	0
Dairy cattle	0.083	0.083	0.090	0.090	0.853 ^a	0.853 ^a	0	0
Poultry—broiler	0	0	0	0	0	0	0	0
Poultry—layer	0	0	0	0	0	0	0	0

^a Highest mean and maximum beef or dairy cattle dietary burden suitable for MRL and STMR estimates for mammalian meat, edible offal and milk.

Farm animal feeding and metabolism studies

No animal feeding studies of dithianon were submitted. The Meeting agreed to extrapolate the residue levels to be expected in ruminant tissues and milk from the goat metabolism studies.

The metabolism studies in lactating goats were performed at actual dose levels of 2.5 and 28 ppm in the first study and of 25 ppm in the feed of the second study. The overdosing factors are calculated as about 2.9 (2.5 ppm ÷ 0.853 ppm), 33 (28 ppm ÷ 0.853 ppm) and 29 (25 ppm ÷ 0.853 ppm), respectively.

Animal commodity maximum residue levels

The expected total residues in milk and edible tissues of ruminants can be extrapolated from the highest TRR found in the goat metabolism studies as follows:

Commodity	Feeding level, ppm	TRR from metabolism study, mg/kg	TRR extrapolated from actual dietary burden, mg/kg
Milk	2.5	< 0.01	< 0.003
Liver		0.07	0.024
Kidney		0.04	0.014
Muscle		Not detected	–
Fat		< 0.01	< 0.003
Milk	28	0.030	0.0009
Liver		0.174	0.0053
Kidney		0.489	0.0149
Muscle		0.013	0.0004
Fat		0.014	0.0004
Milk	25	0.016	0.0006
Liver		0.157	0.0054
Kidney		0.475	0.0162
Muscle		0.014	0.0005
Fat		0.074	0.0025

The extrapolated TRR are for milk, muscle and fat are lower than the LOQ of 0.01 of dithianon in animal products. In case of liver and kidney, the extrapolated TRR range from 0.005–0.02 mg/kg and 0.01–0.02 mg/kg, respectively.

The Meeting noted that the results from metabolism studies on rats, goats and hens show that dithianon is intensively metabolized. In the goat, parent dithianon was detected at low levels (≤ 0.01 mg/kg) and no single metabolite in the extracts was detected > 0.05 mg/kg. Therefore, it is not expected that the calculated TRR in cattle tissues and milk arising from a burden of 0.853 ppm would account for 100% of dithianon or a related metabolite. In case of poultry, the dietary burdens for broiler and layer are zero. The Meeting concluded that the contribution of dithianon arising residues in animal products to the dietary intake is negligible.

The Meeting estimated maximum residue levels of 0.01* mg/kg for meat of mammals, other than marine mammals, edible offal (mammalian), milk, poultry meat, poultry edible offal and eggs. The STMR for milk and the STMR/HR values for mammalian and poultry meat, mammalian and poultry edible offal as well as for eggs are zero.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue (for compliance with the MRL and for estimation of dietary intake) for plant and animal commodities: *Dithianon*.

The residue is not fat-soluble.

MRL recommendations and dietary intake

	Commodity	MRL, mg/kg		STMR or STMR-P	HR or HR-P
CCN	Name	Proposed	previous	mg/kg	mg/kg
TN 0660	Almonds	0.05*		0	0
FS 0013	Cherries	W	5 ^a		
FB 0021	Currants, Black, Red, White	2		0.105	0.89
DF 0269	Dried grapes	3.5		1.03	2.13
MO 0105	Edible offal (mammalian)	0.01*		0	0
PE 0112	Eggs	0.01*		0	0
FB 0269	Grapes	W	3 ^b		
DH 1100	Hops, dry	300	100	64	
FC 0206	Mandarin	W	3		
MM 0095	Meat (from mammals other than marine mammals)	0.01*		0	0
ML 0106	Milks	0.01*		0	0
FP 0009	Pome fruits	1	5	0.15	0.65
PM 0110	Poultry meat	0.01*		0	0
PO 0110	Poultry, Edible offal of	0.01*		0	0
FC 0005	Shaddocks or pomelos	W	3		
FS 0012	Stone fruits	2		0.43	1.6
FB 1235	Table grapes	2		0.63	1.3
FB 1236	Wine grapes	5		0.69 ^c	

W: The recommendation is withdrawn.

^a The recommendation for cherries is withdrawn and replaced by a recommendation for stone fruit.

^b The recommendation for grapes is withdrawn and replaced by separate recommendations for table grapes and wine grapes.

^c Median value for calculation of STMR-P for wine, juice and must.

Dietary intake only

CCN	Commodity name	STMR or STMR-P, mg/kg	HR or HR-P
	Apples, canned	0.009	
DF 0226	Apples, dried	0.015	
JF 0226	Apple juice	0.0045	
	Apple sauce	0.0045	
	Apple syrup	0.006	
	Apple wet pomace	0.33	
	Beer	0.019	
	Cherries, canned	0.024	
	Cherry jam	0.024	

CCN	Commodity name	STMR or STMR-P, mg/kg	HR or HR-P
	Cherry juice	0.024	
JF 0269	Grape juice	0.002 ^a	
	Grape must	0.017 ^a	
	Grape wine	0.002 ^a	
	Grape wet pomace	0.64 ^a	
	Plum puree	0.015	
DF 0014	Prunes	0.22	0.82

^a STMR-P based on median residue of wine grapes.

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Dietary Intakes (IEDIs) of dithianon were calculated for the 13 GEMS/Food cluster diets using STMRs and STMR-Ps estimated by the current Meeting (Annex 3 of the 2013 JMPR Report). The ADI is 0–0.01 mg/kg bw and the calculated IEDIs were 1–7% of the maximum ADI. The Meeting concluded that the long-term intake of residues of dithianon resulting from the uses considered by the current JMPR is unlikely to present a public health concern.

Short-term intake

The International Estimated Short Term Intake (IESTI) for dithianon was calculated for food commodities and their processed fractions for which maximum residue levels were estimated and for which consumption data were available. The results are shown in Annex 4 of the 2013 JMPR Report.

The Meeting noted that for apples and grapes the IESTI calculated according to the maximum GAP exceeded the ARfD of 0.1 mg/kg bw and used an alternative GAP.

For the commodities considered by the JMPR, the IESTI represented 0–40% of the ARfD for the general population and 0–90% of the ARfD for children. The Meeting concluded that the short-term intake of residues of dithianon, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

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DT-712-006	Eichler D.	1986	Rueckstandsuntersuchungen mit Dithianon 750 g/L - Rueckstaende Sauerkirsche. Celamerck GmbH & Co. KG, Ingelheim, Germany Fed. Rep. Unpublished
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DT-712-008	Eichler D.	1986	Rueckstandsuntersuchungen mit Dithianon 750 g/L SC - Rueckstaende Sauerkirsche. Celamerck GmbH & Co. KG, Ingelheim, Germany Fed. Rep. Unpublished
DT-712-028	Bitz K.	1996	Dithianon (CL 37114) 700 g ai/kg WG (SF 09321): Decline curve residue study in cherries (Germany, 1995). Cyanamid Forschung GmbH, Schwabenheim, Germany Fed. Rep. Unpublished
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DT-713-032	Eichler D.	1987	Rueckstandsuntersuchungen mit Pflanzenbehandlungsmitteln: Dithianon – Weintrauben. Celamerck GmbH & Co. KG, Ingelheim, Germany Fed. Rep. Unpublished
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DT-713-034	Anonymous	1988	Plan und Versuchsbericht Rueckstandsversuche - Rueckstaende Weintrauben. Celamerck GmbH & Co. KG, Ingelheim, Germany Fed. Rep. Unpublished
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DT-713-038	Eichler D.	1988	Rueckstandsuntersuchungen mit Pflanzenbehandlungsmitteln: Dithianon - Weintrauben. Celamerck GmbH & Co. KG, Ingelheim, Germany Fed. Rep. Unpublished
DT-713-039	Anonymous	1987	Rueckstandsuntersuchungen mit Pflanzenschutzmitteln - Rueckstaende Weintrauben. Shell Forschung GmbH, Ingelheim, Germany Fed. Rep. Unpublished
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DT-713-127	Anonymous	2001	Dithianon - Essais residus complementaires - Cassis. BASF Agro SAS, Levallois-Perret, France. Unpublished
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DT-790-031	Anonymous	1991	Rueckstandsuntersuchungen mit Pflanzenschutzmitteln - Rueckstaende Hopfen. Dr. Specht & Partner Chemische Laboratorien GmbH, Hamburg, Germany Fed. Rep. Unpublished
DT-790-035	Specht W.	1990	Rueckstandsuntersuchungen auf Dithianon an Hopfen. Dr. Specht & Partner Chemische Laboratorien GmbH, Hamburg, Germany Fed. Rep. Unpublished
DT-790-036	Specht W.	1990	Rueckstandsuntersuchungen auf Dithianon an Hopfen. Dr. Specht & Partner Chemische Laboratorien GmbH, Hamburg, Germany Fed. Rep. Unpublished
DT-790-037	Specht W.	1990	Rueckstandsuntersuchungen auf Dithianon an Hopfen. Dr. Specht & Partner Chemische Laboratorien GmbH, Hamburg, Germany Fed. Rep. Unpublished
DT-790-038	Specht W.	1990	Rueckstandsuntersuchungen auf Dithianon an Hopfen. Dr. Specht & Partner Chemische Laboratorien GmbH, Hamburg, Germany Fed. Rep. Unpublished
DT-790-041	Anonymous	1991	Rueckstandsuntersuchungen mit Pflanzenschutzmitteln - Rueckstaende Hopfen. Dr. Specht & Partner Chemische Laboratorien GmbH, Hamburg, Germany Fed. Rep. Unpublished
DT-790-042	Anonymous	1991	Rueckstandsuntersuchungen mit Pflanzenschutzmitteln - Rueckstaende Hopfen. Dr. Specht & Partner Chemische Laboratorien GmbH, Hamburg, Germany Fed. Rep. Unpublished
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FENBUCONAZOLE (197)

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APPRAISAL

Fenbuconazole was first evaluated for residues and toxicology by the JMPR in 1997, and then evaluated for residues in 2009 and for toxicology in 2012. The 1997 JMPR allocated an ADI of 0–0.03 mg/kg bw. The 2012 JMPR established an ARfD of 0.2 mg/kg bw.

The Meeting recommended a number of maximum residue levels in 1997 and 2009. Those maximum residue levels were adopted by the Codex Alimentarius Commission in 1999, 2000 and 2013 as Codex MRLs.

The 2009 JMPR received the residue trial data on citrus fruits (grapefruit, oranges and lemons). However, it could not estimate a maximum residue level for fenbuconazole in citrus fruits as the residue trials submitted did not match the available GAP.

Fenbuconazole was scheduled by the Fourt-fourth Session of the CCPR for the residue evaluation of citrus fruits. The “Principles and guidance for application of the proportionality concept for estimation of maximum residue limits for pesticides” were adopted by the Codex Alimentarius Commission in 2013.

Results of supervised residue trials on crops

Information on GAP and supervised trial data were submitted to the 2009 JMPR for lemons and oranges and to the 1997 JMPR for grapefruit and oranges.

Citrus fruits

The GAP on citrus fruit in the USA is a maximum of three foliar applications at a rate of 0.14 kg ai/ha with a PHI of 0 day. Nine trials for grapefruit, sixteen trials for oranges and five trials for lemons were conducted in the USA (3×0.28 kg ai/ha, PHI 0 day). As the application rate of those trials submitted to the 1997 and 2009 JMPR was 2 times the GAP rate, the Meeting decided to use the principle of proportionality to select data for estimating a maximum residue level, an STMR value and an HR value for citrus fruit.

The Meeting considered the result from one trial on grapefruit was not appropriate for use in estimating a maximum residue level as the residue concentration in pulp was higher than in the whole fruit.

Scaled residues in the whole fruit of grapefruit were (scaling factor 0.5: 0.28→0.14 kg ai/ha): 0.05, 0.06, 0.07, 0.08 (2), 0.10, 0.17 and 0.24 mg/kg.

Scaled residues in the whole fruit of oranges were (scaling factor 0.5: 0.28→0.14 kg ai/ha): 0.06 (2), 0.07, 0.08, 0.09 (4), 0.10, 0.14, 0.15 (2), 0.17, 0.22, 0.26 and 0.33 mg/kg.

Scaled residues in the whole fruit in lemons were (scaling factor 0.5: 0.28→0.14 kg ai/ha): 0.26, 0.29 (2), 0.35 and 0.42 mg/kg.

To consider a maximum residue level for a crop group, residues in individual crops should be similar (e.g., medians should not differ by more than 5×). The Meeting agreed to estimate a maximum residue level for the group of citrus fruits. In considering whether to combine data to estimate a maximum residue level, the Meeting recognized that the residue populations from trials on grapefruit, oranges and lemons were significantly different according to statistical test (Kruskal-Wallis H-test): the residue population from trials on lemons was different from those on grapefruit and oranges, while the residue populations from trials on grapefruit and oranges were not different according to statistical test (Mann-Whitney U-test). Therefore, the Meeting decided to combine the grapefruit and oranges data sets to estimate a maximum residue level for citrus fruits (except lemons and limes).

The combined residues in the whole fruit of grapefruit and oranges, in rank order, were (n=24): 0.05, 0.06 (3), 0.07 (2), 0.08 (3), 0.09 (4), 0.10 (2), 0.14, 0.15 (2), 0.17 (2), 0.22, 0.24, 0.26 and 0.33 mg/kg.

Scaled residues in pulp of grapefruit were (scaling factor 0.5): < 0.01 (4) and 0.01 mg/kg.

Scaled residues in pulp of orange were (scaling factor 0.5): < 0.01 (5) mg/kg.

The combined residues in pulp of grapefruit and orange were in rank order (n=10): < 0.01 (9) and 0.01 mg/kg.

Based on the scaled residues in the whole fruit of grapefruit and oranges, the Meeting estimated a maximum residue level of 0.5 mg/kg and an STMR value for processing of 0.09 mg/kg for fenbuconazole in citrus fruit (except lemons and limes). Based on the scaled residues in pulp of grapefruit and orange, the Meeting estimated an STMR value of 0.01 mg/kg and an HR value of 0.01 mg/kg for fenbuconazole in citrus fruit (except lemons and limes).

Scaled residues in pulp of lemon were (scaling factor 0.5): < 0.01, 0.016, 0.018, 0.033 and 0.085 mg/kg.

Based on the scaled residues in the whole fruit of lemon, the Meeting estimated a maximum residue level of 1 mg/kg and an STMR for processing of 0.29 mg/kg for fenbuconazole in lemons and limes. Based on the scaled residues in pulp of lemon, the Meeting estimated an STMR value of 0.018 mg/kg and an HR value of 0.085 mg/kg for fenbuconazole in lemons and limes.

Fate of residues during processing

The Meeting received information on the fate of incurred residues of fenbuconazole during the processing of citrus whole fruit (grapefruit and oranges) to juice, dried pulp and cold press oil conducted in the USA in 2009. Based on processing factors for grapefruit and oranges, in combination with STMR for processing estimated for citrus fruits (except lemons and limes) and lemons and limes, the STMR-Ps for juice, dried pulp and oil were calculated as follows.

Processing factors, STMR-P and HR-P for food and feed

Processed commodity	Calculated processing factors*	PF (Mean or best estimate)	Raw agricultural commodity (RAC) STMR		STMR-P (mg/kg)
			mg/kg	RAC	
Juice	< 0.204, < 0.256	< 0.23	0.09	Citrus fruit (except lemons and limes)	0.021
			0.29	Lemons and limes	0.067
Cold press oil	49.0, 66.7	58	0.09	Citrus fruit (except lemons and limes)	5.2
			0.29	Lemons and limes	17
Dried pulp	6.31, 7.74	7.0	0.09	Citrus fruit (except lemons and limes)	0.63

* Processing factors were derived from the two processing studies each on grapefruit or orange. The factor is the ratio of the residue in processed commodity divided by the residue in the RAC.

The Meeting estimated the maximum residue levels of 4 mg/kg ($0.5 \text{ mg/kg} \times 7.0 = 3.5 \text{ mg/kg}$) for deried citrus pulp, 30 mg/kg ($0.5 \text{ mg/kg} \times 58 = 29 \text{ mg/kg}$) mg/kg for citrus oil (except lemons and limes) and 60 mg/kg ($1 \text{ mg/kg} \times 58 = 58 \text{ mg/kg}$) for oil of lemons and limes based on the maximum residue levels of citrus fruit (except lemons and limes) and of lemons and limes.

Residues in animal commodities

Farm animal feeding studies

A lactating dairy cattle feeding study and a laying hen feeding study were submitted to the 1997 JMPR.

Animal commodity maximum residue levels

Dried citrus pulp may be fed to beef cattle, dairy cattle, broilers and layers. But the STMP-P of dried citrus pulp was low at 0.63 mg/kg not contributing significantly to animal dietary burden. The calculated maximum and mean dietary burdens, with addition of dried citrus pulp, to be used for estimating maximum residue levels for commodities of animal origin (both mammals and poultry) were identical to those calculated by the 2009 JMPR.

The Meeting, therefore, confirmed the previous recommendations of the maximum residue levels for fenbuconazole in animal commodities.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for dietary intake assessment.

Definition of the residue (for compliance with the MRL and for estimation of dietary intake, for plant and animal commodities): *fenbuconazole*

The residue is not fat soluble.

Commodity		Recommended MRL, mg/kg		STMR or STMR-P, mg/kg	HR or HR-P, mg/kg
CCN	Name	New	Previous		
FC 0001	Citrus fruit (except Lemons and Limes)	0.5	-	0.01	0.01
OR 0001	Citrus oil, edible (except Lemons and Limes)	30	-	5.2	-
AB 0001	Citrus pulp, dry	4	-	0.63	-
FC 0002	Lemons and Limes (including Citron)	1	-	0.018	0.085
	Oil of Lemons and Limes	60	-	17	-

Commodity name	STMR or STMR-P, mg/kg	HR or HR-P, mg/kg
Citrus juice (except lemons and limes)	0.021	-
Juice of lemons and limes	0.067	-

DIETARY RISK ASSESSMENT***Long-term intake***

In the current evaluation STMRs were estimated for 7 food commodities. Where consumption data were available these STMRs were used in the estimates of dietary intake together with previous MRL recommendations for other food commodities. The results are shown in Annex 3 of the 2013 JMPR Report.

The ADI is 0–0.03 mg/kg bw and the calculated IEDIs were 0–2% of the maximum ADI (0.03 mg/kg bw). The Meeting concluded that the long-term intake of residues of fenbuconazole, resulting from the uses considered by current JMPR, is unlikely to present a public health concern.

Short-term intake

The International Estimated Short Term Intake (IESTI) for fenbuconazole was calculated for 7 food commodities (including processed fractions) for which maximum residue levels were estimated at the present meeting and for which consumption data were available. The results are shown in Annex 4 of the 2013 JMPR Report.

The ARfD is 0.2 mg/kg bw and the calculated IESTI were a maximum of 0% of the ARfD for all population groups. The Meeting concluded that the short-term intake of residues of fenbuconazole, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

FENPYROXIMATE (193)

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EXPLANATION

Fenpyroximate is a pyrazole non-systemic acaricide. It was first evaluated by JMPR in 1995 and then in 1999 and 2010 for maximum residue levels, and in 2004 and 2007 for toxicology. The currently standing recommendations of JMPR are as follows:

ADI: 0–0.01 mg/kg bw (1995)

ARfD: 0.02 mg/kg bw (2007)

Residue definition—Fenpyroximate for compliance with the MRL and for estimation of dietary intake (both for animal and plant commodities). The residue is fat soluble. (1999)

A number of maximum residue levels have been recommended by the 1995, 1999 and 2010 JMPR including those for citrus fruits, pome fruits, grapes, fruiting vegetables other than cucurbits (except sweet corn and mushroom), cucumber, melon (except water melon), tree nuts, dry hops, dried grapes, dried chilli pepper, and cattle liver meat and milk.

The current Meeting received information on the latest use pattern and the supervised residue trials on stone fruits, strawberry, avocado, cucumber, common bean (pods and/or immature seeds and bean fodder), potato, and mints conducted in the USA.

USE PATTERNS

The authorized uses relevant to the supervised trials data submitted to the current Meeting are summarized in Table 1. They can be applied when pests are immature or at a susceptible stage and populations are building, before crop damage occurs.

Table 1 Registered use of fenpyroximate in the USA relevant to the residue evaluation by the current Meeting

Crop	Form g ai/L	F or G	Application						PHI days
			Method	Rate kg ai/ha	Water L/ha	Seasonal kg ai/ha	No.	Interval days	
Stone fruits (Cherry (sweet and tart), peach & plum)	50 EC	F	Foliar	0.117	≥ 748 (ground only)	≤ 0.234	≤ 2	14	7
Low-growing berry (Strawberry)	50 EC	F	Foliar	0.058–0.117	≥ 234 (ground only)	≤ 0.234	≤ 2	14	1
Avocado	50 EC	F	Foliar	0.058–0.117	≥ 889 (ground) ≥ 468 (air)	≤ 0.234	≤ 2	14	1
Cucumber	50 EC	F	Foliar	0.058–0.117	≥ 374 (ground) ≥ 93.5 (air)	≤ 0.234	≤ 2	14	1
		G ^a	Foliar	0.117	≥ 374	≤ 0.117	≤ 1	14	7
Snap beans ^b	50 EC	F	Foliar	0.117	≥ 281 (ground) ≥ 47 (air)	≤ 0.234	≤ 2	14	1
Potato	50 EC	F	Foliar	0.117	≥ 187 (ground) ≥ 47 (air)	≤ 0.234	≤ 2	7	7
Mint (Peppermint, spearmint)	50 EC	F	Foliar	0.058–0.117	≥ 234 (ground only)	≤ 0.234	≤ 2	7	1

^a Do not apply in ultra-low volume equipment

^b Common beans in the Codex Classification.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting considered residue data from supervised field trials conducted in the USA on stone fruits, strawberry, avocado, cucumber, common bean (pods and/or immature seeds and bean fodder), potato, and mints with foliar applications of the fenpyroximate emulsion concentrate (EC) formulation (50 g ai/L nominal concentration).

Application rates and residue concentrations were reported as fenpyroximate. Residue concentrations are recorded unadjusted for recoveries or for residue values in control samples. Where multiple samples were taken from a single plot, individual results are reported, and the calculated average concentration (in parentheses) is used for estimation of maximum residue level. Where trials were conducted in the same location, with the same or similar varieties, same or similar formulations, and same equipment, and at the same or similar timing, they are not regarded as independent and only one result from these trials was chosen for the estimation of a maximum residue level.

Residues from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels and they are underlined.

Crop Group	Commodity	Table No.
Stone fruits	Cherry	Table 2
	Peach	Table 3
	Plum	Table 4
Berries and other small fruits	Strawberry	Table 5
Assorted tropical and subtropical fruit - inedible peel	Avocado	Table 6
Fruiting vegetables, Cucurbits	Cucumber	Table 7
Legume vegetables	Common beans	Table 8
Root and tuber vegetables	Potato	Table 9
Herbs	Mints	Table 10
Legume animal feeds	Bean fodder	Table 11

Stone fruits

Cherry

A total of eight supervised trials on cherries were conducted in California (one), Colorado (one), Michigan (three), New York (one), and Washington (two) in the USA in 2010 (Samoil, 2012a).

In each trial, two foliar applications of the fenpyroximate EC formulation (56 g ai/L) were made at a rate of approximately 0.11 to 0.12 kg ai/ha per application. An adjuvant (e.g. Induce, Silwet L-77, Activator 90, Ad Wet 90, JMS Stylet oil, Nu-Film 17, or Dyne-Amic) was added to the spray solutions, as appropriate. Applications were made on a 13- to 14- day interval, and the cherries were harvested 7 to 8 days after the last treatment.

Two samples of cherries were collected from each treated plot and untreated plot. Specimens were stored frozen and shipped frozen to the analytical laboratory. Samples were processed with dry ice in a Robot Coupe RSI 10U. Processed samples were stored frozen until analysis.

The method of analysis was based LC-MS/MS using multiple reaction monitoring (MRM) in +ESI mode. The LOQ was 0.05 mg/kg for each analyte. Average recovery of cherries at all fortifications was $96.0 \pm 8.8\%$ and $92.8 \pm 6.0\%$ for fenpyroximate and M-1, respectively (n=18). No control samples contained residues at or above the LOQ of the method.

Table 2 Residues of fenpyroximate in cherries from supervised trials conducted with foliar spray in the USA in 2010

CHERRY Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate ^b	M-1	
US GAP (stone fruits)	EC 50	0.117	≥ 748 (ground only)	≤ 2	7				Seasonal Max= 0.234 kg ai/ha Interval=14 days
2010 Tulare, CA (Tulare)	EC 56	0.11 0.11	1330 1320	2	7	Fruits without pits and stems	0.33 0.32 (0.325)	< 0.05 < 0.05	Induce 10438.10-CA90
	EC 56	0.11 0.11	1340 1320	2	7	Fruits without pits and stems	0.41 0.51 (0.46)	< 0.05 < 0.05	Silwet L-77 organo-silicone
	EC 56	0.11 0.11	1330 1310	2	7	Fruits without pits and stems	0.28 0.27 (0.275)	< 0.05 < 0.05	None
2010 Hotchkiss, Co (Montmorency)	EC 56	0.11 0.12	907 982	2	7	Fruits without pits and stems	0.62 0.75 (0.685)	0.0921 0.108	Activator 90 10438.10-CO03
2010 Fennville, MI ^a (Montmorency)	EC 56	0.11 0.11	982 991	2	7	Fruits without pits and stems	0.59 0.58 (0.585)	0.081 0.066	Dyne-Amic modified vegetable oil and organo-silicone surfactant blend 10438.10-MI24
2010 Fennville, MI ^a (Montmorency)	EC 56	0.11 0.11	991 991	2	7	Fruits without pits and stems	0.84 0.90 (0.87)	0.112 0.123	Dyne-Amic modified vegetable oil and organo-silicone surfactant blend 10438.10-MI25
2010 Fennville, MI ^a (Heidelfingen)	EC 56	0.11 0.11	1000 1000	2	7	Fruits without pits and stems	0.36 0.36 (0.36)	< 0.05 < 0.05	Dyne-Amic modified vegetable oil and organo-silicone surfactant blend 10438.10-MI26
2010 Lansing, NY (Galaxy)	EC 56	0.11 0.11	561 561	2	7	Fruits without pits and stems	0.76 0.85 (0.805)	0.122 0.120	Induce 10438.10-NY12
2010 Prosser, WA (Bing)	EC 56	0.11 0.11	1070 1120	2	7	Fruits without pits and stems	0.09 0.10 (0.095)	< 0.05 < 0.05	Ad wet 90 10438.10-WA22
	EC 56	0.11 0.11	1030 1070	2	7	Fruits without pits and stems	0.35 0.33 (0.34)	< 0.05 < 0.05	JMS Stylet oil
	EC 56	0.11 0.11	1060 1100	2	7	Fruits without pits and stems	0.31 0.29 (0.30)	< 0.05 < 0.05	None
2010 Moxee, WA (Bing)	EC 56	0.11 0.11	1050 1320	2	7	Fruits without pits and stems	0.28 0.25 (0.265)	< 0.05 < 0.05	Agri-Dex 10438.10-WA23

DALT: days after the last application

^a Same location^b Average in parentheses

Peach

A total of ten supervised trials on peaches were conducted in Arkansas (one), California (three), Michigan (one), North Carolina (two), New Jersey (two), and Texas (one) in the USA in 2010 (Samoil, 2012b).

In each trial, two foliar applications of the fenpyroximate EC formulation (56 g ai/L) were made at a rate of approximately 0.11 to 0.12 kg ai/ha per application. An adjuvant (Silglow, Induce, Silwet L-77, Pro 90, Agri-Dex, Super Spread 7000, Tricard Silicone, Attach, or Spreader 90) was added to the spray solutions, as appropriate. Applications were made on a 13- to 15- day interval, except for the trials located in Winters, California in which the applications were made on a 7- day interval. The peaches were harvested 6 to 8 days after the last treatment, except for the trials located in Winters, California where samples were collected on DALTs of 2, 7, 11, and 14 days.

Two samples of peaches were collected from each treated plot and untreated plot. Specimens were stored frozen and shipped frozen to the analytical laboratory. Samples were processed with dry ice in a Robot Coupe RSI 10B. Processed samples were stored frozen until analysis.

The method of analysis was based on LC-MS/MS. The LOQ was 0.05 mg/kg for each analyte. Average recovery of peaches at all fortifications was $97.2 \pm 15.5\%$ and $99.8 \pm 10.9\%$ for fenpyroximate and M-1, respectively (n=21). No control samples contained residues at or above the LOQ of the method.

Table 3 Residues of fenpyroximate in peaches from supervised trials conducted with foliar spray in the USA in 2010

PEACH Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate ^c	M-1	
US GAP (stone fruits)	EC 50	0.117	≥ 748 (ground only)	≤ 2	7				Seasonal Max= 0.234 kg ai/ha Interval = 14 days
2010 Clarksville, AR (Cresthaven)	EC 56	0.12 0.12	1200 1210	2	7	Fruits without pits	0.09 0.06 (0.075)	< 0.05 < 0.05	Agri-Dex 10468.10-AR04
2010 Parlier, CA ^a (Crimson Lady)	EC 56	0.11 0.11	804 804	2	7	Fruits without pits	0.09 0.11 (0.10)	< 0.05 < 0.05	Silglow 10468.10-CA93
2010 Parlier, CA ^a (Henry II)	EC 56	0.11 0.11	1070 1080	2	7	Fruits without pits	0.13 0.16 (0.145)	< 0.05 < 0.05	Induce 10468.10-CA94
	EC 56	0.11 0.12	1050 1080	2	7	Fruits without pits	0.16 0.20 (0.18)	< 0.05 < 0.05	Silwet L-77 organo-silicone
	EC 56	0.11 0.11	1060 1070	2	7	Fruits without pits	0.10 0.10 (0.10)	< 0.05 < 0.05	None
2010 Winters, CA (O'Henry)	EC 56	0.11 0.12	1210 1360	2	2	Fruits without pits	0.24 0.28 (0.260)	< 0.05 < 0.05	Pro 90 (interval: 7 days) 10468.10-CA95
					7		0.19 0.20 (0.195)	< 0.05 < 0.05	
					11		0.16 0.16 (0.16)	< 0.05 < 0.05	
					14		0.10 0.16 (0.13)	< 0.05 < 0.05	
	EC 56	0.11 0.12	1200 1380	2	7	Fruits without pits	0.13 0.16 (0.145)	< 0.05 < 0.05	Silwet L-77 organosilicone (interval: 7 days)

PEACH Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate ^c	M-1	
2010 Fennville, MI (Red Haven)	EC 56	0.11 0.11	1040 1040	2	7	Fruits without pits	0.13 0.13 (0.13)	< 0.05 < 0.05	Super Spread 7000 10468.10-mi27
2010 Jackson Springs, NC (Contender)	EC 56	0.11 0.11	1090 1080	2	6	Fruits without pits	0.08 0.09 (0.085)	< 0.05 < 0.05	Induce 10468.10-NC18
	EC 56	0.11 0.11	1090 1090	2	6	Fruits without pits	0.11 0.12 (0.115)	< 0.05 < 0.05	Tricard Silicone organo-silicone
	EC 56	0.11 0.11	1090 1070	2	6	Fruits without pits	0.06 0.06 (0.06)	< 0.05 < 0.05	None
2010 Clayton, NC (Contender)	EC 56	0.11 0.11	1060 1080	2	6	Fruits without pits	0.17 0.13 (0.15)	< 0.05 < 0.05	Induce 10468.10-NC19
2010 Cream Ridge, NJ ^b (Suncrest)	EC 56	0.11 0.11	1310 1320	2	7	Fruits without pits	0.12 0.13 (0.125)	< 0.05 < 0.05	Attach 10468.10-NJ09
2010 Cream Ridge, NJ ^b (Loring)	EC 56	0.11 0.12	1320 1260	2	7	Fruits without pits	0.10 0.08 (0.09)	< 0.05 < 0.05	Attach 10468.10-NJ10
2010 Fredericksburg, TX (Sentinel)	EC 56	0.11 0.11	945 926	2	7	Fruits without pits	0.08 0.07 (0.075)	< 0.05 < 0.05	Spreader 90 10468.10-TX12

DALT: days after the last application

^a Same location

^b Same location

^c Average in parentheses

Plum

A total of six supervised trials on plums were conducted in California (four), Michigan (one), and Oregon (one) in the USA in 2010 (Samoil, 2012c).

In each trial, two foliar applications of the fenpyroximate EC formulation (56 g ai/L) were made at a rate of approximately 0.11 to 0.12 kg ai/ha per application, except the CA97 trial in California where an additional treated plot received two foliar applications made at a rate of approximately 0.57 kg ai/ha, 5× exaggerated rate. An adjuvant (Latron B-1956, Induce, Silglow, Pro 90, Super Spread 7000, or Preference) was added to the tank mix, as appropriate. Applications were made 13 to 15 days apart and the plums were harvested 7 days after the last treatment, except that in the trial in Oregon (OR23 trial), plums were collected 6 days after the last treatment.

Two samples of plums were collected from each treated plot and untreated plot. Specimens were stored frozen and shipped frozen to the analytical laboratory. Samples were processed with dry ice in a Robot Coupe RSI 10B. Processed samples were stored frozen until analysis.

The method of analysis was based on LC-MS/MS. The LOQ was 0.05 mg/kg for each analyte. Average recovery of all fortifications for fenpyroximate was 87.2 ± 10.1 (n=17). Average recovery of all fortifications for M-1 was 87.7 ± 7.4 (n=17). No control samples contained residues at or above the LOQ of the method.

Table 4 Residues of fenpyroximate in plums from supervised trials conducted with foliar spray in the USA in 2010

PLUM Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate ^b	M-1	
US GAP (stone fruits)	EC 50	0.117	≥ 748 (ground only)	≤ 2	7				Seasonal Max= 0.234 kg ai/ha Interval=14 days
2010 Parlier, CA ^a (John W)	EC 56	0.11 0.11	832 842	2	7	Fruits without pits	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Latron B-1956 10469.10-CA96
2010 Parlier, CA ^a (French Prune)	EC 56	0.11 0.11	1330 1320	2	7	Fruits without pits	0.25 0.29 (0.27)	< 0.05 < 0.05	Induce 10469.10-CA97
	EC 56	0.57 0.57	1330 1330	2	7	Fruits without pits	1.84	0.208	Induce (5x rate)
2010 Reedley, CA (Owen T)	EC 56	0.11 0.11	814 823	2	7	Fruits without pits	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Silglow 10469.10-CA98
2010 Gridley, CA (French Prune)	EC 56	0.12 0.12	1150 1160	2	7	Fruits without pits	0.22 0.18 (0.20)	< 0.05 < 0.05	Pro 90 10469.10-CA99
2010 Fennville, MI (Early Golden)	EC 56	0.11 0.11	1070 1060	2	7	Fruits without pits	0.12 0.14 (0.13)	< 0.05 < 0.05	Super Spread 7000 10469.10-MI28
2010 Brooks, OR (Brooks)	EC 56	0.11 0.11	1140 1210	2	6	Fruits without pits	0.08 0.09 (0.085)	< 0.05 < 0.05	Preference 10469.10-OR23

DALT: days after the last application

^a Same location^b Average in parentheses*Berries and other small fruits**Strawberry*

A total of three supervised trials on strawberries were conducted in California (two) and Florida (one) in the USA in 2008 (Hattermann, 2008). In each trial, two foliar applications of the fenpyroximate SC or EC formulation (50 g ai/L nominal) were made at a rate of approximately 0.11 to 0.12 kg ai/ha per application. Applications were made 14 to 15 days apart and the strawberries were harvested 1 day after the last treatment.

Two samples of strawberries were collected from each treated plot and one untreated plot. Specimens were stored frozen and shipped frozen to the analytical laboratory and were processed with dry ice in a HCM-61 Food Processor. Processed samples were stored frozen until analysis.

The method of analysis was based on gas chromatography with nitrogen/phosphorous detection (GC-NPD). The LOQ was 0.01 mg/kg for each analyte. Average recovery of all fortifications was $91.9 \pm 12.0\%$ for strawberry (n=14). No control samples contained residues at or above the LOQ of the method.

A total of five supervised trials on strawberry were conducted in New York (one), North Carolina (one), Minnesota (one), California (one), and Oregon (one) in the USA in 2010 (Carringer, 2011). In each trial, two foliar applications of the fenpyroximate EC formulation (56 g ai/L) were made at a rate of approximately 0.11 to 0.12 kg ai/ha per application. An adjuvant (Induce, Dyne-Amice, or Silwet) was added to the spray solutions, as appropriate. Applications were made 14 to 15 days apart and the strawberries were harvested 1 day after the last treatment.

Two samples of strawberries were collected from each treated plot and one sample of strawberries was collected from each untreated plot. Specimens were stored frozen and shipped frozen to the analytical laboratory and were processed with dry ice in a Hobart food processor equipped with a 1/8 inch plate or a Robot Coupe RSI 45B grinder. Processed samples were stored frozen until analysis.

The method of analysis was based on LC-MS/MS. The LOQ was 0.01 mg/kg and the LOD was 0.003 mg/kg. Average recovery of all fortifications was $88.9 \pm 9.6\%$ for strawberry (n=37). No control samples contained residues at or above the LOQ of the method.

Table 5 Residues of fenpyroximate in strawberries from supervised trials conducted with foliar spray in the USA in 2008 and 2010.

STRAWBERRY Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate _a	M-1	
US GAP (Low-growing berry)	EC 50	0.058- 0.117	≥ 234 (ground only)	≤ 2	1				Seasonal Max = 0.234 kg ai/ha Interval = 14 days
2008 Oviedo, FL (Camarosa)	EC 52	0.11 0.11	273 281	2	1	Fruits	0.61 0.38 (0.495)	0.081 0.049	None 860.1500-08-520- 03c-01
	SC 49	0.11 0.11	273 280	2	1	Fruits	0.59 0.47 (0.53)	0.015 0.014	None
2008 Porterville, CA (Diamante)	EC 52	0.11 0.11	186 187	2	1	Fruits	0.29 0.27 (0.28)	0.057 0.050	None (Water volume less than the GAP minimum) 860.1500-08-520- 03c-02
	SC 49	0.11 0.11	187 187	2	1	Fruits	0.18 0.19 (0.185)	< 0.01 < 0.01	None (Water volume less than the GAP minimum)
2008 Salinas, CA (Albion)	EC 52	0.11 0.11	846 865	2	1	Fruits	0.24 0.18 (0.21)	0.017 0.012	None 860.1500-08-520- 03c-03
	SC 49	0.11 0.12	842 883	2	1	Fruits	0.24 0.23 (0.235)	< 0.01 < 0.01	None
2010 East Williamson, NY (Idea)	EC 56	0.11 0.11	281 281	2	1	Fruits	0.04 0.05 (0.045)	< 0.01 < 0.01	None TCI-10-273-01
	EC 56	0.11 0.11	281 281	2	1	Fruits	0.08 0.03 (0.055)	0.010 < 0.01	Induce
	EC 56	0.11 0.11	281 281	2	1	Fruits	0.06 0.06 (0.06)	< 0.01 < 0.01	Dyne-Amic MSO
	EC 56	0.11 0.11	281 281	2	1	Fruits	0.08 0.07 (0.075)	< 0.01 0.011	Silwet L77 Organo-silicone
2010 Seven Springs, NC (Camino Real)	EC 56	0.11 0.11	1040 1040	2	1	Fruits	0.10 0.10 (0.10)	< 0.01 < 0.01	None TCI-10-273-02
	EC 56	0.11 0.11	421 402	2	1	Fruits	0.16 0.18 (0.17)	< 0.01 < 0.01	Induce
	EC 56	0.11 0.11	421 412	2	1	Fruits	0.11 0.17 (0.14)	< 0.01 < 0.01	Dyne-Amic MSO

STRAWBERRY Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate ^a	M-1	
	EC 56	0.11 0.11	421 402	2	1	Fruits	0.21 0.16 (0.185)	< 0.01 < 0.01	Silwet L77 Organo-silicone
2010 St. Stephen, MN (Honeyoye)	EC 56	0.11 0.11	225 243	2	1	Fruits	0.06 0.04 (0.05)	< 0.003 < 0.003	None TCI-10-273-03
	EC 56	0.11 0.11	225 243	2	1	Fruits	0.03 0.03 (0.03)	< 0.003 < 0.003	Induce
	EC 56	0.11 0.12	225 243	2	1	Fruits	0.07 0.06 (0.065)	< 0.003 < 0.003	Dyne-Amic MSO
	EC 56	0.11 0.11	225 243	2	1	Fruits	0.02 0.04 (0.03)	< 0.003 < 0.003	Silwet L77 Organo-silicone
2010 Salinas, CA (Albion)	EC 56	0.11 0.11	449 477	2	1	Fruits	0.16 0.18 (0.17)	0.033 0.038	None TCI-10-273-04
	EC 56	0.11 0.11	458 477	2	1	Fruits	0.22 0.21 (0.215)	0.037 0.036	Induce
	EC 56	0.11 0.11	449 477	2	1	Fruits	0.23 0.25 (0.24)	0.025 0.026	Dyne-Amic MSO
	EC 56	0.11 0.11	458 468	2	1	Fruits	0.18 0.24 (0.21)	0.033 0.036	Silwet L77 Organo-silicone
2010 Elmira, OR (Benton)	EC 56	0.12 0.12	243 243	2	1	Fruits	0.20 0.18 (0.19)	0.034 0.029	None TCI-10-273-05
	EC 56	0.11 0.12	234 243	2	1	Fruits	0.20 0.18 (0.19)	0.022 0.025	Induce
	EC 56	0.11 0.12	234 243	2	1	Fruits	0.10 0.15 (0.125)	< 0.01 < 0.01	Dyne-Amic MSO
	EC 56	0.12 0.12	243 243	2	1	Fruits	0.14 0.23 (0.185)	0.016 0.034	Silwet L77 Organo-silicone

DALT: days after the last application

^a Average in parentheses

Assorted tropical and subtropical fruit —inedible peel

Avocado

A total of five supervised trials on avocados were conducted in California (four) and Florida (one) in the USA in 2008 and 2009 (Samoil, 2011b).

In each trial, two foliar applications of the fenpyroximate EC formulation (52 g ai/L) were made at a rate of approximately 0.10 to 0.12 kg ai/ha per application. An adjuvant, Omni Supreme Spray (petroleum oil) or First Choice Narrow Range 415 Spray Oil, was added to the tank mix, as appropriate. Applications were made 13 to 17 days apart and the avocados were harvested 1 day after the last treatment.

Two samples each of avocado were collected from each treated plot and untreated plot. Specimens were stored frozen and shipped frozen to the analytical laboratory. Samples were

processed with dry ice in a Hobart food processor. Processed samples were stored frozen until analysis.

The method of analysis was based on gas chromatography coupled to a Mass Selective Detector (MSD) operating in selective ion monitoring (SIM) mode. The LOQ was 0.05 mg/kg. Average recovery of all fortifications was $104.3 \pm 7.3\%$ for avocado (n=18). No control samples contained residues at or above the LOQ of the method.

Table 6 Residues of fenpyroximate in avocado from supervised trials conducted with foliar spray in the USA in 2008 and 2009

AVOCADO Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)	Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate ^b	
US GAP	EC 50	0.058- 0.117	≥ 889 (ground) ≥ 468 (air)	≤ 2	1			Seasonal Max = 0.234 kg ai/ha Interval=14 days
2008 San Luis Obispo, CA (Haas)	EC 52	0.11 0.11	889 907	2	1	Fruits	0.06 < 0.05 (0.055)	Omni Supreme Spray Petroleum Oil 10007.08-CA13
2008 Nipoma, CA (Haas)	EC 52	0.11 0.11	1110 1000	2	1	Fruits	< 0.05 < 0.05 (< 0.05)	Omni Supreme Spray Petroleum Oil 10007.08-CA14
2009 Porterville, CA ^a (Haas)	EC 52	0.12 0.11	917 936	2	1	Fruits	< 0.05 < 0.05 (< 0.05)	First Choice Narrow Range 415 Spray Oil 10007.08-CA15
2009 Porterville, CA ^a (Haas)	EC 52	0.12 0.11	1340 1320	2	1	Fruits	< 0.05 < 0.05 (< 0.05)	First Choice Narrow Range 415 Spray Oil 10007.08-CA16
2008 Homestead, FL (Simmonds)	EC 52	0.10 0.10	1020 1280	2	1	Fruits	0.10 0.10 (0.10)	Omni Supreme Spray Petroleum Oil 10007.08-FL48

DALT: days after the last application

^a Same location

^b Average in parentheses

Fruiting vegetables, Cucurbits

Cucumber

The 2010 Meeting reviewed the data from supervised trials on cucumbers conducted indoor in European countries following GAP for cucumber (indoor) in the USA with PHI of 7 days. The current Meeting received data from supervised trials on cucumber conducted outdoor following US GAP for cucumber (outdoor) with PHI of 1 day.

A total of nine supervised trials on cucumber were conducted in North Carolina (one), South Carolina (two), Georgia (two), Ohio (two), Texas (one), and California (one) in the USA in 2009 (Leonard, 2011a).

In each trial, two foliar applications of the fenpyroximate EC formulation (56 g ai/L) were made at a rate of approximately 0.11 kg ai/ha per application. An adjuvant, Induce, Activator 90, UAP 80/20, Top Surf, or Kinetic, was added to the tank mix, as appropriate. Applications were made on a 13- to 16-day interval and the cucumbers were harvested 1 day after the last treatment.

Two samples of cucumber were collected from each treated plot and untreated plot. Specimens were stored frozen and shipped frozen to the analytical laboratory. Samples were processed with dry ice in a Hobart food processor. Processed samples were stored frozen until analysis.

The method of analysis was based on LC-MS/MS. The LOQ was 0.05 mg/kg for each analyte, and the LOD was 0.01 mg/kg. Average recovery of all fortifications was $109.7 \pm 8.2\%$ and $96.4 \pm 10.4\%$ for fenpyroximate and M-1, respectively, for cucumber (n=19). No control samples contained residues at or above the LOQ of the method.

Table 7 Residues of fenpyroximate in cucumbers from supervised trials conducted with foliar spray outdoor in the USA in 2009

CUCUMBER Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate a	M-1	
US GAP (field)	EC 50	0.058– 0.117	≥ 374 (ground) ≥ 93.5 (air)	≤ 2	1				Seasonal Max= 0.234 kg ai/ha Interval=14 days
Cucumber for fresh consumption									
2009 Charleston, SC (Poinsett 76)	EC 56	0.11 0.11	440 427	2	1	Fruits	0.19 0.15 (0.17)	< 0.05 < 0.05	Activator 90 09032.09-SC*06
2009 Tifton, GA (Straight 8)	EC 56	0.11 0.11	414 413	2	1	Fruits	0.05 0.06 (0.055)	< 0.05 < 0.05	UAP 80/20 09032.09- GA*03
2009 Fremont, OH (Dasher II)	EC 56	0.11 0.11	496 506	2	1	Fruits	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Top Surf 09032.09-OH*01
2009 Weslaco, TX (Poinsett 76)	EC 56	0.11 0.11	403 399	2	1	Fruits	0.08 0.07 (0.075)	< 0.05 < 0.05	Kinetic 09032.09-TX*21
2009 Holtville, CA (Cobra)	EC 56	0.11 0.11	485 490	2	1	Fruits	0.06 0.07 (0.065)	< 0.05 < 0.05	Induce 09032.09-CA44
Pickling cucumber									
2009 Clinton, NC (Cross Country)	EC 56	0.11 0.11	383 381	2	1	Fruits	0.06 0.09 (0.075)	< 0.05 < 0.05	Induce 09032.09- NC08
2009 Charleston, SC (Calypso Hybrid)	EC 56	0.11 0.11	443 428	2	1	Fruits	0.10 0.12 (0.11)	< 0.05 < 0.05	Activator 90 09032.09-SC*05
2009 Tifton, GA (National Pickling)	EC 56	0.11 0.11	413 411	2	1	Fruits	0.07 0.060 (0.065)	< 0.05 < 0.05	UAP 80/20 09032.09-GA*02
2009 Fremont, OH (Sassy)	EC 56	0.11 0.11	500 525	2	1	Fruits	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Top Surf 09032.09- OH*02

DALT: days after the last application

Legume vegetables

Common beans (pods and/or immature seeds)

A total of eight supervised trials on common beans were conducted in California (one), Florida (one), Georgia (one), New York (one), Ohio (two), Washington (one), and Wisconsin (one) in the USA in 2008 (Samoil, 2011a).

In each trial, two foliar applications of the fenpyroximate EC formulation (52 g ai/L) were made at a rate of approximately 0.11 kg ai/ha per application. An adjuvant (Crop Oil COC, Chemnut 80-20 NIS, UAP Surfactant 80/20, Induce, Top Surf, 90 Plus, or Liberate) was added to the spray solutions, as appropriate. Applications were made 13 to 15 days apart and the unshelled immature

beans were harvested 1 day after the last treatment, except for the CA38 trial in which unshelled beans were harvested additionally on 3, 8 and 10 days after the last treatment.

Two samples of unshelled beans were collected from each treated plot and untreated plot; at the CA38 trial, two additional samples were collected from each of the treated plots on each day of harvest. Specimens were stored frozen and shipped frozen to the analytical laboratory. Samples were processed with dry ice in a Hobart Food Chopper. Processed samples were stored frozen until analysis.

The method of analysis was based on LC-MS/MS. The LOQ was 0.05 mg/kg for each analyte. Average recovery of all fortifications was 100.1±12.1% bean (n=38). No control samples contained residues at or above the LOQ of the method.

Table 8 Residues of fenpyroximate in pods and immature beans from supervised trials on common beans conducted with foliar spray in the USA in 2008

COMMON BEANS Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate ^a	M-1	
US GAP	EC 50	0.117	≥ 281 (ground) ≥ 47 (air)	≤ 2	1				Seasonal Max = 0.234 kg ai/ha Interval = 14 days
2008 Davis, CA (Blue Lake bush 274)	EC 52	0.11 0.11	299 290	2	1	Pods with seeds	0.19 0.17 (0.18)	< 0.05 < 0.05	TGI Crop Oil 09942.08-CA38
					3	Pods with seeds	0.12 0.08 (0.10)	< 0.05 < 0.05	
					8	Pods with seeds	0.06 0.07 (0.065)	< 0.05 < 0.05	
					10	Pods with seeds	0.08 0.06 (0.07)	< 0.05 < 0.05	
2008 Citra, FL (Dusky)	EC 52	0.11 0.11	374 365	2	1	Pods with seeds	0.07 0.10 (0.085)	< 0.05 < 0.05	Chemnut 80-20 09942.08-FL37
2008 Tifton, GA (Blue Lake Bush 274)	EC 52	0.11 0.11	449 449	2	1	Pods with seeds	0.13 0.16 (0.145)	< 0.05 < 0.05	Surfactant 80/20 09942.08-GA*13
2008 Freeville, NY (Hystyle)	EC 52	0.11 0.11	318 318	2	1	Pods with seeds	0.08 0.10 (0.09)	< 0.05 < 0.05	Induce 09942.08-NY24
2008 Fremont, OH ^a (Sea Biscuit)	EC 52	0.11 0.11	374 364	2	1	Pods with seeds	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Top Surf 09942.08-OH*09
2008 Fremont, OH ^a (Brio)	EC 52	0.11 0.11	365 374	2	1	Pods with seeds	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Top Surf 09942.08-OH*10
2008 Moxee, WA (Jade)	EC 52	0.11 0.11	374 365	2	1	Pods with seeds	0.19 0.18 (0.185)	< 0.05 < 0.05	90 Plus 09942.08-WA*07
2008 Arlington, WI (Hystyle)	EC 52	0.11 0.11	393 384	2	1	Pods with seeds	0.10 0.07 (0.085)	< 0.05 < 0.05	Liberate 09942.08-WI*17

DALT: days after the last application

^a Average in parentheses

*Root and tuber vegetables**Potato*

A total of sixteen supervised trials on potatoes were conducted in the USA: in New York (two), North Carolina (one), Ohio (one), Michigan (one), Wisconsin (two), New Mexico (one), California (one), Washington (four), and Idaho (two) in 2009 and in Florida (one) in 2010 (Leonard, 2011b).

In each trial, two foliar applications of the fenpyroximate EC formulation (56 g ai/L) were made at a rate of approximately 0.11 to 0.13 kg ai/ha per application. In the ID12 trial, an additional treated plot received two foliar applications made at the 5× exaggerated rate. An adjuvant (Induce, Chem Nut 80/20, Top Surf, Activator 90, Ad Wet 90, or 90 Plus) was added to the spray solutions, as appropriate. Applications were made on a 6- to 8-day interval and the potatoes were harvested 6-7 days after the last treatment, except that in the MI11 and NC18 trials, potatoes were harvested on 0, 3, 7, 11, and 14 or 0, 3, 6, 9, and 12, respectively after the last treatment.

Two samples of potato were collected from each treated plot and untreated plot. In the two decline trials, two additional samples were collected from the treated plot on each day of harvest. Specimens were stored frozen and shipped frozen to the analytical laboratory. Samples were processed with dry ice in a Hobart food processor. Processed samples were stored frozen until analysis.

The method of analysis was based on LC-MS/MS. The LOQ was 0.05 mg/kg for each analyte. Average recovery of all fortifications was $98.3 \pm 6.2\%$ for potatoes (n=58). No control samples contained residues at or above the LOQ of the method.

Table 9 Residues of fenpyroximate in potatoes from supervised trials conducted with foliar spray in the USA in 2009 and 2010

POTATO Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate ^a	M-1	
US GAP (field)	EC 50	0.117	≥ 187 (ground) ≥ 47 (air)	≤ 2	7				Seasonal Max = 0.234 kg ai/ha Interval = 7 days
2009 Freeville, NY (Yukon Gold)	EC 56	0.11 0.11	321 333	2	6	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Induce 10173.09-NY10
2009 North Rose, NY (Superior)	EC 56	0.12 0.11	376 375	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Induce 10173.09-NY11
2009 Clinton, NC (Atlantic)	EC 56	0.11 0.11	292 298	2	0	Tubers	< 0.05 < 0.05	< 0.05 < 0.05	Induce 10173.09-NC18
					3		< 0.05 < 0.05	< 0.05 < 0.05	
					6		< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	
2010 Citra, FL (Red Pontiac)	EC 56	0.11 0.11	375 375	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Chemnut 10173.09-FL07
2009 Laingsburg, MI (FL 1879)	EC 56	0.11 0.11	282 279	2	0	Tubers	< 0.05 < 0.05	< 0.05 < 0.05	Activator 90 10173.09-MI11
					3		< 0.05 < 0.05	< 0.05 < 0.05	
					7		< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	
					11		< 0.05 < 0.05	< 0.05 < 0.05	
					14		< 0.05 < 0.05	< 0.05 < 0.05	

POTATO Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate ^a	M-1	
2009 Arlington, WI ^b (Superior)	EC 56	0.11 0.11	395 399	2	6	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Activator 90 10173.09-WI12
2009 Arlington, WI ^b (Superior)	EC 56	0.11 0.11	200 212	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Activator 90 10173.09-WI16
2009 Wooster, OH (Norland Red)	EC 56	0.13 0.12	354 356	2	6	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Top Surf 10173.09-OH*09
2009 Las Cruces, NM (Red Pontiac)	EC 56	0.12 0.11	288 356	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Induce 10173.09-NM17
2009 Kimberly, ID (Russet Burbank)	EC 56	0.11 0.11	423 428	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Activator 90 10173.09-ID12
	EC 56	0.57 0.57	425 427	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	
2009 Kimberly, ID (Russet Burbank)	EC 56	0.11 0.11	469 470	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Activator 90 10173.09-ID13 (Close to the above)
2009 Prosser, WA (Yukon Gold)	EC 56	0.11 0.11	341 328	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Ad wet 90 10173.09-WA05
2009 Prosser, WA (Russet Burbank)	EC 56	0.12 0.11	274 256	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Ad Wet 90 10173.09-WA06
2009 Moxee, WA ^c (Red Norland)	EC 56	0.12 0.12	388 384	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	90 Plus 10173.09-WA*07
2009 Moxee, WA ^c (Russet (Dillon))	EC 56	0.11 0.11	377 370	2	7	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	90 Plus 10173.09-WA*08
2010 Holtville, CA (Cal White)	EC 56	0.11 0.11	295 293	2	1	Tubers	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Activator 90 10173.09-CA97

DALT: days after the last application

^a Average in parentheses

^b Same location

^c Same location

Herbs

Mints

A total of six supervised trials on mint were conducted in the USA: Washington (three), and Idaho (one) in 2002 (Dorschner, 2005 PR No. 08452), and Wisconsin (two) in 2004 (Dorschner, 2007 PR No.A8542).

In each trial, two foliar applications of the fenpyroximate EC formulation (52 g ai/L) were made at a rate of approximately 0.11 to 0.13 kg ai/ha per application. Applications were made 6 to 8 days apart and the mint was harvested 1 day after the last treatment.

Two samples of mint were collected from each treated plot and untreated plot. Specimens were stored frozen and shipped frozen to the analytical laboratory. Samples were processed with dry ice in a Hobart food processor. Processed samples were stored frozen until analysis.

The method of analysis was based on GC-NPD. The LOQ was 0.05 mg/kg for combined residues of fenpyroximate and M-1. Average recovery of all fortifications was $107.0 \pm 10.4\%$ for mint (n=25). No control samples contained residues at or above the LOQ of the method.

As the method analyses fenpyroximate and M-1 as M-1, no information was available on the concentrations of fenpyroximate alone.

Table 10 Residues of fenpyroximate in mints from supervised trials conducted with foliar spray in the USA

MINT Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)	Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate +M1 ^a	
US GAP	EC 50	0.058- 0.117	≥ 234 (ground only)	≤ 2	1			Seasonal Max= 0.234 kg ai/ha Interval=7 days
2002 Prosser, WA (Spearmint, Native)	EC 52	0.12 0.11	294 286	2	1	Leaves	1.1 1.2 (1.15)	None 08452.02-WA44
2002 Paterson, WA (Peppermint, Black Mitcham)	EC 52	0.12 0.12	279 290	2	1	Leaves	1.9 2.5 (2.2)	None 08452.02-WA45
2002 Prosser, WA (Spearmint, Native)	EC 52	0.13 0.12	475 460	2	1	Leaves	0.56 0.54 (0.55)	None 08452.02-WA46 (different site from 08452.02-WA44)
2002 Nampa, ID (Peppermint, Black Mitcham)	EC 52	0.12 0.12	232 234	2	1	Leaves	2.4 2.5 (2.45)	None 08452.02-ID16
2004 Portage, WI ^b (Spearmint, Scotch)	EC 52	0.12 0.12	322 317	2	1	Leaves	1.0 1.1 (1.05)	None A8542.04-WI23
2004 Protage, WI ^b (Peppermint, Black Mitcham)	EC 52	0.11 0.11	315 304	2	1	Leaves	2.4 2.1 (2.25)	None A8542.04-WI24

DALT: days after the last application

^a Average in parentheses

^b Same location

Legume animal feeds

Bean forage

Common bean plants with pods were sampled one day after the last application (except in one decline study) by cutting the whole plant at soil level. Each of the collected plants were cut into three pieces, top, middle and bottom and shipped frozen to the analytical laboratory and kept frozen until analysis.

The method of analysis was based on LC-MS/MS. The LOQ was 0.05 mg/kg for each analyte. Average recovery of all fortifications was $99.7 \pm 9.8\%$ (n=44). No control samples contained residues at or above the LOQ of the method. Fresh foliage (with pods) samples were analysed.

Table 11 Residues of fenpyroximate in bean forage from supervised trials on common beans conducted with foliar spray in the USA (Samoil, 2011a; PR No. 09942)

COMMON BEANS Year, Location (variety)	Application				DALT	Portion analysed	Residues (mg/kg)		Notes (adjuvant, deviation, etc.) Trial ID
	Form. g ai/L	Rate kg ai/ha	Water L/ha	No			Fenpyroximate ^a	M-1	
US GAP	EC 50	0.117	≥ 281 (ground) ≥ 47 (air)	≤ 2	1				Seasonal Max =0.234 kg ai/ha Interval=14 days
2008 Davis, CA (Blue Lake bush 274)	EC 52	0.11 0.11	299 290	2	1	Foliage	2.07 1.76 (1.915)	1.28 1.15	TGI Crop Oil 09942.08-CA38
					3		1.69 1.61	1.61 1.43	
					8		0.88 0.99	0.79 0.84	
					10		0.83 0.74	0.62 0.52	
2008 Citra, FL (Dusky)	EC 52	0.11 0.11	374 365	2	1	Foliage	0.96 0.83 (0.895)	0.37 0.31	Chemnut 80-20 09942.08-FL37
2008 Tifton, GA (Blue Lake Bush 274)	EC 52	0.11 0.11	449 449	2	1	Foliage	2.16 2.73 (2.445)	0.55 0.53	Surfactant 80/20 09942.08-GA*13
2008 Freeville, NY (Hystyle)	EC 52	0.11 0.11	318 318	2	1	Foliage	3.38 3.45 (3.415)	1.01 1.05	Induce 09942.08-NY24
2008 Fremont, OH ^b (Sea Biscuit)	EC 52	0.11 0.11	374 364	2	1	Foliage	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Top Surf 09942.08-OH*09
2008 Fremont, OH ^b (Brio)	EC 52	0.11 0.11	365 374	2	1	Foliage	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	Top Surf 09942.08-OH*10
2008 Moxee, WA (Jade)	EC 52	0.11 0.11	374 365	2	1	Foliage	1.70 2.04 (1.87)	0.62 0.77	90 Plus 09942.08-WA*07
2008 Arlington, WI (Hystyle)	EC 52	0.11 0.11	393 384	2	1	Foliage	5.10 6.50 (5.80)	0.93 1.01	Liberate 09942.08-WI*17

DALT: days after the last application

^a Average in parentheses^b Same location

FATES OF RESIDUES IN STORAGE AND PROCESSING

In processing

Plum

A processing study was conducted using fresh plum samples taken 7 days after the last treatment in one field trial in Parlier, California, with two applications of fenpyroximate at a rate of 0.57 kg ai/ha each, 5× the GAP rate (Samoil, 2012c). Dried plums were prepared from fresh plums simulating commercial practices by pitting and placing them in dryers set at around 57 °C to 60 °C for 15 to 17 hours until the moisture level reached around 25 to 26%. Fresh and dried samples were shipped frozen to the laboratory, where the samples remained frozen until analysis.

Residues of fenpyroximate and M-1 were analysed in the different plum matrices were determined by LC-MS/MS. The method was validated prior to analysis with a LOQ of 0.05 mg/kg for

fenpyroximate and M-1 in fresh and dried plums. The recoveries of fenpyroximate were 72–107% in fresh plums, and 92–118% in dried plums.

As shown in Table 12, residues of fenpyroximate concentrated during the processing of dried plums.

Table 12 Residues of fenpyroximate in fresh and dried plums

Commodity	Fenpyroximate mg/kg	Processing factor for Fenpyroximate	M-1 mg/kg
Fresh plum	1.84	–	0.208
Dried plum	3.18	1.73	0.316

Potato

A processing study was conducted using potato samples taken 7 days after the last treatment in one field trial in Kimberly, Idaho, with two applications of fenpyroximate at a rate of 0.57 kg ai/ha each, 5× the GAP rate. (Leonard 2011b). Potatoes were processed into flakes, chips, and wet peels by steam peeling, scrubbing, pressing, trimming, cutting, rinsing free starch, precooking in a steam jacketed kettle, cooling, cooking in a steam jacketed kettle, mashing, mixing with additives, drying in a drum dryer, breaking in a mill, and drying, using a procedure that simulated commercial practice. Processed samples and a retained whole potato sample were shipped frozen to the laboratory, where the samples remained frozen until analysis.

Residues of fenpyroximate and M-1 were determined by LC-MS/MS. The method was validated prior to analysis with a LOQ of 0.05 mg/kg for fenpyroximate and M-1 in all matrices. The recoveries for fenpyroximate were 110% in potato tubers, 83% in potato flakes, 90% in potato chips, and 99% in potato wet peels.

The results of the processing study are summarized in Table 13. As residues in fresh and processed potato samples are all less than the LOQ, it was not possible to calculate processing factors.

Table 13 Residues of fenpyroximate in potatoes and their processed commodities

Commodity	Fenpyroximate mg/kg	M-1 mg/kg
Potato (RAC)	< 0.05, < 0.05	< 0.05, < 0.05
Potato flakes	< 0.05, < 0.05	< 0.05, < 0.05
Potato chips	< 0.05, < 0.05	< 0.05, < 0.05
Potato wet peels	< 0.05, < 0.05	< 0.05, < 0.05

Mint

A processing study was conducted using mint samples taken 1 day after the last application in two field trials (one in Prosser, Washington, and the other in Portage, Wisconsin) with two applications of fenpyroximate at a rate of 0.11 to 0.12 kg ai/ha each complying with the GAP rate (Dorschner 2005 and Dorschner 2007). Samples were processed into oil by distilling using a mint still, a procedure that simulated commercial practice. Processed samples and a retained whole mint sample were shipped frozen to the laboratory, where the samples remained frozen until analysis.

Residues of fenpyroximate and M-1 in the different mint matrices were analysed as M-1 by GC with a nitrogen phosphorous detector. The method was validated prior to analysis with a LOQ of 0.05 mg/kg for mint leaves and 0.10 mg/kg for mint oil. The recoveries were 108% and 100% for mint leaves and 97% and 106% for mint oil as reported in Dorschner 2005 and Dorschner 2007, respectively.

The results of the processing study are summarized in Table 14. Although it was not possible to calculate a processing factor for fenpyroximate alone as no concentrations of fenpyroximate alone were reported, the sum of fenpyroximate and M-1 decreased during processing into oil.

Table 14 Residues of fenpyroximate in mint leaves and mint oil

Commodity	Fenpyroximate +M-1 mg/kg	Processing factor for Fenpyroximate +M-1	Reference
Fresh mint	1.1	–	Dorschner 2005 (PR No. 08452)
Mint oil	< 0.10	< 0.09	
Fresh mint	1.01, 1.05	–	Dorschner 2007 (PR No. A8452)
Mint oil	0.254, 0.206	0.25, 0.20	
	Best estimate	0.20	

APPRAISAL

Fenpyroximate is a pyrazole non-systemic acaricide. It was first evaluated by JMPR in 1995 and then in 1999 and 2010 for maximum residue levels, and in 2004 and 2007 for toxicology. The currently standing recommendations of JMPR are as follows:

ADI: 0–0.01 mg/kg bw (1995)

ARfD: 0.02 mg/kg bw (2007)

Residue definition: Fenpyroximate for compliance with the MRL and for estimation of dietary intake (both for animal and plant commodities). The residue is fat soluble. (1999)

The current Meeting received information on the latest use pattern and the supervised residue trials on stone fruits, strawberry, avocado, cucumber, common bean (pods and/or immature seeds and bean fodder), potato and mints conducted in the USA.

Results of supervised residue trials on crops

The Meeting received supervised trial data for fenpyroximate conducted in the USA on stone fruits, strawberry, avocado, cucumber, common bean (pods and/or immature seeds; and bean fodder), potato and mints with foliar applications of the fenpyroximate emulsion concentrate (EC) formulation.

For estimating HR or highest residue, the highest individual residue concentration from the trials conducted in accordance with GAP was used.

Stone fruits

The approved use of fenpyroximate on stone fruits in the USA consists of up to two foliar spray applications with an interval of 14 days at a maximum rate of 0.117 kg ai/ha and a minimum of 748 L/ha of water, the PHI is 7 days. In supervised residue trials, various adjuvants were used with the result that there were no significant difference or trend found between the different adjuvants.

A total of eight supervised trials on cherries were conducted in the USA in 2010. The residues of fenpyroximate in cherries from six independent trials in accordance with US GAP were in rank order: 0.27, 0.34, 0.46, 0.69, 0.81 and 0.87 mg/kg.

The Meeting estimated an STMR of 0.57 mg/kg for cherries.

A total of ten supervised trials on peach were conducted in the USA in 2010. The residues from seven trials in accordance with US GAP were in rank order: 0.08, 0.08, 0.12, 0.13, 0.13, 0.15 and 0.18 mg/kg.

The Meeting estimated an STMR of 0.13 mg/kg for peach.

A total of six supervised trials on plum were conducted in the USA in 2010. The residues from five trials in accordance with US GAP were in rank order: < 0.05, 0.09, 0.13, 0.20 and 0.27 mg/kg.

The Meeting estimated an STMR of 0.13 mg/kg for plum.

The GAP in the USA covers the group of stone fruits; and the STMRs for cherries, peach and plum were within five-fold difference. However, the Meeting decided to estimate two maximum

residue levels, one for cherries and the other for stone fruits except cherries, in order to avoid probability of IESTI for children calculated for peach exceeding the ARfD.

The Meeting therefore estimated a maximum residue level, STMR and HR of 2, 0.57 and 0.90 mg/kg, respectively for cherries.

As the residue populations of peach and plum were similar according to the Mann-Whitney U test, the Meeting decided to combine the data to recommend a maximum residue level for stone fruits except cherries. The combined residues were in rank order (n=12): < 0.05, 0.08, 0.08, 0.09, 0.12, 0.13, 0.13, 0.13, 0.15, 0.18, 0.20 and 0.27 mg/kg.

The Meeting estimated a maximum residue level, STMR and HR at 0.4, 0.13 and 0.29 mg/kg, respectively, for stone fruits, except cherries.

Strawberry

The approved use of fenpyroximate on strawberry in the USA consists of up to two foliar spray applications with an interval of 14 days at a maximum rate of 0.117 kg ai/ha and a minimum of 234 L/ha of water. PHI is 1 day.

A total of three supervised trials on strawberry were conducted in the USA in 2008. In a trial in Porterville, California, the water volume was less than the minimum specified in GAP. However, as the Meeting considered that difference in spray volume would have little impact on terminal residues, the Meeting used the residue data from this trial for the estimation of maximum residue level.

A total of five supervised trials on strawberry were also conducted in the USA in 2010.

The residues of fenpyroximate in strawberry from eight independent trials in accordance with US GAP were in rank order: 0.07, 0.08, 0.19, 0.19, 0.24, 0.24, 0.28 and 0.53 mg/kg.

The Meeting estimated a maximum residue level, STMR and HR at 0.8, 0.215 and 0.59 mg/kg, respectively for strawberry.

Avocado

The approved use of fenpyroximate on avocado in the USA consists of up to two foliar spray applications with an interval of 14 days at a maximum rate of 0.117 kg ai/ha and a minimum of 889 L/ha of water (for ground spray). PHI is 1 day.

A total of five supervised trials on avocado were conducted in the USA in 2008 and 2009. The residues of fenpyroximate in avocado from four independent trials in accordance with US GAP were in rank order: < 0.05 (2), 0.06 and 0.10 mg/kg.

The Meeting estimated a maximum residue level, STMR and HR at 0.2, 0.055 and 0.10 mg/kg respectively for avocado.

Cucumber

The current approved use of fenpyroximate on field grown cucumber in the USA consists of up to two foliar spray applications with an interval of 14 days at a maximum rate of 0.117 kg ai/ha and a minimum of 374 L/ha of water (for ground spray). PHI is 1 day.

A total of nine supervised trials on cucumber were conducted outdoor in the USA in 2009. The residues of fenpyroximate in cucumber from nine independent trials in accordance with US GAP were in rank order: < 0.05 (2), 0.06, 0.07, 0.07, 0.08, 0.08, 0.11 and 0.17 mg/kg.

The Meeting estimated a maximum residue level, STMR and HR at 0.3, 0.07 and 0.19 mg/kg respectively for cucumber. The new recommendation replaces that of the 2010 JMPR (maximum residue level of 0.03 mg/kg).

Common beans (pods and/or immature seeds)

The approved use of fenpyroximate on common beans (US GAP for snap beans) in the USA consists of up to two foliar spray applications with an interval of 14 days at a maximum rate of 0.117 kg ai/ha and a minimum of 281 L/ha of water (for ground spray). PHI is 1 day.

A total of eight supervised trials on common beans were conducted in the USA in 2008. The residues of fenpyroximate in common beans (pods and/or immature seeds) from seven independent trials in accordance with US GAP were in rank order: < 0.05, 0.09, 0.09, 0.09, 0.15, 0.18 and 0.19 mg/kg.

The Meeting estimated a maximum residue level, STMR and HR at 0.4, 0.09 and 0.19 mg/kg respectively for common beans (pods and/or immature seeds).

Potato

The approved use of fenpyroximate on potato in the USA consists of up to two foliar spray applications with an interval of 7 days at a maximum rate of 0.117 kg ai/ha and a minimum of 187 L/ha of water (for ground spray). PHI is 7 days.

A total of sixteen supervised trials on potato were conducted in the USA. The residues of fenpyroximate in potato from fourteen independent trials in accordance with US GAP were in rank order: < 0.05 (14) mg/kg. The residues of fenpyroximate from one trial in which the application rate was 5 times the GAP rate were also < 0.05 mg/kg.

The Meeting estimated a maximum residue level, STMR and HR at 0.05 *, 0 and 0 mg/kg respectively for potato.

Mints

The approved use of fenpyroximate on mint in the USA consists of up to two foliar spray applications with an interval of 7 days at a maximum rate of 0.117 kg ai/ha and a minimum of 234 L/ha of water (for ground spray). PHI is 1 day.

A total of six supervised trials on mint were conducted in the USA. As the method used analyses fenpyroximate and M-1 as M-1, no information was available on the concentrations of fenpyroximate alone. In general, the concentrations of M-1 in food commodities were much lower than those of fenpyroximate but the data from supervised residue trials provided to JMPR so far indicate that M-1 can be present up to 30% of fenpyroximate. The Meeting considered that the information was insufficient to estimate a maximum residue level for mints.

Legume animal feeds*Bean forage*

Common bean plants with pods were sampled by cutting the whole plant at soil level.

The residues of fenpyroximate in foliage of common bean plant from seven independent trials in accordance with US GAP were in rank order: < 0.05, 0.90, 1.87, 1.92, 2.45, 3.42 and 5.80 mg/kg on a fresh weight basis.

The Meeting estimated a median residue and highest residue at 1.92 and 6.50 mg/kg respectively for bean forage (on a fresh weight basis) for the purpose calculating livestock dietary burdens.

Fate of residues during processing

The Meeting received information on the processing of plum into dried plums; potato into potato flakes, chips and wet peels; and mint into mint oils.

As concentration of fenpyroximate was observed in the processing of plums, there was a need to estimate a maximum residue level for dried plum. Using the processing factor of 1.73 shown below, a maximum residue level for dried plum was estimated to be 0.7 mg/kg.

Commodity	Fenpyroximate mg/kg	Processing factor for Fenpyroximate	STMR-(P)	HR-(P)
Fresh plum	1.84	-	0.11	0.29
Dried plum	3.18	1.73	0.18	0.50

As for processing of potato, no processing factors could be calculated as the residues of fenpyroximate were all below the LOQ of 0.05 mg/kg in fresh potato and processed potato products (flakes, chips and wet peels).

As for processing of mint, since no information was available for the concentration of fenpyroximate alone was available, processing factor of fenpyroximate could not be calculated. The best estimate of processing factor for the sum of fenpyroximate and M-1 in the processing of mint to mint oil was 0.20.

Residues in animal commodities

Estimation of dietary burdens

Among commodities reviewed by the 1999, 2010 and the current JMPR, apple wet pomace (STMR-P, 0.05 mg/kg), dry citrus pulp (STMR-P, 0.64 mg/kg), wet grape pomace (STMR-P, 0.06 mg/kg), wet tomato pomace (STMR-P, 0.03 mg/kg), bean forage (median residue, 1.89 mg/kg; and highest residue, 3.415 mg/kg on a fresh weight basis) and potato wet peel (STMR-P, 0.05 mg/kg) can be fed to beef and dairy cattle. There have been no feed items for poultry.

The maximum and mean dietary burdens were calculated using the highest residue and STMR/median residue of fenpyroximate in the above-mentioned commodities on a basis of the OECD Animal Feeding Table. The summary of calculated dietary burdens of fenpyroximate is shown in the following table.

Summary of livestock dietary burdens (ppm of dry matter diet)

	US-Canada		EU		Australia		Japan	
	max	mean	max	Mean	max	mean	Max	mean
Beef cattle	0.15	0.15	0.18	0.18	11.35	3.50	-	-
Dairy cattle	0.07	0.07	3.90 ^a	1.28 ^b	13.21	4.05	-	-

^a Suitable for estimating maximum residue levels for meat, fat, edible offal and milk of cattle (see below).

^b Suitable for estimating STMRs for meat, fat, edible offal and milk of cattle (see below).

Residues in milk and mammalian tissues

The 1999 JMPR reviewed a cattle feeding study conducted at levels equivalent to 1, 3 and 10 ppm in the feed. In the study, fenpyroximate in milk or tissues was measured together with M-1. No information was available on the concentration of fenpyroximate alone. Nonetheless, the 1999 JMPR and 2010 JMPR used the results of this study as the dietary burdens were lower than 1 ppm and the residue concentrations in the tissues and milk were also very low.

In the animal metabolism study, residues of M-1 in tissues and milk were < 0.001 mg/kg and less than fenpyroximate except in the case of liver in which M-1 was present at much higher concentrations. In the animal feeding study, the sum of fenpyroximate and M-1 in kidney was higher than that in liver, and as such, the residue in kidney would be the basis for a maximum residue level for edible offal. In kidney, the concentration of fenpyroximate was significantly higher than that of M-

1. Therefore, the Meeting decided to use the results of animal feeding study recognizing that it would lead to some overestimate of maximum residue level.

The maximum and mean dietary burdens in cattle were 13.21 and 4.05 ppm of dry matter diet respectively. The Meeting noted that the highest maximum dietary burden in cattle, based on animal feed ration in Australia, was higher than the highest feeding level of 10 ppm in feed in the cattle feeding study by about 30%.

As fenpyroximate has not been authorized for use for common beans in Australia, and bean forage is not generally traded internationally, the Meeting decided to use the second highest maximum dietary burden based on the animal feed ration in Europe, where use of fenpyroximate for common bean has been authorized, together with residue levels in tissues and milk at 1, 3 and 10 ppm dose groups. The maximum dietary burden calculated for cattle using the feed ration in Australia without bean forage was 0.21 ppm in dry matter diet.

	Feed level (ppm) for milk residues	Fenpyroximate+M-1 (mg/kg) in milk	Feed level (ppm) for Tissue residues	Fenpyroximate+M-1 (mg/kg) in			
				Muscle	Liver	Kidney	Fat
Maximum residue level beef or dairy cattle							
Feeding study ^a	3	0.0062	3	0.017	< 0.003	< 0.01	0.073
	10	0.013	10	0.049	0.011	0.019	0.159
Dietary burden and highest residue	3.90	0.007	3.90	0.021	0.004	0.011	0.084
STMR beef or dairy cattle							
Feeding study ^b	1	-	1	< 0.01	< 0.003	< 0.003	0.015
	3	0.0062	3	0.015	< 0.003	< 0.003	0.056
Dietary burden and mean residue	1.28	< 0.005	1.28	0.011	< 0.003	< 0.003	0.021

^a highest residues for tissues and mean residue for milk

^b mean residues for tissues and mean residue for milk

The Meeting estimated STMR of 0.005, 0.011, 0.003, 0.003 and 0.021 mg/kg for milk, muscle, liver, kidney and fat, respectively; and HR of 0.021, 0.004, 0.011 and 0.084 mg/kg for muscle, liver, kidney and fat, respectively.

The Meeting estimated maximum residue levels of 0.01* mg/kg for milks, 0.02 mg/kg for edible offal (mammalian) and 0.2 mg/kg (fat) for meat (from mammals other than marine mammals) and withdrew the existing CXLs for cattle milk, kidney, liver and meat.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue for both plant and animal commodities (for compliance with the MRL and for estimation of dietary intake): *fenpyroximate*.

The residue is fat soluble.

Commodity		Recommended MRL, mg/kg		STMR/STMR-P mg/kg	HR/HR-P mg/kg
CCN	Name	New	Previous		
FI 0326	Avocado	0.2	-	0.055	0.10
MO 1280	Cattle kidney	W	0.01*		
MO 1281	Cattle liver	W	0.01*		

Commodity		Recommended MRL, mg/kg		STMR/STMR-P	HR/HR-P
CCN	Name	New	Previous	mg/kg	mg/kg
MM 0812	Cattle meat	W	0.02 (fat)		
ML 0812	Cattle milk	W	0.005* F		
FS 0013	Cherries	2	-	0.57	0.90
VP 0526	Common bean (pods and/or immature seeds)	0.4	-	0.09	0.19
VC 0424	Cucumber	0.3	0.03	0.07	0.19
MO 0105	Edible offal (mammalian)	0.02	-	Liver, 0.003 Kidney, 0.003	Liver, 0.004 Kidney, 0.011
MM 0095	Meat (from mammals other than marine mammals)	0.2 (fat)	-	Muscle, 0.011 Fat, 0.021	Muscle, 0.021 Fat, 0.084
ML 0106	Milks	0.01*	-	0.005	-
VR 0589	Potato	0.05	-	0	0
DF 0014	Prunes	0.7	-	0.18	0.50
FS 0012	Stone fruits (except cherries)	0.4	-	0.13	0.29
FB 0275	Strawberry	0.8	-	0.215	0.59

For calculating animal dietary burden

Commodity		Recommended MRL, mg/kg		STMR/STMR-P	HR/HR-P
CCN	Name	New	Previous	mg/kg	mg/kg
AL 1030	Bean forage			1.92 ^a	5.80 ^a

^a for the purpose of calculating animal dietary burdens. Expressed on an “as received” basis.

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Dietary Intakes (IEDIs) of fenpyroximate were calculated for the 13 GEMS/Food cluster diets using STMRs and STMRPs estimated by the 1999, 2010 and current Meetings, see Annex 3 of the 2013 JMPR Report. The ADI is 0–0.01 mg/kg bw and the calculated IEDIs were 1–7% of the maximum ADI. The Meeting concluded that the long-term intake of residues of fenpyroximate resulting from the uses considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The International Estimated Short-Term Intakes (IESTI) of fenpyroximate were calculated for commodities and their processed commodities using STMRs/STMR-Ps estimated by the current Meeting, see Annex 4 of the 2013 JMPR Report. The ARfD is 0.02 mg/kg and the calculated IESTIs were 0–80% of the ARfD. The Meeting concluded that the short-term intake of residues of fenpyroximate, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

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FLUDIOXONIL (211)

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EXPLANATION

Fludioxonil is a phenylpyrrole fungicide that was reviewed by the JMPR in 2004 (T, R), 2010 (R) and 2012 (R). The compound was listed by the Forty-fourth Session of CCPR for the evaluation by the 2013 JMPR. Residue studies were submitted for pineapple, tomato, fresh peas, dry beans and potato, and processing studies on pineapple, tomato and potato. Additionally, a farm hen feeding study and analytical method to analyse fludioxonil and its metabolites in poultry tissues and eggs were also submitted.

Definition of residue for compliance with the MRLs and estimation of dietary intake in plant commodities: fludioxonil. Definition of residue for compliance with the MRLs and estimation of dietary intake: sum of fludioxonil and its benzopyrrole metabolites, determined as 2,2-difluorobenzo[1,1]dioxole-4-carboxylic acid and expressed as fludioxonil. The residue is fat-soluble.

METHODS OF RESIDUE ANALYSIS

Method GRM025.03A determines fludioxonil and its metabolites oxidisable to CGA192155 (2,2-difluorobenzo[1,3]dioxole-4-carboxylic acid) in poultry tissues and eggs (Sole 2008, 2008a). Samples of muscle, liver and kidney are homogenised and extracted by refluxing with ammonium hydroxide:acetonitrile (80:20 v/v). After filtration, the aqueous phase is acidified and partitioned with toluene following addition of sodium chloride. Conversion of fludioxonil and its metabolites to CGA192155 is carried out by heating in the presence of potassium permanganate and aqueous sodium hydroxide; the oxidation is then quenched with sodium metabisulfite, the extracts are filtered, acidified, and partitioned into dichloromethane:ethyl acetate (80:20 v/v). After evaporation, the residues are dissolved in acetonitrile:water (50:50 v/v) and determined as total fludioxonil by LC-MS/MS. A molecular weight correction factor of 1.23 is applied when calculating procedural recovery values and quantifying residues of CGA192155. The recoveries obtained are shown in Table 1.

Table 1 Recovery of CGA192155 (2,2-difluorobenzo[1,3]dioxole-4-carboxylic acid) expressed as fludioxonil obtained during method validation

Matrix	Level (mg/kg)	Recovery (%)	Mean (%)	RSD (%)	Range (%)
MRM transition 201> 157 m/z					
Eggs	0.01	110, 107, 108, 113, 107	109	2	107-113
	0.1	97, 95, 99, 97, 99	97	2	95-99
	Overall		103	6	95-113
Milk	0.01	74, 84, 92, 98, 87	87	11	74-98
	0.1	78, 78, 79, 76, 80	78	2	76-80
	Overall		83	9	74-98
Muscle	0.01	82, 70, 77, 75, 80	77	6	70-82
	0.1	80, 75, 78, 78, 80	78	3	75-80
	Overall		78	4	70-82
Liver	0.01	86, 86, 85, 85, 89	86	2	85-89
	0.1	88, 87, 88, 87, 87	87	1	87-88
	Overall		87	1	85-89
Kidney	0.01	77, 74, 82, 78, 82	79	4	74-82
	0.1	80, 80, 81, 84, 84	82	3	80-84
	Overall		80	4	74-84
Fat	0.01	78, 81, 78, 76, 77	78	2	76-81
	0.1	77, 79, 81, 78, 80	79	2	77-81
	Overall		78	2	76-81
MRM transition 201>91 m/z					
Eggs	0.01	103, 103, 99, 104, 105	103	2	99-105
	0.1	96, 95, 99, 97, 100	97	2	95-100
	Overall		100	3	95-105
Milk	0.01	80, 82, 85, 92, 81	84	6	80-92

Matrix	Level (mg/kg)	Recovery (%)	Mean (%)	RSD (%)	Range (%)
MRM transition 201> 157 m/z					
Muscle	0.1	79, 81, 81, 77, 80	80	2	77-81
	Overall		82	5	77-92
	0.01	82, 74, 80, 78, 80	79	4	74-82
Liver	0.1	80, 76, 79, 80, 80	79	2	76-80
	Overall		79	3	74-82
	0.01	86, 88, 88, 88, 89	88	1	86-89
Kidney	0.1	87, 86, 87, 86, 87	87	1	86-87
	Overall		87	1	86-89
	0.01	76, 73, 83, 82, 83	79	6	73-83
Fat	0.1	80, 80, 80, 83, 83	81	2	80-83
	Overall		80	4	73-83
	0.01	72, 75, 65, 73, 73	72	5	65-75
	0.1	77, 79, 81, 79, 80	79	2	77-81
	Overall		75	6	65-81

Matrix effects (enhancement or suppression) were greater than 10% for several matrices, and the use of matrix-matched standards is recommended. Standard solutions containing CGA192155 at concentrations ranging from 0.0005 to 0.05 µg/mL (equivalent to 5 to 500 pg of analyte injected on column based on a 10 µL injection) were analysed. The response of the LC-MS/MS system was shown to be linear for CGA192155 primary transition (201.0>157.0 m/z) and the confirmatory transition (201.0>91.0 m/z) over the concentration range tested. The relative standard deviations (RSDs) of recoveries at each fortification level and overall for each matrix tested during method validation were < 20% and therefore according to the EU Guidance (SANCO 3029/99 rev 4. 11/07/00) demonstrate the method has satisfactory repeatability.

The validated limit of quantification for fludioxonil and metabolites as CGA192155 in animal tissues was 0.01 mg/kg for fludioxonil (= 0.0081 mg/kg for CGA192155) when measured as CGA192155 for all animal matrices tested. The stability of CGA192155 was assessed by storing the extracts of representative animal matrices (eggs and liver) refrigerated at 0-9°C and re-analysing them (in quintuplet) after 7 and 9 days of storage. The results showed that the residues were stable in the extracts over these time periods.

USE PATTERNS

All the supervised trials submitted by the manufacturer were conducted in the United States or in Canada. Table 2 shows the registered uses of fludioxonil in USA for the crops relevant to this submission.

Table 2 Use patterns of fludioxonil in USA

Crop	Formulation	Application				DAT (days)
		Method	Maximum Rate	Number	Interval (days)	
Avocado	25%	Foliar spray application	0.245 kg ai/ha	4/year	7-10	0
Beans, dried and succulent, except cowpeas	25%	Foliar spray application	0.245 kg ai/ha	4/year	7	7
Brassica (cole) leafy vegetables	25%	Foliar spray application	0.245 kg ai/ha	4/year	7-10	7
Carrot	25%	Foliar spray application	0.245 kg ai/ha	4/year	7-10	7
Chives	25%	Foliar spray application	0.245 kg ai/ha	4/year	7-10	7
Cucurbits	25%	Foliar spray application	0.245 kg ai/ha	4/year	7-10	1
Ginseng	50%	Drench application or via drip irrigation	0.28 kg ai/ha	4/year	14	14
Herbs, dried and flesh	25%	Foliar spray application	0.245 kg ai/ha	4/year	7-10	7
Kiwifruit	230 g ai/L	In-Line Dip/Drench or aqueous or fruit coating spray application	0.057 kg ai/hL (dip/drench) or 0.24 kg ai/L100,000 kg fruit (spray)	1	na	na

Crop	Formulation	Application				DAT (days)
		Method	Maximum Rate	Number	Interval (days)	
Leafy greens	25%	Foliar spray application	0.245 kg ai/ha	4/year	7–10	0
Lemon	25%	Foliar spray application	0.245 kg ai/ha	1	na	0
Lychee	25%	Foliar spray application	0.245 kg ai/ha	4/year	7–10	0
Pineapple	230 g ai/L	Post-harvest high volume drench and/or directed peduncle spray	0.057 kg ai/hL	1	na	Na
Peas, fresh	479 g ai/L	Seed treatment	0.005 kg ai/L100 kg seed	1	na	Na
Pepper (Bell & Non-Bell)	25%	Foliar spray application	0.245 kg ai/ha	4/year	7–10	0
Potato	230 g ai/L	In-line aqueous spray	0.0045 kg ai/1000 kg tubers	1	na	Na
		High-volume spray	0.005 kg ai/hL	1		
Radish	25%	Foliar spray application	0.245 kg ai/ha	2/crop	7–10	7
Spinach	25%	Foliar spray application	0.245 kg ai/ha	4/year	7–10	0
Tomato	230 g ai/L	In-line drip/drench ^a	0.057 kg ai/hL	1	na	-
	230 g ai/L	High volume, dilute spray ^b	0.0044 kg ai/L1000 kg tomato	1	na	-

Na: not applied;

^a. Dip for approximately 30 seconds and allow fruit to drain.

^b. Must be used in tank mixture with propiconazole

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

Supervised residue trials (149) conducted with fludioxonil in Canada and USA were submitted to the Meeting. Studies were conducted according to GLP, and specified concurrent determination of residues in untreated crops gave residues < LOQ. Residues of fludioxonil arising from use patterns where rate or PHI or $\pm 25\%$ of GAP are underlined and considered for estimation of maximum residue levels and STMRs. In the tables, DAT means days after treatment. In all trials, unless specified, two samples were analysed and the mean residues reported.

Lemon

Five supervised residue trials were conducted in the USA during the 2004-2005 growing season. After harvest, samples were dried and stored deep-frozen for less than 22 months. The results are summarized in Table 3.

Table 3 Residues resulting from fludioxonil application to lemon in USA and Canada (Report: IR-4 PR No. 08297) ^a

State	Crop (Var)	Application			Residue, mg/kg	Trial
		No. (date)	kg ai/ha	DAT		
California, Orange core	Lemon (Lisbon)	1 (11/03/2004)	0.257	0	0.12	08297.04-CA122
California, Orange core	Lemon (Lisbon)	1 (11/10/2004)	0.251	0	0.12	08297.04-CA123
California, Riverside	Lemon (Lisbon)	1 (01/13/2005)	0.245	0	0.12	08297.04-CA124
California, Riverside	Lemon (Lisbon)	1 (03/17/2005)	0.245	0	0.16	08297.04-CA125
California, Porterville	Lemon (Pryor)	1 (03/08/2005)	0.244	0	0.16	08297.04-CA126

Avocado

Six supervised residue trials were conducted in USA in 2003. The results from analysis of treated samples are summarized in Table 4.

Table 4 Residues resulting from fludioxonil application to avocado in USA (Report: IR-4 PR No. 07338)

State	Crop (Var)	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
Florida, Homestad	Avocado (Miguel)	4	0.246–0.251	0	0.06	07338.03-FL22
Texas, Monte Alto	Avocado (Lula)	4	0.241 – 0.245	0	0.02	07338.03-TX*14
California, Porterville	Avocado (Zutano)	4	0.245 – 0.248	0	0.04	07338.03-CA35
California, Nipomo	Avocado (Gwen & Bacon)	4	0.245 – 0.248	0	0.19	07338.03-CA36
California, Irvine	Avocado (Hass)	4	0.245 – 0.250	0	0.11	07338.03-CA37
California, Orosi	Avocado (Hass)	4	0.246 – 0.247	0	0.02	07338.03-CA38

Pineapple

Eight supervised residue trials were conducted in the USA (Hawaii) in 2009. From each site, pineapple fruit were treated twice post-harvest with the test substance in either a dip plus wax followed by a spray directed to the peduncle or a drench plus wax followed by a spray directed to the peduncle. The fruit was allowed to air dry between applications, and samples of pineapple fruit without crowns were collected following the second application, after the test substance had dried. Samples were stored deep-frozen for a maximum of 18 months. The results are summarized in Table 5.

Table 5 Residues of fludioxonil in pineapple after post-harvest treatment (Report: IR-4 PR No. 10203)

Crop (variety)	Application rate, kg/hL	DAT	Residues, mg/kg	Trial
Pineapple (Maui Gold)	0.06 (drench) + 0.87 (spray)	0	6.4	10203.09-HI02
	0.06 (dip) + 0.87 (spray)	0	4.8	
Pineapple (Mg-3)	0.06 (dip) + 0.87 (spray)	0	5.4	10203.09-HI03
	0.06 (drench) + 0.87 (spray)	0	6.1	
Pineapple (Mg-3)	0.06 (drench) + 0.87 (spray)	0	6.6	10203.09-HI04
	0.06 (dip) + 0.87 (spray)	0	5.4	
Pineapple (Maui Gold)	0.06 (dip) + 0.87 (spray)	0	5.4	10203.09-HI05
	0.06 (drench) + 0.87 (spray)	0	5.2	

Cucurbits

Eighteen supervised residue trials were conducted in the USA in 2004 on cantaloupe, cucumber, and squash plants. The results from analysis of treated samples are summarized in Table 6.

Table 6 Residues resulting from fludioxonil application to cucurbits in USA (Report: No. T002039-03)

State	Crop (Var)	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
Illinois, Champaign	Cantaloupe (Super Star)	4	0.238–0.250	1	0.02	4A-FR-04-5178
				8	0.02	
Texas, Wharton	Cantaloupe (Earligold)	4	0.239–0.257	1	0.07	SA-FR-04-5188
				8	0.02	
Georgia, Chula	Cantaloupe (Edisto 47)	4	0.241–0.247	1	0.09	SI-FR-04-5177
				7	0.02	
California, Madera	Cantaloupe (Top Net)	4	0.241–0.247	1	0.20	WC-FR-04-5180
				7	0.14	
California, Live Oak ^a	Cantaloupe (Top Mark)	4	0.245–0.248	1	0.36	WD-FR-04-5182
				7	0.09	
California, Live Oak ^a	Cantaloupe (Durango)	4	0.245–0.246	1	0.13	WD-FR-04-5181
				7	0.12	
Wisconsin, Delavan	Cucumber (Marketmore 86)	4	0.243–0.251	1	0.03	NI-FR-04-5174
				7	< 0.01	
Michigan, Conklin	Cucumber (Marketmore 76)	4	0.243–0.245	1	0.04	NL-FR-04-5173
				7	0.01	
Texas, Wharton	Cucumber (Slice Master Select)	4	0.245–0.250	1	0.06	SA-FR-04-5175
				8	0.03	
Georgia, Chula	Cucumber (Lightning)	4	0.244–0.250	1	0.04	SI-FR-04-5170
				7	< 0.01	

State	Crop (Var)	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
N. Carolina, Rose Hill	Cucumber (Poinsett 79)	4	0.246–0.248	1 7	0.09 < 0.01	SJ-FR-04-5171
Florida, Vero Beach	Cucumber (Straight Eight)	4	0.238–0.248	1 7	0.13 0.02	VF-FR-04-5172
California, Hikman	Cucumber (Poinsett 76)	4	0.243–0.246	1 7	0.05 0.02	WC-FR-04-5176
Illinois, Champaign	Squash, Summer (Lemondrop)	4	0.243–0.268	1 6	0.01 < 0.01	4A-FR-04-5186
New York, Hudson	Squash, Summer (Yellow Straight)	4	0.233–0.252	1 7	0.04 0.01	5E-FR-04-5183
S. Carolina, Elko	Squash, Summer (Lemondrop L)	4	0.244–0.248	1 6	0.08 < 0.01	SJ-FR-04-5184
Florida, Vero Beach	Squash, Summer (Burpee Hybrid Zucchini)	4	0.248–0.252	1 7	0.08 0.02	VF-FR-04-5185
California, Visalia	Squash, Summer (Black Beauty)	4	0.248–0.245	1 7	0.04 < 0.01	WC-FR-04-5187

^a. independent trials, different application dates

Tomato

Twelve post-harvest trials were conducted in the USA in 2008/2009. A food-grade adjuvant was included in each tank mix. Samples were stored deep-frozen for a maximum of 9 months and analysed using Method No. AG-597B. The results are summarized in Table 7.

Table 7 Residues resulting from fludioxonil post-harvest application to tomato in the USA (IR-4 PR No. 10182)

Crop (Variety)	Application rate	DAT	Residues, mg/kg	Trial
Tomato (Shady Lady)	0.06 kg ai/hL; drench/dip	0	0.25/0.28	09-CA98
	0.005 kg ai/1000 kg fruit; in-line spray	0	0.18	
Tomato (Agri-Set 761)	0.06 kg ai/hL; dip	0	0.48	09-FL06
Cherry tomato (Il-7108)	0.06 kg ai/hL; dip	0	0.77	09-FL68
Tomato (Amelia)	0.005 kg ai/1000 kg fruit; in-line spray	0	0.66	09-NC19
	0.06 kg ai/hL, drench/dip	0	0.73/0.47	
	0.06 kg ai/hL; drench/dip	0	1.0/1.1	
Tomato, Cherry (Red Cherry)	0.005 kg ai/1000 kg fruit; in-line spray	0	1.8	09-NY2
	0.06 kg ai/hL; dip	0	0.43	

Peppers (Bell and Non-Bell)

Nineteen supervised residue trials were conducted in the field and in greenhouse on bell and non-bell peppers in USA and Canada in 2005/2006. The results from analysis of treated samples are summarized in Table 8.

Table 8 Residues resulting from fludioxonil application to pepper (bell & non-bell) in USA and Canada

Country, region	Crop (Var)	Field/ greenhouse	Application			Residue, mg/kg	Trial
			No.	kg ai/ha	DAT		
CA, Ontario, Harrow ^a	Bell Pepper (Revolution)	Field	4	0.256 – 0.264	0	< 0.02	IR-4 PR No. 09567.06-ON02
CA, Ontario, Harrow ^a	Bell Pepper (Aristotle)	Field	4	0.249 – 0.286	0	< 0.02	IR-4 PR No. 09567.06-ON03
CA, Ontario, Delhi	Bell Pepper (Crusdaer)	Field	4	0.241 – 0.248	0	0.09	IR-4 PR No. 09567.06-ON04
CA, Quebec	Bell Pepper (Redstart)	Field	4	0.243 – 0.250	0	0.28	IR-4 PR No. 09567.06-QC01
USA, California, Holtville	Bell Pepper (Macabi)	Field	4	0.246 – 0.248	0	0.12	IR-4 PR No. 09567.06-CA45
USA, California, Parlier	Bell Pepper (Baron)	Field	4	0.242 – 0.248	0	0.08	IR-4 PR No. 09567.06-CA46

Country, region	Crop (Var)	Field/ greenhouse	Application			Residue, mg/kg	Trial
			No.	kg ai/ha	DAT		
USA, Florida, Citra	Bell Pepper (Camelot X3R)	Field	4	0.246 – 0.253	0	0.16	IR-4 PR No. 09567.06-FL19
USA, N. Carolina, Raleigh	Bell Pepper (Revolution)	Field	4	0.242 – 0.246	0	0.16	IR-4 PR No. 09567.06-NC07
USA, Florida, Citra	Non-Bell Pepper (Mesilla 242)	Field	4	0.243 – 0.259	0	0.31	IR-4 PR No. 09567.06-FL20
USA, N. Mexico, Las Cruces ^a	Non-Bell Pepper (Joe E. Parker)	Field	4	0.245 – 0.249	0	0.06	IR-4 PR No. 09567.06-NM03
USA, N. Mexico, Las Cruces ^a	Non-Bell Pepper (Joe E. Parker)	Field	4	0.244 – 0.246	0	0.14	IR-4 PR No. 09567.06-NM04
USA, Ohio, Wooster	Non-Bell Pepper (San Ardo)	Field	4	0.244 – 0.245	0	0.07	IR-4 PR No. 09567.06-OH*06
USA, Texas, Weslaco	Non-Bell Pepper (Sonora Anaheim)	Field	4	0.244 – 0.245	0	0.12	09567.06-TX*16
USA, Texas, Weslaco	Bell Pepper (Capistrano)	Field	4	0.244 – 0.248	0	0.13	IR-4 PR No. 09567.06-TX17
Canada, Ontario, Harrow ^a	Pepper (Striker) (bell)	Greenhouse	4	0.245 – 0.247	0	0.21	IR-4 PR No. 09140.05-ON01
Canada, Ontario, Harrow ^a	Pepper (Zamboni) (bell)	Greenhouse	4	0.244 – 0.245	0	0.10	IR-4 PR No. 09140.05-ON06
USA, New Jersey	Pepper (King Arthur) (bell)	Greenhouse	4	0.233 – 0.255	0	0.22	IR-4 PR No. 09140.05-NJ01
USA, Tennessee, Jackson	Pepper (Spartacus F1) (bell)	Greenhouse	4	0.238 – 0.252	0	0.20	IR-4 PR No. 09140.05-TN01
USA, Texas, Weslaco	Pepper (TAM veracruz) (non bell)	Greenhouse	4	0.247 – 0.249	0	0.20	IR-4 PR No. 09140.05-TX01

^a. independent trials, different application days

Lettuce (Head and Leaf)

Fourteen supervised residue trials were conducted in USA in 2001. The results from analysis of treated samples are summarized in Table 9.

Table 9 Residues resulting from fludioxonil application to lettuce in USA (Report: IR-4 PR No. 07131)^a

State	Crop (Var)	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
New York, Freeville	Head Lettuce	4	0.234 – 0.259	0	1.2 (w/ wrapper); ≤ 0.02 (w/o wrapper)	07131.01-NY11 ^a
Florida, Gainesville	Head Lettuce	4	0.243 – 0.247	0	4.6 (w/ wrapper); 0.25 (w/o wrapper)	07131.01-FL15 ^a
New Mexico, Mesilla	Head Lettuce	4	0.235 – 0.248	0	2.0 (w/ wrapper); 0.07 (w/o wrapper)	07131.01-NM04 ^a
Oregon, Aurora	Head Lettuce	4	0.245 – 0.247	0	1.4 (w/ wrapper); 1.4 (w/o wrapper)	07131.01-OR06 ^a
Ohio, Willard	Head Lettuce	4	0.240 – 0.253	0	2.2 (w/ wrapper); 0.50 (w/o wrapper)	07131.01-OH*06 ^a
California, Salinas	Head Lettuce	4	0.244 – 0.252	0	2.0 (w/ wrapper); 1.6 (w/o wrapper)	07131.01-CA*27 ^a
California, Holtville	Head Lettuce	4	0.239 – 0.263	0	0.42 (w/ wrapper); 0.06 (w/o wrapper)	07131.01-CA29 ^a
California, Parlier	Head Lettuce	4	0.247 – 0.252	0	2.8 (w/ wrapper); 0.68 (w/o wrapper)	07131.01-CA31 ^a
Maryland, Salisbury	Leaf lettuce	4	0.245 – 0.249	0	22	07131.01-MD08
Florida, Live Oak	Leaf lettuce	4	0.243 – 0.251	0	16	07131.01-FL16
New Mexico, Mesilla	Leaf lettuce	4	0.251 – 0.262	0	6.7	07131.01-NM05

State	Crop (Var)	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
California, Salinas	Leaf lettuce	4	0.251 – 0.360	0	4.8	07131.01-CA*28
California, Clay Loam	Leaf lettuce	4	0.243 – 0.245	0	10	07131.01-CA30
California, Parlier	Leaf lettuce	4	0.247 – 0.265	0	6.5	07131.01-CA32

^a Only one sample analysed in each case

Spinach

Eleven supervised residue trials were conducted in USA and Canada in 2008. The results from analysis of treated samples are summarized in Table 10.

Table 10 Residues resulting from fludioxonil application to spinach in USA and Canada (Report: IR-4 PR No. 10006)^a

Country/Region	Crop (Var)	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
USA/Maryland, Salisbury	Spinach (Melody)	4	0.245 – 0.247	0	4.6	10006.08-MD22
USA/New York, Ithaca	Spinach (Tyee)	4	0.243 – 0.247	0	1.9	10006.08-NY30
USA/Texas, Weslaco ^a	Spinach (Samish)	4	0.246	0	12	10006.08-TX*02
USA/Texas, Weslaco ^a	Spinach (Space F1)	4	0.243 – 0.247	0	7.5	10006.08-TX03
USA/S. Carolina, Charleston	Spinach (Skookam hybrid)	4	0.239 – 0.246	0	3.4	10006.08-SC*07
USA/Colorado, Fort Collins	Spinach (Spinner)	4	0.247 – 0.260	0	8.3	10006.08-CO13
USA/California, Holtville	Spinach (1B12A)	4	0.236 – 0.251	0	9.8	10006.08-CA18
USA/California, Salinas	Spinach (Whale)	4	0.243 – 0.251	0	4.9	10006.08-CA*17
CAN/Ontario	Spinach (Unipack 151)	4	0.244 – 0.253	0	4.9	10006.08-ON13
CAN/British Columbia	Spinach (Unipack)	4	0.248 – 0.251	0	16	10006.08-BC02
CAN/Quebec	Spinach (Unipack 151)	4	0.235 – 0.258	0	5.8	10006.08-QC04

^a independent trials, different application days

Potato

Five post-harvest trials were conducted in the United States and Canada during 2009 and 2010. From each site, potato tubers were treated as a spray directed to tubers falling from a conveyor belt or moving along a roller table. Samples were stored deep-frozen for a maximum of 11.3 months before analysis. The results are summarized in Table 11.

Table 11 Residues resulting from fludioxonil post-harvest application to potato in Canada and USA (Report: TK0003297)

Country	Crop (Variety)	kg ai/L ton	Sample	DAT	Residues, mg/kg	Trial
Canada	Potato (Ac Chaleur)	0.0045	Roller table	0	2.5	09-ON14 ^{a,b}
				14	3.2	
				31	2.9	
				59	2.9	
USA	Potato (Russet Burbank)	0.0045	Conveyor belt	0	2.9	09-ID19 ^b
				30	0.63	
				231	1.0	
			Surface	0	1.0	
			Spray chamber	0	3.2	
			Brush table	0	1.7	
USA	Potato (Frito Lay 1533)	0.005	Conveyor belt	0	0.66	09-ME04 ^b
USA	Potato (Russet Burbank)	0.0045	Conveyor belt	0	1.5	09-WA32 ^b
				13	1.0	
				32	1.1	
				61	1.1	

Country	Crop (Variety)	kg ai/L ton	Sample	DAT	Residues, mg/kg	Trial
	Potato (Russet Burbank)	0.0046	Conveyor belt	0	1.1	09-WI19 ^b

^a. potato samples were cut in half in the field;

^b. spray directed to tubers falling from conveyor belt or moving along a roller table;

^c. spray directed to tubers placed on a flat surface (i.e. tarp) close together, allowed to dry, turned over, and sprayed again;

^d. spray directed to tubers placed close together inside a spray chamber, allowed to dry, turned over, and sprayed again;

^e. spray directed to tubers placed on a brush table that rolled the potatoes under the spray.

Radish

Six supervised residue trials were conducted in USA in 2004. The results from analysis of treated samples are summarized in Table 12.

Table 12 Residues on radish tops resulting from fludioxonil application to radish in USA (Report: IR-4 PR No. 09019)

State	Crop (Var)	Application			Sample	Residue, mg/kg	Trial
		No.	kg ai/ha	DAT			
New York, Freeville	Radish (Cheriette F1)	2	0.257 – 0.268	7	Tops	4.6	09019.04-NY06
					Root	0.10	
Florida, Citra ^a	Radish (Fireball)	2	0.248 – 0.454	7	Tops	5.8	09019.04-FL14
					Root	0.04	
Florida, Citra ^a	Radish (Fireball)	2	0.245 – 0.250	7	Tops	10	09019.04-FL15
					Root	0.10	
California, Salinas	Radish (Cheriette)	2	0.251 – 0.254	7	Tops	3.0	09019.04-CA*08
					Root	0.08	
Ohio, Willard	Radish (Cabernet)	2	0.251 – 0.256	7	Tops	2.5	09019.04-OH*01
					Root	< 0.02	
Washington Moxee	Radish (Crunchy Royale)	2	0.238 – 0.240	8	Tops	0.45	09019.04-WA*02
					Root	< 0.02	

^a. independent trials, different application days

Peas

Twenty supervised residue trials were conducted on fresh peas with pods in the USA in 1997 after seed treatment at different rates. The results are summarized in Table 13.

Table 13 Residues resulting from fludioxonil seed application at planting to succulent peas with pods in USA (Report: ABR-97097)

State	Crop (Variety)	Rate kg/100 kg seed	DAT	Residues, mg/kg	Trial
Wisconsin, Portage	Pea (Knight)	0.0025	61	< 0.01	MW-SR-705-97
	Pea (Knight)	0.005	61	< 0.01	
	Pea (Knight)	0.012	61	< 0.01	
	Pea (Knight)	0.025	61	< 0.01	
Virginia, Isle of Wight	Pea (Knight)	0.0025	66	< 0.01	NE-SR-308-97
	Pea (Knight)	0.005	66	< 0.01	
	Pea (Knight)	0.012	66	< 0.01	
	Pea (Knight)	0.025	66	< 0.01	
New York, Wayne	Pea (Knight)	0.0025	58	< 0.01	NE-SR-805-97
	Pea (Knight)	0.005	58	< 0.01	
	Pea (Knight)	0.012	58	< 0.01	
	Pea (Knight)	0.025	58	< 0.01	
Washington, Whitman	Pea (Scout)	0.0025	71	< 0.01	OW-SR-632-97
	Pea (Scout)	0.005	71	< 0.01	
	Pea (Scout)	0.125	71	< 0.01	
	Pea (Scout)	0.25	71	< 0.01	

State	Crop (Variety)	Rate kg/100 kg seed	DAT	Residues, mg/kg	Trial
Oregon, Washington	Pea (SP173)	0.005	69	< 0.01	OW-SR-633-97
	Pea (SP173)	0.125	69	< 0.01	
	Pea (SP173)	0.25	69	< 0.01	
	Pea (SP173)	0.25	69	< 0.01	

Snap bean

Eight supervised residue trials were conducted in USA in 2001. The results from analysis of treated samples are summarized in Table 14.

Table 14 Residues in mature snap bean pods resulting from fludioxonil application to snap beans in USA (Report: IR-4 PR No. 07614)^a

State	Crop (Var)	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
New York, Ithaca	Snap Bean	4	0.245	8	0.04	07614.01-NY09
Maryland, Salisbury	Snap Bean	4	0.245	7	0.03	07614.01-MD05
Florida, Gainesville	Snap Bean	4	0.245	7	0.05	07614.01-FL18
Michigan, East Lansing	Snap Bean	4	0.245	7	0.03	07614.01-MI09
Wisconsin, Madison	Snap Bean	4	0.245	7	< 0.02	07614.01-WI08
California, Holtville	Snap Bean	4	0.245	6	0.38	07614.01-CA34
Idaho, Twin Falls	Snap Bean	4	0.245	8	0.05	07614.01-ID05
Ohio, Madison	Snap Bean	4	0.245	6	0.04	07614.01-OH*09

Lima Bean

Eight supervised residue trials were conducted in USA in 2001. The results from analysis of treated samples are summarized in Table 15.

Table 15 Residues resulting from fludioxonil application to lima beans in USA (Report: IR-4 PR No. 07783)

Region	Crop (Var)	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
Maryland, Salisbury ^a	Lima Bean	4	0.245	8	< 0.02	07783.01-MD03
Maryland, Salisbury ^a	Lima Bean	4	0.245	8	< 0.02	07783.01-MD04
N. Carolina, Clinton	Lima Bean	6	0.245	7	0.03	07783.01-NC08
Idaho, Kimberly	Lima Bean	5	0.245	7	0.21	07783.01-ID07
California, Salinas ^a	Lima Bean	4	0.245	6	0.04	07783.01-CA*26
California, Salinas ^a	Lima Bean	5	0.245	8	< 0.02	07783.01-CA*81
Ohio, Freemont	Lima Bean	5	0.245	8	< 0.02	07783.01-OH*11
Georgia, Tifton	Lima Bean	5	0.245	8	0.03	07783.01-GA*08

^a. independent trials, different application days

Dry beans

Nine supervised residue trials were conducted in USA in 2001 using foliar application. The results are summarized in Table 16.

Table 16 Residues resulting from fludioxonil application to dry beans in USA (Report: IR-4 PR No. 07782)

Region	Crop variety	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
California, Salinas	Bean	4	0.245	5	0.22 ^a	07782.01-CA*25
Colorado, Fort Collins	Bean Bill Z	4	0.245	7	0.06	07782.01-CO08
Colorado, Wellington	Bean UI 126	4	0.245	6	0.12	07782.01-CO09

Region	Crop variety	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
Idaho, Kimberly	Bean Pinto	4	0.245	6	<u>0.04</u>	07782.01-ID06
Michigan, Holt	Bean Strike	4	0.245	6	<u>0.02</u>	07782.01-M110
N. Dakota, Velva	Bean Othello	4	0.245	7	<u>0.04</u>	07782.01-ND07
Ohio, Freemont	Bean	4	0.245	8	<u>0.02</u>	07782.01-OH*10
S. Dakota, Brookings	Bean Vista	4	0.245	7	<u>0.23</u>	07782.01-SD04
S. Dakota, Aurora	Bean Vista	6	0.245	7	0.06	07782.01-SD05

^a Residues detected in the “treated samples” were < 0.02 ppm, and in “control samples” were 0.18 ppm and 0.26 ppm from this trial. It is believed that the control & treated samples were inadvertently switched

Parsley

Four supervised residue trials were conducted in USA in 2003. The results from analysis of treated samples are summarized in Table 17.

Table 17 Residues on fresh parsley resulting from fludioxonil application in USA (Report: IR-4 PR No. 07130)^a

State	Crop (Var)	Application			Sample	Residue, mg/kg	Trial
		No.	kg ai/ha	DAT			
Ohio, Willard	Parsley (Dark Green Italian Flat Leaf)	4	0.241–0.247	6	Fresh	<u>2.3</u>	07130.03-OH*04
				6	dried	<u>23</u>	
California, Salinas	Parsley (Italian Dark Green)	4	0.240–0.251	7	Fresh	<u>1.6</u>	07130.03-CA*34
				8	dried	<u>8.9</u>	
Florida, Citra	Parsley (Italian Dark Green)	4	0.239–0.248	7	Fresh	<u>3.9</u>	07130.03-FL21
				7	dried	<u>18</u>	
Oregon, Aurora	Parsley (Italian Plain Leaf)	4	0.244–0.248	6	Fresh	<u>3.2</u>	07130.03-OR05
				6	dried	<u>15</u>	

^a one sample analysed

Ginseng

Four supervised residue trials were conducted in the USA and Canada from 2005 to 2006. Samples of ginseng root were collected 14–15 days after the last application. The results from analysis of treated samples are summarized in Table 18.

Table 18 Residues resulting from fludioxonil application to ginseng in USA and Canada (Report: IR-4 PR No. 09349)^a

Country	Crop (Var)	Application			Residue, mg/kg	Trial
		No.	kg ai/ha	DAT		
CAN, British Columbia	Ginseng	4	0.182 – 0.287	15	<u>0.16</u>	09349.06-BC06
CAN, Ontario	Ginseng	4	0.280 – 0.282	14	<u>0.18</u>	09349.05-ON18
USA, Michigan, Athens	Ginseng	4	0.270 – 0.289	15	<u>0.40</u>	09349.05-MI22
USA, Wisconsin, Stratford	Ginseng	4	0.277 – 0.291	14	<u>1.7</u>	09349.05-WI18

^a highest residue of two samples

RESIDUES IN PROCESSED COMMODITIES

Pineapple

The trial 10203.09-HI05 shown in Table 4 included a processing study. Pineapple fruit (5.62 mg/kg fludioxonil) was processed to juice, that contained residue of 5.40 mg/kg, with a processing factor of 0.96.

Tomato

In one processing study, tomato plants received four foliar applications of fludioxonil (0.24 kg ai/ha), and samples were processed simulating commercial practices (Thompson, 2005; IR-4 PR No. 08124). After washing, the tomatoes were placed in a grinder and the crush was pumped into a hot break system. The crush was heated and processed through a finisher to remove peel and seeds. The resulting juice was concentrated to puree with a vacuum evaporator. After puree sample collection, the remaining puree was condensed into paste. Residues was 0.14 mg/kg in RAC, 0.05 mg/kg in pure (PF=0.36) and 0.15 mg/kg in paste (PF=1.1).

Potato

The trial 09-ID19 shown in Table 8 included a processing study. Residues in tubers were 0.472 mg/kg, in wet peel 0.797 mg/kg (PF=1.69), 0.01 mg/kg in flakes (PF=< 0.02) and 0.018 mg/kg in chips (PF=0.04).

RESIDUES IN ANIMAL COMMODITIES

Farm Animal Feeding Studies

Hen feeding study

A residue transfer study in poultry was carried out with four dosing level groups following a 28-day repeat dose regime via a gelatin capsule (Leslie, 2009; Report No. 1983/108-D2149). Dose levels were 1.54, 4.64 and 15.4 mg/kg feed (AR). Each of the four dosed groups was further sub divided into three sub-groups. Collection of eggs was made in the afternoon following dosing and the following morning immediately prior to dosing, which comprised a single day's sample. Following sacrifice, samples of tissue were homogenised to a fine powder in the presence of dry ice and stored frozen prior to analysis. Samples from the 10× dose group were analysed initially and then those from the lower dose group analysed if residues of fludioxonil were found to be above LOQ. The maximum storage period for eggs and tissues samples was 58 days. Residue levels (sum of fludioxonil and its benzopyrrole metabolites, determined as 2,2-difluorobeno[1,1]dioxole-4-carboxylic acid and expressed as fludioxonil) in eggs as a function of time from the three dosed groups are shown in Table 19.

Table 19 Fludioxonil residue level in eggs (sum of fludioxonil and its benzopyrrole metabolites, determined as 2,2-difluorobeno[1,1]dioxole-4-carboxylic acid and expressed as fludioxonil)

Days after dosing	Equivalent Fludioxonil Residue Level (mg/kg)					
	1.54 ppm		4.64 ppm		15.4 ppm	
	Average	Max	Average	Max	Average	Max
0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
5	< 0.01	< 0.01	0.010	0.013	0.024	0.036
7	< 0.01	< 0.01	< 0.01	< 0.01	0.026	0.032
10	< 0.01	< 0.01	< 0.01	0.011	0.032	0.040
14	< 0.01	< 0.01	0.010	0.012	0.035	0.041
16	< 0.01	< 0.01	< 0.01	< 0.01	0.026	0.028
21	< 0.01	< 0.01	< 0.01	0.010	0.029	0.032
24	< 0.01	< 0.01	< 0.01	< 0.01	0.036	0.040
28	< 0.01	< 0.01	0.011	0.013	0.040	0.052

Residue levels in tissues as a function of feeding level from the three dosed groups are summarised in Table 20. Muscle samples from animals treated at 15.4 ppm per day exhibited residues <LOQ and so further analysis of samples from the lower dose groups was not considered necessary.

Table 20 Fludioxonil residue level in tissues (sum of fludioxonil and its benzopyrrole metabolites, determined as 2,2-difluorobeno[1,1]dioxole-4-carboxylic acid and expressed as fludioxonil)

		Equivalent Fludioxonil Residue Level (mg/kg)			
Dose Rate	Sub group	Muscle	Skin and Fat	Abdominal Fat	Liver
1.54 ppm	A	na	na	na	0.076
	B	na	na	na	0.036
	C	na	na	na	0.026
	Average	na	na	na	0.046
4.64 ppm	A	na	0.012	< 0.01	0.085
	B	na	< 0.01	< 0.01	0.064
	C	na	0.014	< 0.01	0.209
	Average	na	0.012	< 0.01	0.119
15.4 ppm	A	< 0.01	0.035	0.024	0.284
	B	< 0.01	0.039	0.012	0.282
	C	< 0.01	0.030	0.023	0.283
	Average	< 0.01	0.035	0.020	0.283

na = not analysed

One of the highest dosed group of animals remained on the study after the cessation of dosing to monitor the elimination of fludioxonil from eggs and tissues after dosing had been withdrawn – depuration phase. Commensurate with the dosing phase, egg samples were collected twice daily until twelve days after dosing ceased. From this final group, the three sub groups were sacrificed at three, seven, and eleven days after cessation of dosing and edible tissue samples were retained as for the dosing period. The results are shown in Table 21.

Table 21 Summary of equivalent fludioxonil residue levels in egg samples across sub groups during depuration phase.

Number Days after end of dosing	Equivalent Fludioxonil Residue Level (mg/kg)		
	Sub Group A	Sub Group B	Sub Group C
0	0.024	0.035	0.032
1	0.029	0.032	0.028
3	0.024	0.023	0.022
4	Na	< 0.01	< 0.01
6	Na	< 0.01	< 0.01
8	Na	< 0.01	< 0.01
10	Na	na	< 0.01
11	Na	na	< 0.01

na = not available for analysis – animals sacrificed

Fludioxonil was not detected in any of the muscle, fat and liver samples from the depuration study (< LOQ), suggesting rapid elimination of fludioxonil following completion of dosing.

APPRAISAL

Fludioxonil was reviewed by the JMPR in 2004, 2006, 2010 and most recently in 2012. The ADI for fludioxonil is 0–0.4 mg/kg bw and an ARfD was considered unnecessary. Residue studies were submitted by the manufacturer for various crops, in addition to a hen feeding study and analytical method for poultry tissues and eggs.

The residue definition for fludioxonil for plant commodities for compliance with the MRL and estimation of dietary intakes is fludioxonil. For animal commodities the residue is the sum of fludioxonil and its benzopyrrole metabolites, determined as 2,2-difluoro-benzo[1,3]dioxole-4-carboxylic acid and expressed as fludioxonil. The residue is considered fat-soluble.

Methods of analysis

Method GRM025.03A, not previously evaluated by the JMPR, determines fludioxonil and its metabolites oxidisable to 2,2-difluorobenzo[1,3]dioxole-4-carboxylic acid (CGA192155) in poultry tissues and eggs. Samples of muscle, liver and kidney are homogenized, extracted by refluxing with ammonium hydroxide:acetonitrile and the aqueous phase is acidified and partitioned with toluene. Fludioxonil and its metabolites are converted to CGA192155 by heating in the presence of potassium permanganate and sodium hydroxide; the oxidation is quenched with sodium metabisulfite, the extracts are filtered, acidified, and partitioned into dichloromethane:ethyl acetate (80:20 v/v). Residues are determined as total fludioxonil by LC-MS/MS. A molecular weight correction factor of 1.23 is applied when calculating procedural recovery values and quantifying residues of CGA192155. The LOQ for fludioxonil and metabolites as CGA192155 in animal tissues was 0.01 mg/kg for fludioxonil (=0.0081 mg/kg for CGA192155). Residues of CGA192155 were shown to be stable at 0–9 °C for at least 7–9 days of storage.

Data evaluated by the 2004 JMPR showed that fludioxonil and CGA192155 are stable for at least 12 months in frozen muscle and for at least 18 months in frozen liver, milk and eggs.

Results from supervised residue trials on crops

Lemon

Five foliar supervised residue trials were conducted in the USA in lemons in 2004–2005 matching US GAP (1×0.245 kg ai/ha; 0 day PHI). Residues were 0.12 (3) and 0.16 (2) mg/kg.

Residues on lemons from foliar application are covered by the previous recommendation of maximum residue level of 10 mg/kg (Po) for fludioxonil on citrus

Avocado

Six supervised residue trials were conducted in USA in avocado in 2003 complying with US GAP (4×0.245 kg ai/ha; 0 day PHI). Residues were 0.02 (2), 0.04, 0.06, 0.11 and 0.19 mg/kg.

The Meeting estimated a maximum residue level of 0.4 mg/kg and a STMR of 0.05 mg/kg for fludioxonil in avocado.

Pineapple

Fludioxonil is registered in the USA for use in pineapple as a post-harvest high volume drench and/or directed peduncle spray at 1×0.06 kg ai/hL. Eight supervised residue trials were conducted in the USA (Hawaii) in 2009 using a dip plus wax or drench application at 0.06 kg ai/hL followed by a spray directed to the peduncle at 0.87 kg ai/hL. Residues ranged from 4.8 to 6.6 mg/kg (n=8).

As no trials were conducted according to GAP, the Meeting could not estimate a maximum residue level for fludioxonil in pineapple.

Fruiting vegetables, Cucurbits

Eighteen supervised residue trials were conducted in the USA in 2004 complying with the US GAP for cucurbits (4×0.245 kg ai/ha; 1 day PHI).

Residues in cantaloupe were (n=6) 0.02, 0.07, 0.09, 0.13, 0.20 and 0.36 mg/kg.

Residues in cucumber were: (n=7) 0.03, 0.04 (2), 0.05, 0.06, 0.09 and 0.13 mg/kg.

Residues in summer squash were: (n=5) 0.01, 0.04 (2) and 0.08 (2) mg/kg

The median residues found in the three individual commodities were within a 5 times range, allowing a recommendation to be made for the cucurbits crop group.

As the residue populations are not statistically different, the Meeting agreed they could be combined as (n=18) 0.01, 0.02, 0.03, 0.04 (4), 0.05, 0.06, 0.07, 0.08 (2), 0.09 (2), 0.13 (2), 0.20 and 0.36 mg/kg.

The Meeting recommended a maximum residue level of 0.5 mg/kg and a STMR of 0.065 mg/kg for fludioxonil in fruiting vegetables, cucurbits.

The Meeting withdrew its previous recommendation of 0.03 mg/kg for Melons, except watermelon, and of 0.3 mg/kg for summer squash.

Tomato

Fludioxonil is registered in the USA for use on tomatoes as a post-harvest in line dip/drench at 1×0.06 kg ai/hL or high volume spray at 0.0044kg ai/1000 kg tomatoes (combined with propiconazole in a tank mix).

Residues in tomatoes from six trials at GAP using the dip or drench application were: 0.28, 0.43, 0.48, 0.73, 0.77 and 1.1 mg/kg (if drench and drip was used in one trial, only the highest residue was selected). Three trials conducted at GAP using spray application gave residues of 0.18, 0.66 and 1.8 mg/kg.

Residue data from the two application types were similar and could be combined for residues of 0.18, 0.28, 0.43, 0.48, 0.66, 0.73, 0.77, 1.1 and 1.8 mg/kg (n=9).

The Meeting estimated a maximum residue level of 3 mg/kg and a STMR of 0.66 mg/kg for fludioxonil in tomato (Po).

The Meeting withdrew its previous maximum residue level recommendation for fludioxonil in tomato of 0.5 mg/kg.

Peppers (Bell & Non-Bell)

Currently, there is a MRL of 1 mg/kg for fludioxonil in Peppers, sweet, based European trials matching the GAPs of Italy and Austria.

The GAP of the USA consists of 4×0.245 kg ai/ha; 0 day PHI. The current Meeting received 14 supervised field residue trials on bell (sweet pepper) and non-bell peppers (including chili pepper) from the USA and Canada and five greenhouse trials matching US GAP.

Residues in the field trials for sweet peppers were < 0.02 (2), 0.08, 0.09, 0.12, 0.13 (2), 0.16 (2) and 0.28 (2) mg/kg. Residues for non-bell peppers were 0.06, 0.07, 0.12 and 0.14 mg.

Residues found in the greenhouse trials were 0.10, 0.20, 0.21 and 0.22 mg/kg for sweet pepper and 0.20 mg/kg for non-bell peppers.

These data indicate that the current MRL of 1 mg/kg would accommodate the expected fludioxonil residues resulting in non-bell peppers when applied according to US GAP. The Meeting agreed to extend the previous recommendation of 1 mg/kg to peppers.

Based on the data on non-bell peppers (0.06, 0.07, 0.12, 0.14 and 0.20 mg) and a factor of 10, the Meeting estimates a maximum residue level of 4 mg/kg and a STMR of 1.2 mg/kg for dried chili peppers.

Leafy vegetables

Currently, there is a MRL of 10 mg/kg in Head lettuce, based on indoor trials matching the Italian GAP, and a MRL of 10 mg/kg in Mustard greens based on trials matching the GAP of the USA.

In the USA, GAP in leafy greens is 4×0.245 kg ai/ha; 0 day PHI. Twenty five trials were conducted in USA in 2001 in lettuce and spinach according to GAP were submitted to this Meeting. Additionally, trials evaluated by the 2004 JMPR according to GAP were also considered. Six trials conducted in USA in 2004 in radish tops were not at GAP.

Residue in head lettuce (with wrapper leaves) were (n=8) 0.42, 1.2, 1.4, 2.0 (2), 2.2, 2.8 and 4.6, mg/kg.

Indoor trials conducted in Europe in head lettuce at Italian GAP evaluated by the 2004 JMPR gave residues (n=11) ranging from 0.72 to 6 mg/kg, median of 2.7 mg/kg.

Residues in leafy lettuce were (n= 6) 4.8, 6.5, 6.7, 10, 16 and 22 mg/kg.

Residues in spinach were (n= 11) 1.9, 3.4, 4.6, 4.9 (2), 5.8, 7.5, 8.3, 9.8, 12 and 16 mg/kg.

Residues in watercress from trials evaluated in 2004 (USA GAP) were 4.2 and 4.5 mg/kg.

Residues in mustard greens from trials evaluated in 2004 (USA GAP) ranged from 0.06 to 7.1 mg/kg, median of 1.2 mg/kg (n=9).

The median residues found in the individual commodities from trials conducted matching USA GAP were outside the 5 times range, not allowing a recommendation for leafy vegetable group.

The Meeting therefore, estimated a maximum residue level of 40 mg/kg and a STMR of 8.3 mg/kg for fludioxonil in leafy lettuce

The Meeting estimated a maximum residue level of 30 mg/kg and a STMR of 5.8 mg/kg for fludioxonil in spinach.

The Meeting agreed that there were insufficient trials to estimate a maximum residue level for watercress.

The Meeting confirmed its previous recommendation of 10 mg/kg for fludioxonil in head lettuce and mustard greens.

Potato

Currently, there is a MRL of 0.02 mg/kg for potato, based on the Australian GAP as a seed treatment.

Fludioxonil is registered in the USA for use in potatoes as a post-harvest in line spray at 0.0045 kg ai/1000 kg tubers. Five trials were conducted in the USA and Canada in 2009/2010 matching the US GAP, giving residues of 0.66, 1.1, 1.5, 1.7 and 2.9 mg/kg.

The Meeting estimated a maximum residue level of 5 mg/kg and a STMR of 1.5 mg/kg for fludioxonil in potato (Po).

The Meeting withdrew its previous recommendation for fludioxonil in potatoes of 0.02 mg/kg.

Radish

Six supervised residue trials were conducted in the USA in 2004 matching US GAP (2×0.245 kg ai/ha; 7 days PHI). Residues in the radish tops were: < 0.02 (2), 0.04, 0.08, and 0.10 (2) mg/kg.

The Meeting estimated a maximum residue level of .3 mg/kg and a STMR of 0.06 mg/kg for fludioxonil in radish.

Legume vegetables

Currently, there is a MRL of 0.3 mg/kg for beans, except broad beans and soya beans and for peas (pods and succulent=immature seeds), based on the GAP of France.

The GAP in USA for beans (dried and succulent, except cow beans) is 4×0.245 kg ai/ha; 7 days PHI). In eight trials conducted in snap beans (common beans) from the USA, matching US GAP, residues in snap beans pods were: < 0.02, 0.03 (2), 0.04 (2), 0.05 (2) and 0.38 mg/kg.

Based on the US data on snap beans, the Meeting estimated a maximum residue level of 0.6 mg/kg and a STMR of 0.04 mg/kg for fludioxonil in Beans, except broad bean and soya bean. The Meeting withdrew its previous recommendation of 0.3 mg/kg for beans, except broad bean and soya bean.

In seven trials conducted in lima beans in the USA according to US GAP, residues in succulent shelled beans were: < 0.02 (4), 0.03, 0.04 and 0.21 mg/kg.

The Meeting estimated a maximum residue level of 0.4 mg/kg and a STMR of 0.02 mg/kg for fludioxonil in Beans, Shelled. The Meeting agreed to withdraw its previous recommendation of 0.03 mg/kg for Beans, Shelled.

Fludioxonil is registered in USA to be used in peas as a seed treatment at 0.005 kg ai/100 kg seed. Five trials conducted at US GAP gave residues in mature fresh peas with pods of < 0.01 (5) mg/kg. Fifteen trials conducted at higher or lower GAP rate gave the same results.

The Meeting confirms its previous recommendation of 0.3 mg/kg for peas (pods and succulent=immature seeds).

Beans (dry)

Currently, there is a Codex MRL of 0.07 mg/kg for beans (dry) based on Spanish GAP.

Seven trials were conducted in USA in 2001 according to US GAP (4×0.245 kg ai/ha; 7 days PHI) gave residues in dry beans of 0.02 (2), 0.04 (2), 0.06, 0.12 and 0.23 mg/kg. In two trials harvested earlier or with 6 applications gave residues in the same range.

The Meeting estimated a maximum residue level of 0.5 mg/kg and a STMR of 0.04 mg/kg for fludioxonil in beans (dry) The Meeting withdrew its previous recommendation of 0.07 mg/kg for Beans (dry).

Herbs

Currently, there is a Codex MRL of 10 mg/kg for fludioxonil in fresh basil and chives and of 50 mg/kg for dried basil and chives.

The Meeting received four supervised residue trials in parsley from the USA matching US GAP in herbs (4×0.245 kg ai/ha; 7 days PHI). Residues in fresh parsley were 1.6, 2.3, 3.2 and 3.9 mg/kg and in dry parsley 8.9, 15, 18 and 23 mg/kg.

Data submitted to the 2004 JMPR matching US GAP showed residue of 1.8 and 3.9 mg/kg on fresh chives and 1.9 and 3.0 mg/kg on fresh basil, 14 and 31 mg/kg on dry chives and 15 and 24 mg/kg on dry basil.

The residues found in the individual fresh or dried commodities from trials conducted according to USA GAP are in the same range, and they are combined for allowing recommendations for herbs, fresh and dried.

The residues of fludioxonil in fresh parsley, basil and chives were considered similar and could be combined giving residues of 1.6, 1.8, 1.9, 2.3, 3.0, 3.2 and 3.9 (2) mg/kg.

The Meeting recommended a maximum residue level of 9 mg/kg and a STMR of 2.65 mg/kg for fludioxonil in herbs.

The residue data sets of fludioxonil from dried parsley, basil and chives were also considered similar and could be combined giving residues of 8.9, 14, 15 (2), 18, 22, 24 and 31 mg/kg.

The Meeting recommended a maximum residue level of 60 mg/kg and a STMR of 16.5 mg/kg for fludioxonil in dried herbs, except dried hops.

The Meeting agreed to withdraw its previous recommendations for chives and basil of 10 mg/kg and for dried chives and basil of 50 mg/kg.

Ginseng

Four supervised residue trials were conducted in the USA and Canada from 2005 to 2006 according to GAP (4×0.245 kg ai/ha; 14 days PHI). Residues were 0.16, 0.18, 0.40 and 1.7 mg/kg.

The Meeting recommends a maximum residue level of 4 mg/kg and a STMR of 0.29 mg/kg for fludioxonil in ginseng.

Residues in processed commodities

Pineapple fruit (5.62 mg/kg fludioxonil) processed to juice contained a residue of 5.40 mg/kg, with a processing factor (PF) of 0.96. However, as no maximum residue level recommendation on the raw commodity was made, the Meeting could not make an assessment of residues for pineapple juice.

Tomatoes containing 0.14 mg/kg of fludioxonil were processed to paste (0.15 mg/kg), giving a PF of 1.1. Processing factors estimated by the 2004 JMPR were 1.1, 1.4, 1.5 and 1.6. The best estimated processing factor for tomato paste is 1.4. Based on a STMR of 0.66 mg/kg for tomato, the Meeting estimated a of STMR-P of 0.924 mg/kg for tomato paste

Tomatoes was also processed to puree (0.05 mg/kg) giving a PF of 0.36. The Meeting estimated a STMR-P of 0.236 mg/kg for tomato puree.

The best estimate PF for tomato juice (2004 JMPR) was 0.22. The Meeting estimated a STMR-P of 0.145 mg/kg for fludioxonil.

Potato tubers containing 0.472 mg/kg fludioxonil were processed into chips. Residues were 0.797 mg/kg in wet peel (PF=1.69), 0.01 mg/kg in flakes (PF < 0.02) and 0.018 mg/kg in chips (PF of 0.04).

The Meeting estimated a STMR-P of 0.06 mg/kg for fludioxonil in potato chips (STMR in potato is 1.5 mg/kg).

Residues in animal commodities

Farm animal dietary burden

Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are provided in Appendix IX of the FAO manual. The calculations were made according to the animal diets from US-Canada, EU, Australia and Japan in the Table (Appendix IX of the FAO manual). The STMR, STMR-Ps were estimated at the present Meeting. Dietary burden calculations are provided in Annex 5 of the 2013 JMPR Report.

Livestock dietary burden for fludioxonil, ppm of dry mater diet

Commodity	US-Canada		EU		Australia		Japan	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	0.029	0.018	0.56 ^a	0.27 ^c	0.24	0.13	0.017	0.017
Dairy cattle	0.39	0.18	0.57 ^{a,b}	0.27 ^d	0.24	0.11	0.02	0.018
Poultry-broiler	0.017	0.017	0.38 ^e	0.19 ^f	0.035	0.035	0.002	0.002
Poultry-layer	0.017	0.017	0.38	0.19	0.035	0.035	0.002	0.002

^a Highest maximum beef or dairy cattle dietary burden suitable for maximum residue level estimated for mammalian tissues

^b Highest maximum dairy cattle dietary burden suitable for maximum residue level estimated for mammalian milk

^c Highest mean beef or dairy cattle dietary burden suitable for STMR estimated for mammalian tissues.

^d Highest mean dairy cattle dietary burden suitable for STMR estimated for milk.

^e Highest maximum poultry dietary burden suitable for maximum residue level estimated for poultry tissues

^f Highest mean poultry dietary burden suitable for maximum residue level estimated for poultry tissues

Animal feeding study

A feeding study on poultry submitted to the current Meeting was conducted with fludioxonil at 1.54, 4.64 and 15.4 mg/kg feed on a 28-day daily dose regime via gelatine capsules.

Residues in eggs from the 15.4 ppm dose level hens were < 0.01 mg/kg 3 days after the initiation of dosing, increased to 0.024 mg/kg fludioxonil eq. (max. of 0.036 mg/kg), and reached 0.04 mg/kg at day 28. The Mean level during the study was 0.025 mg/kg and a maximum of 0.052 mg/kg fludioxonil eq. Eggs from the 4.64 ppm group had a mean and a maximum residue of 0.01 and 0.013 mg/kg fludioxonil eq., respectively. No residues were found in eggs from the 1.54 ppm dose group.

Only liver samples from the 1.54 ppm group were analysed, giving a mean of 0.05 mg/kg eq. (0.03 to 0.08 mg/kg).

In the 4.64 ppm group, residues in skin/fat (including abdominal fat) ranged from < 0.01 to 0.01 mg/kg eq. and residues in liver ranged from 0.06 to 0.21 mg/kg eq. (mean of 0.12 mg/kg).

In the 15.4 mg/kg ppm group, residues in muscle were < 0.01, from 0.01 to 0.04 mg/kg eq. in skin and fat (mean of 0.03 mg/kg) and 0.28 mg/kg eq. in liver.

A depuration study conducted at 15.4 ppm dosing level demonstrated that residues in the eggs ranged from 0.02 to 0.04 mg/kg eq. up to 3 days after termination of the study and were not detected further. Fludioxonil was not detected in any of the muscle, fat or liver samples, suggesting rapid elimination of fludioxonil following completion of dosing.

Animal commodity maximum residue levels

A feeding study in cattle evaluated by the 2004 JMPR showed that residues of fludioxonil and its metabolites found in the highest feeding level dose group (5.5 ppm) were 0.014–0.017 mg/kg in liver, 0.022–0.025 mg/kg in kidney (LOQ of 0.05 mg/kg) and none was detected in fat (< 0.05 mg/kg) or muscle (< 0.01 mg/kg). The highest and median residues in milk were 0.019 and 0.01 mg/kg, respectively (LOQ of 0.01 mg/kg). The feeding level in this study is about 10 times higher than the highest dietary burden estimated for cattle at this Meeting (0.57 ppm).

The Meeting confirmed its maximum residue level recommendation of 0.05* mg/kg for edible offal (mammalian), and 0.01* mg/kg for meat (from mammals other than marine mammals) and milks.

Based on an estimated dietary burden for poultry of 0.07 ppm and a metabolism study, the 2004 JMPR had estimated that residues of fludioxonil and metabolites were unlikely to be found in poultry commodities and recommended maximum residue levels of 0.05* mg/kg for eggs, 0.01* mg/kg for poultry meat and 0.05* mg/kg for poultry edible offal and STMRs of 0 mg/kg for eggs, poultry meat and poultry edible offal.

The highest calculated poultry dietary burden calculated by the current Meeting was 0.38 ppm. As the feeding study showed that no residues are expected at a dietary burden of 1.54 ppm (lowest dose tested), the Meeting confirmed that no residues are expected in poultry commodities.

The Meeting recommended a maximum residue level of 0.01* mg/kg and a STMR of 0 for fludioxonil in poultry edible offal and eggs.

The Meeting confirmed its previous recommendation of 0.01* mg/kg for poultry meat.

RECOMMENDATION

The residue definition: for plant commodities for compliance with the MRL and estimation of dietary intakes: *fludioxonil*.

For animal commodities the residue is the sum of fludioxonil and its benzopyrrole metabolites, determined as 2,2-difluoro-benzo[1,3]dioxole-4-carboxylic acid and expressed as fludioxonil.

The residue is fat-soluble.

CCN	Commodity name	Recommended maximum residue level (mg/kg)		STMR (P) mg/kg
		New	Previous	
FI 0326	Avocado	0.4		0.05
HH 0772	Basil	W	10	
DH 0772	Basil, dry	W	50	

CCN	Commodity name	Recommended maximum residue level (mg/kg)		STMR (P) mg/kg
		New	Previous	
VP 0061	Beans, except broad bean and soya bean	0.6	0.3	0.04
VP 0062	Beans (shelled)	0.4		0.02
VD 0071	Beans (dry)	0.5	0.07	0.04
VC 4199	Melons	W	0.03	
HH 0727	Chives	W	10	
DH 0727	Chives, dry	W	50	
	Chili pepper, dry	2		1.2
DH 0092	Dried herbs, except dried hops	60		16.5
PE 0112	Eggs	0.01*	0.05*	0
VC 0045	Fruiting vegetables, Cucurbits	0.5		0.065
VR 0604	Ginseng	4		0.29
HH 0092	Herbs	9		2.65
VL 0483	Lettuce, leafy	40		8.3
VP 0063	Peas (pods and succulent=immature seeds)	0.6	0.3	0.04
VO 0051	Peppers	1		0.18
VO 0445	Peppers, sweet (including pimento or pimiento)	W	1	
VR 0589	Potato	5 (Po)	0.02	1.5
	Potato chips			0.06
PO 0111	Poultry, edible offal of	0.01*	0.05*	0
VR 0494	Radish	20		3.8
VP 4453	Snap beans	0.6		0.04
VL 0502	Spinach	30		5.8
VO 0448	Tomato	3	0.5	0.66
	Tomato purée			0.236
	Tomato juice			0.145
	Tomato paste			0.924

DIETARY RISK ASSESSMENT

Long-term intake

The IEDI of fludioxonil based on the STMRs estimated by this and previous Meetings for the 13 GEMS/Food regional diets were 2–6% of the maximum ADI of 0–0.4 mg/kg bw (see Annex 3 of the 2013 Report). The Meeting concluded that the long-term dietary intake of residues of fludioxonil is unlikely to present a public health concern.

Short-term intake

The 2004 JMPR decided that an ARfD for fludioxonil is unnecessary. The Meeting therefore concluded that the short-term dietary intake of fludioxonil residues is unlikely to present a public health concern.

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FLUTOLANIL (205)

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EXPLANATION

Flutolanil is a systemic fungicide with protective and curative actions. It was evaluated by JMPR in 2002 for the first time for toxicologically and for residues. The 2002 JMPR allocated an ADI of 0–0.09 mg/kg bw, and ARfD unnecessary. It also determined that the definition of residues should be flutolanil for plant commodities (for compliance with MRLs and for estimation of dietary intake) and flutolanil and transformation products, (containing the 2-trifluoromethylbenzoic acid moiety), expressed as flutolanil, for animal commodities (for compliance with MRLs and for estimation of dietary intake). It recommended a maximum residue level for rice, husked; rice, polished; rice bran, unprocessed; rice straw and fodder, dry; tissues of cattle goats, pigs, sheep and poultry; milks; and eggs.

The current Meeting received information on analytical methods, storage stability, use patterns and supervised trials to support estimation of maximum residue levels for broccoli, cabbage and mustard greens.

RESIDUE ANALYSIS

Analytical methods

The Meeting received information on the analytical method used for the determination of flutolanil which is based on the method XAM-65, LC-MS method, and which was originally developed for analysis of flutolanil and its metabolite M-4 in cotton seed and corn grain. It has been modified for the determination of flutolanil and its metabolite M-4 in Brassica vegetables (Corley, 2009a, b and c).

Flutolanil was extracted from broccoli or mustard green samples with acetone. Samples were partitioned twice with ethyl acetate:dichloromethane (1:9). The top layers were dried down and reconstituted in acetone. Following clean-up on a Florisil column, eluates were dried down and reconstituted in mobile phase. Flutolanil in cabbage samples was extracted with methanol:water (1:1, v/v). The analysis was carried out using LC-MS/MS (electro-spray ionization mode; molecular ion of 324 (m+H⁺) m/z and product ion of 282 m/z).

The modified XAM-65 method was validated for the determination of residues of flutolanil in broccoli, cabbage and mustard greens at three different fortification levels, 0.05, 0.5 and 5 mg/kg. Recoveries were 96–110%, 97–106% and 83–110% for broccoli, cabbage and mustard greens, respectively. These were all within the acceptable range of 70–110%, with the relative standard deviation below 10% (Table 1).

Table 1 Recovery results obtained for the determination of flutolanil by the modified method XAM65

Matrix	Fortification level (mg/kg)	N	Recoveries (%)				Mean (%)	RSD (%)
Broccoli	0.05	3	109,	110,	97		105	6.9
	0.5	3	103,	101,	96		100	3.6
	5	3	97,	103,	108		103	5.4
Cabbage	0.05	3	105,	102,	103		103	1.5
	0.5	3	102,	104,	106		104	1.9
	5	3	98,	100,	97		98	1.6
Mustard greens	0.05	4	98,	88,	88,	83	89	7.0
	0.5	4	94,	99,	101,	109,	101	6.2
	5	3	92,	103,	100,	110	101	7.4

The calculated limit of detection (LOD), limit of quantification (LOQ) and lowest level of method validation (LLMV) are shown in Table 2.

Table 2 LOD, LOQ and LLMV of the modified method XAM65 for flutolanil in the matrices relevant to the current review

Matrix	LOD (mg/kg)	LOQ (mg/kg)	LLMV (mg/kg)
Broccoli	0.01	0.03	0.05
Cabbage	0.005	0.015	0.05
Mustard greens	0.008	0.02	0.05

Stability of pesticide residues in stored analytical samples

Storage stability studies were conducted on broccoli in conjunction with supervised trials. Flutolanil in the frozen condition was stable up to 569 days at -22–4 °C (102–114% remaining) in broccoli, 297 days at -29–10 °C (95–101% remaining) in cabbage and 519 days at -22–4 °C (107–114% remaining) in mustard greens. The concurrent recovery spike extracted and analysed along with the storage stability samples showed 95% and 111% recoveries for flutolanil. In the supervised residue trial studies, samples were stored frozen for periods shorter than the respective period tested for the storage stability studies. The storage stability data indicate that the compound was stable under the conditions that the samples were held between sampling and analyses (Corley, 2009a, b and c).

Table 3 Stability of flutolanil in frozen Brassica vegetables

Matrix	Fortification level (mg/kg)	Storage (days)	% Remaining		Concurrent recovery (%) ^a
			Actual	Average	
Broccoli	0.5	569 (-22–4 °C)	114, 102, 104	107 ± 6	111 (at 0.05 mg/kg) 103 (at 5 mg/kg)
Cabbage	0.5	297 (-29–10 °C)	101, 97, 95	98 ± 5	111 at 0.5 mg/kg
Mustard greens	0.5	519 (-22–4 °C)	114, 107, 112	111 ± 4	98 (at 0.05 mg/kg) 95 (at 5 mg/kg)

^a Analyses conducted on the same day

USE PATTERNS

The authorized uses relevant to the supervised trials data submitted to the current Meeting are summarized in Table 4.

Table 4 Registered uses of flutolanil in the USA relevant to the residue evaluation by the current Meeting

Crop	Form g ai/L	Application					PHI days
		Method	Rate kg ai/ha	Water L/ha	Timing	No.	
Brassica leafy vegetables (Head and stem Brassica) (Brassica leafy greens) (Turnip greens)	WP 700	In-furrow or Directed spray	0.863	> 28	At planting	1	–
		Soil drench			At planting	1	45
		Banded application directed at plant bases		281–468	Immediately after transplanting	1	

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting considered residue data from supervised field trials conducted in the USA on broccoli, cabbage and mustard greens with flutolanil WP formulation (700 g ai/kg nominal concentration).

Application rates and residue concentrations were reported as flutolanil. Residue concentrations are recorded unadjusted for recoveries or for residue values in control samples. Where multiple samples were taken from a single plot, individual results are reported, and the calculated average concentration (in parentheses) is used for estimation of maximum residue levels. Where trials were conducted in the same location, with the same or similar varieties, same or similar formulations,

and the same equipment, and at the same or similar timing, they are not regarded as independent and only one result from these trials was chosen for the estimation of a maximum residue level.

Residues from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels and they are underlined.

Crop Group	Commodity	Table No.
Brassica vegetables	Broccoli	Table 5
	Cabbage	Table 6
	Mustard greens	Table 7

Brassica vegetables

Broccoli

A total of eleven field trials were conducted across the USA. Each field trial site consisted of one untreated control plot and one treated plot. Common cultural practices were followed to maintain the broccoli crop. Additional maintenance pesticides and fertilizers were used at all of the sites (except CA66) to produce a commercial quality crop. No adjuvants were used in any of the trials. At all the trials, a single ground application directed in a narrow band at the base of the transplants or over the seed furrow was made at the time of seeding or immediately after transplanting. All applications were made using appropriate equipment, and the carrier volume was sufficient to provide adequate dispersal of the test substance. At the NJ34 trial, the treated area was calculated using the narrow band into which the test substance was sprayed instead of using the entire row width. This resulted in an under-application of the test substance by 45% at the NJ34 trial. At all the trials, the untreated samples were harvested before or simultaneously with the treated samples by different people. Samples were harvested using techniques simulating commercial practices. The commercially mature broccoli heads (including stems and jacket leaves) were harvested 56–106 days after the application.

The samples were analysed using the modified XAM-65 method for both Flutolanil (parent) and its metabolite M-4. No detectable residues of flutolanil or M-4 above the lowest level of method validation (0.05 mg/kg) were found in any of the untreated samples. An apparent flutolanil residue of approximately 0.02 mg/kg was found in the untreated control sample from the OH*11 trial. Also, apparent flutolanil residues of approximately 0.01 mg/kg and 0.009 mg/kg (at or below the calculated LOD) were found in the treated samples from the same trial. All other apparent peaks occurring at or around the retention times for flutolanil and M-4 were below the calculated limit of detection for both compounds and well below the lowest calibration standard.

Table 5 Residues of flutolanil in broccoli from supervised trials conducted in the USA in 2006 (Corley, 2009a; PR No. 09263)

Broccoli Year, Location (variety)	Application				DAT	Portion analysed	Residues (mg/kg)		Trial ID
	Method	Timing	Rate kg ai/ha	No			Flutolanil ^b	M-4	
2006 Salinas, CA (Patron)	Directed at transplant base	Transplants	848	1	68	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	CA*62
2006 Salinas, CA ^a (Marathon)	Directed at transplant base	Transplants (4–5 leaf stage)	841	1	68	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	CA*63
2006 Salinas, CA ^a (Everest)	Directed at transplant base	Transplants	841	1	76	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	CA*64

Broccoli Year, Location (variety)	Application				DAT	Portion analysed	Residues (mg/kg)		Trial ID
	Method	Timing	Rate kg ai/ha	No			Flutolanil ^b	M-4	
2006 Holtville, CA (Triathalon)	Directed at transplant base	Transplant	869	1	98	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	CA65
2006 Irvine, CA (Packman F1)	Directed at transplant base	Seedling	819	1	64	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	CA66
2006 Salisbury, MD (De Cicco)	Directed in narrow band over transplant	Transplant (2 leaf stage)	844	1	62	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	MD11
2006 Bridgeton, NJ (Packman)	Directed at transplant base	Transplant	461	1	54	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	NJ34
2006 Las Cruces, NM (Packman)	Directed at transplant base	Seedling	866	1	83	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	NM07
2006 Willard, OH (Packman)	Directed at transplant base	Transplants	845	1	56	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	OH*11
2006 Aurora, OR (General)	Directed at open seed furrow	Seed (at planting)	864	1	78	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	OR18
2006 Weslaco, TX (Heritage)	Directed at open seed furrow	Seed (at planting)	854	1	106	Flower heads	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	TX25

DAT: days after treatment

^a Same location.

^b Average residue concentration in parentheses

Cabbage

A total of nine field trials were conducted across the USA. Each field trial site consisted of one untreated control plot and one treated plot. Common cultural practices were followed to maintain the cabbage crop. Additional maintenance pesticides and fertilizers were used at all of the sites to produce a commercial quality crop. No adjuvants were used in any of the trials. At all the trials, a single ground application directed in a narrow band at the base of the plant or over the seed furrow was made at the time of transplanting or seeding. All applications were made using appropriate equipment, and the carrier volume was sufficient to provide adequate dispersal of the test substance. At all the trials, the untreated samples were harvested before the treated samples. Samples were harvested using techniques simulating commercial practices. The commercially mature cabbage heads were harvested 62–138 days after the application.

The samples were analysed using the modified XAM-65 method for both flutolanil and its metabolite M-4. No detectable residues of flutolanil or M-4 above the lowest level of method validation (0.05 mg/kg) were found in any of the untreated control samples.

Table 6 Residues of flutolanil in cabbage from supervised trials conducted in the USA in 2005 (Corley, 2009b; PR No. 08840)

Cabbage Year Location (variety)	Application				DAT	Portion analysed	Residues (mg/kg)		Trial ID
	Method	Timing	Rate kg ai/ha	No			Flutolanil ^a	M-4	

Cabbage Year Location (variety)	Application				DAT	Portion analysed	Residues (mg/kg)		Trial ID
	Method	Timing	Rate kg ai/ha	No			Flutolanil ^a	M-4	
2005 Salinas, CA. (Charmant)	Directed at plant base	3–4 leaf stage	842	1	78	Heads (with wrapper leaves)	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05 < 0.05	CA*106
2005 Brighton, CO. (Blue Lagoon)	Directed at plant base	Vegetative	828	1	81	Heads (with wrapper leaves)	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05 < 0.05	CO14
2005 Citra, FL (Bravo)	Directed at plant base	Transplant	853	1	83	Heads (with wrapper leaves)	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05 < 0.05	FL41
2005 Tifton, GA (Primax)	Directed over seed furrow	Seed	853	1	97	Heads (with wrapper leaves)	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05 < 0.05	GA*12
2005 North Rose, NY. (Blue Thunder)	Directed at plant base	3–4 leaf stage	857	1	84	Heads (with wrapper leaves)	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05 < 0.05	NY13
2005 Freeville, NY. (Amtrak)	Directed at plant base	4 leaf stage	807	1	92	Heads (with wrapper leaves)	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05 < 0.05	NY14
2005 Charleston, SC. (Fortuna)	Directed at plant base	Seedling	883	1	85	Heads (with wrapper leaves)	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05 < 0.05	SC*03
2005 Weslaco, TX (Blue Vantage)	Directed over seed furrow	Seed	846	1	138	Heads (with wrapper leaves)	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05 < 0.05	TX*26
2005 Arlington, WI (Blue Vantage)	Directed at plant base	Transplant	862	1	62	Heads (with wrapper leaves)	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05 < 0.05	WI19

DAT: days after treatment

^a Average residue concentration in parentheses

Leafy vegetables

Mustard greens

A total of ten field trials were conducted across the USA. Each field trial site consisted of one untreated control plot and one treated plot. Common cultural practices were followed to maintain the greens (mustard) crop. Additional maintenance pesticides and fertilizers were used at all of the sites to produce a commercial quality crop. No adjuvants were used in any of the trials. At all the trials, a single ground application directed in a narrow band over the seed furrow was made at the time of seeding. All applications were made using appropriate equipment, and the carrier volume was sufficient to provide adequate dispersal of the test substance. At the NC11 & NJ16 trials, the treated area was calculated using the narrow band into which the test substance was sprayed instead of using the entire row width as specified by the protocol. This resulted in an under-application of the test substance by 34% and 74% at the NC11 & NJ16 trials respectively. At all the trials, the untreated samples were harvested before the treated samples. Samples were harvested using techniques simulating some commercial practices. The commercially mature mustard greens were harvested 31–63 days after the application.

The samples were analysed using the modified XAM-65 method. The samples were analysed for both Flutolanil (parent) and its metabolite M-4. The two treated samples from the CA67 trial showed residues of 0.06 and 0.05 mg/kg of flutolanil. Residues of flutolanil and/or M-4 ranging from approximately 0.01 to 0.03 mg/kg were detected in treated samples from some of the trials. However, these residues were well below the LLMV and around or below the calculated LOQ making the

numbers unquantifiable. No detectable residues of flutolanil or M-4 above the lowest level of method validation (0.05 mg/kg) were found in any of the untreated control samples.

Table 7 Residues of flutolanil in mustard greens from supervised trials conducted in the USA in 2006 (Corley, 2009c; PR No. 08760)

Mustard greens Year, Location (variety)	Application				DAT	Portion analysed	Residues (mg/kg)		Trial ID
	Method	Timing	Rate kg ai/ha	No			Flutolanil ^a	M-4	
2006 Holtville, CA (Mizuna)	Directed at open seed furrow	Seed (at planting)	868	1	48	Plants	0.05 0.06 (0.055)	< 0.05 < 0.05	CA67
2006 Citra, FL (Florida Broadleaf)	Directed at open seed furrow	Seed (at planting)	879	1	37	Plants	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	FL25
2006 Clinton, NC (Southern Giant Curled)	Directed over Seed Furrow	Seed (at planting)	557	1	42	Plants	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	NC11
2006 Bridgeton, NJ (Southern Curled)	Directed over Seed Furrow	Seed (at planting)	219	1	41	Plants	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	NJ16
2006 Las Cruces, NM (Southern Giant Curled)	Directed at open seed furrow	Seed (at planting)	862	1	54	Plants	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	NM08
2006 Willard, OH (Savanna)	Directed over Seed Furrow	Seed (at planting)	843	1	31	Plants	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	OH*23
2006 Charleston, SC (Florida Broadleaf Mustard)	Directed over Seed Furrow	Seed (at planting)	859	1	54	Plants	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	SC*08
2006 Jackson, TN (Florida Broadleaf)	Directed at open seed furrow	Seed (at planting)	848	1	63	Plants	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	TN11
2006 Weslaco, TX (Florida Broadleaf)	Directed at open seed furrow	Seed (at planting)	848	1	46	Plants	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	TX*27
2006 Arlington, WI (Florida Broadleaf)	Directed at open seed furrow	Seed (at planting)	845	1	49	Plants	< 0.05 < 0.05 (< 0.05)	< 0.05 < 0.05	WI16

DAT: days after treatment

^a Average residue concentration in parentheses

APPRAISAL

Flutolanil was evaluated by JMPR in 2002 for the first time toxicologically and for residues. The 2002 JMPR allocated an ADI of 0–0.09 mg/kg bw and ARfD unnecessary. It also determined that the definition of residues should be flutolanil for plant commodities (for compliance with MRLs and for estimation of dietary intake) and flutolanil and transformation products containing the 2-trifluoromethylbenzoic acid moiety, expressed as flutolanil for animal commodities (for compliance with MRLs and for estimation of dietary intake) and recommended a maximum residue level for rice, husked; rice, polished; rice bran, unprocessed; rice straw and fodder, dry; tissues of cattle goats, pigs, sheep and poultry; milks; and eggs.

The current Meeting received information on analytical methods, storage stability, use patterns and supervised trials to support estimation of maximum residue levels for broccoli, cabbage and mustard greens.

Methods of analysis

The Meeting received information on the analytical method used for the determination of flutolanil. Flutolanil in broccoli or mustard green was extracted with acetone and flutolanil in cabbage was extracted with methanol:water (1:1, v/v). Acetone extract or methanol extract was partitioned with ethyl acetate:dichloromethane (1:9) and the top layer was dried down and reconstituted in acetone. Following clean up on a Florisil column, eluates were dried down, reconstituted in mobile phase. The analysis is carried out using LC-MS/MS (electro-spray ionization mode; molecular ion of 324 ($m+H^+$) m/z and product ion of 282 m/z).

This method was found to be suitable for the determination of residues of flutolanil in broccoli, cabbage and mustard greens with recoveries of 83–110%, 97–106% and 83–110%, respectively, for these matrices at fortification levels 0.05–5 mg/kg.

The LOQ was 0.05 mg/kg for broccoli, cabbage and mustard green.

Stability of pesticide residues in stored analytical samples

Storage stability studies were conducted on broccoli in conjunction with supervised trials.

Flutolanil in the frozen condition was stable up to 569 days at -22 to -4 °C (102–114% remaining) in broccoli, 297 days at -29 – -10°C (95–101% remaining) in cabbage and 519 days at -22 to -4 °C (107–114% remaining) in mustard green.

In the supervised residue trial studies, samples were stored frozen for periods shorter than the respective periods tested for the storage stability studies.

Results of supervised residue trials on crops

The Meeting considered residue data from supervised field trials conducted in the USA on broccoli, cabbage and mustard green with a flutolanil WP formulation (700 g ai/kg nominal concentration).

Brassica vegetables

The approved use of flutolanil in the USA on the crop group Brassica leafy vegetables (including Brassica vegetables) consists of one application at a rate of 0.863 kg ai/ha either as an in-furrow or directed spray (minimum of 28 L/ha) or as soil drench at planting (PHI of 45 days), or, when transplanted, as a banded application directed at plant bases immediately after transplanting (281–468 L/ha).

According to the review of information on environmental fate by the 2002 JMPR, flutolanil is strongly adsorbed to most soils and is classified as low mobility through soil.

Broccoli

A total of eleven field trials were conducted across the USA. At all the trials, a single ground application directed in a narrow band at the base of the transplants or over the seed furrow was made at the time of seeding or immediately after transplanting. The commercially mature broccoli heads (including stems, and jacket leaves) were harvested 56–106 days after the application.

Residues of flutolanil in broccoli from trials in accordance with US GAP were all < 0.05 mg/kg (9). The Meeting estimated a maximum residue level of 0.05 * mg/kg. As flutolanil is applied at the time of planting or immediately after transplanting and flutolanil is unlikely to be taken up from soil by crops, the Meeting estimated an STMR of 0 mg/kg.

Cabbages, Head

A total of nine field trials were conducted across the USA. At all the trials, a single ground application directed in a narrow band at the base of the plant or over the seed furrow was made at the time of transplanting or seeding. The commercially mature cabbage heads were harvested 62–138 days after the application.

Residues of flutolanil in head cabbages from trials in matching US GAP were all < 0.05 mg/kg (9). The Meeting estimated a maximum residue level of 0.05* mg/kg. Applying the same rational as for broccoli on soil uptake, the Meeting estimated an STMR of 0 mg/kg. The Meeting also estimated a highest residue of 0 mg/kg for the purpose of calculating livestock dietary burdens.

Leafy vegetables

Mustard greens

A total of ten field trials were conducted across the USA. At all the trials, a single ground application directed in a narrow band over the seed furrow was made at the time of seeding. The commercially mature mustard greens mustard were harvested 31–63 days after the application.

Residues of flutolanil in mustard greens from trials matching US GAP were < 0.05 (7) and 0.055 mg/kg. The Meeting estimated a maximum residue level of 0.07 mg/kg. The Meeting estimated an STMR of 0.05 mg/kg.

Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead Brassicas; and Brassica leafy vegetables

The GAP in the USA covers the crop group Brassica leafy vegetables, including head and stem Brassica, Brassica leafy vegetables and turnip greens. As this GAP involves one application at planting or immediately after transplanting, residues in commodities in this group harvested at their maturity are expected to be very low, as was observed in the trials on broccoli, cabbage and mustard greens.

Consequently, the Meeting decided to extend the recommendations for maximum residue levels of 0.05* mg/kg and STMRs of 0 mg/kg for broccoli and head cabbage to the group Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead Brassicas (VB 0040); and the recommended maximum residue level of 0.07 mg/kg and STMRs of 0.05 mg/kg for mustard greens to Brassica leafy vegetables (VL 0054).

Residues in animal commodities

Estimation of dietary burdens

The Meeting noted that in addition to rice grain, rice bran, rice hulls and rice straw from which dietary burdens were calculated by the 2002 JMPR, cabbages can also be fed to beef and dairy cattle and laying hens. Although both the STMR and highest residue of head cabbages were estimated to be 0 mg/kg and therefore not impacting on animal dietary burden, as the OECD Animal Feeding Table had been revised since the last evaluation, the maximum and mean dietary burdens were re-calculated using the highest residue and STMR/median residue of the above-mentioned commodities on a basis of the updated OECD Animal Feeding Table. The summary of calculated dietary burdens is shown in the following table.

Summary of livestock dietary burdens (ppm of dry matter diet)

	US-Canada		EU		Australia		Japan	
	max	Mean	max	Mean	max	mean	Max	mean
Beef cattle	0.372	0.372	0.822	0.411	5.83 ^a	3.37 ^b	4.90	2.64
Dairy cattle	0.372	0.372	0.789	0.584	2.78 ^c	1.96 ^d	2.24	1.22
Broiler	0.278	0.278	0.189	0.189	0.599	0.599	0.094	0.094
Layer	0.278	0.278	0.094	0.094	0.599 ^e	0.599 ^f	0.378	0.378

^a Suitable for estimating maximum residue levels for meat, fat and edible offal of cattle.

^b Suitable for estimating STMRs for meat, fat and edible offal of cattle.

^c Suitable for estimating maximum residue level for milk of cattle.

^d Suitable for estimating STMR for milk of cattle.

^e Suitable for estimating maximum residue levels for meat, fat, edible offal of poultry.

^f Suitable for estimating STMRs for meat, fat, edible offal of poultry.

Residues in milk and mammalian tissues

The 2002 JMPR reviewed a cattle feeding study conducted at levels equivalent to 39, 116 and 388 ppm in the feed.

The maximum and mean dietary burdens in cattle were 2.78 and 1.96 ppm of dry matter diet respectively for estimating a maximum residue level and STMR for milk; and 5.83 and 3.37 ppm respectively for estimating maximum residue levels and STMRs for tissues. The maximum residue levels, STMRs and highest residues for relevant commodities of animal origin were estimated using the residue levels in tissues and milk at 39 ppm feeding group.

	Feed level (ppm) for milk residues	Flutolanil* (mg/kg) in milk	Feed level (ppm) for tissue residues	Flutolanil * (mg/kg) in			
				Muscle	Liver	Kidney	Fat
Maximum residue level beef or dairy cattle							
Feeding study ^a	39	< 0.05	39	< 0.05	2.0	0.79	0.06
Dietary burden and highest residue	2.78	< 0.004	5.83	< 0.007	0.299	0.118	0.009
STMR beef or dairy cattle							
Feeding study ^b	39	< 0.05	39	< 0.05	1.7	0.42	0.05
Dietary burden and mean residue	1.96	< 0.003	3.37	< 0.004	0.147	0.036	0.004

^a highest residues for tissues and mean residue for milk

^b mean residues for tissues and mean residue for milk

* From the common moiety method

The Meeting estimated STMRs of 0.147 and 0.036 mg/kg for liver and kidney respectively. As the residues in meat were < 0.05 mg/kg in any of feeding groups, the Meeting confirmed the existing STMR for meat at 0 mg/kg. Since the calculated STMR for milk was less than one tenth of the LOQ, the Meeting decided to use the existing STMR of 0 mg/kg.

The Meeting confirmed the previous maximum residue level recommendations of 0.05* and 0.05* mg/kg for milks and meat (from mammals other than marine mammals), and estimated a maximum residue level of 0.5 mg/kg for edible offal (mammalian) and withdrew the previous recommendations for liver and kidney.

Residues in eggs and poultry tissues

The 2002 JMPR reviewed a chicken feeding study conducted at levels equivalent to 0.78, 2.4 and 7.8 ppm in the feed. The maximum of calculated poultry dietary burden was 0.60 ppm.

At the lowest feeding level in the feeding study, residues from the common moiety method were all < 0.05 mg/kg in the eggs and all tissues tested. As a result the Meeting confirmed the existing maximum residue levels for eggs, poultry meat and poultry, edible offal of 0.05 * mg/kg.

At all feeding levels, residues did not exceed the LOQ of 0.05 mg/kg in eggs, muscle, fat or skin. The Meeting therefore confirmed the previously estimated STMRs of 0 mg/kg for these commodities.

Residues in the liver were below 0.05 mg/kg in the lowest and middle feeding groups but were detected at 0.08, 0.10 and 0.20 mg/kg in the highest feeding group. The Meeting, therefore also confirmed the STMR of 0.05 mg/kg for poultry, edible offal of.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue for plant commodities (for compliance with MRLs and for estimation of dietary intake): flutolanil.

Definition of the residue for animal commodities (for compliance with MRLs and for estimation of dietary intake): flutolanil and transformation products containing the 2-trifluoromethylbenzoic acid moiety, expressed as flutolanil.

The residue is not fat-soluble.

Commodity		Recommended MRL, mg/kg		STMR/STMR-P
CCN	Name	New	Previous	mg/kg
VL 0054	Brassica leafy vegetables	0.07	-	0.05
VB 0040	Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead brassicas	0.05*	-	0
MO 0105	Edible offal (mammalian)	0.5	-	Liver, 0.147 Kidney, 0.036
MO 0098	Kidney of cattle, goats, pigs and sheep	W	0.1	
MO 0099	Liver of cattle, goats, pigs and sheep	W	0.2	

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Dietary Intakes (IEDIs) of flutolanil were calculated for the 13 GEMS/Food cluster diets using STMRs estimated by the 2002 and current Meetings (Annex 3). The ADI is 0–0.09 mg/kg bw and the calculated IEDIs were 0–1% of the maximum ADI. The Meeting concluded that the long-term intake of residues of flutolanil resulting from the uses considered by the current JMPR is unlikely to present a public health concern.

Short-term intake

The 2002 JMPR decided that an ARfD is unnecessary. The Meeting therefore concluded that the short-term intake of residues of flutolanil is unlikely to present a public health concern.

REFERENCES

Code.	Author	Year	Title, Institute, Report reference
09263	Corley, J	2009a	Flutolanil: Magnitude of the Residue on Broccoli
08840	Corley, J	2009b	Flutolanil: Magnitude of the Residue on Cabbage
08760	Corley, J	2009c	Flutolanil: Magnitude of the Residue on Greens (Mustard)

GLYPHOSATE (158)

First draft prepared by Dr Dugald MacLachlan, Department of Agriculture, Fisheries and Forestry, Australia

EXPLANATION

Glyphosate was listed in the Periodic Re-evaluation Programme of the Thirty-fourth Session of the CCPR for residue review by 2005 JMPR. It has been reviewed by the JMPR in 1986 (TR), 1987 (R), 1988 (R), 1994 (R), 1997 (TR), 2004 (T), 2005 (R) and 2011 (R).

For the current evaluation the Meeting received critical data required for the estimation of MRLs for glyphosate tolerant rape (with the *gat* trait).

The glyphosate tolerant crops with the *gat* trait have been inserted with a glyphosate N-acetyltransferase gene which inactivates glyphosate by converting it to N-acetylglyphosate, making it the main metabolite in plant commodities. The Meeting received data on glyphosate metabolism in glyphosate tolerant rape crops, methods of residue analysis, storage stability, use patterns (USA and Canada), data from supervised residue trials and processing studies.

Trivial and systematic chemical names of all glyphosate related compounds referenced in the study reports submitted for the evaluation of the use of glyphosate on maize and soya bean with the *gat* trait are shown below in Table 1. These genetically modified crops lead to a different metabolic pathway of glyphosate in plants than in conventional crops or crops genetically modified to contain the CP4-EPSPS gene making them tolerant for glyphosate.

Table 1 List of reference compounds used in various study reports, including reports evaluated in previous JMPR reports

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
Gly	metabolite 1/parent glyphosate N-(phosphonomethyl)glycine C ₃ H ₈ NO ₅ P DPX-B2856	Rat, goat, hen
AMPA	metabolite 2 AMPA (aminomethyl)phosphonic acid H ₂ NCH ₂ PO ₃ H IN-YB726	Rat, goat, hen
NA-AMPA	metabolite 6 N-acetyl AMPA [(acetylamonio)methyl]phosphonic acid CH ₃ C(O)NHCH ₂ PO ₃ H ₂ IN-EY252	Rat, goat, hen
NA-Gly	metabolite 9 N-acetylglyphosate N-acetyl-N-(phosphonomethyl)glycine IN-MCX20	Rat, goat, hen

METABOLISM AND ENVIRONMENTAL FATE

Plant metabolism

The Meeting received information on the fate of glyphosate after single pre-emergence application followed by three foliar applications on rape crops containing the *gat* gene. Studies were conducted with [phosphonomethyl- ^{14}C] glyphosate under glasshouse conditions at a total rate of approximately 7.5 kg ai/ha.

The metabolism of [^{14}C] glyphosate was investigated in 0827 rape plants containing the *gat* gene [Chapleo & McLachlan, 2010, DuPont-26109]. A single pre-emergence soil application (4.5 kg ai/ha) followed by three foliar applications (each 1.0 kg ai/ha at the 2 and 5 leaf stage and 1 week before maturity) were made of an aqueous solution containing [^{14}C] glyphosate (SL formulation and 2% ammonium sulphate salt). The intervals between the four applications were 48, 9 and 83 days, respectively. Rape plants were harvested as immature foliage (midway between the 2nd and 3rd foliar applications), immediately prior to the last application (pods with seeds, foliage) and finally at maturity whereupon plants were separated into seeds and foliage fractions. After homogenization tissues were extracted with 0.1% formic acid (aqueous):methanol (96:4, v/v) followed by enzyme (α -amylase then amyloglucosidase and cellulase), alkaline (NaOH, 0.1 N, 60 °C, 6 hours) then acid (HCl, 1.0 N, 60 °C, 6 hours) digestion. Extracts containing ≥ 0.01 mg/kg were analysed by HPLC and the identification of residues accomplished with reference to authenticated reference standards.

Table 2 Identification of radioactivity in plants and seed

	Harvest 1		Harvest 2			Harvest 3	
	Foliage		Immature pods (with seeds)		Foliage	Mature seeds	
TRR (mg equiv/kg)	5.98		1.27		1.55	2.15	
				%TRR			
Extracted	97		80		96	96	
glyphosate		3.0		ND		ND	21
N-acetylglyphosate		90		80		93	51
AMPA		1.4		ND		ND	1.9
N-acetyl AMPA		3.4		ND		ND	15
Unidentified		ND		ND		ND	7.1 ^a
Unextracted	2.7		20		3.6	3.5	

ND = not detected

^a Multiple components, no single component > 1% TRR or 0.022 mg equiv/kg.

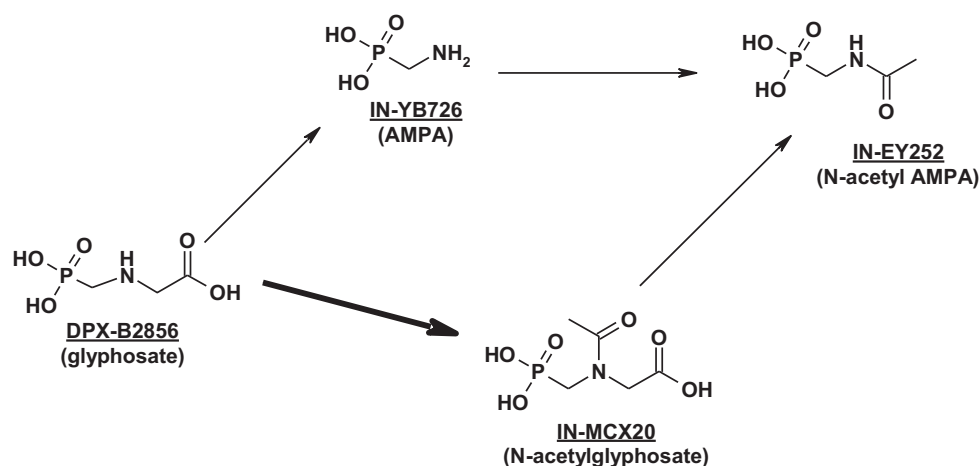


Figure 1 Proposed metabolic pathway for [^{14}C] glyphosate in 0827 rape seed (canola) plants containing the *gat* gene

RESIDUE ANALYSIS

Analytical methods

The Meeting received information on methods for the determination of glyphosate and some of its metabolites in rape commodities (DuPont 27816 Rev 1). The methods were similar to those reviewed by the 2011 JMPR and are suitable for measuring residues in rape commodities.

Residues of glyphosate, N-acetylglyphosate, N-acetyl AMPA, and AMPA were extracted from forage, seed, and meal in 96% aqueous 0.1% formic acid/4% methanol. Clean-up included partitioning with methylene chloride and passage through a C₁₈ SPE cartridge. A portion of the C₁₈ purified sample was further cleaned-up on an anion exchange cartridge before analysis for glyphosate, N-acetylglyphosate and N-acetyl AMPA with glyphosate internal standard. Another aliquot of the C₁₈ purified extract was further cleaned-up on a cation exchange cartridge before analysis for AMPA with AMPA internal standard.

Residues of glyphosate, N-acetylglyphosate, N-acetyl AMPA, and AMPA were extracted from oil via direct partition into 0.02 M phosphoric acid, with methylene chloride present to retain the oily components. An aliquot of the aqueous sample was diluted prior to analysis for glyphosate, N-acetylglyphosate, N-acetyl AMPA, and AMPA after addition of both glyphosate and AMPA internal standards to each sample. The sample was injected twice, once for analysis of glyphosate, N-acetylglyphosate and N-acetyl AMPA and a second time for AMPA. The LOQ was 0.05 mg/kg for each analyte (glyphosate and metabolites). Mean recoveries for forage, seed, refined oil and meal samples fortified at levels that ranged from 0.05 to 30 mg/kg were acceptable ranging from 78 ± 9.7% to 97 ± 14% for the various analytes.

Stability of pesticide residues in stored analytical samples

The 2005 and 2011 JMPR meetings evaluated data on the storage stability of glyphosate residues (and metabolites) in plant commodities that included commodities with high oil content (corn and soya bean), and in animal commodities. The studies concluded residues in high oil commodities are stable for more than 12 months freezer storage. The longest storage interval in the current trials was 302 days.

USE PATTERNS

Glyphosate is registered as an herbicide on a wide variety of crops. Information on registered uses was made available to the Meeting and those uses of relevance to this evaluation, which are supported by supervised residue trials and based on label information provided by the manufacturers, are summarized in Table 3.

Table 3 Table of use patterns

Crop	Country	Method	Growth stage	Rate kg ai/ha	No.	L/ha	PHI (days)	Comment
Rape seed tolerant varieties, <i>gat</i> gene	Canada	Broadcast spray (ground or aerial)	Pre-emergence	0.68	–		na	
		Broadcast spray (ground or aerial)	0–6 leaf stage	0.3–0.68	–	50–100	7	
		Broadcast spray (ground or aerial)	Pre-harvest	0.9	–	50–100	7 ^a	
Rape seed tolerant varieties, <i>gat</i> gene	USA (pending)	Broadcast spray (ground or aerial)	pre-emergence (A)	≤ 1.7 (seasonal max 1.7 kg/ha pre-emergence)	≥ 1			The combined total per year for pre- and post-emergent (A+B) = (1.7 + 0.84) =
		Broadcast	from crop	≤ 0.84	–single or		60	

Crop	Country	Method	Growth stage	Rate kg ai/ha	No.	L/ha	PHI (days)	Comment
		spray, in crop (over-the- top), ground or aerial	emergence to 6 leaf stage (B)	If two applications 0.42 at the 1–3 leaf stage + 0.42 at < 6 leaf stage but > 10 days apart.	split			2.5 kg ai/ha. The combined total max of post emergence applications = 0.84 kg ai/ha/year

^a Pods are green to yellow; most seeds are yellow to brown. Apply when crop has < 30% grain moisture, typically 7–14 days before harvest

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised residue trials of foliar treatments of glyphosate for the following crops:

Application rates were reported as glyphosate acid equivalents (parent). Unquantifiable residues are shown as below the reported LOQ (e.g. < 0.05 mg/kg). Residues, application rates and spray concentrations have been rounded to two figures. Residue data are recorded unadjusted for percentage recoveries or for residue values in control samples. Where multiple analyses were conducted on a single sample, the average value is reported. Where results from separate plots with distinguishing characteristics such as different formulations, varieties or treatment schedules were reported, results are listed for each plot.

Residues from the trials conducted according to critical GAP have been used for the estimation of maximum residue levels, STMR and HR values. Those results are underlined.

The Meeting received supervised residue trials on glyphosate tolerant rape containing the *gat* trait. Supervised residue trials on glyphosate tolerant rape (containing the *gat* trait) were conducted in the USA and Canada in 2009 (DuPont 27816 Rev 1). Residues in seeds are shown in Table 5. The maximum frozen storage interval was 302 days. Oil and meal processing samples were stored for 34 and 46 days, respectively.

Table 4 Summary of sprayers, plot sizes and field sample sizes in the supervised trials

Crop	Location	Year	Sprayer	Plot size	Sample size
Rape	Canada (Portage la Prairie)	2009	ATV mounted CO ₂ boom 6 nozzles	3 × 20 m ²	0.5–0.6 kg seed 1.3–1.4 kg forage
Rape	Canada (Dundurn)	2009	ATV mounted CO ₂ boom 6 nozzles	3 × 20 m ²	0.5–0.55 kg seed 1.2–4.5 kg forage
Rape	Canada (Gibbons)	2009	ATV mounted CO ₂ boom 6 nozzles	3 × 20 m ²	0.5–0.9 kg seed 1.0–1.8 kg forage
Rape	Canada (Fort Sasks)	2009	ATV mounted CO ₂ boom 6 nozzles	3 × 20 m ²	0.7–1.0 kg seed 1.4–1.8 kg forage
Rape	Canada (Waldheim)	2009	ATV mounted CO ₂ boom 6 nozzles	3 × 20 m ²	0.7–1.3 kg seed 1.0–1.4 kg forage
Rape	Canada (Wakaw)	2009	ATV mounted CO ₂ boom 6 nozzles	3 × 20 m ²	0.15–0.65 kg seed 1.0–1.4 kg forage
Rape	Canada (Rosthern)	2009	ATV mounted CO ₂ boom 6 nozzles	3 × 20 m ²	0.55–0.7 kg seed 1.2–1.9 kg forage
Rape	Canada (Wellwood)	2009	ATV mounted CO ₂ boom 6 nozzles	3.6 × 20 m ²	0.5–0.8 kg seed 1.0–1.3 kg forage
Rape	Canada (Wellwood)	2009	Tractor mounted/ATV mounted CO ₂ boom 6 nozzles	3.6 × 20 m ² 3 × 20 m ²	0.5–1.4 kg seed 1.0–1.7 kg forage
Rape	Canada (Franklin)	2009	Tractor mounted/ATV mounted CO ₂ boom 6 nozzles	3 × 20 m ²	0.6–1.0 kg seed 1.0–1.9 kg forage
Rape	USA (Frenchtown)	2009	Backpack CO ₂ boom 4 nozzles	7.3 × 22 m ²	0.9–1.6 kg seed 2.0–2.2 kg forage
Rape	USA (Erie)	2009	Backpack CO ₂ boom 4 nozzles	6 × 15 m ² 12 × 24 m ²	0.5 or 28 for oil pro kg seed 1.1 kg forage

Crop	Location	Year	Sprayer	Plot size	Sample size
Rape	USA (Perley)	2009	Backpack CO ₂ boom 4 nozzles	12 × 18 m ²	0.5–1.0 kg seed 1.0–1.5 kg forage
Rape	USA (Jamestown)	2009	Backpack CO ₂ boom 4 nozzles	6 × 15 m ² 12 × 24 m ²	1.0 or 28 for oil pro kg seed 1.1–1.2 kg forage
Rape	USA (Montpellier)	2009	Backpack CO ₂ boom 4 nozzles	6 × 15 m ²	1.0–1.1 kg seed 1.2 kg forage
Rape	USA (Jerome)	2009	Tractor/ATV mounted boom	7.3 × 15 m ² 7.3 × 38 m ²	1.0 or 27 for oil pro kg seed 1.3–1.4 kg forage
Rape	USA (Ephrata)	2009	ATV mounted CO ₂ boom 6 nozzles	3 × 61 m ²	1.3–2.8 kg seed 1.0–2.1 kg forage

Table 5 Residues of glyphosate and its metabolites in seeds of glyphosate tolerant rape (containing the *gat* trait). All residue concentrations are expressed in glyphosate equivalents (DuPont 27816 Rev 1)

Trial, state, country, year (variety)	N	kg ai/ha	L/ha	last treatment, timing	DALA	matrix	Gly	NA-gly	AMPA	NA-AMPA	Tot MRL	Tot diet
Portage la Prairie, MB Canada 2009 DP-Ø73496-4	3 (30 75)	0.685 0.68 0.885	100 100 90	PRE BBCH 14 BBCH 87	8	seed	1.3	0.46	< 0.05	0.05	<u>1.8</u>	<u>1.8</u>
Dundurn, SK Canada 2009 DP-Ø73496-4	3 (42 89)	0.69 0.67 0.90	100 100 100	PRE BBCH 14–16 BBCH 89	7	seed	9.0	0.22	0.05	< 0.05	<u>9.2</u>	<u>9.2</u>
Gibbons, AB Canada 2009 DP-Ø73496-4	3 (44 78)	0.66 0.66 0.91	100 100 100	PRE BBCH 14–16 BBCH 83–84	7	seed	2.1	0.30	< 0.05	< 0.05	<u>2.4</u>	<u>2.4</u>
	3 (44 78)	0.67	100	PRE	7	seed	2.3	0.48	< 0.05	< 0.05	2.8	2.8
		0.67	100	BBCH 14–16	11		2.2	0.37	< 0.05	ND	2.6	2.6
		0.93	100	BBCH 83–84	12		2.3	0.38	ND	< 0.05	2.7	2.7
					18		3.5	0.39	< 0.05	< 0.05	3.9	3.9
Fort Saskatchewan, AB Canada 2009 DP-Ø73496-4	3 (48 72)	0.67 0.68 0.88	100 100 100	PRE BBCH 14–16 BBCH 84	7	seed	0.82	0.61	ND	< 0.05	<u>1.4</u>	<u>1.5</u>
	3 (48 72)	0.67 0.67 1.2	100 100 100	PRE BBCH 14–16 BBCH 81	7	seed	1.4	0.96	ND	< 0.05	<u>2.4</u>	<u>2.4</u>
Waldheim, SK Canada 2009 DP-Ø73496-4	3 (41 90)	0.70 0.69 0.92	100 100 100	PRE BBCH 16 BBCH 89	7	Seed	2.2	0.46	ND	< 0.05	<u>2.7</u>	<u>2.7</u>
	3 (41 90)	0.70 0.68 0.92	100 100 100	PRE BBCH 16 BBCH 88–89	7	Seed	2.7 c0.05	0.34	ND	< 0.05	<u>3.0</u>	<u>3.1</u>
Wakaw, SK Canada 2009 DP-Ø73496-4	3 (50 93)	0.69 0.67 0.91	100 100 50	PRE BBCH 16 BBCH 80	6	Seed	4.9 c0.27	0.69	0.06	ND	<u>5.6</u>	<u>5.6</u>
	3 (48 87)	0.70 0.70 0.90	100 100 100	PRE BBCH 14–51	6	Seed	7.2 c0.13	3.1	0.08	< 0.05	<u>10</u>	<u>10</u>

Trial, state, country, year (variety)	N	kg ai/ha	L/ha	last treatment, timing	DALA	matrix	Gly	NA-gly	AMPA	NA-AMPA	Tot MRL	Tot diet
				BBCH 80								
										Mean	<u>7.8</u>	<u>7.8</u>
Rosthern, SK Canada 2009 DP-Ø73496-4	3 (42 93)	0.69 0.68 0.92	100 100 100	PRE BBCH 15–16 BBCH 85	6	Seed	3.1	0.29	< 0.05	< 0.05	<u>3.4</u>	<u>3.5</u>
	3 (42 93)	0.69 0.68 0.91	100 100 100	PRE BBCH 15–16 BBCH 85	6	Seed	2.4	0.28	< 0.05	< 0.05	<u>2.7</u>	<u>2.7</u>
										Mean	<u>3.05</u>	<u>3.1</u>
Wellwood, MB Canada 2009 DP-Ø73496-4	3 (34 87)	0.68 0.68 0.89	100 100 90	PRE BBCH 15 BBCH 89	6	Seed	0.91	2.8	< 0.05	< 0.05	<u>3.7</u>	<u>3.8</u>
	3 (34 87)	0.68 0.67 0.90	100 100 90	PRE BBCH 15 BBCH 89	6	Seed	0.82	1.6	ND	< 0.05	<u>2.4</u>	<u>2.4</u>
										Mean	<u>3.05</u>	<u>3.1</u>
Franklin, MB Canada 2009 DP-Ø73496-4	3 (34 87)	0.70 0.67 0.88	100 100 91	PRE BBCH 15 BBCH 89	6	Seed	0.41	0.34	ND	ND	<u>0.75</u>	<u>0.77</u>
	3 (34 87)	0.68 0.69 0.91	100 100 91	PRE BBCH 15 BBCH 89	6	Seed	0.46	0.34	ND	ND	<u>0.80</u>	<u>0.82</u>
										Mean	<u>0.775</u>	<u>0.795</u>
Frenchtown, NJ USA 2009 DP-Ø73496-4	2 (34)	1.8 0.63	281 280	PRE 6 leaf	55	Seed	ND	0.30	ND	0.05	0.31	0.38
Erie, ND USA 2009 DP-Ø73496-4	2 (28)	1.75 0.63	281 280	PRE BBCH 15	62	Seed	ND	0.52 c0.05	ND	0.10	0.53	0.66
	3 (28 55)	0.70 0.71 4.5	94 94 94	PRE BBCH 15 BBCH 85	7	Seed	0.61	56	< 0.05	1.1	57	57
Perley, MN USA 2009 DP-Ø73496-4	2 (28)	1.79 0.62	94 94	PRE BBCH 15	61	Seed	0.36 c1.5	1.4 c2.2	ND c0.08	0.08	1.8	1.9
					64		0.37	1.9	ND	0.08	2.3	2.3
					66		0.05	1.2	ND	0.08	1.3	1.4
					71		ND	0.96	ND	0.08	1.0	1.1
					76 82		0.05 ND	1.3 1.1	ND ND	0.08 0.05	1.3 1.1	1.4 1.1
Jamestown, ND USA 2009 DP-Ø73496-4	2 (33)	1.75 0.64	94 94	PRE BBCH 16	60	Seed	< 0.05	1.9	ND	0.55	1.9	2.5
	3 (33 54)	0.72 0.72 4.6	187 94 187	PRE BBCH 16 BBCH 85	6	Seed	4.8	12	< 0.05	0.27	17	17
Montpelier, ND USA 2009 DP-Ø73496-4	2 (33)	1.73 0.64	94 94	PRE BBCH 15	60	seed	< 0.05 c0.08	0.31	ND	0.06	0.35	0.42
	3 (33 54)	0.72 0.72 0.93	47 47 187	PRE BBCH 15 BBCH 85	6	Seed	0.71	14	ND	0.34	<u>15</u>	<u>15</u>
Jerome, ID USA 2009 DP-Ø73496-4	2 (32)	1.8 0.64	178 186	PRE BBCH14–16	69	Seed	ND	0.32	ND	< 0.05	0.33	0.38
	3 (32, 62)	0.67 0.68 4.5	176 186 196	PRE BBCH14–16 BBCH 89	7	Seed	14	0.47	0.13	ND	14.5	15

Trial, state, country, year (variety)	N	kg ai/ha	L/ha	last treatment, timing	DALA	matrix	Gly	NA-gly	AMPA	NA-AMPA	Tot MRL	Tot diet
Ephrata, WA USA 2009 DP-Ø73496-4	2 (20)	1.8 0.62	140 140	PRE 6 leaf	77	Seed	ND	0.26	ND	< 0.05	0.27	0.32
					80		ND	0.23	ND	< 0.05	0.24	0.29
					83		ND	0.23	ND	< 0.05	0.24	0.29
					87		ND	0.24	ND	< 0.05	0.25	0.30
					91		ND	0.20	ND	< 0.05	0.21	0.26
					98		ND	0.19	ND	< 0.05	0.20	0.26
	2 (20)	1.7 0.62	47 47	PRE 6 leaf	66	Seed	ND	0.08	ND	ND	0.09	0.11

For additional containment, tents were used to cover the field plots at the Canadian locations. The tents were a white mesh material that reflected some light, resulting in taller, thinner plants than typical. The tents also created a warmer, more humid environment which served to prolong flowering and to delay maturity beyond what was normal for un-tented canola in the area. Consequently, the trials ran late into the season, it was harder to determine staging and timing, and in some provinces the crops were affected by frost before sampling occurred, despite efforts to protect the plants from frost damage by re-covering the plots with the tents following the third application. The use of mesh tents is unlikely to significantly affect residues in seed or forage.

Samples of forage were collected at times after planting typical for use of the crop as forage.

Table 6 Residues of glyphosate and its metabolites in forage of glyphosate tolerant rape (containing the *gat* trait). All residue concentrations are expressed in glyphosate equivalents (DuPont 27816 Rev 1).

Trial, state, country, year (variety)	N	kg ai/ha	L/ha	last treatment, timing	DALA	matrix	Gly	NA-gly	AMPA	NA-AMPA	Tot MRL	%moisture (corrected)
Portage la Prairie, MB Canada 2009 DP- Ø73496-4	2 (30)	0.685 0.68	100 100 90	PRE BBCH 14	35	forage	ND	0.32	ND	ND	<u>0.32</u>	85 (2.1DM)
Dundurn, SK Canada 2009 DP-Ø73496-4	2 (42)	0.69 0.67	100 100 100	PRE BBCH 14–16	70	Forage	ND	0.19	< 0.05	ND	<u>0.24</u>	78 (1.1DM)
Gibbons, AB Canada 2009 DP-Ø73496-4	2 (44)	0.66 0.66	100 100	PRE BBCH 14–16	62	Forage	ND	0.42	ND	ND	0.42	79
	2 (44)	0.67 0.67	100 100	PRE BBCH 14–16	35 38 41 48 55 62	Forage	ND	0.94	ND	< 0.05	<u>0.99</u>	79 (4.7DM)
							ND	0.38	ND	ND	0.38	
							ND	0.73	ND	ND	0.73	
							ND	0.45	ND	ND	0.45	
							ND	0.39	ND	ND	0.39	
							ND	0.50	ND	ND	0.50	
Fort Saskatchewan, AB Canada 2009 DP- Ø73496-4	2 (48)	0.67 0.68	100 100	PRE BBCH 14–16	64	Forage	ND	0.43	ND	ND	0.43	79
	2 (48)	0.67 0.67	100 100	PRE BBCH 14–16	64	Forage	ND	0.25	ND	ND	0.25	76
	Mean										<u>0.34</u>	(1.5DM)
Waldheim, SK Canada 2009 DP-Ø73496-4	2 (41)	0.70 0.69	100 100	PRE BBCH 16	76	Forage	ND	0.74	ND	ND	<u>0.74</u>	66
	2 (41)	0.70 0.68	100 100	PRE BBCH 16	76	Forage	ND	1.3	ND	< 0.05	1.4	68
	Mean										<u>1.1</u>	(3.3DM)
Wakaw, SK Canada 2009 DP-Ø73496-4	2 (50)	0.69 0.67	100 100	PRE BBCH 16	82	Forage	ND	0.14	ND	ND	<u>0.14</u>	71 (0.48DM)
	2 (48)	0.70 0.70	100 100	PRE BBCH 14–51	76	Forage	ND	ND	ND	ND	< 0.05	71

Trial, state, country, year (variety)	N	kg ai/ha	L/ha	last treatment, timing	DALA	matrix	Gly	NA-gly	AMPA	NA-AMPA	Tot MRL	%moisture (corrected)
Rosthern, SK Canada 2009 DP-Ø73496-4	2 (42)	0.69 0.68	100 100	PRE BBCH 15–16	82	Forage	0.17	0.19	ND	ND	0.36	74
	2 (42)	0.69 0.68	100 100	PRE BBCH 15–16	82	Forage	< 0.05	0.10	ND	ND	0.15	75
	Mean										0.26	(1.0DM)
Wellwood, MB Canada 2009 DP-Ø73496-4	2 (34)	0.68 0.68	100 100	PRE BBCH 15	35	Forage	ND	0.79	ND	ND	0.79	79
	2 (34)	0.68 0.67	100 100	PRE BBCH 15	35	Forage	ND	0.60	ND	ND	0.60	82
	Mean										0.70	(3.6DM)
Franklin, MB Canada 2009 DP-Ø73496-4	2 (34)	0.70 0.67	100 100	PRE BBCH 15	35	Forage	ND	0.48	ND	ND	0.48	82
	2 (34)	0.68 0.69	100 100	PRE BBCH 15	35	Forage	ND	0.40	ND	ND	0.40	81
	Mean										0.44	(2.4DM)
Frenchtown, NJ USA 2009 DP-Ø73496-4	2 (34)	1.8 0.63	281 280	PRE 6 leaf	40	Forage	ND	0.54	ND	ND	0.54	78 (2.5DM)
Erie, ND USA 2009 DP-Ø73496-4	2 (28)	1.75 0.63	281 280	PRE BBCH 15	30	Forage	ND	0.91	ND	ND	0.91	82 (5.1DM)
Perley, MN USA 2009 DP-Ø73496-4	2 (28)	1.79 0.62	94 94	PRE BBCH 15	27	Forage	ND	1.2	ND	< 0.05	1.2	85 (8.0DM)
					30		ND	0.98	ND	ND	0.98	
					33		ND	0.66	ND	< 0.05	0.71	
					41		ND	0.90	ND	ND	0.90	
					48		ND	0.58	ND	ND	0.58	
Jamestown, ND USA 2009 DP-Ø73496-4	2 (33)	1.75 0.64	94 94	PRE BBCH 16	32	Forage	< 0.05	3.4	ND	0.13	3.6	78 (16.4DM)
					32		< 0.05	3.4	ND	0.13	3.6	
					32		ND	0.08	ND	ND	0.08	
					32		ND	0.08	ND	ND	0.08	
					32		ND	0.08	ND	ND	0.08	
Jerome, ID USA 2009 DP-Ø73496-4	2 (32)	1.8 0.64	178 186	PRE BBCH14–16	45	Forage	ND	0.41	ND	ND	0.41	75 (1.6DM)
					45		ND	0.41	ND	ND	0.41	
					45		ND	0.41	ND	ND	0.41	
					45		ND	0.41	ND	ND	0.41	
					45		ND	0.41	ND	ND	0.41	
Ephrata, WA USA 2009 DP-Ø73496-4	2 (20)	1.8 0.62	140 140	PRE 6 leaf	55	Forage	ND	0.18	ND	ND	0.18	76 (2.5DM)
					58		ND	0.10	ND	ND	0.10	
					62		ND	0.09	ND	ND	0.09	
					69		ND	0.14	ND	ND	0.14	
					76		ND	0.38	ND	ND	0.38	
					83		ND	0.56	ND	< 0.05	0.61	
					55		ND	0.08	ND	ND	0.08	
					55		ND	0.08	ND	ND	0.08	

For additional containment, tents were used to cover the field plots at the Canadian locations. The tents were a white mesh material that reflected some light, resulting in taller, thinner plants than typical. The tents also created a warmer, more humid environment which served to prolong flowering and to delay maturity beyond what was normal for un-tented canola in the area. Consequently, the trials ran late into the season, it was harder to determine staging and timing, and in some provinces the crops were affected by frost before sampling occurred, despite efforts to protect the plants from frost damage by re-covering the plots with the tents following the third application. The use of mesh tents is unlikely to significantly affect residues in seed or forage.

Processing studies on grain

A processing study was undertaken in rape seed from rape plants containing event DP-Ø73496-4 modified with the *gat* gene (Shepard, 2013; DuPont-27816 Rev 1). Rape plots were treated with

approximately 5.85 kg ai/ha, as applications of 0.68, 0.68 and 4.5 kg ai/ha, with application timings pre-emergence, 6 leaf stage (BBCH 16) and 7 days pre-harvest. Two different processing procedures (cold-pressing and solvent extraction) were trialled and samples of refined oil and meal collected for analysis.

Cold pressing

Rape seed samples were pressed in an expeller to mechanically remove a portion of the crude oil. Resulting products were meal (cold press) and expelled crude oil. Cold press meal was collected and placed in frozen storage. Crude oil was filtered and processed in the same manner as the combined crude oil from the solvent extraction procedure described below. Cold press refined oil was collected separately and placed into frozen storage.

Solvent Extraction Procedure

Rape seed/kernel was flaked in a flaking roll with a gap setting of 0.28 to 0.38 mm. Flakes were heated to 82–99 °C and held for 10 to 15 minutes in the temperature range. Flakes were then pressed (expelled) in an expeller to mechanically remove a portion of the crude oil. Resulting products were presscake and expelled crude oil. Residual crude oil remaining in the solid material (presscake) exiting the expeller was extracted with hexane.

Presscake was placed in stainless steel batch extractors and submerged in 49–60 °C solvent (hexane). After 30 minutes, the miscella (hexane and crude oil) was drained and fresh hexane added to repeat the cycle two more times. The final two washes were for 15–30 minutes each. After the final draining, the solvent was removed from extracted presscake (meal) using a stream of warm air. Meal was collected and placed into frozen storage.

Miscella was passed through a laboratory vacuum evaporator to separate the crude oil and hexane. Crude oil was heated to 91–96 °C for hexane removal.

Crude oil samples recovered from the expeller and solvent extraction were filtered and combined into a container. Percent free fatty acid (FFA) of the crude oil was determined. Oil was placed in a water bath after pre-treatment with 85% phosphoric acid. Oil was mixed for 29–31 minutes at 40–44 °C. After the pre-treatment, an amount of 12 N baumé sodium hydroxide was added to the oil. Samples were mixed for 19 to 21 minutes at 40–44 °C and then for 9–11 minutes at 65–70 °C. Neutralized oil was then centrifuged to separate the refined oil and soapstock. Refined oil was decanted and filtered. Refined oil was collected and placed in frozen storage.

There was marked reduction in canola oil to non-detectable levels from the residues on the raw agricultural commodity. There was concentration in meal up to 1.8× for glyphosate and N-acetylglyphosate residues. Concentration and reduction of residues was the similar for both cold press and solvent extraction processes. Average meal processing factors were 0.787 and 0.563 for cold press and solvent extraction processes for glyphosate residues and 1.45 and 1.10 for N-acetylglyphosate residues.

Table 7 Results of processing rape seed into oil

Location	kg ai/ha	DALA		Gly	NA-gly	AMPA	NA-AMPA	Total	PF _{total}
Erie, ND USA 2009 DP- Ø73496-4	0.70 0.71 4.5	7	RAC	0.61 c0.05	56 c0.09	0.023 c0.05	1.1 c0.05	57.73	–
			Refined oil—cold press	ND	ND	ND	ND	< 0.05	< 0.0009
			Refined oil—solvent ext	ND	ND	ND	ND	< 0.05	< 0.0009
			Meal—cold press	0.93	88	< 0.05	1.9	90.86	1.57
			Meal—solvent ext	0.75	80	ND	1.6	82.35	1.43

Location	kg ai/ha	DALA		Gly	NA-gly	AMPA	NA-AMPA	Total	PF _{total}
Jamestown, ND USA 2009 DP- Ø73496-4	0.72 0.72 4.6	6	RAC	4.8	12	< 0.05	0.27	17.11	
			Refined oil—cold press	ND	ND c0.05	ND	ND	< 0.05	< 0.003
			Refined oil—solvent ext	ND	ND	ND	ND	< 0.05	< 0.003
			Meal—cold press	2.5	22	< 0.05	0.66	25.19	1.47
			Meal—solvent ext	1.7	17	< 0.05	0.62	19.34	1.13
Jerome, ID USA 2009 DP- Ø73496-4	0.67 0.68 4.5	7	RAC	14	0.47	0.13	ND	14.6	
			Refined oil—cold press	ND	ND	ND	ND	< 0.05	< 0.003
			Refined oil—solvent ext	ND	ND	ND	ND	< 0.05	< 0.003
			Meal—cold press	4.0	0.45	0.05	< 0.05	4.539	0.311
			Meal—solvent ext	1.3	0.24	ND	< 0.05	1.563	0.107

Calculated processing factors for processed rape seed are summarized in Table 8. Processing factors are based on total glyphosate free acid equivalents

Table 8 Summary of calculated processing factors

Commodity	PF _{total}	Best estimate PF _{total}
Refined oil—cold press	< 0.0009 < 0.003 < 0.003	< 0.003
Refined oil—solvent extracted	< 0.0009 < 0.003 < 0.003	< 0.003
Meal—cold pressed	0.311 1.47 1.57	1.47
Meal—solvent extracted	0.107 1.13 1.43	1.13

Residues in the edible portion of food commodities

No data submitted.

National residue definition

Not applicable.

APPRAISAL

Glyphosate is an herbicide with uses on many crops, conventional and glyphosate tolerant. Glyphosate has been evaluated several times with the initial evaluation in 1986 and the latest in 2011 where the use of glyphosate on glyphosate tolerant crops was reviewed.

The 2011 JMPR established a residue definition for compliance with MRLs for plant commodities as the sum of glyphosate and N-acetyl-glyphosate, expressed as glyphosate in the case of soya bean and maize and glyphosate for other crops. The definition of the residue for compliance with MRL for animal commodities is the sum of glyphosate and N-acetyl-glyphosate, expressed as glyphosate. For estimation of dietary intake it is the sum of glyphosate, AMPA, N-acetyl-glyphosate

and N-acetyl AMPA, expressed as glyphosate. The toxicology of glyphosate was re-evaluated by the 2011 JMPR which estimated group ADI of 0–1 mg/kg bw for the sum of glyphosate, N-acetyl-glyphosate, AMPA and N-acetyl-AMPA. The same Meeting confirmed that an ARfD was unnecessary.

For the current evaluation data have been submitted covering the use on genetically modified rape crops containing the *gat* trait (glyphosate-N-acetyl transferase or GAT gene). These crops inactivate glyphosate by converting it to N-acetyl-glyphosate. The Meeting received information on glyphosate metabolism in genetically modified rape containing the *gat* trait, methods of residue analysis, GAP information, supervised residue trials on *gat* rape crops and the fate of residue during storage and processing.

To assist uniform interpretation of GAP application rates have been expressed in terms of glyphosate acid equivalents (ae), unless indicated otherwise.

Metabolites referred to in the appraisal were addressed by their common names:

N-acetyl-glyphosate	N-acetyl-N-(phosphonomethyl)glycine
AMPA	aminomethyl phosphonic acid
N-acetyl-AMPA	[(acetylamino)methyl]phosphonic acid.

Plant metabolism

The metabolic fate of [¹⁴C] glyphosate in *gat* rape plants was examined following a single pre-emergence soil application of 4.5 kg ae/ha, followed by three foliar applications at 1.0 kg ae/ha at three different growth stages (2 and 5 leaf stage and 1 week before harvest). Rape plants were harvested as immature foliage, immediately prior to the final application and at maturity (PHI 7 days).

N-acetyl-glyphosate was the major metabolite in immature foliage (90% TRR; 5.4 mg/kg glyphosate equivalents). Glyphosate, AMPA and N-acetyl-AMPA were also detected accounting for 3.0, 1.4 and 3.4% of TRR respectively. At the intermediate harvest prior to the final application the only glyphosate related compound detected in foliage and immature pods (with seeds) was N-acetyl-glyphosate representing 93% TRR in foliage and 80% TRR in immature pods (with seeds). The residue in seeds at harvest, seven days after the final application, comprised glyphosate (21% TRR; 0.45 mg/kg), N-acetyl-glyphosate (51% TRR; 1.1 mg/kg), AMPA (1.9% TRR; 0.04 mg/kg) and N-acetyl-AMPA (15% TRR; 0.32 mg/kg).

The proposed pathway of glyphosate in rape plants with the *gat* trait is deactivation to N-acetyl-glyphosate which can be further metabolized to N-acetyl-AMPA and AMPA. The metabolism is similar to that observed for maize and soya bean crops with the *gat* trait previously reviewed by the 2011 JMPR.

Methods of Analysis

The Meeting received description and validation data for analytical methods for residue analysis of glyphosate and its metabolites in various plant commodities using LC-MS/MS. The LOQs are 0.05 mg/kg.

Stability of pesticide residues in stored analytical samples

No new information was received on the stability of glyphosate and its residues in samples stored frozen. The periods of demonstrated stability reported by the 2011 JMPR for other high oil and high protein crops cover the frozen storage intervals used in the residue studies.

Definition of the residue

The 2011 JMPR reviewed glyphosate metabolism studies in tolerant maize and soya bean containing the *gat* trait. Glyphosate, AMPA, N-acetyl-glyphosate and N-acetyl-AMPA were the major components of the residue in both maize and soya bean. In seeds from *gat* rape, N-acetyl-glyphosate

was the major component of the residue (51% TRR) followed by glyphosate (21% TRR) and N-acetyl AMPA (15% TRR). In *gat* rape forage, N-acetyl glyphosate was the major metabolite (90–93% TRR).

To accommodate the use of glyphosate on rape plants containing the *gat* trait the Meeting concluded that the previously established residue definition for enforcement in plants of “glyphosate” should be replaced by “*the sum of glyphosate and N-acetyl-glyphosate expressed as glyphosate*” for soya bean, maize and rape crops and remain “*glyphosate*” for all other crops.

Based on the above the Meeting agreed to amend the previous definition for glyphosate for compliance with MRL for plant commodities as follows:

Definition of the residue for compliance with MRL (for plant commodities): for soya bean, maize and rape - *sum of glyphosate and N-acetyl-glyphosate, expressed as glyphosate*, and for other crops - *glyphosate*.

The Meeting confirmed the residue definition for estimation of dietary intake as (for plant and animal commodities: *glyphosate, N-acetyl-glyphosate, AMPA and N-acetyl AMPA, expressed as glyphosate*).

Results of supervised residue trials on crops

The Meeting received supervised residue trial data for glyphosate on glyphosate-tolerant rape (*gat* trait).

For estimation of maximum residue levels for rape crops glyphosate and N-acetyl glyphosate levels are summed and expressed as glyphosate equivalents.

For estimation of the residue levels for dietary risk assessment of glyphosate in *gat* crops, in general all four analytes may be present in significant amounts. In the *gat* modified rape, N-acetyl glyphosate is the major residue found in rape seed, followed by glyphosate and N-acetyl AMPA. AMPA is a minor component of the residue and is included in the sum of residues when AMPA is reported as < LOQ.

The current Meeting received field trials performed in the USA and Canada involving glyphosate tolerant rape containing the *gat* trait. GAP for Canada is for application pre-emergence at 0.68 kg ae/ha, post-emergence at the 0–6 leaf stage at 0.3–0.68 kg ae/ha followed by a pre-harvest application at 0.9 kg ae/ha (PHI 7 days).

Residues of glyphosate and N-acetyl-glyphosate in rape seed trials matching Canada GAP were: 0.775, 1.8, 1.9, 2.4, 2.85, 3.05, 3.05, 7.8, 9.2 and 15 mg/kg (n=10). The Meeting estimated a maximum residue level of 30 mg/kg for glyphosate in rape seed to replace its previous recommendation of 20 mg/kg.

Corresponding total residues, for dietary intake estimation, were: 0.795, 1.8, 1.95, 2.4, 2.9, 3.1, 3.1, 7.8, 9.2 and 15 mg/kg. The Meeting estimated an STMR for glyphosate in rape seed of 3.0 mg/kg.

It was assumed that rape forage is plant material available from 25 days after planting. Residues in rape forage matching Canada GAP were: 0.4, 0.48, 1.0, 1.1, 1.5, 1.6, 2.1, 2.4, 2.5, 2.5, 3.3, 3.6, 4.7, 5.1, 8.0 and 16 mg/kg (dry matter basis). The Meeting estimated median and highest residues for glyphosate in rape forage of 2.25 and 16 mg/kg respectively, both on a dry-matter basis.

Fate of residues during processing

The Meeting received information on the nature of residues under simulated processing condition on the fate of incurred residues of glyphosate during the processing of rape seeds. Calculated processing factors for total glyphosate acid equivalents (combined results of the four metabolites) are summarized below.

Summary of calculated processing factors and estimated STMR-P values

Commodity	PF _{total}	Best estimate PF _{total}	STMR _{RAC} (mg/kg)	STMR _{RAC} ×PF

				(mg/kg)
Refined oil-cold press	< 0.0009 < 0.003 < 0.003	< 0.003	3.0	< 0.009
Refined oil-solvent extracted	< 0.0009 < 0.003 < 0.003	< 0.003		< 0.009
Meal-cold pressed	0.311 1.47 1.57	1.47		4.41
Meal-solvent extracted	0.107 1.13 1.43	1.13		3.39

The estimated STMR-P values in oil are lower than the previous values reported by the 2011 JMPR (previous 0.093 mg/kg) while the STMR-P estimated for rape seed meal is higher (previous 2.3 mg/kg).

Residues in animal commodities

Animal commodity maximum residue levels

The current evaluation has not led to recommendations that would alter the dietary burdens calculated using the livestock intake figures employed by the 2011 JMPR. The glyphosate dietary burdens for cattle (dairy and beef) were based on grass, cotton seed and barley grain while those for poultry were based on barley, soya bean grain and soya bean hulls and as such do not require a re-evaluation of animal commodity maximum residues levels.

RECOMMENDATIONS

On the basis of the data obtained from supervised residue trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

Definition of the residue for compliance with MRL (for plant commodities) for soya bean, maize and rape: *sum of glyphosate and N-acetyl-glyphosate, expressed as glyphosate*, and for other crops - *glyphosate*.

The Meeting confirmed the residue definition for estimation of dietary intake as (for plant and animal commodities): *glyphosate, N-acetyl-glyphosate, AMPA and N-acetyl AMPA, expressed as glyphosate*.

Definition of the residue for compliance with MRL (for animal commodities): *sum of glyphosate and N-acetyl-glyphosate, expressed as glyphosate*.

Definition of the residue for estimation of dietary intake (for plant and animal commodities): *glyphosate, N-acetyl-glyphosate, AMPA and N-acetyl AMPA, expressed as glyphosate*.

The residue is not fat soluble.

Table of recommendations

Commodity		Recommended MRL (mg/kg)		STMR or STMR-P (mg/kg)
CCN	Name	New	Previous	
SO 0495	Rape seed	30	20	3.0
	Rape forage			2.25 (highest residue 16)
OR 0495	Rape seed oil, edible			0.009
	Rape seed meal			4.41

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDI) of glyphosate for the 13 GEMS/Food regional diets, based on estimated STMRs were in the range 0–1% of the maximum ADI of 1 mg/kg bw for the sum of glyphosate, *N*-acetyl glyphosate, AMPA and *N*-acetyl AMPA, expressed as glyphosate. The Meeting concluded that the long-term intake of residues of glyphosate, *N*-acetyl glyphosate, AMPA and *N*-acetyl AMPA from uses that have been considered by the JMPR is unlikely to present a public health concern. The results are shown in Annex 4 of the JMPR 2013 Report.

Short-term intake

The International Estimated Short Term Intake (IESTI) of glyphosate was not calculated. The 2004 and 2005 JMPR concluded that it was unnecessary to establish an ARfD for glyphosate. The Meeting therefore concluded that short-term dietary of glyphosate residues is unlikely to present a risk to consumers.

REFERENCES

Code	Author	Year	Title, Institute & Report reference
DuPont 26109	Chapleo, S and McLachlan, T	2010	The metabolism of [¹⁴ C] glyphosate in 0827 canola. E. I. du Pont de Nemours and Company. DuPont Report No. DuPont 26109. Unpublished.
DuPont 27816 Rev 1	Shepard, E	2013	Magnitude and decline of glyphosate related residues in forage and seed of genetically modified canola event DP-Ø73496-4 and magnitude of glyphosate related residues in canola event DP-Ø73496-4 seed process fractions following applications of Touchdown Total® Herbicide—Locations in the United States and Canada, season 2009. E. I. du Pont de Nemours and Company. DuPont Report No. DuPont 27816, Revision No. 1. Unpublished.

IMAZAPIC (266)

*First draft prepared by Dr Yukiko Yamada, Ministry of Agriculture, Forestry and Fisheries,
Tokyo, Japan*

EXPLANATION

Imazapic is an imidazolinone herbicide developed for the control of grasses and broadleaf weeds in a variety of crops. Like all other imidazolinone herbicides, its mode of action is the inhibition of acetohydroxy acid synthase (AHAS or ALS) which catalyses the production of three branched chain amino acids, valine, leucine, and isoleucine, required for protein synthesis and cell growth.

Imazapic has been registered in a number of countries and was included in the Codex Priority List in 2009 as a new compound for evaluation by the current JMPR.

The Meeting received information on physical and chemical properties, animal and plant metabolism, environmental fate, analytical methods, storage stability, use patterns, supervised trials, processing and farm animal feeding.

IDENTITY

ISO common name: Imazapic

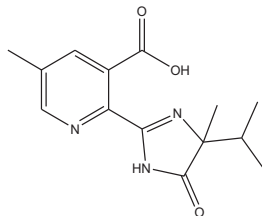
Chemical name

IUPAC: 2-[(RS)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-5-methylnicotinic acid

CAS: 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methyl-3-pyridinecarboxylic acid

CAS Registry No.: 104098-48-8

CIPAC No.: None yet

Structural formula:

Molecular formula: C₁₄H₁₇N₃O₃

Molecular weight: 275.3

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

Property	Results	Reference
Appearance	White powdered solid	IA-301-002 Cortes D. <i>et al.</i> , 1993a
Odour:	Odourless (room temperature)	A-301-002 Cortes D. <i>et al.</i> , 1993a
Melting point:	206 °C	2012/1010149 Kroehl T. 2012a
Boiling point:	Decomposes prior to boiling	2012/1010149 Kroehl T. 2012a
Temperature of decomposition	ca. 210 °C	2012/1010149 Kroehl T. 2012a
Solubility in water	In distilled water 1.92 g/L (15 °C), 2.23 g/L (25 °C) 2.63 g/L (35 °C).	IA-311-001 Mangels G. 1986b
Vapour pressure:	ca. 2.7×10^{-9} Pa (20 °C) ca. 7.5×10^{-9} Pa (25 °C) (Extrapolation from measurements at 150°C to 190 °C) $< 1.3 \times 10^{-5}$ Pa (1×10^{-7} mmHg) (25 °C) (Triplicate test system using gas saturation method)	2012/1010149 Kroehl T. 2012a IA-306-001 Mangels G., 1986a
Volatility, Henry's Law Constant at	1.6×10^{-6} Pa m ³ /mole (Calculation by dividing vapour pressure by water solubility)	
Octanol-water partition coefficient at (logPow)	0.054 (Average logPow uncorrected for dissociation using initial concentration of 0.88, 0.42, 0.06 and 0.04 mg/L in n-octanol) No significant effect of pH (4-10) on logPow.	IA-315-003 Morelli D. 1993a
Dissociation in water	pKa: 3.9 (calculation from potentiostatic titration) pKa: 3.1 and 11.4 (by spectrophotometry)	IA-322-003 Mangels G. 1986c

Technical material

Property	Results	Reference

Appearance:	White fine powdery solid	2012/1010149 Kroehl T. 2012a
Odour	Odourless at room temperature	2012/1010149 Kroehl T. 2012a
Relative density:	Tapped bulk density, 0.38 g/ml (24 °C) Untapped bulk density, 0.24 g/ml (24 °C)	IA-301-002 Cortes D. <i>et al.</i> 1993a
Solvent solubility at 25 °C:	mg/mL g/100 mL of solvent* Hexane 0.0084 -- Toluene 1.48 0.135 Methanol 50.9 5.07 Dichloromethane 89.2 9.58 Acetone 18.9 1.93 Acetonitrile 12.9 1.33 Dimethyl sulfoxide 310 41.8 Deionized water 2.15 0.215 pH 5 Buffer 36.0 3.69 pH 7 Buffer 479 68.1 pH 9 Buffer 518 76.5 * corrected for solution density	IA-310-001 Teeter D. 1992a
Hydrolysis:	Stable in pH 5, 7 and 9 buffers (25°C)	IA-322-004 Mangels G. 1992a
Photolysis:	Rapid photolysis in sterilized water with the following six photo-degradation products, each of which accounted for 10% of the dose: - Carbon dioxide - 5-methyl-3-pyridinecarboxylic acid - 2-[(1-carbamoyl-1,2-dimethylpropyl) carbamoyl]-5- methyl nicotinic acid (CL 290210) - 5-ethyl-2,3-pyridine dicarboxylic acid - 2-carbamoyl-5-methyl-nicotinic acid - 2-carbamoyl-5-methyl-3-nicotinic acid Several other photoproducts were present at less than 10% of the dose. DT ₅₀ under continuous irradiation: 0.30 day (7.2 h) at pH 5 0.25 day (6.0 h) at pH 7 0.26 day (6.24 h) at pH 9	IA-630-002 Ta, 1994a
Dissociation in water:	pKa: 2.0, 3.6 and 11.1 (by UV spectrophotometry).	IA-322-002 Melcer M. 1993a

Formulations

- Soluble concentrate (SL) formulations containing 25, 90 or 240 g ai/L
- Emulsifiable concentrate (EC) formulations containing 22 or 240 g ai/L.
- Water dispersible granule (WG) formulations containing 175, 525 or 700 g ai/kg.

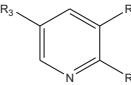
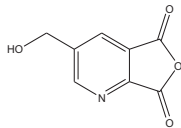
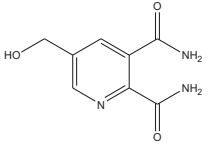
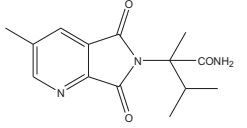
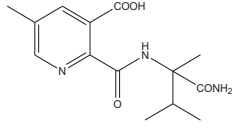
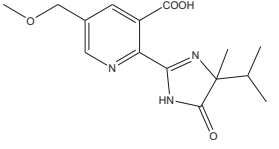
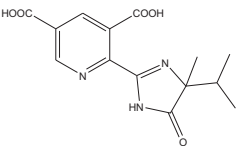
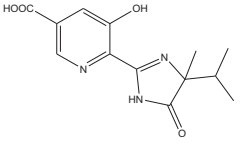
Except 240 SL and 700 WG, each of these formulations contain one or two other active ingredient(s).

METABOLISM AND ENVIRONMENTAL FATE

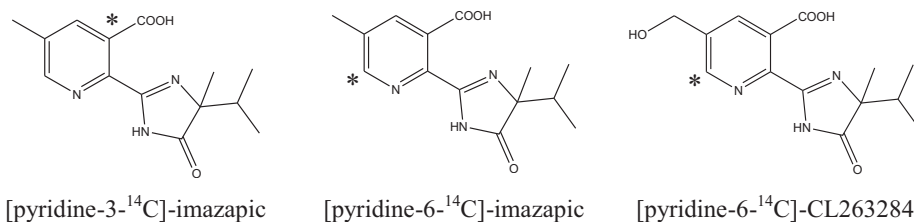
The following links code number and structure or description of the compound appearing in the various metabolism and environmental fate studies.

Structure of compounds appearing in metabolism and environmental fate studies

Code (MW)	IUPAC chemical name	Structure	Found in
Imazapic (275.3)	2-(4-isopropyl-4-methyl-5-oxo-imidazolin-2-yl)-5-methyl-nicotinic acid		Livestock (goat, hen), rat, Plants (soya bean, sugar cane, peanut, Bermuda grass) Soil
CL263284 M715H001 (M5) (291)	2-(4-isopropyl-4-methyl-5-oxo-imidazolin-2-yl)-5-hydroxymethyl-nicotinic acid		Livestock (goat) rat) Plants (soya bean, sugar cane, peanut, Bermuda grass) Soil
CL189215 M715H002 (M4) (453)	5-[(β-glucopyranosyloxy)methyl]-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-nicotinic acid		Plants (soya bean, sugar cane, peanut, Bermuda grass)
M6-D/M6-H (291)	3-(hydroxymethyl)-7-isopropyl-7-methyl-6H-pyrido[2,3-f][1,4]diazocine-5,8,10-trione		Plant (Bermuda grass)
M6-J2 (293)	10-hydroxy-3-(hydroxymethyl)-7-isopropyl-7-methyl-9,10-dihydro-6H-pyrido[2,3-f][1,4]diazocine-5,8-dione		Plant (Bermuda grass)
M6-J3 (275)	-		Plant (Bermuda grass)
M2-B (167)	Left: 3,7-dihydroxy-7H-furo[3,4-b]pyridin-5-one Right: 5-hydroxy-2-		Plant (Bermuda grass)

Code (MW)	IUPAC chemical name	Structure	Found in
	(hydroxymethyl)pyridine-3-carboxylic acid		
M1-C (183)	[1] 5-hydroxypyridine-2,3-dicarboxylic acid [2] 3-hydroxypyridine-2,5-dicarboxylic acid [3] 2-hydroxypyridine-3,5-dicarboxylic acid	 R1=COOH, R2 = COOH, R3 = OH or R1=COOH, R2 = OH, R3 = COOH or R1=OH, R2 = COOH, R3 = COOH	Plant (Bermuda grass)
M2-A (179)	3-(hydroxymethyl)furo [3,4-b]pyridine-5,7-dione		Plant (Bermuda grass)
M1-B (195)	5-(hydroxymethyl)-pyridine-2,3-dicarboxamide		Plant (Bermuda grass)
CL 303459 (275)	2,3-dimethyl-2-(3-methyl-5,7-dioxo-pyrrolo[3,4-b]pyridin-6-yl)butanamide		Rat
CL 290610 (292)	2-[(1-carbamoyl-1,2-dimethylpropyl)carbamoyl]-5-methylnicotinic acid		Rat
CL 299263	2-(4-isopropyl-4-methyl-5-oxo-imidazolin-2-yl)-5-methoxymethyl nicotinic acid		Soil
CL 312622	2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3,5-pyridine-dicarboxylic acid		Soil
CL 354825	5-carboxy-3-hydroxypyridine imidazolinone		Soil

The metabolism and distribution of imazapic in animals and plants and the fate of imazapic in the environment were investigated using the following $^{14}\text{C}/^{13}\text{C}$ -radiolabelled compounds.



In the descriptions below, the application rates are all in acid equivalents.

Animal metabolism

The Meeting received information on the results of studies on lactating goats and laying hens which were fed isotope-labelled imazapic or CL263284.

Metabolism studies on laboratory animals including rats were reviewed in the framework of toxicological evaluation by the current JMPR and the relevant information is summarized below.

Rat

A metabolism study using rats was evaluated and described in detail by the WHO Panel. Radiolabelled imazapic administered by oral gavage was rapidly and extensively absorbed, minimally metabolized, and excreted primarily in the urine after single dose of 10 or 1000 mg/kg bw, or repeated low dose of 10 mg/kg bw per day over 14 days to rats. Biliary excretion was minimal. The majority of radioactivity was excreted as the unchanged parent compound within the first 6 hours post-dosing. Less than 2% of the administered dose (AD) was detected in the carcass with trace amounts detected in blood, kidneys and liver of the high dose group; however, radiolabelled test substance was not detected in any other organs. There was no evidence of accumulation. Imazapic and its metabolites were not excreted in expired air. Parent compound accounted for 94% of the AD in the urine and 2.3% of the AD in the faeces. The metabolites produced from oxidation, reduction and hydrolysis, including CL 263284, CL 280442 and several other unidentified metabolites, accounted for a total of approx. 6% AD in the urine and faeces.

Lactating goats

Imazapic

A lactating goat was orally given single encapsulated doses of [pyridine-6-¹⁴C]- and [pyridine-6-¹³C]-imazapic daily for 5 consecutive days at a dose of 254 mg/day, equivalent to 175 ppm of test material in the diet, based on the actual food consumption during the treatment period (Sharp and Thalacker, 1999a). A control goat was given placebo capsules for 5 days. Urine and faeces samples were collected daily. Milk samples were collected twice daily. The animals were sacrificed approximately 23 hours after the last dose, and liver, kidneys, fat, bile, muscle, blood, and gastrointestinal (GI) tract and its contents were collected. All samples, except the bile and GI tract and its contents, were analysed for radioactivity content.

Samples were analysed by LSC after combustion. Selected tissue (liver, kidney, muscle and fat) and milk extracts and ¹⁴C-sample eluents were analysed using HPLC and TLC to determine the metabolic profile. The limits of detection were 0.001–0.004 mg/kg with sample sizes of 0.2–5 g. Kidney, liver, muscle and selected milk samples were extracted and analysed for ¹⁴C-imazapic, CL 263284 (imazapic alcohol metabolite) and CL 312622 (5-acid imidazolinone metabolite). Fat (omental and renal) was not extracted and analysed because the concentration of radioactive residues was < 0.010 mg/kg.

Among 90.7% of the total administered radioactivity (TAR) recovered, urine contained 81.7% and faeces 6.7% of TAR with cage wash and wipe accounted 1.2% and 1.2% respectively of

TAR. This indicate that urinary excretion is the major route of elimination from body. Approximately 75% of each daily dose was excreted in the urine in the 24-hours following each dose administration.

From milk 0.03% TAR was recovered and from the edible tissues and blood collected contained 0.01% TAR.

The radioactive residues in the milk from pm milking, the first collection of milk after each capsule administration ranged from 0.045 mg eq/kg (Day 1) to 0.078 mg eq/kg (Day 5), expressed in mg/kg-equivalents of imazapic. The radioactive residues in the milk from am milking, the second milk collection after each capsule administration, ranged from 0.012 to 0.014 mg eq/kg, lower than those in the milk from pm milking. The calculated daily radioactivity residue levels in milk ranged from 0.026 mg eq/kg (Day 1) to 0.037 mg eq/kg (Day 5). The total amount of radioactivity in milk ranged from 53.4 to 83.9 µg eq per day.

Among the tissues collected and analysed, the kidney contained 0.275 mg/kg, liver 0.033 mg/kg, muscle 0.010 mg/kg, blood 0.086 mg/kg and fat 0.003 mg/kg, expressed in mg/kg-equivalents of imazapic.

The results of the TRR in lactating goats are presented in the following table.

Table 1 Total radioactive residues (TRR) in goat treated with ^{14}C -imazapic.

Sample	TRR (mg/kg)*	Imazapic	
		mg/kg	% TRR
Milk (48 h p.m.)	0.058	0.039	66.8
Milk (120 h p.m.)	0.078	0.051	65.0
Kidney	0.275	0.234	85.0
Liver	0.033	0.016	49.1
Muscle	0.010	0.003	33.8

* expressed in mg/kg-equivalents of imazapic.

Parent ^{14}C -imazapic was the only major residue detected in tissues and milk.

In another study (Kao, 1993a), lactating goats were orally treated with a mixture of [pyridine-6- ^{13}C]- and [pyridine-6- ^{14}C]-imazapic. Feeding level for each of two goats was equivalent to 2.0 or 11.8 ppm in the diet daily for 7 consecutive days. One goat was used as a control. Samples of blood, milk and excreta were collected daily and either refrigerated or stored frozen. After seven days of dosing, the goats were sacrificed and the tissues (kidney, liver, muscle, and fat) were collected approximately 20 hours after the last dose. Tissue samples were stored frozen.

Samples were analysed by LSC either after combustion or by direct analysis. The validated detection limit of the radioassay method was approximately 0.01 mg/kg for milk, blood, and all tissues except fat with a validated sensitivity of 0.02 mg/kg. Extracts of the kidney and faeces and aliquots of urine were analysed by reverse phase radio-HPLC with two different phases used for analysis of the kidney.

Elimination of radioactive residues in the urine accounted for 67.2% and 94.0% of the TAR for the low and high doses, respectively. The radioactivity excreted in the faeces represented 7.0% and 9.6% of the TAR for the low and high doses, respectively.

The TRR in the daily collected blood and milk samples were < 0.01 mg eq/kg at both dose levels. The TRR in liver and muscle were < 0.01 mg eq/kg and < 0.02 mg eq/kg in fat regardless of the dose level. The TRR in the kidney was < 0.01 mg eq/kg from the goat dosed at 2.0 ppm and 0.05 mg eq/kg from the goat dosed at 11.8 ppm.

93% of TRR in kidney of the high-dose goat were extracted with acetonitrile and methanol. Analysis of the extract by reverse phase HPLC showed imazapic at 30% TRR (0.02 mg/kg), CL 263284 (hydroxymethyl imazapic) at 8% TRR (< 0.01 mg/g) and unknown A at 7% TRR (< 0.01 mg/kg). An unresolved peak near the solvent front comprised 33% TRR (0.02 mg/kg).

Analysis of the kidney extract by reverse phase HPLC using two different HPLC phases with comparison to reference standards confirmed the identification of the components.

HPLC analysis of the urine showed that radioactive residue was essentially unmetabolized imazapic. HPLC analysis of extracts of faeces showed the presence of imazapic (58% TRR) and the lesser amount of hydroxymethylated metabolite CL 263284 (9% of TRR).

CL 263284

A study (Kao, 1994a) was conducted using the [pyridine-6-¹⁴C]-radiolabelled hydroxymethyl imazapic (CL 263284) fed in capsule to lactating goats daily for seven days. Feeding levels for each of two goats were equivalent to 2.33 or 14.5 ppm of feed. One goat was used as a control. Samples of blood, milk and excreta were collected daily. After seven days of dosing, the goats were sacrificed, and the tissues kidney, liver, muscle and fat were collected 20 hours after the last dose. CL 283284 was eliminated via urine (15–18% of the applied dose) and faeces (82% and 68% of the applied dose at low dose and high dose respectively). The TRR in the daily blood and milk samples and those in liver, muscle, and omental fat were all less than 0.01 mg eq/kg, for both feeding levels. The TRR in kidney was < 0.01 mg eq/kg for low dose and 0.03 mg eq/kg for high dose. Analysis of the extract of kidney from the high dose goat showed that 9% (< 0.01 mg/kg) of the extracted TRR was CL 263284, and the remaining residue was predominantly a labile component M1 (78% TRR, 0.02 mg/kg), possibly a salt of CL 263284, which converted to CL 263284 on exposure to aqueous buffer.

Laying hens

Laying hens were orally dosed with a mixture of [pyridine-6-¹³C]- and [pyridine-6-¹⁴C]-imazapic in capsules (Gatterdam, 1993a). Feeding levels for three groups, each containing 8 hens, were 0, 2.1, or 11.4 ppm in feed daily for 7 consecutive days.

Eggs were collected twice daily and, after compositing, were refrigerated. After 7 days of dosing, the hens were sacrificed and blood and tissues (liver, kidney, muscle and skin with adhering fat) were collected approximately 22 hours after the last dose. Tissue samples were composited for each group and stored frozen at -20 °C.

Samples were analysed by LSC either after combustion or by direct analysis. The validated limit of detection of the radioassay method was approximately 0.01 mg/kg for eggs, blood, and all tissues.

TRR in the all egg samples and all tissue and blood samples were less than 0.01 mg eq/kg. Total recovery of radioactivity in excreta was 90.6% and 95.2% for the low and high dose, respectively.

Study 2 (Afzal, 1994a)

A study was conducted on laying hens with the [pyridine-6-¹⁴C]-radiolabelled hydroxymethyl imazapic (CL 263284). Hens were dosed orally, with feeding levels for each group at 2.14 or 10.9 ppm in diet daily for seven days. After seven days, the hens were sacrificed and the tissues (liver, kidney, muscle and skin with adhering fat) were collected for analysis approximately 22 hours after the final dose. Total recovery of radioactivity in excreta was 85.3% and 88.6% for the low and high doses, respectively. Residues in all tissues, liver, kidney, muscle, skin with adhering fat, blood and eggs, were less than 0.01 mg eq/kg. In summary, orally administered CL 263284, the hydroxymethyl metabolite of imazapic was mainly eliminated from the hen through excreta. No detectable (< 0.01 mg eq/kg) radioactive CL 263284-derived residues were found in eggs or edible tissues.

Proposed metabolic pathway of imazapic in animals

A proposed metabolic pathway for imazapic in rat and the lactating goats is presented in Figure 1. The majority of orally dosed imazapic was eliminated unchanged, mostly via urine (goats) and excreta (hens). The radioactive residues in edible tissues, milk or eggs were very low. In lactating goats, residues remaining in kidney were mostly unchanged parent with a minor amount of CL263284. In laying hens the studies with oral administration of either imazapic or its hydroxymethyl metabolite

did not result in detectable residues in any tissues or eggs. In the case of rats, imazapic was also primarily eliminated rapidly, unchanged, via urine. A small amount of the total dose excreted via faeces, consisted mostly of unchanged parent with minor amounts of metabolites CL 303459, CL 263284 and CL 290610 together with even lower amounts of several unknown radioactive components. Some amount of imazapic remaining in the body of animals did not go through extensive metabolism with minor oxidation to produce hydroxylated metabolite and in the case of rats, another metabolism to produce two minor metabolites through possibly hydrolysis.

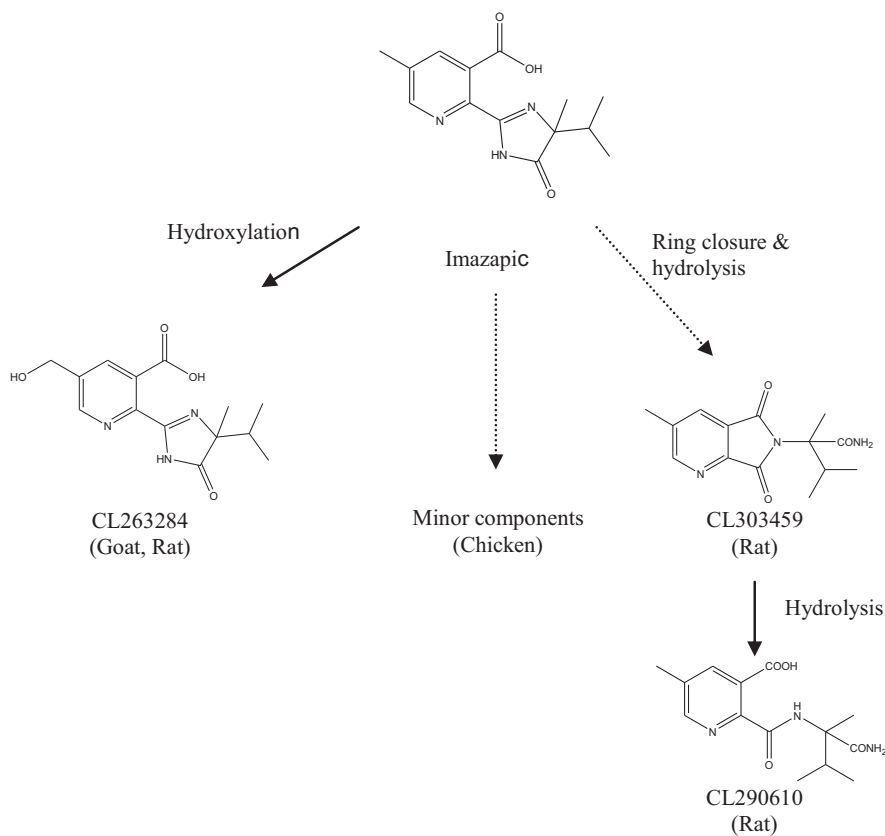


Figure 1 Proposed metabolic pathway of imazapic in animals

Plant metabolism

The Meeting received information on the fate of imazapic in sugar cane, peanuts, Bermuda grass and transgenic soya beans.

Sugar cane

Study 1 (Mangels, 1988a)

A metabolism study was conducted to investigate [pyridine-6-¹⁴C]-imazapic in sugar cane variety CP 65-357. [¹⁴C]-labelled imazapic was mixed with unlabelled imazapic and applied to the soil surface as a pre-emergence treatment at a rate approximating 150 g/ha by spraying 200 mL of the

aqueous solution of the compound onto the soil. The test was carried out under natural climatic conditions using one test plot of 0.6×3.1 m size and one control plot.

At harvest, approximately 13 months after pre-emergence treatment, mature sugar canes were cut above the soil and the outer leaves were removed by hand. The stalks were cut into thirds and each third was cut into pieces of 15–20 cm length.

All plant samples were frozen after collection and shipped to the analytical laboratory over dry ice. Twelve pieces from each section were combined and ground to a fine consistency in the presence of solid CO_2 . The radioactive residues present in the sugar canes were determined by combustion and liquid scintillation counting (LCS).

Radioassays of the stalk samples indicated that there were no detectable ^{14}C residues present in the harvest samples (< 0.005 mg/kg).

Study 2 (Grosshans, 2009a)

In another study, the metabolism of [pyridine-6- ^{14}C]-imazapic was investigated in sugar cane grown in plastic boxes ($0.365 \text{ m} \times 0.56 \text{ m}$) filled with a sandy loam soil. The cultivation of the crop and the plant uptake part of the study was conducted in a greenhouse. A calculated amount of ^{14}C -imazapic was dissolved in blank formulation solution (DG formulation with adjuvant BAS 160 00 S in water). This resulted in a nominal target rate of 245 g ai/ha (corresponding to spray volumes of approximately 220 L/ha). The formulation was applied as a pre-emergence treatment using an automatic spray track system.

Sugar cane plants were sampled at 63, 96, 151 and 236 DAT and adult plants were split into leaves and stalks.

Frozen samples (sugar cane forage, leaves or stalks) were mixed with dry ice and homogenized using a Stephan mill. Weighed homogenized subsamples were extracted three times with methanol and twice with water. The methanol extracts of the three steps were combined and adjusted to a defined volume. Aliquots of the combined extracts were measured by Liquid Scintillation Counting (LSC). The residue was further extracted in the same way with appropriate volumes of water (twice). The aqueous extracts were also combined, adjusted to a defined volume, and aliquots of the combined aqueous extracts were radioassayed by LSC as well. Based on the sum of radioactive counts found in the methanol and aqueous extracts, the ERR is calculated. The residue remaining after methanol and water extraction of each sample was air dried, and the weight of the remaining sample was determined. The samples were homogenized using an analytical mill prior to combustion analysis of aliquots for the determination of the PES. The PES after methanol and water extraction of sugar cane samples accounted only for low concentrations, therefore no further processing was attempted.

Additional extraction procedures were carried out to get further information about the extractability of radioactive residues. Solvents or solvent mixtures were used which are applied in residue analytical methods: A three step extraction method with methanol / 25 mM HCl (6/4, v/v; Method SOP-PA.0288); and a three step extraction method with methanol / acetone / water (1/1/1, v/v/v; Method M 2253.01).

The calculated total radioactive residues of the growing sugar cane forage sampled 63 DAT of pre-emergence treatment with ^{14}C -imazapic accounted for 0.0358 mg/kg (Table 2). The TRR of forage sampled 96 DAT was lower with 0.0161 mg/kg. On 151 DAT, small plants were sampled as forage material (TRR 0.0222 mg/kg). The leaves (TRR) and stalks (TRR) of full grown plants sampled 15 DAT contained TRR of 0.0242 and 0.0086 mg/kg respectively. At the last sampling date of 236 DAT, leaves and stalks of the adult plants contained residues at 0.0151 mg/kg and 0.0039 mg/kg, respectively.

Table 2 TRRs in sugar cane samples after pre-emergence treatment with [pyridine-6-¹⁴C]-imazapic

Matrix	Days after Treatment	TRRs in Treated Sugar Cane Matrices	
		Determined by Direct Combustion (mg eq/kg)*	Sum of Extracted Radioactive Residue and PES (mg eq/kg)*
Forage	63	0.0424	0.0358
Forage	96	0.0169	0.0161
Forage ^a	151	0.0220	0.0222
Leaves ^b	151	0.0266	0.0242
Stalks ^b	151	0.0075	0.0086
Leaves ^b	236	0.0162	0.0151
Stalks ^b	236	0.0048	0.0039

PES = post extraction solid (after solvent extraction)

* Expressed in mg-imazapic equivalents/kg.

^a young small plants

^b adult plants

The extraction profiles of radioactive residues from sugar cane leaves and stalks are summarized in Table 3.

High percentage (82.0–84.4% TRR) of the radioactive residues in forage (63, 96 and 151 DAT) was extracted, most of which (77.1 to 80.0%) extracted with methanol. The additional water extraction released only 3.2 to 4.4% TRR. Most of the extracted radioactive residues were water-soluble (48.1 to 79.0% TRR). The residual radioactive residues accounted for 15.6 to 19.7% TRR (0.0032 to 0.0064 mg eq/kg).

Equally high percentage (78.1–83.6% TRR) of radioactive residues in leaves (151 and 236 DAT) were extracted, most of which extracted with methanol (72.3 to 78.6%). The additional water extraction released only 5.1 to 5.8% TRR. Most of the extracted radioactive residues were water-soluble (71.5 to 75.8% TRR). The residual radioactive residues accounted for 16.4 and 21.9% TRR (0.0033 and 0.0040 mg eq/kg).

Slightly lower but still quite high percentage (63.4–81.9% TRR) of radioactive residues in stalks (151 and 236 DAT) was extracted, most of which extracted with methanol (59.2 to 78.4%). The additional water extraction released 3.4 to 4.2% TRR. Most of the extracted radioactive residues were water-soluble (63.3 to 65.2% TRR). The residual radioactive residues accounted for 18.1 and 36.6% TRR (0.0014 and 0.0016 mg eq/kg).

Table 3 Extracted radioactive residues from sugar cane samples after pre-emergence treatment with [pyridine-6-¹⁴C]-imazapic

(a) Distribution of radioactive residues among methanol extracts, aqueous extracts, total extracted radioactive residue and PES of various matrices

Matrix	DAT	TRR Sum of Extracted Residue and PES (mg/kg)*	Distribution of Radioactive Residues							
			Combined Methanol Extract		Combined Aqueous Extract		Total Extracted Radioactive Residue		PES	
			(mg/kg)*	(%TRR)	(mg/kg)*	(%TRR)	(mg/kg)*	(%TRR)	(mg/kg)*	(%TRR)
Forage	63	0.0358	0.0282	78.7	0.0012	3.3	0.0294	82.0	0.0064	18.0
Forage	96	0.0161	0.0124	77.1	0.0005	3.2	0.0129	80.3	0.0032	19.7
Forage ¹	151	0.0222	0.0177	80.0	0.0010	4.4	0.0187	84.4	0.0035	15.6
Leaves ²	151	0.0242	0.0190	78.6	0.0012	5.1	0.0202	83.6	0.0040	16.4
Stalks ²	151	0.0086	0.0067	78.4	0.0003	3.4	0.0070	81.9	0.0016	18.1
Leaves ²	236	0.0151	0.0109	72.3	0.0009	5.8	0.0118	78.1	0.0033	21.9
Stalks ²	236	0.0039	0.0023	59.2	0.0002	4.2	0.0025	63.4	0.0014	36.6

DAT=days after treatment

PES=post extraction solid

* Expressed in mg-imazapic equivalents/kg.

(b) Partition of methanol extracts into organic solvent and water (See Table 3a above)

Matrix	DAT	Organosoluble				Water Soluble (water phase)	
		Dichloromethane Extract (alkaline conditions)		Ethyl Acetate Extract (acidic conditions)			
		(mg/kg)*	(%TRR)	(mg/kg)*	(%TRR)	(mg/kg)*	(%TRR)
Forage	63	0.0038	10.7	0.0085	23.7	0.0172	48.1
Forage	96	0.006	3.8	ne	ne	0.0123	76.7
Forage ^a	151	0.0022	9.8	ne	ne	0.0175	79.0
Leaves ^b	151	0.0021	8.5	ne	ne	0.0183	75.8
Stalks ^b	151	0.0014	16.0	ne	ne	0.0054	63.3
Leaves ^b	236	n.m.	n.m.	ne	ne	0.0108	71.5
Stalks ^b	236	n.m.	n.m.	ne	ne	0.0025	65.2

n.m.= not measured by LSC

ne = not extracted with ethyl acetate.

*= Expressed in mg-imazapic equivalents/kg.

^a Young small plants

^b Adult plants

The identification of metabolites was based on HPLC analyses of the concentrated extracts and/or clean-up fractions either via solvent partition or fractionation. The parent compound and the metabolites were assigned by comparison of the retention times with synthesized and certified reference compounds. All the quantification of the parent compound and its metabolites was based on the HPLC analyses of the concentrated extracts or clean-up fractions obtained from the individual matrices using two different HPLC methods with radio-detection. The results of identification and characterization are shown in Table 4.

Imazapic was found in all samples investigated (5.7 to 41.3% TRR, 0.0005 to 0.0058 mg/kg). In addition, the hydroxymethyl metabolite CL263284 was detected in all samples investigated (10.1 to 44.5% TRR, 0.0005 to 0.0139 mg eq/kg). Its glucoside CL189215 was found only in forage and leaves (2.7 to 8.0% TRR, 0.0005 to 0.0019 mg/kg) and could not be identified in stalks. Some HPLC peaks in the chromatograms could be characterized by their chromatographic behavior.

In samples taken up to 151 DAT, the degree of identification was 55.1 to 69.0% of the TRR. Additional 14.7 to 30.5% TRR could be characterized for its chromatographic, SPE fractionation, partition or extraction behavior.

Since the extractability of the 236 DAT stalk and leaves samples was lower, only 21.3 and 34.7% TRR, respectively, only known metabolites could be identified. Additional 29.9 and 29.7% TRR could be characterized in stalks and leaves, respectively.

Table 4 Characterization and identification of radioactive residues in sugar cane samples after pre-emergence treatment with [pyridine-6-¹⁴C]-imazapic

Component	Forage 63 DAT mg/kg (% TRR)	Forage 96 DAT mg/kg (% TRR)	Forage 151 DAT mg/kg (% TRR)	Leaves 151 DAT mg/kg (% TRR)	Stalks 151 DAT mg/kg (% TRR)	Leaves 236 DAT mg/kg (% TRR)	Stalks 236 DAT mg/kg (% TRR)
Imazapic	0.0058 (16.4)	0.0051 (31.4)	0.0040 (18.0)	0.0027 (11.0)	0.0026 (41.3)	0.0010 (5.7)	0.0005 (11.2)
CL263284	0.0139 (38.7)	0.0061 (37.6)	0.0094 (42.5)	0.0108 (44.5)	0.0010 (15.8)	0.0045 (26.3)	0.0005 (10.1)
CL189215	nd	nd	0.0011 (5.1)	0.0019 (8.0)	nd	0.0005 (2.7)	nd
Total identified and characterized ^a	0.0306 (85.6)	0.0135 (83.7)	0.0206 (93.2)	0.0217 (89.4)	0.0051 (82.2)	0.0111 (64.4)	0.0023 (51.1)

DAT = Days after last treatment

nd = not detected

^a in extracted radioactive residues (ERR)

The TRR in adult sugar cane parts were low (leaves 0.024 mg eq/kg and 0.015 mg eq/kg and stalks 0.009 and 0.004 mg eq/kg for the 151 DAT and 236 DAT, respectively). Most of the radioactive residues were extracted with methanol, and only minor portions subsequently with water. The major radioactive components in the extracts were identified as unchanged parent, the 5-hydroxymethyl metabolite CL263284 and its glucose conjugate CL189215 (in forage and leaves only). The glucose conjugate CL189215 was not present in sugar cane stalks.

Peanut

A metabolism study was conducted with [pyridine-6-¹⁴C]-imazapic in peanuts of variety NC7 (Wu, 1993a). The plants were kept in outdoor test plots. Both untreated and treated plots had total area of 1.2 × 2.4 m of sandy loam soil. Radiolabelled imazapic in a 2ASU formulation was applied to peanut plants at a rate of approximately 72 g ai/ha 30 days post-emergence. Pre-harvest (green plant) samples were collected at 0, 31, and 61 DAT. At harvest (131 DAT) hay and peanuts were collected. Soil samples were taken prior to and just after application and at harvest.

Samples were frozen after collection and shipped to the analytical laboratory over dry ice. Each mature harvest sample was separated into hay, hulls, and nutmeat. Green plants sampled at 0, 31, and 61 DAT and hay were first cut into small pieces and then homogenized in dry ice and/or liquid nitrogen. Nutmeat and hull were also ground in dry ice and/or liquid nitrogen. Levels of radioactivity in soil and plant matrices were determined by combusting subsamples in a sample oxidizer. All combustions were performed in triplicate.

Crop samples were sequentially extracted with methanol:water:acetone (1:1:1) and methanol:water (80:20) containing 2% hydrochloric acid except for nutmeat, which was extracted only with the former. HPLC of the peanut green plant, hay, hull, and nutmeat extracts was performed on a Supelco C₁₈ reversed-phase column using an acetonitrile and phosphate buffer gradient system.

The TRR in all plant parts were determined by combustion. Additionally, the TRR was calculated by summing of the ERR extracted with methanol:acetone:water (1:1:1, v/v/v) and the PES. A summary of the TRR values in peanut plant matrices collected at various time intervals is shown in Table 5.

The TRR in the peanut plant declined significantly from 4.23 mg eq/kg at 0 DAT in green plants to 0.216 mg eq/kg (hay). The TRR in nutmeat at 131 DAT was low at 0.022 mg eq/kg (nutmeat)

Table 5 TRR in peanut plant samples after 30 days post-emergence treatment with [pyridine-6-¹⁴C]-imazapic

Matrix	Days after Treatment	TRRs in Treated Sugar Cane Matrices	
		Determined by Direct Combustion (mg eq/kg)*	Sum of Extracted Radioactive Residue and PES (mg eq/kg)*
Plant	0	4.230	4.756
Plant	31	0.067	0.071
Plant	61	0.094	0.085
Hay	131	0.216	0.197
Hull	131	0.086	0.089
Nutmeat	131	0.022	0.016

PES =post extraction solid (after solvent extraction)

* Expressed in mg-imazapic equivalents/kg.

The extraction profiles of radioactive residues from peanut plant samples are summarized in Table 6.

The radioactive residue in peanut plant samples (green plant, hay, hull, and nutmeat) was initially extracted with methanol:water:acetone (1:1:1, v/v/v). Table 9 shows that 76–96% of the TRR in peanut samples was extracted with aqueous methanol:acetone. In order to get sufficient solid residue after solvent extraction for further process of the unextracted radioactivity, fresh peanut samples, with the exception of nutmeat, were extracted with methanol:water:acetone (1:1:1). The resultant residue after solvent extraction containing 6–20% of the TRR was then further processed by extraction with methanol:water (80:20) containing 2% hydrochloric acid. An additional 3–8% of the TRR was extracted into the acid methanol:water mixture. In the case of the green plant (0 DAT), the residue after solvent extraction with 2% HCl-methanol:water was subjected to a third extraction by using methanol:water (80:20) containing 0.5 M sodium hydroxide. An additional 30% of the unextracted fraction (1% of TRR) was soluble in the base methanol:water mixture. Following extraction of the hay with acid:methanol:water, the resulting residue was treated with *Aspergillus* cellulase at 37 °C for 72 hours which solubilized about 36% of ¹⁴C-residues in the marc (4% of TRR). The results suggest the presence of glycosidic linkage of the residues with endocons in the peanut hay.

Table 6 Extracted radioactive residues from peanut plant samples after 30days post-emergence treatment with [pyridine-6-¹⁴C]-imazapic

Matrix	DAT	TRR Sum of Extracted Radioactive Residue and PES (mg eq/kg)*	Extracted Radioactive Residue (extracted with methanol:acetone:H ₂ O (1:1:1, v/v/v))		PES	
			(mg eq/kg)*	(%TRR)	(mg eq/kg)*	(%TRR)
Plant	0	4.756	4.561	95.9	0.195	4.1
Plant	31	0.071	0.058	81.2	0.013	18.8
Plant	61	0.085	0.076	88.9	0.009	11.1
Hay	131	0.197	0.156	79.2	0.041	20.8
Hull	131	0.089	0.073	81.9	0.016	18.1
Nutmeat	131	0.016	0.012	76.4	0.004	23.6

DAT=days after treatment

PES =post extraction solid (after solvent extraction)

* Expressed in mg-imazapic equivalents/kg.

The nature of the radioactive components in the extracts of peanut samples was characterized first by matching the HPLC profile with the reference compounds. The identification of metabolites was then accomplished by isolating them from peanut plant (61 DAT) and harvest peanut hay. Structural characterization of the isolated metabolites was confirmed by mass spectral analysis. The results of identification and quantification are shown in Table 7.

The [¹⁴C]-Imazapic accounted for 76% TRR in the green plant at 0 DAT, 2% in the plant at 31 DAT, 3% in the plant at 61 DAT, 3% in the hay, 2% in the hull, and 1% in the nutmeat. Residues of imazapic in all samples, except at 0 DAT, were < 0.01 mg/kg. This indicates imazapic was significantly metabolized.

The metabolite CL263284 accounted for 1% of the TRR (0.048 mg/kg) in the plant at 0 DAT, 12% (< 0.01 mg/kg) in the plant at 31 DAT, 12% (0.010 mg/kg) in the plant at 61 DAT, 28% (0.055 mg/kg) in the hay, 28% (0.025 mg/kg) in the hull, and 8% (0.001 mg/kg) in the nutmeat, showing increase over time.

The metabolite CL189215, which is glycoside of CL263284, accounted for 2% of the TRR (0.095 mg/kg) in the plant at 0 DAT, 32% (0.023 mg/kg) in the plant at 31 DAT, 46% (0.039 mg/kg) in the plant at 61 DAT, 16% (0.032 mg/kg) in the hay, 36% (0.032 mg/kg) in the hull, and 35% (0.006 mg/kg) in the nutmeat.

No other component of the extracted ¹⁴C-residue from the immature plant and harvest samples exceeded 10% TRR as determined by HPLC. The concentration was all less than 0.01 mg eq/kg, with the exception of one component (0.014 mg eq/kg) detected in the hay.

Table 7 Characterization and identification of radioactive residues in peanut plant samples after 30 days post-emergence treatment with [pyridine-6-¹⁴C]-imazapic

Component	Plant (0 DAT)		Plant (31 DAT)		Plant (61 DAT)		Hay (131 DAT)		Hull (131DAT)		Nutmeat (131DAT)	
	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)
Imazapic	3.615	76	0.001	2	0.003	3	0.006	3	0.002	2	< 0.001	1
CL 189215	0.095	2	0.023	32	0.039	46	0.032	16	0.032	36	0.006	35
CL 263284	0.048	1	0.009	12	0.010	12	0.055	28	0.025	28	0.001	8
Unknown	-	< 1	0.004	6	0.005	6	0.014	7	0.002	2	< 0.001	1

DAT=days after treatment

Bermuda grass

A metabolism study was conducted to investigate metabolism of [pyridine-6-¹⁴C]-imazapic in Bermuda grass (Fung, 1999a). The Bermuda grass was treated when approximately 51 cm tall (62 days after sprigging) with a blank formulation for the control plot or a single post-emergence application of [¹⁴C]-imazapic at an actual rate of approximately 203 g ai/ha and a spray volume of 300 L/ha for the treated plot. The field portion of the study was conducted in outdoor test plots. Both treated and untreated plots had total area of 0.9 × 4.6 m of loam soil. Bermuda grass forage samples were collected within three hours after application (0 DAT) and at 15, 32, and 49 DAT. Bermuda grass foliage for hay samples was cut at 68 days after treatment.

Samples were frozen after collection and shipped to the analytical laboratory over dry ice. Bermuda grass samples were cut with a pair of shears into small pieces (approximately 5 cm long) and ground to fine powder in two steps with dry ice. The TRR in all plant parts were determined by combustion. Additionally, the Bermuda grass samples were each extracted sequentially with an aqueous methanol/acetone mixture followed by sequential extraction with acidified aqueous methanol, aqueous acid, and aqueous base. The post-extraction solids were treated sequentially with enzymes, 10 N NaOH reflux, and 6 N HCl reflux to attempt releasing of the bound residues. The aqueous methanol/acetone extract, the combined sequential extracts and the post-extraction solids wash were each analysed by HPLC on a reversed phase C₁₈ column.

A summary of the TRR in Bermuda grass samples collected at various time intervals is shown in Table 8. The increased residue concentration in the hay compared to 49 DAT forage is attributed to the dehydration of the grass.

Table 8 TRR in Bermuda grass samples after post-emergence treatment with [pyridine-6-¹⁴C]-imazapic

Matrix	Days after Treatment	TRRs in Treated Sugar Cane Matrices	
		Determined by Direct Combustion (mg eq/kg)*	Sum of Extracted Radioactive Residue and PES (mg eq/kg)*
Forage	0	8.25	8.29
Forage	15	4.58	3.92
Forage	32	2.73	2.42
Forage	49	0.77	0.78
Hay	68	0.92	0.83

PES =post extraction solid (after solvent extraction)

* Expressed in mg-imazapic equivalents/kg.

The extraction profiles of the radioactive residues from Bermuda grass are summarized in Table 9.

The incurred residues extracted by the neutral aqueous methanol/acetone solvent decreased from 98% for the 0 DAT sample, to the range of 69% to 51% for the 15 to 49 DAT samples, and about 35% for the hay sample at 68 DAT. A significant amount of the radioactivity ranging from

12.6% TRR in the 15 DAT sample to 27% TRR in the 68 DAT hay was extracted with dilute acid and base. Thus, the total extracted radioactive residues were 84% to 101% of the TRR in forage, and 74% of the TRR in hay.

The remaining radioactivity in the residues after solvent extraction (PES) accounted for about 2–3% of the TRR in the 15 and 32 DAT samples, 10% of the TRR in the 49 DAT sample, and 31% of the TRR in the 68 DAT sample. Treatment of the PES with enzymes cellulase and pepsin released only a very small amount of the bound residues (< 5% TRR) suggesting that the unextracted residues in the PES did not contain glycoside or peptide bonds. Following enzymatic treatment, the resulting solids were subjected to base (NaOH) and acid (HCl) hydrolyses under reflux. The acid and base hydrolyses steps also released a very small amount of radioactive residues: < 1% TRR in the 15 and 32 DAT samples, 4.3% TRR in the 49 DAT sample, and 8.0% TRR in the 68 DAT sample. The results suggest that portions of the radiolabelled carbon have been incorporated into undefined plant constituents.

Table 9 Extracted radioactive residues from Bermuda grass samples after post-emergence treatment with [pyridine-6-¹⁴C]-imazapic

Matrix	Days after Treatment	TRR (mg/kg)*	Distribution of Radioactive Residues									
			MeOH:Acetone: H ₂ O Extract		Extracts ^a (MeOH:HCl:H ₂ O , 1 N HCl, 1 N NaOH)		Rinse of PES by Methanol:Water (1:1)		Extracted Radioactive Residue		PES after Rinse	
			(mg/kg) *	(%TRR)	(mg/kg) *	(%TRR)	(mg/kg) *	(%TRR)	(mg/kg) *	(%TRR)	(mg/kg) *	(%TRR)
Forage	0	8.29	8.05	97.6	0.22	2.7	0.02	0.3	8.29	100.6	< 0.01	0.1
Forage	15	3.92	3.14	68.6	0.58	12.6	0.14	3.0	3.86	84.2	0.12	2.7
Forage	32	2.42	1.70	62.1	0.43	15.6	0.20	7.2	2.33	84.9	0.06	2.3
Forage	49	0.78	0.39	51.2	0.21	27.3	0.11	13.7	0.71	92.2	0.08	10.2
Hay	68	0.83	0.32	34.8	0.25	27.0	0.11	12.4	0.68	74.2	0.29	31.2

TRR=calculated sum of the extracted residues (MAH, MHH and PES wash), different solubilizates from the PES and the final residue (values not given in this table)

PES =post extraction solid (after solvent extraction)

^a combined sequential extracts of (1) methanol: HCl: H₂O, (2) 1 N HCl and (3) 1 N NaOH

* Expressed in mg-imazapic equivalents/kg.

The chemical structure of the parent compound and its putative Bermuda grass metabolites were confirmed by the characteristic ions detected in the Liquid Chromatography - Electrospray Positive Ion Mass Spectrometry (LC-ESP/PIMS) of the purified metabolites and, where available, by authentic reference standard compounds.

When the aqueous methanol/acetone extract, the combined sequential extracts and the post-extraction solids wash were each analysed by HPLC on a reversed phase C₁₈ column, there were 11 discernible regions or peaks, designated as M1 (the most polar) through M10 (the least polar), detected on the radiochromatograms. The chromatographic patterns were compared with those obtained from the known reference compounds including parent compound imazapic, hydroxymethyl analog CL 263284, glucose conjugate CL 189215, 3,5-dicarboxylic acid analog CL 312622, CL 290610 and CL 397695. Chromatography of the isolates of some of the regions or peaks by HPLC on Hypercarb graphitic column and other solid support showed that these peaks were comprised of multiple components as illustrated below:

The enzymes, acid, and base hydrolyzates of the samples from Bermuda grass hay and forage contained radioactivity which was too low to conduct HPLC analysis.

The metabolites detected in Bermuda grass forage and hay are summarized in Table 10.

Imazapic was extensively metabolized in Bermuda grass and accounted for only about 6% of the TRR at 15 DAT. Quantitatively, CL 263284 and CL 189215 were the major Bermuda grass metabolites of imazapic. Although M1 accounted for up to 26.8% of TRR in the grass samples at various time intervals, it was comprised of at least twelve groups of multi-radioactive components.

The 0 DAT (about three hours after application) sample extracts showed a main chromatographic peak that coincided with the standard of the parent compound (89.3% of TRR). In addition, several radioactive residue components including hydroxymethyl metabolite CL 263284 (0.7% TRR) and its glucose conjugate CL 189215 (1.0% TRR) and minor residue fractions M2, M3, M3A, M6, and M8 through M10 of varying quantities were detected. The proportions of these radioactive residue fractions/or metabolites changed with time.

At 15 DAT, the hydroxymethyl metabolite CL 263284 became the single most prominent residue component (30.2% TRR) and the quantity was maintained at > 20% TRR at 32 and 49 DAT, then declined to 8.4% TRR at 68 DAT. The increase of CL 263284 and its glucoside conjugate CL 189215 contents in the grass sample coincided with the decline of the parent compound from about 89% of the TRR at three hours after application to 6% TRR at 15 DAT, 3% TRR at 49 and 2% TRR at 68 DAT.

In addition to the CL 263284 metabolite, a significant amount of highly polar metabolites in the M1 fraction were formed at 15 DAT (20.6% TRR) and at 49 and 68 DAT (~27% TRR). Among at least 12 groups of multi-radioactive components of M1 fraction, groups M1-B and M1-C were present at about 0.1 mg/kg at 15 DAT. Their chemical structures are shown to be multi-substituted pyridine derivatives. M1-B was characterized as 5-hydroxymethyl-nicotinamide derivative and additionally M2-A 5-hydroxymethylquinolic acid anhydride. Some other minor fractions were also identified.

Table 10 Characterization and identification of radioactive residues in Bermuda grass samples after post-emergence treatment with [pyridine-6-¹⁴C]-imazapic

Components	Forage (0 DAT)		Forage (15 DAT)		Forage (32 DAT)		Forage (49 DAT)		Hay (68 DAT)	
	(mg/kg)*	(%TRR)*	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)
Imazapic (M7)	7.37	89.3	0.27	5.9	0.08	3.1	0.02	2.6	0.02	2.3
M1 (>12 groups of multi-components)	0.24	3.0	0.95	20.6	0.67	24.2	0.20	26.8	0.25	26.9
M2 (M2-A + M2-B)	0.10	1.3	0.29	6.4	0.13	4.9	0.04	4.9	0.02	2.6
M3 (> 5 components)	0.04	0.5	0.18	4.0	0.19	6.9	0.02	3.0	0.02	2.5
M3A (~ 28 components)	0.03	0.4	0.10	2.2	0.11	4.0	0.05	7.1	0.04	4.0
CL189215 (M4)	0.08	1.0	0.17	3.9	0.14	5.3	0.08	9.2	0.08	9.2
CL263284 (M5)	0.06	0.7	1.38	30.2	0.60	22.0	0.16	20.5	0.08	8.4
M6 (>12 components)	0.08	0.9	0.18	4.0	0.12	4.4	0.05	7.1	0.04	4.8
M8 (> 6 components)	0.13	1.5	0.13	2.7	0.12	4.4	0.02	2.3	0.04	4.6
M9 (>18 components)	0.05	0.6	0.08	1.8	0.07	2.7	0.02	3.2	0.03	3.0
M10 (>16 components)	0.05	0.6	0.07	1.6	0.07	2.6	0.03	3.7	0.03	2.8
Total	8.23	99.8	3.80	83.3	2.30	84.5	0.69	90.4	0.65	71.1

* The values of mg/kg for individual metabolites (M1 to M10) were the sum of mg/kg values obtained from the aqueous methanol-acetone extract, the combined sequential extracts and the post-extraction solids wash except that in case of < 0.01 mg/kg in one of the extract, the sum of mg/kg values was calculated from the sum of % TRR times TRR in mg/kg in the grass or hay.

** The values of % TRR for individual metabolites (M1 to M10) were the sum of % TRR values obtained from the aqueous methanol/acetone extract, the combined sequential extracts and the post-extraction solids wash.

Transgenic soya beans

A metabolism study was conducted in 2011 to investigate metabolism of [pyridine-3-¹⁴C]-imazapic in transgenic soya bean variety BPS-CV127-9 in which the *csr1-2* gene encoding an altered AtAHASL protein was inserted to make the host tolerant to imidazolinone herbicides (Dohn and Estigoy, 2012a). [¹⁴C]-imazapic in DG formulation was sprayed once at BBCH growth stage 65 with an application rate of 80.1 g/ha to the above-ground portion of soya beans plants. This application rate is equivalent to 4.6 times the maximum anticipated label rate. Soya bean forage was harvested approximately one hour after application and hay was harvested 35 days after treatment. Soya bean straw, pods, and seeds were harvested when mature, 97 days after treatment.

Samples were frozen after collection and shipped to the analytical laboratory over dry ice. They were ground to a fine consistency in the presence of solid CO₂ using a food processors. The moisture content of hay and seed was measured by drying subsamples at 105 °C. Portions (25 g of forage, hay, straw, and pods, 50.7 g of soya bean seed) of the processed samples were subjected to sequential solvent extraction. Samples were extracted sequentially by 100% methanol (two times), followed by 100% water and methanol:water:1N HCl (60:39:1,v:v:v). The radioactive residue remaining in the PES samples was measured by combustion analysis and LSC counting. The TRR were calculated as the sum of extracted radioactivity (ERR) and radioactivity recovered in the PES.

The TRR of soya bean forage was 0.689 mg eq/kg, soya bean hay 0.241 mgeq/kg, soya bean seed 0.014 mg eq/kg, soya bean straw 0.092 mg eq/kg and soya bean pod 0.042 mg eq/kg as shown in Table 11. The extraction procedure released 77.8% to 98.4% of the TRR.

Table 11 TRR in transgenic soya bean samples following foliar application of [pyridine-3-¹⁴C]-imazapic

Matrix	Days after Treatment	TRRs in Treated Soya Bean Matrices	
		Determined by Direct Combustion (mg eq/kg)*	Sum of Extracted Radioactive residue and PES (mg eq/kg)*
Forage	0	0.689	0.673
Hay	35	0.241	0.240
Seeds	97	0.014	0.015
Straw	97	0.092	0.088
Pods	97	0.042	0.045

PES = post extraction solid (after solvent extraction)

* Expressed in mg-imazapic equivalents/kg.

The extraction profiles of radioactive residues from soya bean forage, hay, straw, hull and seed are summarized in Table 12. As a consequence of low residual radioactive residues (PES), no further processing was conducted on PES.

The residue extracted from forage 0 DAT was 0.662 mg eq/kg (98.4% of the TRR calculated to be 0.673 mg eq/kg). The methanol extract contained 92.1% of the radioactive residues (0.620 mg eq/kg), the aqueous fraction 5.2% (0.035 mg eq/kg), and the acidic methanol 1.1% of the radioactivity (0.007 mg eq/kg). The PES contained residue of 0.011 mg eq/kg (1.6% of the TRR).

The residue extracted from hay 35 DAT was 0.221 mg eq/kg (92.1% of the TRR calculated to be 0.270 mg eq/kg). The methanol extracts contained 76.7% of the radioactive residues (0.184 mg eq/kg) and the aqueous fraction 12.9% (0.031 mg eq/kg). The acidic methanol extracted 2.5% of the radioactivity (0.006 mg eq/kg) and was not further analysed. The PES contained residue of 0.019 mg eq/kg (7.9% of TRR).

The residue extracted from seeds 97 DAT was 0.013 mg eq/kg (86.7% of the TRR calculated to be 0.015 mg eq/kg). The methanol extracts contained 46.7% of the radioactive residues (0.007 mg eq/kg) and the aqueous fraction 26.7% (0.004 mg eq/kg). The acidic methanol extracted 13.3% of the radioactivity (0.002 mg eq/kg). The PES had 0.002 mg eq/kg of radioactive residue (13.3% of TRR).

The residue extracted from straw 97 DAT was 0.072 mg eq/kg (81.8% of the TRR calculated to be 0.088 mg eq/kg). The methanol extracts contained 59.1% of the radioactive residues (0.052 mg eq/kg) and the aqueous fraction 17.0% (0.015 mg eq/kg). The acidic methanol extracted 5.7% of the radioactivity (0.005 mg eq/kg). The PES had 0.016 mg eq/kg of radioactive residue (18.2% of TRR).

The residue extracted from pods 97 DAT was 0.035 mg eq/kg (77.8% of the TRR calculated to be 0.045 mg eq/kg). The methanol extracts contained 33.3% of the radioactive residues (0.015 mg eq/kg) and the aqueous fraction 24.4% (0.011 mg eq/kg). The acidic methanol extracted 20.0% of the radioactivity (0.009 mg eq/kg). The PES had 0.010 mg eq/kg of radioactive residue (22.2% of TRR).

Table 12 Extracted radioactive residues from transgenic soya bean samples following foliar application of [pyridine-3-¹⁴C]-imazapic

Matrix	Days after Treatment	TRR Sum of ERR and PES (mg/kg)	Distribution of Radioactive Residues									
			Combined Methanol Extract		Combined Aqueous Extract		Acidic Methanol Extract		Extracted Radioactive Residue		PES	
			(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)
Forage	0	0.673	0.620	92.1	0.035	5.2	0.007	1.1	0.662	98.4	0.011	1.6
Hay	35	0.240	0.184	76.7	0.031	12.9	0.006	2.5	0.221	92.1	0.019	7.9
Seeds	97	0.015	0.007	46.7	0.004	26.7	0.002	13.3	0.013	86.7	0.002	13.3
Straw	97	0.088	0.052	59.1	0.015	17.0	0.005	5.7	0.072	81.8	0.016	18.2
Pods	97	0.045	0.015	33.3	0.011	24.4	0.009	20.0	0.035	77.8	0.010	22.2

PES = post extraction solid (after solvent extraction)

(mg/kg): Expressed in mg-imazapic equivalents/kg.

The methanol and water extracts of the forage and hay samples were combined and, after concentration, characterized by reverse phase HPLC. The radioactive residue detected in the acidic extract of soya bean forage and hay was insignificant and no further analyses were performed on these extracts. Representative portions (20% of each extract) of methanol, aqueous and acidic methanol extracts of the soya bean straw, soya bean pods and soya bean seeds were combined and liquid/liquid extracted with hexane. The hexane and the aqueous/methanol phases were assayed by LSC. No radioactive residue was detected in the hexane portions and no further analysis was done on these fractions. The aqueous/methanol portions were concentrated and characterized by reverse phase HPLC. Imazapic and the metabolites CL263284 and CL189215 were identified by co-chromatography of the extracts with reference standards. The results of identification and quantification are shown in Table 13.

A mixture of the methanol and water extracts of forage (0 DAT) containing 0.655 mg eq/kg of residue was analysed. The primary component of the residue was imazapic (0.605 mg/kg, 89.9% of the TRR) with other minor components that did not individually exceed 3.4% TRR. The total identified and characterized residues were 97.3% of the TRR.

The most abundant component of the residue in a mixture of the methanol and water extracts of hay (35 DAT) was imazapic (0.087 mg/kg, 36.3% of the TRR). Imazapic was metabolized to a large number of components including a low amount of a component with the retention time matching that of the analytical standard CL189215, the glucoside of hydroxymethyl imazapic (CL263284) (0.006 mg/kg, 2.5% of the TRR). The total identified and characterized residues were 90.4% of the TRR.

The analysis of a mixture of methanol, water and acidic extracts of seeds (97 DAT) indicated that imazapic was metabolized to a large number of components. Imazapic comprised 0.0030 mg/kg (20.0% of the TRR), and imazapic metabolites CL189215, the glucoside, and CL263284, hydroxymethyl imazapic, comprised 4.7% TRR (0.0007 mg/kg) and 0.7%TRR (0.0001 mg/kg), respectively. A significant radioactive peak (0.0034 mg eq/kg, 22.7% TRR) was very polar and consisted of multiple components by analysis using a Hypercarb method. Multiple minor components were detected at very small concentrations (≤ 0.0014 mg eq/kg). The total identified and characterized residues were 88.7% of the TRR.

Imazapic was the most abundant component of the residue at 0.013 mg/kg (14.8% of the TRR) in a mixture of methanol, water and acidic extracts of straw (97 DAT). The imazapic metabolites CL189215 and CL263284 comprised 6.8% TRR (0.006 mg/kg) and 2.3% TRR (0.002 mg/kg), respectively. The amount of polar radioactive residue (0.004 mg/kg, 4.5% TRR) was less than that seen in the seed and pod. Multiple minor components indicated that metabolism of imazapic was complex and extensive. The total identified and characterized residues were 84.1% of the TRR.

Imazapic comprised 0.004 mg/kg (8.9% of the TRR), and imazapic metabolites CL189215, the glucoside, and CL263284, hydroxymethyl, comprised 4.4% TRR (0.002 mg/kg) and 2.2% TRR (0.001 mg/kg), respectively in a mixture of methanol, water and acidic extracts of pods (97 DAT). As in the seed, significant radioactive residue (0.007 mg/kg, 15.6% TRR) was polar. Multiple minor degradates were present as seen in the straw and bean samples. The total identified and characterized residues were 80.0% of the TRR.

Table 13 Characterization and identification of radioactive residues in transgenic soya bean samples following foliar application of [pyridine-3-¹⁴C]-imazapic

Components	Forage 0 DAT (mg/kg) (%)TRR)		Hay 15 DAT (mg/kg) (%)TRR)		Seeds 32 DAT* (mg/kg) (%)TRR)		Straw 49 DAT* (mg/kg) (%)TRR)		Pods 68 DAT* (mg/kg) (%)TRR)	
Imazapic	0.605	89.9	0.087	36.3	0.0030	20.0	0.013	14.8	0.004	8.9
CL189215	ND		0.006	2.5	0.0007	4.7	0.006	6.8	0.002	4.4
CL263284	ND		ND		0.0001	0.7	0.002	2.3	0.001	2.2
M5	ND		ND		0.0004	2.7	ND		0.002	4.4
M6	ND		0.004	1.7	0.0009	6.0	0.005	5.7	0.001	2.2
M18-19	ND		0.004	1.7	0.0001	0.7	0.007	8.0	0.003	6.7
M23	ND		ND		ND		0.005	5.7	ND	
M25-26	ND		0.008	3.3	0.0003	2.0	0.002	2.3	0.001	2.2
M35	ND		0.006	2.5	0.0003	2.0	ND		ND	
M36	ND		0.022	9.2	ND		0.009	10.2	ND	
M37	ND		0.004	1.7	ND		ND		ND	
M39-40	ND		0.0018	7.5	ND		0.006	6.8	0.001	2.2
M42	0.005	0.7	ND		ND		ND		ND	
M45-46	0.007	1.0	0.007	2.9	0.0007	4.7	0.004	4.5	0.001	2.2
M52	0.016	2.4	ND		ND		ND		ND	
M53/M63	0.023	3.4	ND		0.0003	2.0	ND		ND	
Total of the above	0.655	97.3	0.176	73.3	0.0102	68.0	0.057	64.8	0.023	51.1
Other characterized components at concentration 0.003 mg/kg	None		0.015	6.3	none		0.003	3.4	none	
Other characterized components at concentration ≤0.002mg/kg	None		0.026	10.8	0.003	20.0	0.014	15.9	0.013	28.9
Total identified and characterized	0.655	97.3	0.217	90.4	0.0133	88.7	0.074	84.1	0.037	80.0
Acidic methanol extraction	0.007	1.0	0.006	2.5	Included in the above		Included in the above		Included in the above	

* The extracts (methanol + aqueous + acidic) for these samples were combined and analysed by HPLC

ND = not detected

No phytotoxicity was observed in this study.

Despite extensive metabolism, imazapic was the main component in all soya bean matrices. The concentration of imazapic declined from 0.605 mg/kg in forage collected approximately 1 hour

after application to 0.087 mg/kg in the hay sample collected 35 days after application, and then to 0.013 mg/kg in the straw sample collected 97 days after application. Imazapic measured as a percentage of the TRR declined from 89.9% of the TRR in forage to 36.3% of the TRR in hay, and then to 14.8% of the TRR in straw. The imazapic concentration was 0.0030 mg/kg (20.0% of the TRR) in seed, and 0.004 mg/kg (8.9% of the TRR) in pods.

Proposed metabolic pathway of imazapic in plants

[¹⁴C]-Imazapic used for pre-emergence treatment of sugar cane plant or post-emergence treatment of peanut, Bermuda grass plants or transgenic soya bean, was rapidly metabolized over time with significant decline of imazapic concentration and increase of the concentrations of the 5-hydroxymethyl metabolite CL263284 and its glucoside CL189215. There were very low radioactive residues remaining in the soya bean seeds, peanut seeds and sugar cane stalks at the time of harvest. Except for Bermuda grass, the predominant residue was either imazapic, CL263284 or CL189215 with varying ratios. A number of more polar components were found from the extracts of soya bean and Bermuda grass matrices. Such polar components found from the Bermuda grass extracts include nicotinic acid derivatives, 5-hydroxymethylniconinamide derivative and 5-hydroxymethylquinolia acid anhydride, potentially oxidized from the hydroxymethyl metabolite.

Imazapic was very rapidly metabolized in plants by oxidative hydroxylation of the 5-methyl substituent to form a 5-hydroxymethyl metabolite CL263284. Subsequently, the hydroxymethyl metabolite was either rapidly conjugated with glucose to produce a prominent metabolite component CL 189215 or further metabolized to form more polar components.

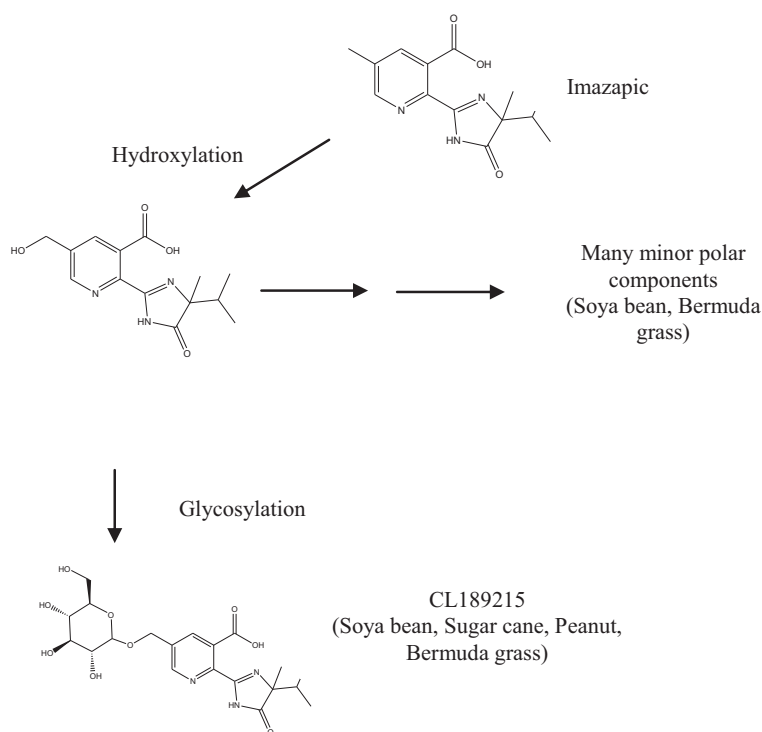


Figure 2 Proposed metabolic pathway of imazapic in plants

Environmental fate in soil

The Meeting received information on aerobic soil metabolism, photodegradation on soil, anaerobic aquatic metabolism, hydrolysis, photodegradation in water and residues in succeeding crops. Since imazapic is a herbicide with ground or aerial spray, aerobic degradation in soil, soil photolysis (some

included in the Physical and Chemical Properties Section), hydrolysis rate and products (included in the Physical and Chemical Properties Section) and rotational crop were relevant to the current evaluation.

Aerobic soil metabolism

The characteristics of soils used in the aerobic soil metabolism studies are summarized in Table 14.

Table 14 Characteristics of soils used in laboratory studies

Study reference	Location	Type	% Sand	% Silt	% Clay	Bulk Density (dry soil; g/cc)	CEC (MEQ/100g)	% Moisture at 1/3 bar	% Organic Matter	pH
Madsen, 1993 a	Princeton	Sandy Loam	60	30	10	1.26	8.2	17.2	1.3	5.2
Ta, 1997	Princeton	Sandy Loam	62	25	13	-	9.1	14.1	1.5	6.8 ^b
Ta, 1994b	Princeton	Sandy Loam	55	29	16	-	5.1	14.7	0.6	5.4 ^b

- = not reported

^a IA-620-003 and IA-630-001

^b pH in CaCl₂

Study 1 (Madsen, 1993a)

The aerobic soil metabolism of ¹⁴C-Imazapic was studied in Princeton sandy loam soil. [Pyridine-6-¹⁴C]-imazapic was dissolved in acetonitrile and applied to the soil at the rate equivalent to 0.14 kg/ha and kept under aerobic conditions in the dark. Water was added to the soil to bring the moisture of the soil to 75–80% of field capacity. At intervals of 0, 7, 14, 31, 62, 91, 122, 183, 274, and 365 days after soil treatment, the potassium hydroxide traps were analysed for ¹⁴CO₂ by LSC. At the same intervals, the ethylene glycol and sulphuric acid traps were assayed for the ¹⁴C-volatile materials.

The soil was extracted three times with 0.5N aqueous sodium hydroxide and the humic acid was removed by acid precipitation. The aqueous fulvic acid fraction was partitioned with methylene chloride. The humic acid fraction was rinsed with ethyl acetate and the rinse was combined with the methylene chloride partition. The methylene chloride partition was then poured through sodium sulfate. The sodium sulfate was then rinsed with methylene chloride. The extract was then evaporated to dryness. The residue was dissolved in methanol:water (1:1 v:v) and aliquots were analysed by LSC. The extracted soil was finally combusted to determine the bound residues. The solvent extractions were concentrated and analysed by HPLC.

After 12 months of incubation approximately 0.9% of the applied dose was mineralized to ¹⁴CO₂. No other radiolabelled volatile compounds were detected, which indicates that volatilization of the parent compound and other metabolites did not occur. Approximately 70.8% of the applied imazapic remained intact after 12 months. Carbon dioxide was the only major metabolite detected which derived from ¹⁴C-imazapic. No significant degradation of imazapic occurred during 12 months of incubation. The unextracted radioactivity varied from 1.8 to 8.0% of the total applied dose during the 365 days of incubation (Table 15).

Table 15 Material balance for aerobic soil metabolism of [pyridine-6-¹⁴C]-imazapic

DAT	% of Applied radioactivity									
	Total extracted	Soil extract I	Imazapic	Humic acid	Soil extract II	Imazapic	Unextracted residue	KOH	H ₂ SO ₄	Ethylene glycol
0	94.3	94.3	84.1	4.7	-	-	5.7	0.0	0.0	0.0
7	92.7	92.7	81.6	6.7	-	-	7.3	0.3	0.0	0.0
14	100.3	100.3	77.4	8.3	-	-	7.3	0.3	0.0	0.0
31	100.9	100.9	77.0	5.4	-	-	3.6	0.4	0.0	0.0
62	83.7	83.7	71.5	10.8	-	-	5.8	0.4	0.0	0.0

DAT	% of Applied radioactivity										
	Total extracted	Soil extract I	Imazapic	Humic acid	Soil extract II	Imazapic	Unextracted residue	KOH	H ₂ SO ₄	Ethylene glycol	Total
91	81.3	81.3	76.8	5.0	-	-	8.0	0.6	0.0	0.0	89.9
122	91.9	79.5	71.2	8.3	12.4	6.2	4.3	0.6	0.0	0.0	96.8
183	96.2	86.3	60.6	9.2	9.9	4.9	5.5	0.8	0.0	0.0	102.5
274	85.2	85.2	71.8	6.7	-	-	4.7	0.8	0.0	0.0	90.7
365	96.0	83.5	62.4	12.9	12.5	8.4	1.8	0.9	0.0	0.0	98.7
											Mean: 98.1

DAT=days after treatment

Imazapic was found to be very persistent in soil under an aerobic condition, with about 70% remaining after 1 year.

Study 2 (Ta, 1997a)

The aerobic soil metabolism of [pyridine-6-¹⁴C]-imazapic and its metabolites, CL263284, CL312622 and CL299263 was studied in Princeton Sassafras sandy loam soil. Each of the radiolabelled compounds listed above was dissolved in water and each solution was applied separately to the soil at the rate equivalent to 0.14 kg/ha and kept under aerobic conditions at 25 °C in the dark. Water was added to the soil to bring the moisture of the soil to 75% of 0.33 bar. At intervals of 0, 3, 7, 14, 21, 28, 60, 90 and 120 days after treatment with radiolabelled imazapic, CL 263284, CL 312622 and CL 299263, the sodium hydroxide traps were analysed for ¹⁴CO₂ by LSC. At the same intervals, the extracted foam plugs and ethylene glycol traps were assayed for the ¹⁴C-volatile materials. For each compound the soil was extracted three times with 0.5 N aqueous sodium hydroxide. The extracted radioactive residues was filtered through C-18 OH then eluted with methanol:water (1:1 v/v). The solvent was concentrated and analysed by HPLC and HPLC/MS. The extracted soil was combusted to determine the bound residues. No samples were taken at 3 and 7 days for CL 299263 and at 60 days for CL 312622. One sterile soil sample from each incubation group at 28 and 60 days after incubation were analysed as described above.

At 120 days after incubation under non-sterile conditions, approximately 11, 30, 43, and 41% of the applied dose was recovered as ¹⁴CO₂ from ¹⁴C-imazapic, CL 299263, CL 263284, and CL 312622, respectively (Table 16). No volatile compounds were detected in the glycol traps or in the foam plugs from any of the compounds tested. Under sterile conditions, no CO₂ or volatiles were detected in any traps. At 120 days after incubation under non-sterile condition approximately 81% of the parent was still present. Several metabolites less than 5%TAR such as CL 312622 (1.7%) and CL 354825 (4.1%) were also generated. Degradate CL 263284 was formed in a small amount but as data showed its instability, it was not included in the Table.

Approximately 80, 10, 0 and 4% of the applied dose of imazapic, CL 299263, CL 263284, and CL 312622, respectively, remained after 120 days. Under sterile conditions, the total recoveries of radioactivity ranged from approximately 92–95, 99–104, 99–104, and 86–90% of the applied dose of imazapic, CL 299263, CL 263284 and CL 312622, respectively.

Table 16 Material balance and ratio of degradates found in aerobic soil metabolism of [pyridine-6-¹⁴C]-imazapic and its metabolites.

% of Total Applied Radioactivity							
Treatment with ¹⁴ C-imazapic							
DAT	Imazapic	CL312622	CL354825	Others	CO ₂	Unextracted	Total
0	96.0	0.6	0.1	3.4	0.0	0.7	101
3	91.6	0.9	0.5	4.2	1.6	1.9	101
7	86.7	1.4	1.8	4.9	3.2	3.0	101
14	87.5	1.7	1.5	3.5	4.4	3.4	102
21	81.4	2.3	1.9	3.8	5.1	3.8	99
28	82.4	1.9	1.6	4.1	6.1	4.5	101
60	81.4	1.9	2.9	3.6	7.4	5.5	102
90	81.8	2.0	3.1	2.7	9.2	5.4	104
120	80.5	1.7	4.1	3.2	10.9	6.1	106

% of Total Applied Radioactivity							
Treatment with ¹⁴ C-imazapic							
DAT	Imazapic	CL312622	CL354825	Others	CO ₂	Unextracted	Total
Sterile							
28	88.8	0.6	0.0	2.8	0.0	2.7	95
60	84.3	1.5	0.6	2.4	0.0	3.1	92
Treatment with ¹⁴ C-CL299263							
DAT	CL299263	CL312622	CL354825	Others	CO ₂	Unextracted	Total
0	89.6	3.2	1.0	2.4	0.0	2.1	98
14	35.9	43.6	7.2	4.5	2.5	5.5	99
28	18.2	41.1	15.0	9.4	7.1	5.8	97
60	15.3	26.1	24.0	8.4	15.6	8.6	98
90	9.5	6.7	33.6	7.9	25.4	9.1	93
120	10.1	5.0	34.0	6.4	29.8	10.2	96
Sterile							
28	96.2	3.7	0.0	2.5	0.0	2.4	104
60	89.2	3.4	0.0	2.6	0.0	3.5	99
Treatment with ¹⁴ C-CL263284							
DAT	CL263284	CL312622	CL354825	Others	CO ₂	Unextracted	Total
0	87.0	7.7	0.2	3.6	0.0	0.9	99
3	0.8	88.0	1.0	5.4	1.6	1.8	99
7	0.9	82.2	3.3	6.5	3.2	2.4	99
14	0.0	77.2	5.8	6.2	4.9	3.4	98
21	0.0	65.7	10.5	9.2	7.9	4.0	97
28	0.0	60.5	12.6	9.5	9.7	5.4	98
60	0.0	31.0	24.7	16.4	21.2	7.3	101
90	0.0	10.5	30.2	13.6	32.2	7.8	95
120	0.0	6.8	31.7	12.9	42.8	8.0	102
Sterile							
28	88.6	4.9	0.0	7.6	0.0	2.7	104
60	82.8	5.4	0.0	7.6	0.0	3.4	99
Treatment with ¹⁴ C-CL312622							
DAT	CL312622	CL354825		Others	CO ₂	Unextracted	Total
0	98.5	0.7		3.7	0.0	1.1	104
3	93.1	1.5		3.8	0.4	1.7	101
7	88.7	5.0		2.5	1.9	2.7	101
14	75.9	7.7		3.8	4.5	3.8	96
28	57.6	15.1		5.9	10.0	6.0	95
90	14.9	35.3		7.6	29.5	9.7	97
120	3.6	37.9		6.9	40.6	9.4	99
Sterile							
28	89.0	0.0		0.0	0.0	1.0	91
60	78.8	0.0		0.0	6.2	1.0	87

DAT=days after treatment

The data were evaluated by plotting the remaining percentage of imazapic, CL299263, CL263284, and CL312622 versus time and the half-lives were estimated assuming a first order kinetic. The half-life of imazapic, CL 299263, CL 263284, and CL 312622 were 133, 12, < 0.5 and 36 days, respectively. For all four compounds studied the unextracted radioactivity varied from 0.7 to 10.2% of the total applied dose during the 120 days of incubation.

Under sterile conditions, all of the compounds tested remained intact after 2 months of incubation and there was no detectable level of evolved CO₂ trapped in NaOH. The results indicate that microbial activity is required for the degradation of imidazolinone herbicides in soil.

Photodegradation on soil surface

The soil photolysis of [pyridine-6-¹⁴C]-Imazapic was studied in Princeton Sassafras sandy loam soil (Ta, 1994b). The ¹⁴C-Imazapic was dissolved in water and applied to the soil at the equivalent rate of about 0.08 kg/ha and exposed continuously for up to 30 days by light from a xenon-arc lamp which had been filtered to remove wavelengths shorter than 290 nm. Control samples were maintained in the

dark. The temperature was maintained at 25°C during the course of the study. The output of the lamp was set to 0.35 w/m² at 340 nm, which is comparable to mid-autumn sunlight in Princeton, NJ, USA. At intervals of 0, 1, 3, 7, 14, 21 and 30 days after treatment of soil with ¹⁴C-imazapic the soil samples were extracted two times with 0.5 M aqueous sodium hydroxide. The NaOH extracts were combined and the pH was adjusted to 1.7 with HCl, and then filtrated through celite. The clear filtrates were then subjected to solid phase extraction using C18-OH three times with methanol followed by three washings with acidified (pH 1.7) Millipore water. The radioactivity was eluted from the cartridges with methanol/water (1/1 v/v). The extract was concentrated and analysed by TLC and HPLC. The soil were dried and then assayed by combustion to determine the bound residues.

A mass balance and the ratio of degradates at each sampling point is shown in Tables 17 and 18. One major product was formed, the diacid CL312622 which accounted for up to 11% of the applied dose. Several minor photoproducts formed, each of which accounted for less than 6.2% of applied dose. The control samples were stable, with less than 4% degradation, throughout the course of the study.

Table 17 Mass balance of photodegradation of imazapic

Days	% of Total Applied Dose					
	Irradiated Extracted	Unextracted	Total	Control Extracted	Unextracted	Total
0	100.8	0.5	101.2	100.8	0.5	101.2
1	97.0	2.3	99.2	98.6	0.9	99.4
3	94.8	3.2	98.0	101.6	1.3	102.8
7	93.0	2.7	95.7	95.6	1.5	97.0
14	90.7	3.2	93.9	94.5	1.8	96.3
21	92.1	3.0	95.2	96.7	2.7	99.3
30	90.2	3.3	93.5	94.9	2.8	97.7

Table 18 Ratio of photodegradation products

Days	% of Total Extract			
	Irradiated		Control	
	Imazapic	CL312622	Imazapic	CL312622
0	94.0	2.1	94.0	2.1
1	89.5	3.5	94.9	1.0
3	83.3	5.9	93.7	1.9
7	84.3	5.2	92.9	2.5
14	80.2	8.7	92.6	3.1
21	78.4	9.6	92.1	3.5
30	74.8	11.0	89.0	4.2

The decline of imazapic can be described by first-order kinetics. The half-life was calculated as 106 days.

Hydrolysis

[Pyridine-6-¹⁴C]-Imazapic was dissolved in acetonitrile and applied to the water + soil at a nominal rate of 0.125 µg/g soil (equivalent to about 0.14 kg/ha) and kept under anaerobic conditions with nitrogen gas in the dark at 25 °C (Madsen, 1993b). At intervals of 0, 7, 14, 31, 60, 91, 121, 182, 274 and 366 days after treatment, the potassium hydroxide traps were analysed for ¹⁴CO₂ by LSC. At the same intervals, the ethylene glycol and sulphuric acid traps were assayed for the ¹⁴C-volatile materials.

The analysis of the water was accomplished by centrifuging the samples and decanting the water. The entire water sample's pH was adjusted to approximately 1.7 with 6 N HCl then filtered through the C₁₈ cartridge. The C₁₈ cartridge was eluted with methanol:water (1:1 v:v). The concentrated samples were then analysed by LSC and HPLC-MS. The soil was extracted three times with 0.5 N aqueous sodium hydroxide and the humic acid was removed by acid precipitation. The aqueous fulvic acid fraction was partitioned with methylene chloride. The humic acid fraction was

rinsed with ethyl acetate and combining the rinse with the methylene chloride partition. The methylene chloride partition was then poured through sodium sulfate. The sodium sulfate was then rinsed with methylene chloride. The extract was then evaporated to dryness. The residue was dissolved in methanol:water (1:1, v:v) and aliquots were analysed by LSC. The extracted soil was finally combusted to determine the bound residues. The solvent extractions were concentrated and analysed by HPLC-MS.

After 366 days of anaerobic aquatic incubation, 0.5% of the applied dose was mineralized to $^{14}\text{CO}_2$. No other radiolabelled volatile compounds were collected. Volatilization of the parent compound and other metabolites did not occur. The measured concentration of imazapic decreased from 92.1% (35.7% in the soil extract and 56.4% in the water) at day 0 to 83.0% (54.3% in the soil extract and 28.7% in the water) of the applied dose after 366 days of incubation (Table 2.3/9). This indicates that imazapic is stable against hydrolysis.

Proposed degradation pathway of imazapic in soil under aerobic condition

Imazapic degrades in soil under aerobic conditions, leading to eventual mineralization. Three metabolites were identified as CL263284, CL312622 and CL354825. The rapid degradation of CL 299263 in soil under aerobic conditions proceeds via formation of the diacid metabolite, CL312622, the hydroxy acid, CL354825 and by mineralization to CO_2 . Degradation of imazapic, although much slower than that of CL 299263, gave the same metabolites, and ultimately CO_2 . It is concluded that the routes of degradation for the two imidazolinones proceed through common intermediates. Since the hydroxy methyl derivative, CL263284, was rapidly transformed in the same fashion, this is proposed as an intermediate in the metabolism of imazapic.

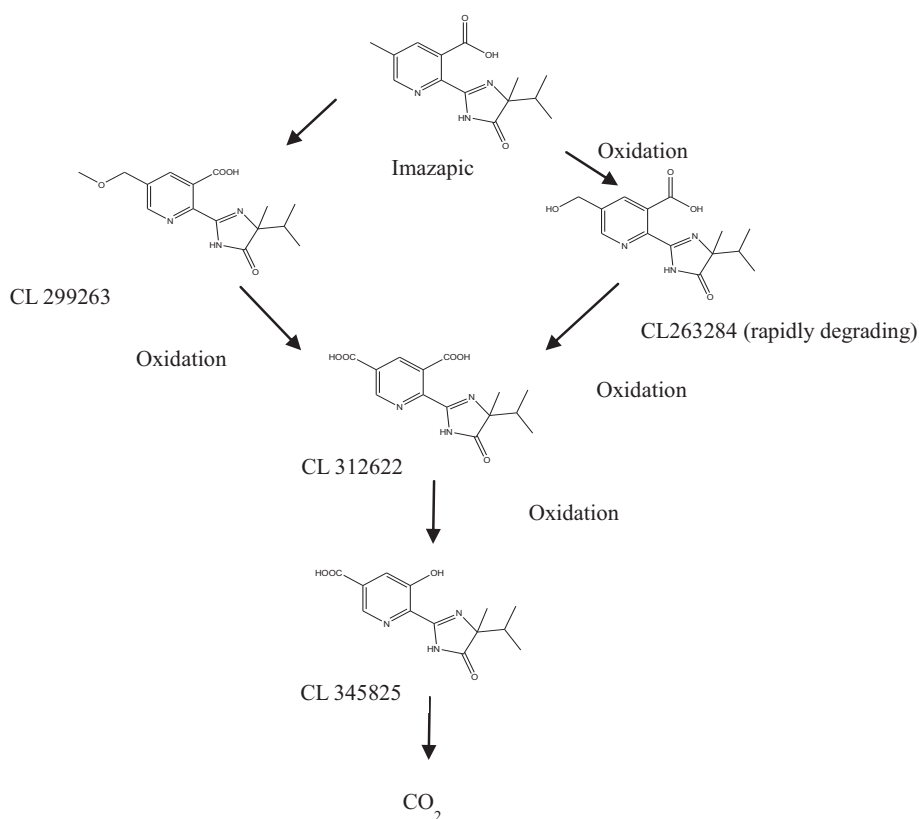


Figure 3 Proposed degradation pathway of imazapic in soil under aerobic condition

*Metabolism and Distribution in Succeeding Crops**Confined Rotational Crop Study*

The metabolism and distribution of imazapic in succeeding crops were investigated using [pyridine-6-¹⁴C]- or [pyridine-6-¹³C]-imazapic (Afzal, 1993a).

The field phase of the study was conducted in Madera California from July 1991 through December 1992. Three field plots (labelled A – C, 0.9 × 3.7 m, 0.9 × 5.5 m and 0.9 × 7.3 m, respectively) were treated with ¹⁴C-labelled imazapic at the rate equivalent to approximately 772 g ai/ha. Ninety days (90 Plant back interval (PBI)) and 120 days (120 PBI) after treatment, Plot A was planted with barley in subplots 1 and 2, respectively. At 270 days after treatment (270 PBI), Plot B was planted with barley, cotton and maize in subplots 1, 2 and 3, respectively. Similarly, 300 days after treatment (300 PBI), Plot C was planted with cotton, maize, lettuce and carrots in subplots 1 to 4, respectively. Three test plots D–F were used to grow the corresponding control crops. Soil core samples were taken prior to treatment, immediately following treatment, at planting and at crop sampling (mid-maturity and harvest). All cores were 46 cm deep except immediately after treatment where they were 30 cm.

Samples were frozen after collection and shipped to the analytical laboratory over dry ice. All unprocessed samples from the field were stored frozen (ca. -20 °C) until the time of analysis. All crops sampled at mid-maturity were composited for analysis on a whole plant basis except for carrots where only the root was composited. Samples taken at crop maturity were separated and the following crop parts were analysed: (a) barley straw and grain (removed from seed head); (b) cotton seed and linters (separated from seed); (c) maize fodder (dried stalk + cob + leaves + husks) and grain (removed from cob), (d) carrot root and (e) whole lettuce plants.

Fifty to 100 g of crop sample were homogenized with a mixture of high purity grade water:methanol:acetone (1:1:1). The sample to solvent ratio used for extraction was 1/10 (w/v). The supernatant was filtered through qualitative filter paper. The homogenization process was repeated once more and the supernatant was collected. The supernatants from the first and second extraction were pooled and triplicate aliquots were used for radioactivity measurement by LSC. Residual radioactive residues (PES) after drying were weighed and combusted in triplicate aliquots. The PES in barley straw (120 PBI and 270 PBI planting) and grain contained residues > 0.01 mg/kg. Therefore, they were digested with 2% HCl in MeOH:H₂O (80:20) overnight and homogenized twice with a polytron homogenizer using a tissue to solvent ratio of approximately 1/10 (w/v). The supernatants were pooled and triplicate aliquots were used for radioactivity measurement by LSC. The final residues were air-dried and combusted in triplicate aliquots to determine the amount of unextracted radioactivity.

Selected soil samples at application, planting and different crop sampling intervals containing radioactive residue of > 0.01 mg/kg were extracted twice for approximately 1 hour with water:methanol:acetone (1:1:1) using a mechanical shaker. Celite (30%) was added to aid filtration and the extracts were filtered and pooled. Triplicate aliquots were used for radioactivity measurement by LSC. The PES were air-dried and triplicate aliquots combusted. Soil samples containing residues > 0.01 mg/kg were subjected to mild acid hydrolysis with 2% HCl (80:20 MeOH:H₂O 1/10 w/v) using a mechanical shaker for 1 h. This procedure was repeated once, and the resulting supernatants were pooled and analysed in triplicates by LSC. The final residues were air-dried and combusted in triplicate aliquots.

HPLC of the soil and crop extracts was performed on a Supelco C₁₈ reversed phase column using an acetonitrile and phosphate buffer gradient system.

The TRR in all crop and soil samples were determined by combustion. A summary of the TRR values in rotational crop matrices collected at different plant back intervals is shown in Table 19 and those in soil samples in Table 20.

The TRR in barley and maize samples show the tendency to be higher in samples obtained from longer plant back interval. The TRR in crop samples were quite low with the highest in 270

DAT barley straw at 0.070 mg eq/kg. The TRR in edible portions of rotational crops were lower with the highest in 270 PBI barley grain at 0.045 mg eq/kg. The TRR in 270 PBI lettuce and carrots were < 0.01 mg eq/kg.

Table 19. TRR in rotational crop matrices after soil application of [pyridine-6-¹⁴C]-imazapic

Matrix	Plant back interval	TRR Determined by Direct Combustion (mg eq/kg)*
Barley plant	90	< 0.004
	120	0.009
	270	0.023
Barley straw	90	0.013
	120	0.056
	270	0.070
Barley grain	90	0.014
	120	0.030
	270	0.045
Maize forage	270	0.010
	300	0.016
Maize fodder	270	0.019
	300	0.028
Maize grain	270	0.007
	300	0.008
Cotton seed	270	0.017
	300	0.009
Cotton linters	270	0.015
	300	0.009
Lettuce	270	0.006
Carrots	270	< 0.004

* Expressed in mg-imazapic equivalents/kg.

Radioactive residues remained largely confined to the top 0–8 cm soil horizon throughout the course of the study. At 0 DAT, the TRR in soil of 0–8 cm depth ranged from 0.026 to 0.095 mg/kg while the TRR in deeper soil layers were mostly < 0.004 mg/kg. The TRR in soil of 0–8 cm depth declined to the range of < 0.04 to 0.078 mg/kg at the different plant back intervals.

Table 20 TRR in soil samples after soil application of [pyridine-6-¹⁴C]-imazapic

Days after Treatment	TRR Determined by Direct Combustion (mg eq/kg)* at Various Soil Depth			
	0-8 cm	8-30 cm	30-46 cm	46-61 cm
Plot A				
-1	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
0	0.057 / 0.029	< 0.004 / < 0.004	< 0.004 / < 0.004	na
90	0.044 / 0.078	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
120	0.023 / 0.019	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
244	0.019 / 0.008	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
262	0.021 / 0.027	0.006 / 0.010	0.005 / < 0.004	< 0.004 / < 0.004
297	0.010 / 0.013	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
308	0.015 / 0.032	0.007 / 0.013	0.004 / 0.005	< 0.004 / < 0.004
Plot B				
-1	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
0	0.065 / 0.095	< 0.004 / < 0.004	< 0.004 / < 0.004	Not analysed.
270	0.018 / 0.049	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004

Days after Treatment	TRR Determined by Direct Combustion (mg eq/kg)* at Various Soil Depth			
	0-8 cm	8-30 cm	30-46 cm	46-61 cm
332	0.015 / 0.012	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
332	0.012 / 0.013	< 0.004 / 0.007	< 0.004 / < 0.004	0.005 / < 0.004
364	< 0.004 / 0.012	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
399	0.009 / 0.016	0.004 / 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
406	0.009 / 0.007	0.005 / 0.005	< 0.004 / < 0.004	< 0.004 / < 0.004
493	0.012 / 0.019	0.006 / 0.010	0.006 / 0.009	< 0.004 / < 0.004
Plot C				
-1	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
0	0.026 / 0.046	< 0.004 / < 0.004	< 0.004 / < 0.004	Not analysed
300	0.006 / 0.025	< 0.004 / < 0.004	0.005 / < 0.004	0.007 / < 0.004
351	0.011 / 0.014	0.005 / 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
361	0.006 / 0.014	0.006 / 0.006	0.007 / 0.007	< 0.004 / < 0.004
364	0.015 / 0.010	0.007 / 0.008	< 0.004 / < 0.004	< 0.004 / < 0.004
374	0.005 / 0.005	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
375	0.009 / 0.012	0.005 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
436	0.008 / 0.008	< 0.004 / < 0.004	< 0.004 / < 0.004	< 0.004 / < 0.004
442	0.005 / 0.011	0.005 / 0.005	0.005 / < 0.004	< 0.004 / < 0.004
493	0.008 / 0.007	0.006 / < 0.004	0.005 / < 0.004	< 0.004 / < 0.004

* Expressed in mg-imazapic equivalents/kg.

The extraction profile of radioactive residues from rotational crop matrices is summarized in Table 21 and that from soil samples in Table 22.

The efficiency of extraction of radioactive residues in crop samples was 56.5–90.8% with a mixture of methanol:water:acetone (1:1:1). The unextracted portion of the TRR in selected crops was subjected to mild hydrolysis with 2% HCl in MeOH/H₂O (80:20) which released an additional 9–18% of the radioactivity. The remaining unextracted residues (PES) accounted for ≤ 0.01 mg/kg in all crops.

Table 21 Extracted radioactive residues from rotational crops after soil application of [pyridine-6-¹⁴C]-imazapic

Matrix	Plant back interval	TRR ^a (mg eq/kg)*	Solvent extract ^b (mg eq/kg)* (%TRR)		2% HCl ^c (mg eq/kg)* (%TRR)		PES (mg eq/kg)* (%TRR)	
Barley forage	90	< 0.004	No extraction attempted due to low TRR.					
	120	0.009	No extraction attempted due to low TRR.					
	270	0.023	0.018	79.2	-	-	0.005	20.8
Barley straw	90	0.013q	0.007	56.5	-	-	0.006	43.5
	120	0.056	0.041	72.4	0.005	8.92	0.010	18.7
	270	0.070	0.053	76.4	0.007	10.0	0.010	13.6
Barley grain	90	0.014	0.009	66.8	-	-	0.005	33.2
	120	0.030	0.023	75.2	-	-	0.007	24.8
	270	0.045	0.033	73.8	0.004	8.89	0.008	17.3
Maize forage	270	0.010	No extraction attempted due to low TRR.					
	300	0.016	0.015	90.8	-	-	0.001	9.2
Maize fodder	270	0.019	0.014	76.0	-	-	0.005	24.0
	300	0.028	0.018	63.5	0.005	17.9	0.005	18.6
Maize grain	270	0.007	No extraction attempted due to low TRR.					

Matrix	Plant back interval	TRR ^a (mg eq/kg)*	Solvent extract ^b (mg eq/kg)* (%TRR)		2% HCl ^c (mg eq/kg)* (%TRR)		PES (mg eq/kg)* (%TRR)	
	300	0.008	No extraction attempted due to low TRR.					
Cotton seed	270	0.017	0.013	74.0	-	-	0.004	26.0
	300	0.009	No extraction attempted due to low TRR.					
Cotton linters	270	0.015	0.011	70.5	-	-	0.004	29.5
	300	0.009	No extraction attempted due to low TRR.					
Lettuce	270	0.006	No extraction attempted due to low TRR.					
Carrots	270	< 0.004	No extraction attempted due to low TRR.					

PES = post extraction solid (after solvent extraction)

^a Sum of extracts and PES, if extraction was performed, otherwise TRR combusted. Expressed in mg-imazapic equivalents/kg

^b extracted with methanol:acetone:H₂O (1:1:1)

^c extracted with 2% HCl (methanol:H₂O, 80:20)

* Expressed in mg-imazapic equivalents/kg.

Extracted residues from soil using a mixture of methanol:water:acetone (1:1:1) declined with time from 83% of TRR (0.054 mg eq/kg) at 0 DAT to 38% of TRR (0.007 mg eq/kg) by the last harvest (493 DAT). Exhaustive extraction of soil PES in selected soil samples (90 DAT, 300 DAT and 308 DAT) showed that a majority (34–52% of TRR; 0.013–0.015 mg eq/kg) of the radioactivity was extracted following mild acid hydrolysis with 2% HCl in MeOH/H₂O (80:20). The low residues in soil PES (≤ 0.01 mg/kg) precluded further characterization.

Table 22 Extracted radioactive residues from soil samples after soil application of [pyridine-6-¹⁴C]-imazapic

Days after Treatment	Sampling Timing	TRR ^a (mg eq/kg)*	Solvent extract ^b (mg eq/kg)* (%TRR)		2% HCl ^c (mg eq/kg)* (%TRR)		PES (mg eq/kg)* (%TRR)	
0	Application	0.065	0.054	82.7	-	-	0.011	17.3
90	90 PBI Planting	0.044	0.023	52.1	0.015	34.1	0.006	13.8
120	120 PBI Planting	0.019	0.010	53.6	-	-	0.009	46.4
270	270 PBI Planting	0.018	0.005	28.2	-	-	0.013	71.8
297	90 PBI Planting Barley Harvest	0.013	0.007	50.4	-	-	0.006	49.6
300	300 PBI Planting	0.025	0.005	21.5	0.013	52.0	0.007	26.5
308	120 PBI Planting Barley Harvest	0.032	0.010	32.5	0.015	46.9	0.007	20.6
332	270 PBI Planting Barley Mid Harvest	0.015	0.007	47.8	-	-	0.008	52.2
364	300 PBI Planting Maize Mid Harvest	0.015	0.006	35.4	-	-	0.009	64.6
399	270 PBI Planting Barley Harvest	0.016	0.004	27.1	-	-	0.012	72.9
406	270 PBI Planting Maize Harvest	< 0.010	No extraction attempted due to low TRR.					
436	300 PBI Planting Carrot Harvest	< 0.010	No extraction attempted due to low TRR.					
442	300 PBI	0.010	No extraction attempted due to low TRR.					

Days after Treatment	Sampling Timing	TRR ^a (mg eq/kg)*	Solvent extract ^b		2% HCl ^c		PES	
			(mg eq/kg)*	(%TRR)	(mg eq/kg)*	(%TRR)	(mg eq/kg)*	(%TRR)
	Planting Maize Harvest							
493	270 PBI Planting Cotton Harvest	0.019	0.007	37.5			0.012	62.5
493	300 PBI Planting Cotton Harvest	< 0.010	No extraction attempted due to low TRR.					

PES = post extraction solid (after solvent extraction)

^a Sum of extracts and PES, if extraction was performed, otherwise TRR combusted. Expressed in mg-imazapic/kg.

^b extracted with methanol:acetone:H₂O (1:1:1)

^c extracted with 2% HCl (methanol:H₂O 80:20)

* Expressed in mg-imazapic equivalents/kg.

Structural characterization of imazapic in 0 DAT soil extract was performed by thermospray LC-MS. HPLC chromatograms obtained from crop sample extracts suggested the presence of CL 263284 and CL 189215 based on the retention time of reference compounds. The identity of CL 189215 was confirmed both by retention time comparison with a synthetic reference compound and -glucosidase hydrolysis. Because of the low concentrations of CL 189215 and CL 263284 (0.005-0.031 mg/kg combined) no spectroscopic identification was possible. All other components of the crop residues were < 0.01 mg/kg.

Imazapic was the principal component of the residue in all extracted soil fractions at all planting (49–74%; 0.012–0.048 mg eq/kg) and crop sampling intervals (16–49%; 0.003–0.005 mg eq/kg). The identity of the parent in soil was confirmed by mass spectrometry. Furthermore, the radioactivity released from the PES following hydrolysis with 2% HCl in MeOH/H₂O (80:20) indicated that a majority of the radiocarbon accounted for the unaltered parent. One polar unknown component was detected at all intervals, however, its concentration was in all cases < 0.01 mg/kg. All other radioactive components were < 5% of the TRR and were insignificant.

The extracted ¹⁴C-residues from crops were used to determine the metabolic profile of imazapic following HPLC analysis. The two major metabolites detected in crop extracts were the hydroxymethyl derivative of parent, CL 263284, and the corresponding glucoside, CL 189215. Since the two components were not completely resolved in either of the gradient HPLC methods, their concentrations in crop extracts are reported as a sum of the two components. Characterization of the residue components were performed on HPLC by comparing the retention time of each component with known reference compounds.

Barley straw: The unaltered parent imazapic was a minor component of TRR (< 10%) for 120 DAT and 270 DAT planting intervals. The two major radioactive components corresponded to CL 263284 and CL 189215, collectively accounting for 37 and 44% of TRR (0.021 and 0.031 mg /kg) for 120 PBI and 270 PBI, respectively. One minor component designated as a polar unknown metabolite was detected accounting for 2.7% and 4.2% of TRR (0.002 and 0.003 mg eq/kg) at the two planting intervals.

Barley grain: Imazapic was the major component of the TRR (23%; 0.007 mg/kg) for 120 PBI and depleted to 9.6% of the TRR (0.004 mg eq/kg) for 270 PBI. CL 263284 and CL 187215 collectively constituted 18% and 33% of the TRR (0.006 and 0.015 mg/kg) for 120 and 270 PBI, respectively. The minor polar unknown metabolite accounted for 1.5–4.2% of TRR (< 0.001–0.002 mg eq/kg) at the two intervals. The radiocarbon released from barley straw PES and grain PES after hydrolysis with 2% HCl in MeOH:H₂O (80:20) was not amenable to HPLC or TLC characterization.

Maize forage and fodder: The major components of the radioactive residue were CL 263284 and CL 189215. Collectively they accounted for 31% of the TRR (0.006 mg/kg) in fodder for 270 day

PBI; 28% of the TRR (0.005 mg/kg) in forage for 300 day PBI and 28% of the TRR (0.008 mg/kg) in fodder for 300 day PBI. The parent was a minor component accounting for 0.001 mg/kg or less in these samples. The polar metabolite in all cases was < 0.01 mg/kg.

Cotton: The major components of the organosoluble residue corresponded to CL 263284 and CL 189215. Imazapic constituted 23% (0.004 mg/kg) and 17% (0.003 mg/kg) of the TRR in cotton seed and linters for 270 PBI interval, respectively. The minor polar component was insignificant accounting for <10% (0.001 mg/kg) of the TRR in cotton seed and linters for the 270 PBI.

Lettuce and carrots planted 300 DAT showed no significant residues (0.006 and < 0.004 mg eq/kg), respectively.

The metabolites found in rotational crop matrices (barley and maize) are summarized in Table 23.

Table 23 Metabolites found in barley and maize matrices after soil application of [pyridine-6-¹⁴C]-imazapic

Barley												
Component	Straw (90 PBI)		Grain (90 PBI)		Straw (120 PBI)		Grain (120 PBI)		Straw (270 PBI)		Grain (270 PBI)	
	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)
Imazapic	Not analysed		Not analysed.		0.003	5.5	0.007	23	0.004	5.4	0.004	9.6
CL 189215 + CL 263284					0.021	37	0.006	18	0.031	44	0.015	33
Polar unknown					0.002	2.7	< 0.001	1.5	0.003	4.2	0.002	4.2
Maize												
Component	Forage (270 PBI)		Fodder (270 PBI)		Grain (270 PBI)		Forage (300 PBI)		Fodder (300 PBI)		Grain (300 PBI)	
	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)	(mg/kg)	(%TRR)
Imazapic	Not analysed		< 0.001	2.5	Not analysed		0.001	7.3	< 0.001	3.5	Not analysed	
CL 189215 + CL 263284			0.006	31			0.005	28	0.008	28		
Polar unknown			0.002	8.0			0.007	41	< 0.001	5.7		

While the major component in soil was imazapic, the principal components of the residue in barley, maize and cotton were CL 263284 and CL 189215, the hydroxymethyl derivative of imazapic and the corresponding glucose conjugate, respectively. The metabolic pathway in rotational crops is proposed to be the hydroxylation of the methyl group on the pyridine ring to the hydroxymethyl group followed by conjugation with glucose, similar to the metabolic pathway of most of plants.

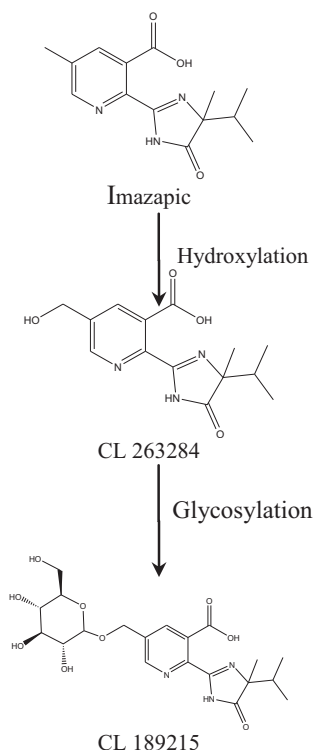


Figure 4 Proposed metabolic pathway in rotational crops (barley, maize)

RESIDUE ANALYSIS

Analytical methods

The Meeting received descriptions and validation data (including concurrent recovery data) for analytical methods for residues of imazapic and its metabolites CL263284 and CL189215.

Analytical methods for plant matrices

The descriptions of the analytical methods used in supervised residue trials are shown below.

All of these methods showed good linearity with a correlation coefficient ≥ 0.99 . There were no interferences at the analyte concentration higher than 30% of LOQ. Additional information on method performance is described later.

Method SOP-PA.0288

Analyte: Imazapic, CL263284 and CL189215
 Matrix: Sugar cane (cane, sugar, molasses) and soya bean (seed, oil, hull, flake, meal toasted meal)
 LOQ: 0.01 mg/kg for each analyte.
 Description: Residues are extracted from sugar cane or sugar using methanol:water:1M HCl (60:39:1, v/v/v) with shaking and centrifugation as necessary. and an aliquot is taken and diluted with 0.1% formic acid in water: 0.1% formic acid in methanol (50:50, v/v). Residues in molasses are extracted in the same manner and an aliquot is taken and diluted with 0.1% formic acid in water:0.1% formic acid in methanol (50:50, v/v).
 The final extracts are filtered and the determination is performed by LC-MS/MS (for quantification: imazapic, 276.2 $\rightarrow$ 231.2; CL263284, 292.2 $\rightarrow$ 247.3; CL189215, 454.2 $\rightarrow$ 292.4 and for confirmation: imazapic, 276.2 $\rightarrow$ 163.2; CL263284, 292.2 $\rightarrow$ 179.1;

CL189215, 454.2 → 179.1). Mobile phase solution A, 0.1% formic acid in water; and mobile phase solution B, 1% formic acid in methanol (same for other HPLC separation).
 Reference: Leite, 2008a; Leite and Souza, 2009a; Resende and Takahashi, 2010a;

Method SOP-PA.0249

Analyte: Imazapic
 Matrix: Rice grain and soya bean (seed)
 LOQ: 0.05 mg/kg
 Description: Residues are extracted from samples using methanol:water:1M HCl (60:39:1, v/v/v) in a homogenizer. An aliquot is taken, the volume reduced and diluted with water. The pH is adjusted to 2.1 with 1 M HCl solution. An aliquot is partitioned with dichloromethane. An aliquot of the organic phase is evaporated to dryness and the residue dissolved with 0.1% formic acid in water:0.1% formic acid in methanol (50:50, v/v). The determination is performed by LC-MS/MS (for quantification: imazapic, 276.2 → 231.2; CL263284, 292.2 → 247.3; CL189215, 454.2 → 292.4 and for confirmation: imazapic, 276.2 → 163.2; CL263284, 292.2 → 179.1; CL189215, 454.2 → 179.1).
 Reference: Borges, 2003a; Leite, 2005a; Borges, 2004a; Borges, 2004b; Borges, 2004c

Method LAADL R0001.01

Analyte: Imazapic
 Matrix: Maize (grain)
 LOQ: 0.1 mg/kg
 Description: Imazapic is extracted from maize with acidic aqueous methanol using an ultrasonic extractor. The analyte is partitioned with methylene chloride from aqueous acid solution. The methylene chloride is evaporated and reconstituted in 50% methanol in pH 2.5 water for cation exchange clean-up. Imazapic is eluted with a saturated KCl in methanol solution, partitioned with methylene chloride, evaporated to dryness and diluted in Milli-Q water for HPLC analysis. The final determination is performed by HPLC-UV with UV detection at 254 nm.
 Reference: Steling, 1998a

Method SOP-PA.0231

Analyte: Imazapic and CL263284
 Matrix: Rice (grain)
 LOQ: 0.05 mg/kg for each analyte.
 Description: Based on method R0001.01. Residues of imazapic are extracted with methanol:water:1M HCl (60:39:1, v/v/v) and the solution is filtered over Celite. The extract is concentrated, and after addition of lead acetate and water, the pH is adjusted to 6.2 with NaOH. Following centrifugation and addition of water, the pH is adjusted to 2.1 with HCl. The solution is solvent-extracted with dichloromethane, and the dichloromethane phase is evaporated to dryness. The residue is dissolved in a solution of methanol:water (1:1, v/v) and cleaned up with an SCX cartridge rinsed with methanol. The residue is eluted from the cartridge with KCl-saturated methanol, evaporated to dryness and dissolved in water at pH 2.5. The solution is again solvent-extracted with dichloromethane, the dichloromethane phase evaporated to dryness and the residue dissolved in water. The final analysis is performed with HPLC with UV detection at 254 nm.
 Reference: Dantas C., 2003a; Steling C., 2001a; Steling C., 2001b; Steling C., 2001c;

Method M2253.01

Analyte: Imazapic and CL263284
 Matrix: Wheat (grain, forage, stubble), chickpea (seed, forage), barley (grain, forage), peanut (nutmeat, hull)
 LOQ: 0.1 mg/kg for each analyte.
 Description: Residues of imazapic and CL263,284 are extracted from the sample in acetone:methanol:water (1:1:1). Organic layers are removed and samples are centrifuged after addition of 10% lead acetate. The aqueous sample is then cleaned up, using resin AG 1-X8 anion exchange, partitioning with methylene chloride and subsequent benzene sulfonic acid (SCX) cation exchange solid phase extraction (SPE). Determination is performed by HPLC with UV detection and external standards.

Reference: Minoura, 1995a; Minoura, 1995b; Minoura, 1995c; Minoura, 1995d; Minoura, 1995e; Minoura, 1995f; Minoura, 1995g; Nejad H., 1993a; Nejad and Cenni, 1997b

Method M3114

Analyte: Imazapic, CL263284 and CL189215
Matrix: Bermuda grass (forage, hay), big bluestem grass (forage, hay), grass mixture (forage, hay)
LOQ: 0.5 mg/kg for each analyte.
Description: Residues are extracted from grass samples with methanol:water:1 M HCl (60:39:1, v/v/v). The extract is cleaned up, using precipitation, centrifugation and solid phase extraction techniques. Determination is performed by capillary electrophoresis equipped with a high sensitivity cell and UV detection at 240 nm and external standards
Reference: Duan and Nejad, 1999a; Nejad, 1999a

Method M2599

Analyte: Imazapic, CL263284 and CL189215
Matrix: Peanut (hay)
LOQ: 0.1 mg/kg for each analyte.
Description: Residues are extracted from the sample with methanol:water:1 M HCl (60:39:1, v/v/v). The extract is then cleaned up, using precipitation, centrifugation and solid phase extraction techniques. Determination is performed by capillary electrophoresis equipped with a high sensitivity cell and UV detection at 240 nm and external standards.
Reference: Nejad H., 1998a

Method L741/1

Analyte: Imazapic
Matrix: Rape (seed, foliage, straw)
LOQ: 0.05 mg/kg for each analyte.
Description: The extract is partitioned with dichloromethane after adjusting the pH to 2 with HCl. Subsequently, the extract is evaporated to dryness and the residue dissolved in methanol/water (1:1, v/v). Following SCX cartridge clean-up, separation and quantification of imazapic is accomplished by reverse phase HPLC with UV detection at 254 nm.
Reference: Anonymous, 1998a

Method M2379

Analyte: Imazapic, CL263284 and CL189215
Matrix: Peanut (nutmeat, hull)
LOQ: 0.1 mg/kg for each analyte.
Description: Residues are extracted from samples using methanol:water: 1M HCl (60:39:1, v/v/v). The extract is then cleaned up, using precipitation, centrifugation and solid phase extraction techniques. Determination is performed by capillary electrophoresis equipped with a high sensitivity cell and UV detection at 240 nm and external standards.
Reference: Nejad H., 1995a; Nejad H., 1994a; Nejad H., 1994b; Safarpour M., 1994a

Method 2463

Analyte: Imazapic, CL263284 and CL189215
Matrix: Wheat (grain, forage, straw, hay)
LOQ: 0.1 mg/kg for each analyte.
Description: Residues are extracted from samples using methanol:water: 1M HCl (60:39:1, v/v/v) in a homogenizer. An aliquot is taken and diluted with 0.1% formic acid in water: 0.1% formic acid in methanol (50:50, v/v). The final extracts are filtered and the determination is performed by LC-MS/MS (for quantification: imazapic, 276.2 → 231.2; CL263284, 292.2 → 247.3; CL189215, 454.2 → 292.4 and for confirmation: imazapic, 276.2 → 163.2; CL263284, 292.2 → 179.1; CL189215, 454.2 → 179.1).
Reference: Nejad and Cenni, 1995a; Nejad and Cenni, 1996a

Method SOP-PA.0288

The recoveries from sugar cane matrices or soya bean matrices (fortification range, 0.01-1.0 mg/kg) were within the acceptable range for all fortification levels and matrices tested (Table 25). Good linearity was observed in the range of 0.100 to 2.00 ng/mL for sugar cane matrices and 0.020 to 2.00 ng/mL for soya bean matrices. The repeatability relative standard deviations for all commodities and all fortification levels were below 15%.

Table 25 Recovery results obtained for the analysis of sugar cane matrices and soya bean matrices with Method SOP-PA.0288

Matrix	Analyte	No.	Fortification Level (mg/kg)	Transition 1* for quantification			Transition 2** for confirmation		
				Mean (%)	SD (%)	RSD (%)	Mean (%)	SD (%)	RSD (%)
Sugar cane matrices									
Sugar cane	Imazapic	5	0.01	108	4.5	4.1	108	4.5	4.1
		5	0.10	90	4.8	5.3	95	11	12
		5	1.0	104	5.5	5.3	104	5.5	5.3
	CL263284	5	0.01	108	4.5	4.1	108	4.5	4.1
		5	0.10	91	3.7	4.1	99	1.3	1.4
		5	1.0	110	0.0	0.0	106	5.5	5.2
	CL189215	5	0.01	102	8.0	7.8	99	7.2	7.3
		5	0.10	95	10	11	95	4.3	4.6
		5	1.0	108	4.5	4.1	106	5.5	5.2
Sugar	Imazapic	5	0.01	102	4.5	4.4	97	9.0	9.3
		5	0.10	98	4.5	4.6	101	9.3	9.3
		5	1.0	92	6.8	7.4	90	4.1	4.6
	CL263284	5	0.01	97	13	13	101	7.1	6.9
		5	0.10	94	3.5	3.7	95	4.9	5.2
		5	1.0	101	6.1	6.0	101	5.8	5.7
	CL189215	5	0.01	90	13	14	92	6.1	6.6
		5	0.10	92	4.5	4.9	89	6.0	6.7
		5	1.0	89	6.2	7.0	88	5.1	5.7
Molasses	Imazapic	5	0.01	102	4.5	4.4	100	6.7	6.7
		5	0.10	94	4.3	4.6	91	1.3	1.4
		5	1.0	98	1.9	1.9	97	1.9	2.0
	CL263284	5	0.01	97	10	10	94	10	11
		5	0.10	84	3.0	3.6	85	4.5	5.3
		5	1.0	100	0.0	0.0	100	0.0	0.0
	CL189215	5	0.01	99	6.9	6.9	89	4.8	5.3
		5	0.10	87	6.4	7.3	91	3.5	3.9
		5	1.0	97	3.4	3.5	103	6.4	6.2
Soya bean matrices									
Seeds	Imazapic	5	0.01	96	4	5	94	7	7
		5	1.0	93	1	1	93	1	1
	CL263284	5	0.01	102	5	5	85	4	5
		5	1.0	100	2	2	100	2	2
	CL189215	5	0.01	88	4	4	-	-	-
		5	1.0	102	2	2	-	-	-
Oil	Imazapic	5	0.01	92	4	5	101	5	5
		5	1.0	101	2	2	100	3	3
	CL263284	5	0.01	83	2	2	82	2	2
		5	1.0	95	3	3	93	5	5
	CL189215	5	0.01	93	3	3	90	8	9
		5	1.0	101	9	9	96	8	8
Flaked soya bean	Imazapic	5	0.01	103	5	4	101	3	3
		5	1.0	97	3	3	99	4	4
	CL263284	5	0.01	112	4	4	102	5	5
		5	1.0	102	3	3	100	4	4

Matrix	Analyte	No.	Fortification Level (mg/kg)	Transition 1* for quantification			Transition 2** for confirmation		
				Mean (%)	SD (%)	RSD (%)	Mean (%)	SD (%)	RSD (%)
Meal	CL189215	5	0.01	106	2	1	85	7	8
		5	1.0	99	4	4	98	3	3
	Imazapic	5	0.01	94	4	4	99	5	5
		5	1.0	92	3	4	92	3	4
	CL263284	5	0.01	100	8	8	75	4	5
		5	1.0	82	1	1	82	5	6
Toasted meal	CL189215	5	0.01	108	8	7	-	-	-
		5	1.0	84	4	5	-	-	-
	Imazapic	5	0.01	97	9	9	107	7	7
		5	1.0	85	3	4	85	4	4
	CL263284	5	0.01	89	10	12	95	8	9
		5	1.0	76	3	4	76	2	3
	CL189215	5	0.01	105	5	5	-	-	-
		5	1.0	77	3	4	-	-	-

* imazapic: 276 → 231; CL263284: 292 → 247; CL189215: 454 → 292

** imazapic: 276 → 163; CL263284: 292 → 179; CL189215: 454 → 179

An independent laboratory validation of Method SOP-PA.0288 was conducted for the determination of imazapic, CL 263284 and CL 189215 in sugar cane matrices (Grosshans, 2009b) and soya bean matrices (Robaugh, 2012a). Fortification levels used are 0.01 and 0.1 mg/kg for sugar cane matrices (Table 26) and 0.01 and 0.5 mg/kg for soya bean matrices (Table 27).

The recoveries were within the acceptable range for all fortification levels and matrices tested. Good linearity was observed in the range of 0.100 to 2.00 ng/mL for sugar cane matrices and 5.00 to 200 ng/g for soya bean matrices. The repeatability relative standard deviations for all sugar cane matrices at all fortification levels were below 20% using matrix-matched standards, except for metabolite CL189215 in molasses at a fortification level of 0.01 mg/kg, where the RSD was 25%; and those for all soya bean matrices were below 30% a fortification level of 0.01 mg/kg and below 10% at the other fortification levels, using matrix-matched standards.

Table 26 Recovery results obtained during independent laboratory validation of Method SOP-PA.0288 for sugar cane matrices

Matrix	Analyte	No.	Fortification Level (mg/kg)	Transition 1* for quantification			Transition 2** for confirmation		
				Mean (%)	SD (%)	RSD (%)	Mean (%)	SD (%)	RSD (%)
1 st set of analysis									
Sugar cane	Imazapic	5	0.01	83	6.7	8.1	87	11	12
		5	0.10	81	1.8	2.2	82	1.8	2.2
	CL263284	5	0.01	30	1.2	3.9	31	2.2	7.0
		5	0.10	44	1.8	4.2	44	1.5	3.5
	CL189215	5	0.01	63	8.6	14	54	11	21
		5	0.10	62	2.2	3.6	60	2.3	3.8
Sugar	Imazapic	5	0.01	90	3.9	4.4	87	3.1	3.6
		5	0.10	93	2.4	2.6	96	1.4	1.5
	CL263284	5	0.01	47	1.6	3.4	47	2.6	5.5
		5	0.10	71	0.8	1.2	70	1.7	2.4
	CL189215	5	0.01	89	3.3	3.7	82	7.4	9.0
		5	0.10	104	2.8	2.7	104	2.9	2.8
Molasses	Imazapic	5	0.01	57	6.8	12	48	9.3	19
		5	0.10	70	1.7	2.5	71	0.7	0.9
	CL263284	5	0.01	28	1.3	4.8	26	5.1	20
		5	0.10	40	1.0	2.4	39	0.7	1.7

Matrix	Analyte	No.	Fortification Level (mg/kg)	Transition 1* for quantification			Transition 2** for confirmation		
				Mean (%)	SD (%)	RSD (%)	Mean (%)	SD (%)	RSD (%)
	CL189215	5	0.01	- ^a	- ^a	- ^a	45	23	51
		5	0.10	53	13	24	46	4.5	9.7
2 nd set of analysis using matrix-matched standards									
Sugar cane	Imazapic	5	0.01	105	5.5	5.3	108	3.8	3.5
		5	0.10	90	1.9	2.2	90	4.2	4.7
	CL263284	5	0.01	109	3.9	3.6	109	2.5	2.3
		5	0.10	100	2.6	2.6	99	1.6	1.6
	CL189215	5	0.01	105	11	10	91	5.6	6.2
		5	0.10	103	3.1	3.1	105	4.5	4.3
Sugar	Imazapic	5	0.01	105	3.4	3.2	106	2.0	1.9
		5	0.10	98	1.9	2.0	100	3.2	3.2
	CL263284	5	0.01	103	3.6	3.5	103	2.1	2.0
		5	0.10	101	2.2	2.2	100	3.1	3.1
	CL189215	5	0.01	106	12	11	106	4.5	4.3
		5	0.10	103	2.3	2.3	101	1.4	1.4
Molasses	Imazapic	5	0.01	115	4.3	3.8	111	3.8	3.4
		5	0.10	93	1.6	1.8	92	3.6	3.9
	CL263284	5	0.01	115	3.8	3.3	113	11	10
		5	0.10	92	1.8	1.9	94	1.8	1.9
	CL189215	5	0.01	106	27	25	117	17	15
		5	0.10	102	5.0	4.9	92	5.9	6.5

* imazapic: 276 → 231; CL263284: 292 → 247; CL189215: 454 → 292; used for quantification

** imazapic: 276 → 163; CL263284: 292 → 179; CL189215: 454 → 179; used for confirmation

^a due to low sensitivity, no peaks above 3 fold signal to noise ratio detectable

Table 27 Recovery results obtained during independent laboratory validation of Method SOP-PA.0288 for soya bean matrices

Matrix	Analyte	No.	Fortification Level (mg/kg)	Transition 1* for quantification		
				Mean (%)	SD (%)	RSD (%)
Seed	Imazapic	5	0.01	90	10	11
		5	0.5	93	5	5
	CL263284	5	0.01	91	14	16
		5	0.5	90	4	4
	CL189215	5	0.01	80	15	19
		5	0.5	91	7	7
Oil	Imazapic	5	0.01	99	3	3
		5	0.1	109	1	3
	CL263284	5	0.01	98	5	5
		5	0.1	89	5	6
	CL189215	5	0.01	114	5	4
		5	0.1	110	2	2
Hulls	Imazapic	8	0.01	78	11	14
		5	2.0	99	4	4
	CL263284	8	0.01	92	19	21
		5	2.0	93	6	6
	CL189215	5	0.01	83	4	5
		5	2.0	85	3	3

* imazapic: 276 → 231; CL263284: 292 → 247; CL189215: 454 → 292

Method SOP-PA.0249

The recoveries from rice grain (Borges, 2004a, c) and in soya bean seed (Borges, 2004a, c) at fortification levels of 0.05 and 5.0 mg/kg were within the acceptable range (Tables 28 and 29). Good linearity was observed in the range of 0.500 to 10.0 ng/mL for rice grain and soya bean seed. The repeatability relative standard deviations for all commodities and all fortification levels were below 10%.

Table 28 Recovery results obtained for the analysis of imazapic in rice grain with Method SOP-PA.0249

Matrix	Analyte	No.	Fortification Level (mg/kg)	Transition 1* for quantification			Transition 2** for confirmation		
				Mean (%)	SD (%)	RSD (%)	Mean (%)	SD (%)	RSD (%)
Grain	Imazapic	15	0.05	94	4.7	5.0	94	5.0	5.4
		15	5.0	105	6.6	6.3	105	6.8	6.5

* imazapic: 276.0 → 231.0

** imazapic: 276.0 → 163.0

Table 29 Recovery results obtained or the analysis of imazapic in rice grain with Method SOP-PA.0249

Matrix	Analyte	No.	Fortification Level (mg/kg)	Transition 1* for quantification			Transition 2** for confirmation		
				Mean (%)	SD (%)	RSD (%)	Mean (%)	SD (%)	RSD (%)
Seed	Imazapic	5	0.05	95	3.6	3.8	95	3.3	3.5
		5	5.0	96	6.5	6.8	97	5.9	6.1

* imazapic: 276.0 → 231.0

** imazapic: 276.0 → 163.0

Method LAADL R0001.01

Although the method was not subjected to formal validation, the method showed recoveries of 92 and 96% (n=1) at the fortification levels of 0.1 and 0.2 mg/kg.

Method SOP-PA.0231

The recoveries of imazapic from rice grain at fortification levels of 0.05 and 0.5 mg/kg were within the acceptable range (Table 30). Good linearity was observed in the range of 5.0 to 100 ng/mL (2003/3001442) or 5.0 to 50 ng/mL (2001/3001704, -05 and -06). The repeatability relative standard deviations for all fortification levels were below 15%.

Table 30 Recovery results obtained for analysis of imazapic in rice grain with Method SOP-PA.0231

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)
Grain (2003/3001442)	Imazapic	2	0.05	96
		2	0.50	93
Grain (2001/3001704) (2001/3001705) (2001/3001706)	Imazapic	2	0.05	94
		2	0.51	88

Method 2253.01

The recoveries of imazapic and CL263284 from chick-pea matrices (Minoura, 1995b and 1995e), barley matrices (Minoura, 1995c and 1995f), wheat matrices (Minoura, 1995a, 1995d and 1995g), and

peanut matrices (Nejad, 1993a)(Table 31) at fortification levels from 0.10 to 0.50 mg/kg (wheat stubble up to 5.0 mg/kg) were all within the acceptable range (Table 31).

Table 31 Recovery results obtained for analysis of imazapic and CL 263284 in various plant matrices with Method 2253.01

Matrix		Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Crop	Portion						
Chickpea	Seed	Imazapic	2	0.10	84		
			2	0.50	74		
		Total	4	0.10-0.50	79	5.9	7.4
		CL263284	2	0.10	75		
			2	0.50	69		
		Total	4	0.10-0.50	72	3.5	4.9
	Forage	Imazapic	2	0.10	72		
			2	0.50	69		
		Total	4	0.10-0.50	70	1.8	2.6
		CL263284	2	0.10	82		
			2	0.50	73		
		Total	4	0.10-0.50	77	5.8	7.5
Wheat	Grain	Imazapic	2	0.10	74		
			2	0.50	90		
		Total	4	0.10-0.50	82	9.5	12
		CL263284	2	0.10	69		
			2	0.50	85		
		Total	4	0.10-0.50	77	9.5	12
	Forage	Imazapic	2	0.10	103		
			2	0.50	87		
		Total	4	0.10-0.50	95	11	12
		CL263284	2	0.10	90		
			2	0.50	82		
		Total	4	0.10-0.50	86	8.5	9.9
	Stubble	Imazapic	2	0.10	93		
			2	0.50	98		
			2	1.0	100		
			2	5.0	94		
		Total	8	0.10-5.0	96	4.3	4.5
		CL263284	2	0.10	78		
			2	0.50	79		
			2	1.0	95		
			2	5.0	91		
		Total	8	0.10-5.0	86	7.9	9.3
Barley	Grain	Imazapic	2	0.10	80		
			2	0.50	86		
		Total	4	0.10-0.50	83	5.5	6.6
		CL263284	2	0.10	73		
			2	0.50	83		
		Total	4	0.10-0.50	78	6.4	8.3
	Forage	Imazapic	2	0.10	87		
			2	0.50	103		
		Total	4	0.10-0.50	95	9.5	10
		CL263284	2	0.10	92		
			2	0.50	78		
		Total	4	0.10-0.50	85	12	14

Matrix		Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Crop	Portion						
Peanut	Nutmeat	Imazapic	3	0.10	85	8.9	10
			3	0.50	82	11	13
			3	1.0	85	6.4	7.5
			3	5.0	83	7.7	9.2
		CL263284	3	0.10	79	2.8	3.5
			3	0.50	86	5.5	6.4
			3	1.0	82	4.9	6.0
			3	5.0	83	5.4	6.5
	Hull	Imazapic	3	0.10	78	3.2	4.1
			3	0.50	85	4.3	5.0
			3	1.0	70	2.8	4.0
			3	5.0	76	3.5	4.5
		CL263284	3	0.10	110	11	10
			3	0.50	98	9.8	10
			3	1.0	87	2.9	3.4
			3	5.0	87	4.9	5.6

An independent laboratory validation of Method M 2253.01 was conducted for the determination of imazapic and CL 263284 in peanut hull and peanut meat at fortification levels of 0.10 and 0.50 mg/kg (Nejad and Cenni, 1997b)(Table 32). The recoveries were within the acceptable range for all fortification levels. The repeatability relative standard deviations for both commodities over all fortification levels were below 20%.

Table 32 Recovery results obtained during independent laboratory validation of Method M2253.01 for peanut matrices

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Peanut hull	Imazapic	2	0.10	100		
		2	0.50	93		
	Total	4	0.10-0.50	97	10	10
	CL263284	2	0.10	100		
		2	0.50	85		
	Total	4	0.10-0.50	92	10.0	10
Peanut meat	Imazapic	2	0.10	86		
		2	0.50	76		
	Total	4	0.10-0.50	81	9.1	11
	CL263284	2	0.10	89		
		2	0.50	89		
	Total	4	0.10-0.50	89	2.4	2.7

Method M3114

An independent laboratory validation of Method M 3114 was conducted for the determination of imazapic, CL 263284 and CL 189215 in grass at fortification levels of 0.50–50 mg/kg (Duan and Nejad, 1999a)(Table 32).

The recoveries of these analytes from grass matrices were within the acceptable range. The repeatability standard deviations were below 15%.

Table 32 Recovery results obtained during independent laboratory validation of Method M3114 for grass matrices

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Bermuda grass forage	Imazapic	2	0.50	85		
		2	1.0	80		
		2	50	87		
	Total	6	0.50-50	84	4.9	5.8
	CL263284	2	0.50	87		
		2	1.0	84		
		2	50	90		
	Total	6	0.50-50	87	5.2	6.0
	CL189215	2	0.50	89		
		2	1.0	84		
		2	50	90		
	Total	6	0.50-50	87	4.3	4.9
Bermuda grass hay	Imazapic	2	0.50	76		
		2	1.0	81		
		2	50	65		
	Total	6	0.50-50	74	8.1	11
	CL263284	2	0.50	78		
		2	1.0	84		
		2	50	68		
	Total	6	0.50-50	76	8.4	11
	CL189215	2	0.50	78		
		2	1.0	85		
		2	50	65		
	Total	6	0.50-50	76	10	14
Big Bluestem grass forage	Imazapic	2	0.50	80		
		2	1.0	84		
		2	50	73		
	Total	6	0.50-50	79	5.6	7.1
	CL263284	2	0.50	77		
		2	1.0	83		
		2	50	71		
	Total	6	0.50-50	77	6.1	8.0
	CL189215	2	0.50	81		
		2	1.0	85		
		2	50	74		
	Total	6	0.50-50	80	5.8	7.2
Big Bluestem grass hay	Imazapic	2	0.50	73		
		2	1.0	73		
		2	50	71		
	Total	6	0.50-50	72	2.0	2.8
	CL263284	2	0.50	69		
		2	1.0	84		
		2	50	72		
	Total	6	0.50-50	75	7.0	9.4
	CL189215	2	0.50	71		
		2	1.0	84		
		2	50	72		
	Total	6	0.50-50	76	6.7	8.9
Grass mixture forage	Imazapic	2	0.50	77		
		2	1.0	91		
		2	50	84		
	Total	6	0.50-50	84	7.4	8.9
	CL263284	2	0.50	82		
		2	1.0	93		
		2	50	91		
	Total	6	0.50-50	89	6.0	6.8

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
	CL189215	2	0.50	80		
		2	1.0	93		
		2	50	84		
	Total	6	0.50-50	85	6.9	8.1
Grass mixture hay	Imazapic	2	0.50	84		
		2	1.0	78		
		2	50	77		
	Total	6	0.50-50	80	5.0	6.3
	CL263284	2	0.50	84		
		2	1.0	77		
		2	50	76		
	Total	6	0.50-50	79	5.9	7.5
	CL189215	2	0.50	90		
		2	1.0	83		
		2	50	83		
	Total	6	0.50-50	85	5.5	6.5

Method M2599

An independent laboratory validation of Method M 3114 was conducted for the determination of imazapic, CL 263284 and CL 189215 in peanut hay at fortification levels of 0.10–0.40 mg/kg (Duan and Nejad, 1998a)(Table 33). The recoveries were within the acceptable range. The repeatability standard deviations were below 15%.

Table 33 Recovery results obtained during independent laboratory validation of Method M2599 for peanut hay

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Peanut hay	Imazapic	2	0.10	73		
		2	0.20	72		
		2	0.40	73		
	Total	6	0.10-0.40	73	4.9	6.8
	CL263284	2	0.10	82		
		2	0.20	81		
		2	0.40	84		
	Total	6	0.10-0.40	82	3.4	4.2
	CL189215	2	0.10	76		
		2	0.20	72		
		2	0.40	75		
	Total	6	0.10-0.40	74	3.8	5.2

Method L 741/1

The recoveries of imazapic from rape matrices at fortification levels of 0.05 and 0.5 mg/kg were within the acceptable range (Table 34). Good linearity was observed in the range of 0.5 to 100 ng/mL. The repeatability relative standard deviations for all fortification levels were below 15%.

Table 34 Recovery results obtained for analysis of imazapic in rape seed matrices with Method L 741/1

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Foliage Straw Grain	Imazapic	2	0.05	92		
		2	0.5	81		
	Total	4	0.05-0.5	86	8	10

M 2379

The recoveries of imazapic and CL263284 from peanut matrices at fortification levels from 0.10 to 0.50 mg/kg were within the acceptable range (Table 35). The repeatability standard deviations were below 15%.

Table 35 Recovery results obtained for analysis of imazapic, CL263284 and CL189215 in peanut matrices with Method M 2379

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Peanut meat	Imazapic	2	0.10	80		
		2	0.20	83		
		2	0.50	90		
	Total	6	0.10-0.50	90	4.4	4.9
	CL263284	2	0.10	93		
		2	0.20	89		
		2	0.50	93		
	Total	6	0.10-0.50	93	6.7	7.2
	CL189215	2	0.10	75		
		2	0.20	75		
		2	0.50	84		
	Total	6	0.10-0.50	83	7.1	8.5
Peanut hull	Imazapic	2	0.10	91		
		2	0.20	91		
		2	0.50	89		
	Total	6	0.10-0.50	84	6.5	7.8
	CL263284	2	0.10	99		
		2	0.20	91		
		2	0.50	89		
	Total	6	0.10-0.50	91	4.1	4.5
	CL189215	2	0.10	87		
		2	0.20	84		
		2	0.50	79		
	Total	6	0.10-0.50	78	4.7	6.0

The extraction efficiency was investigated using peanut hay obtained 131 days after the treatment of plants with ^{14}C -labelled imazapic (Nejad, 1994b). Two separate samples of peanut hulls containing ^{14}C -residues were extracted with methanol:water:1N hydrochloric acid (60:39:1, v/v/v). Triplicate 30 mL aliquots from the control and each of the ^{14}C -treated sample extracts were evaporated and peanut residue was dissolved in a total of 5 mL methanol, sonicated and centrifuged. Triplicate 0.5 mL of each subsample were combusted using an oxidizer and subjected to liquid scintillation counting (LSC). Aliquots of approximately 250 mg of unextracted peanut hulls from control and treated plants were also combusted and subjected to LSC.

The average percentage of extracted radioactive residues were 73% (range 71–76%) compared with the radioassay result.

An independent laboratory validation of Method M 2379 was conducted for the determination of imazapic, CL 263284 and CL 189215 in peanut matrices at fortification levels of 0.10–0.50 mg/kg (Safarpour, 1994a)(Table 36). The recoveries were within the acceptable range. The repeatability standard deviations were below 20%.

Table 36 Recovery results obtained during independent laboratory validation of Method M 2379 for peanut matrices

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Peanut meat	Imazapic	2	0.10	89		
		2	0.20	88		
		2	0.50	85		
	Total	6	0.10-0.50	87	8.1	9.3
	CL263284	2	0.10	89		
		2	0.20	98		
		2	0.50	96		
	Total	6	0.10-0.50	94	6.1	6.5
	CL189215	2	0.10	74		
		2	0.20	68		
		2	0.50	80		
	Total	6	0.10-0.50	73	11.5	16
Peanut hull	Imazapic	2	0.10	77		
		2	0.20	102		
		2	0.50	92		
	Total	6	0.10-0.50	90	11.3	13
	CL263284	2	0.10	77		
		2	0.20	105		
		2	0.50	95		
	Total	6	0.10-0.50	92	13.1	14
	CL189215	2	0.10	60		
		2	0.20	77		
		2	0.50	76		
	Total	6	0.10-0.50	71	8.7	12

Method M 2463

An independent laboratory validation of Method M 2463 was conducted for the determination of imazapic, CL 263284 and CL 189215 in wheat matrices at fortification levels of 0.10–0.50 mg/kg (Nejad and Cenni, 1995a)(Table 37). The recoveries were within the acceptable range. The repeatability standard deviations were below 15%.

Table 37 Recovery results obtained during independent laboratory validation of Method M 2463 for wheat matrices

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Straw	Imazapic	2	0.10	95		
		2	0.20	86		
		2	0.50	92		
	Total	6	0.10-0.50	91	7	8
	CL263284	2	0.10	91		
		2	0.20	87		
		2	0.50	97		
	Total	6	0.10-0.50	91	6	7

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Hay	CL189215	2	0.10	77		
		2	0.20	75		
		2	0.50	80		
	Total	6	0.10-0.50	77	4	5
	Imazapic	2	0.10	80		
		2	0.20	81		
		2	0.50	82		
	Total	6	0.10-0.50	81	10	13
	CL263284	2	0.10	81		
		2	0.20	84		
		2	0.50	86		
Forage	CL263284	2	0.10	81		
		2	0.20	84		
		2	0.50	86		
	Total	6	0.10-0.50	84	10	11
	CL189215	2	0.10	81		
		2	0.20	81		
		2	0.50	80		
	Total	6	0.10-0.50	80	4	5
	Imazapic	2	0.10	74		
		2	0.20	86		
		2	0.50	88		
Grain	Imazapic	2	0.10	74		
		2	0.20	86		
		2	0.50	88		
	Total	6	0.10-0.50	82	8	9
	CL263284	2	0.10	75		
		2	0.20	89		
		2	0.50	91		
	Total	6	0.10-0.50	85	8	9
	CL189215	2	0.10	76		
		2	0.20	88		
		2	0.50	86		
Grain	Imazapic	2	0.10	85		
		2	0.20	85		
		2	0.50	89		
	Total	6	0.10-0.50	86	3	4
	CL263284	2	0.10	81		
		2	0.20	83		
		2	0.50	90		
	Total	6	0.10-0.50	84	4	5
	CL189215	2	0.10	80		
		2	0.20	83		
		2	0.50	82		
	Total	6	0.10-0.50	82	2	2

The extraction efficiency was investigated using barley straw from the confined rotational crop study (Nejad and Cenni, 1996a). Two separate samples of barley straw containing ^{14}C -residues were extracted with methanol:water:1N hydrochloric acid (60:39:1, v/v/v). Duplicate 3 mL aliquots from the control and each of the ^{14}C -containing sample extracts were assayed by LSC. The post-extraction solids were collected and combusted and also subjected to LSC.

The average percentage of extracted radioactive residues was 67% compared with the radioassay results.

Analytical methods for animal matrices

The descriptions of the analytical methods related to the current review are shown below.

All of these methods showed good linearity with a correlation coefficient ≥ 0.99 . There were no interferences at the analyte concentration higher than 30% of LOQ. Additional information on method performance is described later.

Method M 3188

Analyte: Imazapic and CL263284
 Matrix: Milks
 LOQ: 0.01 mg/kg for each analyte.
 Description: Residues are extracted from the sample with acidic water. Precipitation, centrifugation and solid phase extraction (SPE) techniques are used for sample clean-up. Measurement of imazapic and CL263284 is accomplished by capillary electrophoresis (CE) equipped with a high sensitivity flow cell and a UV detector set at 240 nm. Results are calculated as imazapic and CL 263284 by the direct comparison of the peak heights in the sample to those of external standards. Confirmation of residues > 0.01 mg/kg for each compound is provided by LC/MS of the final extract.
 Reference: Sweeney and Nejad, 1998a

Method M 3222

Analyte: Imazapic and CL263284
 Matrix: Tissues
 LOQ: 0.05 mg/kg for each analyte.
 Description: Residues are extracted from the sample with acidic methanol water. Precipitation, centrifugation and solid phase extraction (SPE) techniques are used for sample clean-up. Measurement of imazapic and CL 263284 is accomplished by capillary electrophoresis (CE) equipped with a high sensitivity flow cell and a UV detector set at 240 nm. Results are calculated as imazapic and CL 263284 by the direct comparison of the peak heights in the sample to those of external standards.
 Reference: Sweeney and Nejad, 1998b

Method M 3223

Analyte: Imazapic and CL263284
 Matrix: Milk fat and tissue fat
 LOQ: 0.01 mg/kg in milk and 0.05 mg/kg in tissue fat for each analyte.
 Description: Residues are extracted from bovine milk fat and tissue fat with acidic acetonitrile in hexane. Filtration, solvent partitioning and solid phase extraction (SPE) techniques are used for sample clean-up. Measurement of imazapic and CL263284 is accomplished by HPLC/MS (positive ion electrospray ionization tandem mass spectrometry). Results are calculated as imazapic and CL263284 by the direct comparison of the peak area in the sample to those of external standards.
 Reference: Boner and Nejad, 1999a

M 3188

An independent laboratory validation of Method M 3188 was conducted for the determination of imazapic and CL 263284 in cattle milk at fortification levels of 0.01–1.0 mg/kg (Sweeney and Nejad, 1998a)(Table 38). The recoveries were within the acceptable range. The repeatability standard deviations were below 15%.

Table 38 Recovery results obtained during independent laboratory validation of Method M 3188 for milk

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Bovine milk	Imazapic	2	0.01	89		
		3	0.02	95		
		2	1.0	91		
	Total	7	0.01-1.0	92	3	4

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
	CL 263284	2	0.01	87		
		3	0.02	92		
		2	1.0	91		
	Total	7	0.01-1.0	90	3	3

M 3222

An independent laboratory validation of Method M 3222 was conducted for the determination of imazapic and CL 263284 in cattle tissues at fortification levels of 0.5–1.0 mg/kg (Sweeney and Nejad, 1998a)(Table 39). The recoveries were within the acceptable range. The repeatability standard deviations were below 15%.

Table 39 Recovery results obtained during independent laboratory validation of Method M 222 for tissues

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Bovine muscle	Imazapic	2	0.05	74		
		2	0.10	74		
		2	1.0	81		
	Total	6	0.05-1.0	76	4	5
	CL263284	2	0.05	89		
		2	0.10	77		
		2	1.0	77		
	Total	6	0.05-1.0	81	6	8
Bovine kidney	Imazapic	3	0.05	79	1	1
		2	0.10	79		
		2	1.0	85		
	Total	7	0.05-1.0	81	5	6
	CL263284	3	0.05	88	7	8
		2	0.10	81		
		2	1.0	84		
	Total	7	0.05-1.0	85	6	7
Bovine liver	Imazapic	2	0.05	79		
		2	0.10	83		
		2	1.00	82		
	Total	6	0.05-1.00	81	2	3
	CL263284	2	0.05	78		
		2	0.10	83		
		2	1.0	78		
	Total	6	0.05-1.0	80	4	4

The extraction efficiency was investigated using goat milk and kidney from metabolism study (Nejad, 1999b). Two separate samples each of treated milk and kidney tissue containing ^{14}C -residues were analysed for imazapic and CL 263284 by Method M 3188 (milk) and M 3222 (kidney) respectively. With both methods, quantification of residues is made by capillary electrophoresis and UV detection. For milk samples, triplicate 1 mL aliquots of extracted and unextracted milk were assayed by using LSC. For the kidney samples, prior to extraction, the samples were combusted to determine total radioactive residue (TRR). The respective extracts were counted for determination of extraction efficiency.

The extraction procedure used in method M 3188 (milk) yielded a total extractability of 94% for milk (based on total ^{14}C recovery) using 22.1 mL of a 6 N HCl:water:10% lead acetate (0.1:20:2, v/v/v) extraction.

The extraction procedure used in method M 3222 (kidney) yielded a total extractability of 88% in kidney (based on total carbon-14 recovery) using 150 mL of an HCl:water:methanol (1.5:58.5:90, v/v/v) extraction and a 5-minute extraction time.

CE analysis of the treated milk indicated an average of 0.060 mg/kg imazapic compared to 0.051 mg/kg using HPLC radioassay. CE analysis of the treated kidney indicated an average of 0.271 mg/kg imazapic compared to 0.234 mg/kg using HPLC radioassay. No detectable residues for CL 263284 were found in milk or kidney.

M 3223

An independent laboratory validation of Method M 3223 was conducted for the determination of imazapic and CL 263284 in milk fat and tissue fat at fortification levels of 0.01–0.2 or 0.05–1.0 mg/kg respectively (Sweeney and Nejad, 1998a)(Table 40). The recoveries were within the acceptable range. The repeatability standard deviations were below 15%.

Table 40 Recovery results obtained during independent laboratory validation of Method M 3223 for fat

Matrix	Analyte	No.	Fortification Level (mg/kg)	Mean (%)	SD (%)	RSD (%)
Bovine milk fat	Imazapic	2	0.01	106		
		2	0.02	102		
		2	0.20	104		
	Total	6	0.01-0.20	104	8	8
	CL263284	2	0.01	100		
		2	0.02	104		
		2	0.20	92		
	Total	6	0.01-0.20	99	11	11
Bovine tissue fat	Imazapic	2	0.05	91		
		2	0.10	94		
		2	1.00	104		
	Total	6	0.05-1.00	96	12	12
	CL263284	2	0.05	100		
		2	0.10	88		
		2	1.00	97		
	Total	6	0.05-1.00	95	8	8

Stability of pesticide residues in stored analytical samples

The Meeting received information on freezer storage stability of imazapic and two of its metabolites in various plant and animal commodities.

Frozen samples were homogenized and fortified with test compound. The fortified homogenate was stored in deep freezer. After each specified period, a portion of sample was analysed for test compound. The stability results are expressed as average percentage of the nominal fortification and are not corrected for the procedural recoveries. In order to account for possible variations over the time investigated, the mean procedural recovery results are given in addition.

Table 41 summarized the storage conditions, storage periods and percent remaining after each period

Table 41 Stability of imazapic in frozen plant matrices

Matrix.	Storage period (month)	Imazapic % remaining	Procedural recovery	CL 263284 % remaining	Procedural recovery	CL 189215 % remaining	Procedural recovery
Soya bean matrices fortified at 0.1 mg/kg, stored at <-20 °C and analysed with Method SOP-PA.0288 (Leite, Alves, 2011a)							
Seed	0	105	-	107	-	107	-
	1	101	103	101	103	102	108
	2	100	97	92	99	93	106
	3	93	91	104	103	105	107
	7	69	81	75	89	97	103
	10	134	148	111	123	124	124
Laminated bean	0	93	-	95	-	90	-
	1	94	104	98	108	95	111
	3	93	95	93	104	88	89
Defatted meal	0	94	-	101	-	92	-
	1	102	110	105	107	107	126
	3	90	93	107	97	97	100
Toasted Defatted meal	0	103	-	101	-	98	-
	1	115	101	105	107	111	126
	3	93	99	107	97	100	90
Oil	0	110	-	111	-	106	-
	1	95	92	86	102	83	100
	3	109	104	100	110	108	116
Wheat matrices fortified at 0.5 mg/kg, stored at <-10 °C and analysed with Method M 2463 (Nejad H., 1999a)							
Grain	14	91	90	91	91	83	90
	18	89	108	102	104	82	98
	24	102	100	112	106	85	103
Straw	14	87	88	92	91	79	78
	18	86	93	93	98	80	89
	24	92	87	92	92	87	77
Hay	14	84	90	82	92	83	92
	18	74	92	75	89	77	95
	24	92	103	84	108	88	108
Forage	14	85	88	79	89	79	85
	18	86	90	97	87	84	95
	24	71	85	70	87	71	90
Sugar cane matrices fortified at 0.1 mg/kg, stored at ≤-20 °C and analysed with Method SOP-PA.0288 (Leite and Goncalves, 2010a)							
Cane	0 d	101	-	108	-		
	31 d	84	89	97	91		
	62 d	84	93	97	97		
	91 d	89	92	96	94		
	185 d	80	85	74	79		
	276 d	72	84	73	75		
	367 d	85	95	100	93		
	731 d	70	86	74	89		
Peanut matrices fortified at 1 mg/kg, stored at -25 to -5°C Method M 2379 (nutmeat & hull) or M 2599 (hay) (Nutmeat and hull: Nejad and Xu, 2000a)(Hay: Nejad and Xu, 2000b)							
Nutmeat	1	84	96	87	98	80	87
	5	81	86	83	92	84	91
	6	74	81	76	85	76	86
	12	70	89	75	93	78	96
	18	71	81	62	84	66	83
	24	80	78	85	81	82	77
Hull	1	89	79	87	78	81	78
	5	111	101	122	113	84	79
	6	84	90	86	88	97	96
	12	74	83	81	84	84	86
	18	83	82	68	85	74	85
	24	80	95	83	93	83	96

Matrix.	Storage period (month)	Imazapic % remaining	Procedural recovery	CL 263284 % remaining	Procedural recovery	CL 189215 % remaining	Procedural recovery
Hay	0	81	77	110	87	100	83
	3	73	84	83	88	82	83
	6	61	86	84	93	78	90
	12	53	77	68	85	63	81
	18	64	92	80	100	74	98
	24	75	87	103	96	100	96

Table 42 Stability of imazapic in frozen animal matrices

Matrix	Storage period (month)	Imazapic % remaining	Procedural recovery	CL 263284 % remaining	Procedural recovery
Cattle milk fortified at 1 mg/kg, stored frozen (no information on the temperature) and analysed with Method M 3188 (Naumann and Nejad, 1999a)					
Cattle milk	1	89	87	87	88
	3	95	97	95	97
	6	88	90	92	90
Cattle tissues fortified at 1 mg/kg, stored frozen (no information on the temperature) and analysed with Method M 3222 (Sweeney and Nejad, 1999a)					
Muscle	1	84	84	66	72
	3	78	83	80	76
	5	80	80	82	78
	8	79	79	75	77
Kidney	1	85	87	75	82
	3	87	90	83	86
	5	86	90	85	93
	8	77	82	76	78
Liver	1	81	80	78	72
	3	82	88	82	86
	5	79	82	89	81
	8	78	77	81	76

The stability of imazapic and its metabolites CL 263,284 and CL 189,215 was also investigated in standard calibration solutions diluted in 0.1% formic acid in water: 1% formic acid in methanol (1:1, v/v) and stored at 5±3 °C in the dark. The standard solutions contained 0.400 ng/mL per analyte. After 32 days, fresh standard calibration solutions were diluted by the above solution mixture, and the results obtained for the stored standard solutions were compared to the results obtained for the fresh standard solutions.

The storage stability of standard calibration solutions containing imazapic and its metabolites in 0.1% formic acid in water: 1% formic acid in methanol (1:1, v/v) was demonstrated for a period of 32 days when stored at 5±3 °C in the dark.

USE PATTERNS

Imazapic is used to control broad leaf and grassy weeds. It is formulated as a liquid or granular product either as a solo product or in combination with other active substances for use on pulses, cereal grains, grasses for sugar, oilseeds, and straw, forage and fodder of cereal grains. It is registered in a number of countries for crops with pre-emergence and post emergence applications.

The authorized uses relevant to the supervised trials data submitted to the current Meeting is summarized in Table 43.

Table 43 Registered use of imazapic relevant to the residue evaluation by the current Meeting

Country	Formulation Type and g/kg or g/l (Other ai)	F, G, or P	Application				Application rate per treatment		PHI days
			Method	No. per crop and season	Interval days	Timing	Water L/ha	Max Rate kg ai/ha	
Cereal grains: Maize									
Brazil	WG 525* (imazapyr)	F	Ground spraying	1	nr	Post emergence	100-250	0.0525	96
Brazil	WG 525* (imazapyr)	F	Aerial spraying	1	nr	Post emergence	40-50	0.0525	96
Cereal grains: Rice									
Brazil	SL 25* (imazapyr)	F	Ground spraying	1-2	14-21	Post emergence between 4 leaves and 1 tiller of rice	100-250	0.025	60
Brazil	SL 25* (imazapyr)	F	Aerial spraying	1-2	14-21	Post emergence between 4 leaves and 1 tiller of rice	40-50	0.025	60
Brazil	WG 175* (imazapyr)	F	Ground spraying	1-2	-	Post emergence between 2 leaves and 1 tiller of rice	100-200	0.0245	60
Brazil	WG 175* (imazapyr)	F	Aerial spraying	1-2	-	Post emergence between 2 leaves and 1 tiller of rice	40-50	0.0245	60
Cereal grains: Wheat									
Australia	WG 525* (imazapyr)	F	spraying	1	nr	Post emergence 2 to 6 leaf stage	70	0.011	nr
Australia	EC 22* (imazapyr)	F	spraying	1	nr	Post emergence 4 leaf (Z14) to flag leaf (Z37)	50	0.021	nr
Grasses for sugar or syrup production: Sugar cane									
Argentina	WG 700	F	spraying	1	nr	30–45 days before planting	100-150	0.35	392
Australia	SL 240	F	spraying	1	nr	After planting before emergence of cane	200	0.096	nr
Brazil	WG 700	F	spraying	1	nr	30-45 days before planting	200-250	0.245	283
Costa Rica	WG 700	F	spraying	1	nr	Within first 10 days of planting Pre-emergence to weed	250-300	0.175	85
Guatemala	WG 700	F	spraying	1	nr	Within first 10 days of planting Pre-emergence to weed	250-300	0.175	85
Oilseeds: Peanut									
Brazil	WG 700	F	spraying	1	nr	30-45 days before planting	200-250	0.098	70
USA	SL 240	F	spraying	1	nr	Early post emergence	47-94	0.067	90
USA	WG 700	F	spraying	1	nr	Early post emergence	min. 94	0.071	90
Oilseeds: Rape seed									
Australia	WG 525* (imazapyr)	F	spraying	1	nr	Early post emergence 2-6 leaf stage	70	0.0288	nr
Straw, fodder and forage of cereal grains and grasses, except grasses for sugar production (including buckwheat fodder): Bermuda grass, brome grass blue grass, wheat grass, pasture, rangeland, etc.									
USA	SL 240	F	spraying	1	nr	Post emergence (spring & summer, 100% green-up; winter, dormant or full green-up)	18.7-94	0.22	-

nr: not required when used as directed.

* for imidazolinone-tolerant varieties only

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received residue data from supervised field trials conducted on soya bean (including GM soya bean) in Brazil, maize in Brazil, rice in Brazil, wheat in Australia, sugar cane in Argentina, Australia, Brazil, Costa Rica and Guatemala, Peanut in Brazil and the USA, rape seed in Australia and grasses (animal feedstuffs) in the USA.

Application rates and residue concentrations were reported as imazapic. Residue concentrations are recorded unadjusted for recoveries or for residue values in control samples. Where multiple samples were taken from a single plot, individual results are reported, and the calculated average concentration is used for estimation of maximum residue level. Where trials were conducted

in the same location, with the same or similar varieties, same or similar formulations, and same equipment, and at the same or similar timing, they are not regarded as independent and only one result from these trials was chosen for the estimation of a maximum residue level.

Residues from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels and they are underlined.

In many of the following trials, plants resistant to imidazolinone pesticides were used. They are classified into two different categories. The first category is non-GM plants (maize, rape seed, rice, wheat) showing the tolerance due to the mutation(s) of endogenous AHAS gene from conventional breeding technique. and their variety names have "CL" in them. The second category is GM plants (so far soya bean only) to which mutated AHAS gene of Arabidopsis was introduced for imidazolinone tolerance.

Crop Group	Commodity	Table No.
Pulses	Soya beans	Table 44
Cereal grains	Maize	Table 45
	Rice	Table 46
	Wheat	Table 47
Grasses, for sugar or syrup production	Sugar cane	Table 48
Oilseed	Peanut	Table 49
	Rape seed	Table 50
Legume animal feed	Peanut hay	Table 51
Straw, fodder and forage of cereal grains and grasses (including buckwheat fodder)(straws and fodders dry)	Wheat straw and fodder, dry	Table 52
	Hay or fodder (dry) of grasses	Table 53
Miscellaneous fodder and forage crops	Rape seed forage	Table 54

Pulses

Soya beans

During the 2006/2007 growing season, eight field trials were carried out in Brazil to determine the residues levels of imazapic in soya bean after treatment with a WG mix formulation of imazapic and imazapyr. In all trial sites, one trial plot was untreated to provide control samples, and one trial plot received one post-emergence application at a rate of 0.0175 kg imazapic/ha (and 0.0525 kg imazapyr/ha), 60 days before harvest (BBCH 24–75). In three trials, the application was performed 40, 60, 80, 100 and 120 days before harvest, each on a separate plot. Samples were taken 60 days after the application (DALA) in all trials; but in three trials, additional samplings were performed 40, 80, 100 and 120 DALA. The soya bean samples were stored frozen until analysis. Soya bean samples were analysed for imazapic using Method SOP-PA.0249. The limit of quantification was 0.05 mg/kg.

During the 2007/2008 growing season, a field trial was carried out in Brazil to determine the residues levels of imazapic in soya bean after treatment with a mix formulation of imazapic and imazapyr. One trial plot was untreated to provide control samples, and one trial plot received one foliar post-emergence spray application at a rate of 0.0175 kg imazapic/ha (and 0.0525 kg imazapyr/ha), either 40, 60, 80, 100 or 120 days before harvest. Samples were taken 40, 60, 80, 100 or 120 days after the application. The soya bean samples were analysed for imazapic and the two metabolites using Method SOP-PA.0288. The limit of quantification was 0.01 mg/kg for each analyte.

During the 2010 growing season, two field trials were carried out in Brazil to determine the residues levels of imazapic in soya bean after treatment with a mix formulation of imazapic and imazapyr. At both trial sites, one trial plot was untreated to provide control samples, and four trial plots received one foliar post-emergence spray application at a rate of 0.0175 kg imazapic/ha (and 0.0525 kg imazapyr/ha), 20, 40, 60 or 80 days before harvest. Samples of soya bean grain were taken 20, 40, 60 and 80 days after the application. Soya bean samples were analysed for residues using Method SOP-PA.0288.

During the 2011 growing season, five field trials were carried out in Brazil to determine the residues levels of imazapic in transgenic soya bean after treatment with a mix formulation of imazapic and imazapyr. At all trial sites, one trial plot was untreated to provide control samples, and one trial plot received one post-emergence application at a rate of 0.0175 kg imazapic/ha (and 0.0525 kg imazapyr/ha), 60 days before harvest (BBCH 66–73). At one trial with five plots, the application was performed 20, 40, 60, 80 and 100 days before harvest. Samples of soya bean grain were taken 60 days after the application (DALA) at all trials; at one trial, additional samplings were performed 20, 40, 80 and 100 DALA, and at one trial aspirated grain fractions were also sampled. Soya bean samples were analysed for residues using Method SOP-PA.0288.

Table 44 Residues of imazapic in imidazolinone-tolerant soya beans from supervised trials conducted in Brazil

Report-No. Location (trial no.) (Variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
GAP in Brazil	Ground spray	0.014- 0.018	1	PHI 60						
	Aerial spray	0.014- 0.018	1	PHI 60						
2008/1097470 Uberaba Minas Gerais, BRA (EC-CD-BRVA/ 1088-06) (CV 603)	n.r.	0.0175	1 04.03.07 13.02.07 23.01.07 03.01.07 14.12.06	40 60 80 100 120	grain grain grain grain grain	0.19 0.23 < 0.05 < 0.05 < 0.05	na na na na na	na na na na na		
2008/1097470 Santo Antonio de Posse Sao Paulo, BRA (EC-CD-BRUA/ 1088-06) (CV 603)	n.r.	0.0175	1 19.02.07 30.01.07 10.01.07 21.12.06 01.12.06	40 60 80 100 120	grain grain grain grain grain	0.08 < 0.05 < 0.05 < 0.05 < 0.05	na na na na na	na na na na na		
2008/1097470 Brasilia Distrito Federal do Brasil, (BRA) (EC-R-BRUC/ 1088-06) (CV 603)	n.r.	0.0175	1 09.02.07	60	grain	0.10	na	na		
2008/1097470 Santo Antonio de Goias Goias, BRA (EC-R-BRUB/ 1088-06) (CV 603)	n.r.	0.0175	1 05.02.07	60	grain	0.15	na	na		
2008/1097470 Uberaba Minas Gerais, BRA (EC-R-BRVA/ 1088-06)	n.r.	0.0175	1 13.02.07	60	grain	0.25	na	na		

Report-No. Location (trial no.) (Variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
(CV 603)										
2008/1097470 Santo Antonio de Goias Goias, BRA (EC-CD-BRUB/ 1088-06) (CV 603)	n.r.	0.0175	1 25.02.07 05.02.07 16.01.07 27.12.06 07.12.06	40 60 80 100 120	grain grain grain grain grain	0.15 0.08 < 0.05 < 0.05 < 0.05	na na na na na	na na na na na		
2008/1097470 Santo Antonio de Posse Sao Paulo, BRA (EC-R-BRUA/ 1088-06) (CV 603)	n.r.	0.0175	1 30.01.07	60	grain	< 0.05	na	na		
2008/1097470 Londrina Parana, BRA (EC-R-BRTA/ 1088-06) (CV 603)	n.r.	0.0175	1 03.01.07	60	grain	< 0.05	na	na		
2010/1010261 Santo Antonio de Posse Sao Paulo, BRA (G080102) (CV 127)	spray	0.0175	1 13.02.08 24.01.08 04.01.08 15.12.07 25.11.07	40 60 80 100 120	grain grain grain grain grain	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.03 < 0.03 < 0.03 < 0.03 < 0.03	
2012/3000423 Castro Parana, BRA (G100579) (BRZ 08 200151)	spray	0.0175	1 22.04.11	60	grain	0.07	< 0.01	0.01	0.09	
2010/1127505 Ponta Grossa Parana, BRA (G100005) (L 08)	spray	0.0175	1 24.03.10 04.03.10 12.02.10 23.01.10	20 40 60 80	grain grain grain grain	< 0.01 0.02 0.07 0.03	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 0.02 0.02	< 0.03 0.04 0.10 0.06	
2010/1127505 Santo Antonio de Posse Sao Paulo, BRA (G100006) (CV 127)	spray	0.0175	1 13.05.10 23.04.10 04.04.10 14.03.10	20 40 60 80	grain grain grain grain	< 0.01 < 0.01 0.05 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.03 < 0.03 0.07 0.03	
2012/3000423 Ponta Grossa Parana, BRA (G100575) (BRZ 08 200151)	spray	0.0175	1 20.05.11 30.04.11 10.04.11 21.03.11 01.03.11	20 40 60 80 100	grain grain grain grain grain	< 0.01 < 0.01 0.05 0.12 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 0.01 < 0.01	< 0.03 < 0.03 0.07 0.14 < 0.03	
2012/3000423 Senador Canedo Goias, BRA (G100576) (BRZ 5384)	spray	0.0175	1 31.01.11	60	grain	< 0.01	< 0.01	< 0.01	< 0.03	

Report-No. Location (trial no.) (Variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
2012/3000423 Anapolis Goias, BRA (G100577) (BRZ 5384)	spray	0.0177	1 04.02.11	60	grain	< 0.01	< 0.01	< 0.01	< 0.03	
2012/3000423 Santo Antonio de Posse Sao Paulo, BRA (G100578) (BRZ 08)		0.0175	1 12.05.11	60	grain	0.23	< 0.01	0.02	0.26	

Cereal Grains

Maize

One maize field trial was conducted in Brazil during the 1997 growing season. The trial consisted of an untreated control plot and two treated plots. The treated plots received a single application of a mix formulation of imazapic and imazapyr at growth stage BBCH 17–19 at a rate of either 0.0525 or 0.105 kg imazapic/ha. The maize samples were taken manually at 96 days after treatment. Maize RAC samples were analysed for residues using Method LAADL R0001.01. The limit of quantification was 0.1 mg/kg.

During the 2010/2011 growing season, four field trials were carried out in Brazil to determine the residues of imazapic in imidazolinone tolerant maize after treatment with a mix formulation of imazapic and imazapyr. At all trial sites, one trial plot was untreated to provide control samples, and one trial plot received one post-emergence application at a rate of 0.0525 kg imazapic/ha, 96 days before harvest (BBCH 13-17). At two trials, the application was performed 89, 96 and 103 days before harvest. Samples were taken 96 days after the application at all trials; at two trials, additional samples were obtained 89 and 103 DALA. Maize RAC samples were analysed for residues using Method SOP-PA.0288 with a limit of quantification (LOQ) of 0.01 mg/kg.

Table 45 Residues of imazapic in imidazolinone-tolerant maize from supervised trials conducted in Brazil

Report-No. Location (trial no.) (Variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
GAP in Brazil	Ground spray	0.0525	1	PHI 96						
	Aerial spray	0.0525	1	PHI 96						
# IA-731-007 Goiania Goias, BRA (Cargill / IMI 1)	Spray	0.0525	1 06.01.97	96	grain	< 0.1	na	na		7-9 leaves
		0.105				< 0.1	na	na		
# 2011/1104555 Santo Antonio de Posse Sao Paulo, BRA (G100192) (Dow 2B710CL)		0.0525	1 29.07.10 22.07.10	89 96	grain grain	< 0.01 < 0.01	na na	na na		G14 G14
			15.07.10	103	grain	< 0.01	na	na		G14

Report-No. Location (trial no.) (Variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
# 2011/1104555 Senador Canedo Goiás, BRA (G100193) (Clearfield)		0.0525	1 28.07.10 21.07.10 14.07.10	89 96 103	grain grain grain	< 0.01 < 0.01 < 0.01	na na na	na na na		G17 G15 G13
# 2011/1104555 Engenheiro Coelho Sao Paulo, BRA (G100194) (Dow 2B710CL)		0.0525	1 22.09.10	96	grain	< 0.01	na	na		G14
# 2011/1104555 Jaboticabal Sao Paulo, BRA (G100195) (Dow 2B710CL)		0.0525	1 07.10.10	96	grain	< 0.01	na	na		G15

Rice

During the 2000/2001 growing season, one field trial was carried out in Brazil to determine the residues of imazapic in rice grain after treatment with a mix formulation of imazapic and imazapyr. One trial plot was untreated to provide control samples, and one trial plot received two post-emergence spray applications at a rate of 0.0375 kg ai/ha each and a retreatment interval of 14–17 days. Samples were taken at physiological maturity 60, 75 and 90 days after the last application. Rice RAC samples were analysed for residues using Method SOP-PA.0231. The limit of quantification was 0.05 mg/kg.

During the 2000/2001 growing season, one field trial was carried out in Brazil to determine the residues of imazapic in rice grain after treatment with a mix formulation of imazapic and imazapyr. One trial plot was untreated to provide control samples, and two trial plots received two post-emergence spray applications, each at a rate of 0.01875 or 0.0375 kg ai/ha, respectively. The retreatment interval was 17 days. Samples were taken at physiological maturity, 60 days after the last application (DALA), at all plots. Rice RAC samples were analysed for residues using Method SOP-PA.0231.

During the 2000/2001 growing season, another field trial was carried out in Brazil to determine the residues of imazapic in rice grain after treatment with a mix formulation of imazapic and imazapyr. One trial plot was untreated to provide control samples, and two trial plots received two post-emergence spray applications, each at a rate of 0.01875 or 0.0375 kg ai/ha, respectively. The retreatment interval was 13 days. Samples were taken at physiological maturity, 60 days after the last application, at all plots. Rice RAC samples were analysed for residues using Method SOP-PA.0231.

During the 2002/2003 growing season, four field trials were carried out in Brazil to determine the residues of imazapic in rice grain after treatment with a mix formulation of imazapic and imazapyr. One trial plot was untreated to provide control samples. In one trial site, the treated plot received two post-emergence spray applications at a rate of 0.025 kg ai/ha each. In three trials, two separate plots received two post-emergence spray applications, each at a rate of 0.025 or 0.05 kg ai/ha, respectively. The retreatment interval was 17–52 days. Samples were taken at physiological maturity, 60 days after the last application at all plots. In the trial treated with the lower rate only, samples were collected at 50, 55, 65 and 70 DALA in addition. Rice RAC samples were analysed for residues using Method SOP-PA.0249. The limit of quantification was 0.05 mg/kg.

During the 2002/2003 growing season, four field trials were carried out in Brazil to determine the residues of imazapic in rice grain after treatment with a mix formulation of imazapic and imazapyr. One trial plot was untreated to provide control samples. At one trial site, the treated plot received two post-emergence spray applications at a rate of 0.015 kg imazapic/ha each. At three trials, two separate plots received two post-emergence spray applications, each at a rate of 0.015 kg imazapic/ha (+0.045 kg imazapyr/ha) or 0.030 kg imazapic/ha (+0.090 kg imazapyr/ha), respectively. The retreatment interval was 17-52 days. Samples were taken at physiological maturity, 60 days after the last application at all plots. At the trial treated with the lower rate only, samples were collected at 50, 55, 65 and 70 DALA in addition. Rice RAC samples were analysed for residues using Method SOP-PA.0231.

Table 46 Residues of imazapic in imidazolinone-tolerant rice from supervised trials conducted in Brazil

Report-No. Location (trial no.) (Variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
GAP in Brazil	Ground spray Aerial spray	0.0245	1	PHI 60						
		0.0245	1	PHI 60						
# 2001/3001704 Cachoeirinha Rio Grande do Sul, BRA (CDR/H/2001/617/ BRTB) (IRGA 417 CL)	Spray	0.0375	2 05.03.01 16.02.01 02.02.01	60 75 90	grain	< 0.05 < 0.05 < 0.05	na na na	na na na		post- emerg.
# 2001/3001705 Cachoeirinha Rio Grande do Sul, BRA (R/H/2001/618/BRTB) (IRGA 417 CL)	Spray	0.01875	2 15.03.01	60	grain	< 0.05	na	na		post- emerg.
		0.0375				< 0.05	na	na		
# 2001/3001706 Uruguaiana Rio Grande do Sul, BRA (R/H/2001/674/BRTB) (Americana,, (AS 3510))	Spray	0.01875	2 07.12.00	60	grain	< 0.05	na	na		post- emerg.
		0.0375				< 0.05	na	na		
# 2004/3000911 Sao Vicente do Sul Rio Grande do Sul, BRA (CD/H/2003/523/BRT) (IRGA 422 CL)	Spray	0.025	2 03.03.03 27.02.03 22.02.03 17.02.03 12.02.03	50 55 60 65 70	grain	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	na na na na na	na na na na na		booting booting elongation elongation elongation
# 2004/3000911 Sao Vicente do Sul Rio Grande do Sul, BRA (R/H/2003/524/BRT) (IRGA 422 CL)	Spray	0.025	2 22.02.03	60	grain	< 0.05	na	na		booting
		0.05				< 0.05	na	na		

Report-No. Location (trial no.) (Variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
# 2004/3000911 Uruguiana Rio Grande do Sul, BRA (R/H/2003/525/BRT) (XP 701 CL)	Spray	0.025 0.05	2 16.01.03	60	grain	< 0.05 < 0.05	na na	na na		1-2 leaves
# 2004/3000911 Cachoeirinha Rio Grande do Sul, BRA (R/H/2003/526/BRT) (XP 701 CL)	Spray	0.025 0.05	2 19.02.03	60	grain	< 0.05 < 0.05	na na	na na		booting
# 2003/3001442 # 2003/3001441 Sao Vicente do Sul Rio Grande do Sul, BRA (CD/H/2003/519/BRT) (IRGA 422 CL)		0.02975	2 03.03.03 27.02.03 22.02.03 17.02.03 12.02.03	50 55 60 65 70	grain	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	na na na na na	na na na na na		n.r. flowering infloresc. emerg. booting booting elongation
# 2003/3001442 # 2003/3001441 Sao Vicente do Sul Rio Grande do Sul,		0.02975	2 22.02.03	60	grain	< 0.05	na	na		booting
BRA (R/H/2003/520/BRT) (Tec XP 701 CL)		0.0595				< 0.05	na	na		
# 2003/3001442 # 2003/3001441 Cachoeirinha Rio Grande do Sul, BRA (R/H/2003/521/BRT) (XP 701 CL)		0.02975 0.0595	2 19.02.03	60	grain	< 0.05 < 0.05	na na	na na		booting
# 2003/3001442 # 2003/3001441 Uruguiana Rio Grande do Sul, BRA (R/H/2003/522/BRT) (IRGA 422 CL)		0.02975 0.0595	2 16.01.03	60	grain	< 0.05 < 0.05	na na	na na		1-2 leaves

Wheat

Five wheat field trials were conducted in Australia during the 1997 and 1998 growing seasons. The trials consisted of an untreated control plot and two (3 trials) or three (2 trials) treated plots. The treated plots received a single application of WG formulation of imazapic. Two trials were treated with either 35, 52.5 or 70 g ai/ha. Three trials were treated at a rate of either 21 or 35 g ai/ha. Wheat forage samples were collected 1–4 times, 0–42 days after treatment. Samples of grain and straw were

taken at normal harvest, 93–113 days after the application. The samples were analysed for residues using HPLC. The limit of quantification was 0.05 mg/kg.

Table 47 Residues of imazapic in imidazolinone-tolerant wheat from supervised trials conducted in Australia

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
GAP in Australia	Spray	0.021	1	-						
# 2000/1023962 Galore New South Wales AUS (573/AU/97/01/SN01)	Spray	0.035 0.0525 0.07	1	96 96 96	grain grain grain	< 0.05 < 0.05 < 0.05	na na na	na na na		post- emerg.
# 2000/1023962 Wongan Hills Western Australia AUS (573/AU/97/01/WA01)		0.035 0.0525 0.07	1	113 113 113	grain grain grain	< 0.05 < 0.05 < 0.05	na na na	na na na		post- emerg.
# 2000/1023962 Burabadji Western Australia AUS (573/AU/98/08/WA01)		0.021 0.035	1	93 93	grain grain	< 0.05 < 0.05	na na	na na		advanced tillering (Z25)
# 2000/1023962 Manoora South Australia AUS (573/AU/98/08/SA01)		0.021 0.035	1	95 95	grain grain	< 0.05 < 0.05	na na	na na		stem elongation 1-2 nodes

Grasses for sugar or syrup production

Sugar cane

One sugar cane field trial was conducted in Argentina during the 1996/1997 growing season. The trial consisted of an untreated control plot and a treated plot. The treated plot received a single application of a WG formulation of imazapic as pre-treatment at a rate of 350 g ai/ha, 38 days pre-plantation. The sugar cane samples were taken at 392 days after treatment. Sugar cane RAC samples were analysed for residues of BAS 715 H (imazapic) using Method LAADL R0002 with a limit of quantification of 0.05 mg/kg.

Two residue trials on sugar cane were conducted in Guatemala and two in Costa Rica during the growing season 2007-2008. Three test plots were established at each trial site. Treatment 1 was the untreated plot and provided control samples for analysis. For one trial each in Costa Rica and Guatemala, the Treatment 2 plot was designated as a RAC plot (non-processing) and received one pre-plant incorporated application of a WG formulation of imazapic, targeting a rate of 0.245 kg ai/ha. The Treatment 3 plot was designated as a processing plot and received one pre-emergence application of a WG formulation of imazapic targeting the 5× rate of 1.225 kg ai/ha. For the remaining two trials, the Treatment 2 plot was designated as a RAC plot (non-processing) and received one pre-emergence application at a targeted a rate of 0.245 kg ai/ha. The 'Treatment 3' plot was designated as a processing plot and received one pre-emergence application of a WG formulation of imazapic targeting the 5× rate of 1.225 kg ai/ha. At about 150 days after the last application, whole cane samples for RACs were

collected from the 'Treatment 2' and untreated plots at all sites. At about 300 DALA, commercially mature, whole cane samples for RACs and processing samples were collected.

Residues of imazapic in sugarcane RAC were determined using SOP-PA.0288. The limit of quantification (LOQ) of the method was 0.01 mg/kg for imazapic and its two metabolites.

Four residue trials on sugar cane were conducted in Australia during the growing season 1996/97. Three test plots were established on each site, one untreated control plot and two plots treated once with a WG formulation of imazapic, targeting a rate of either 0.144 or 0.288 kg ai/ha. Two trials were treated pre-emergence and two post-emergence at the 'spike' growth stage. The spray volume was 119 l/ha. At 211–217 days after the application, sugar cane foliage and cane samples were collected. Residues of imazapic in sugar cane matrices were determined using Method L 741. The limit of quantification (LOQ) of the method was 0.05 mg/kg.

During 2006 growing season, five field trials were carried out in representative sugar cane growing areas in Brazil to determine the residues levels of imazapic and its two metabolites in sugar cane after treatment with a WG formulation of imazapic. At all trial sites, two trial plots were untreated to provide control samples, and two trial plots each received one pre-plant incorporated application at a rate of 0.245 kg ai/ha. In one untreated and one treated plot at four sites, the whole cane samples were harvested (BBCH 30) at 150 days after the last application. At one trial, the 150 DALA samples were not collected due to the insufficient crop productivity. In one control and one treated plot at all five sites, the mature cane samples were harvested at 360 to 365 days after treatment (BBCH 49). The samples were analysed according to SOP-PA.0288 for the determination of imazapic and its metabolites residues with a limit of quantification (LOQ) of 0.01 mg/kg for each analyte.

Table 48 Residues of imazapic in sugar cane from supervised trials conducted in Argentina, Australia, Brazil, Costa Rica and Guatemala

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
GAP in Argentina	Spray	0.35	1	PHI						
GAP in Australia	Spray	0.096	1	392						
GAP in Brazil		0.245	1	nr						
GAP in Costa Rica	Spray	0.175	1	283						
GAP in Guatemala	Spray	0.175	1	85						
# IA-790-011 Lules Tucuman, ARG (Famailla 8116)	Spray	0.35	1 03.06.96		cane	< 0.05	na	na		PPI
# 1997/1007121 Home Hill North Queensland AUS (173/AU/96/20/QU06)		0.144	1 28.08.96	217	foliage cane	< 0.05 < 0.05	na na	na na		pre- emerg. (post pit)
		0.288			foliage cane	< 0.05 < 0.05	na na	na na		
# 1997/1007121 Bunderberg Queensland, AUS (173/AU/96/21/QU05)		0.144	1 04.09.96	211	foliage cane	< 0.05 < 0.05	na na	na na		post- emerg. (spike')
		0.288			foliage cane	< 0.05 < 0.05	na na	na na		

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
# 1997/1007121 Bunderberg Queensland, AUS (173/AU/96/20/QU11)		0.144 0.288	1 04.09.96	211	foliage cane foliage cane	< 0.05 < 0.05 < 0.05 < 0.05	na na na na	na na na na		pre- emerg.
# 1997/1007121 Bunderberg Queensland, AUS (173/AU/96/20/QU12) (138)		0.144 0.288	1 04.09.96	211	foliage cane foliage cane	< 0.05 < 0.05 < 0.05 < 0.05	na na na na	na na na na		post- emerg. (‘spike’) (5 cm height)
# 2008/7012758 Carrillos Alajuela, CRI (RCN R06486) (Mex 50)		0.245 1.225	1 20.03.07	153 299 299 299	cane cane cane cane	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.03 < 0.03 < 0.03 < 0.03	PPI pre- emerg.
# 2008/7012758 Tacares Alajuela, CRI (RCN R06487) (Mex 50)		0.245 1.225	1 20.03.07	153 299 299 299	cane cane cane cane	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.03 < 0.03 < 0.03 < 0.03	pre- emerg.
# 2008/7012758 La Gomera Escuintla, GTM (RCN R06488) (CP-731547)		0.245 1.225	1 09.03.07	148 310 310 310	cane cane cane cane	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.03 < 0.03 < 0.03 < 0.03	PPI pre- emerg.
# 2008/7012758 Ceiba Amelia Escuintla, GTM (RCN R06489) (CP-731547)		0.245	1 16.12.06	148	cane	< 0.01	< 0.01	< 0.01	< 0.03	pre- emerg.
# 2009/1094340 Uberlandia Minas Gerais, BRA (EC-R-BRVA/1084-06)		0.245	1 20.12.06	150 360-365	cane cane	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.03 < 0.03	0
# 2009/1094340 Campo Alegre Goias, BRA (EC-R-BRVB/1084-06)		0.245	1 20.12.06	360-365	cane	< 0.01	< 0.01	< 0.01	< 0.03	0
# 2009/1094340 Santo Antonio de Posse Sao Paulo, BRA (EC-R-BRUA/1084-06) (SP 801816)		0.245	1 22.11.06	150 360-365	cane cane	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.03 < 0.03	0
# 2009/1094340 Piracicaba Sao Paulo, BRA (EC-R-BRUB/1084-06) (SP 801816)		0.245	1 06.11.06	150 360-365	cane cane	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.03 < 0.03	0

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
# 2009/1094340 Santo Antonio de Posse Sao Paulo, BRA (EC-R-BRUC/1084-06) (SP 801816)		0.245	1 22.11.06	150 360-365	cane cane	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.03 < 0.03	0

Oilseeds

Peanut

One peanut field trial was conducted in Brazil during the 1996/1997 growing season. The trial consisted of an untreated control plot and two treated plots. The treated plots received a single post-emergence application of a WG formulation of imazapic at a rate of either 0.070 or 0.140 kg ai/ha, 22 days after planting. Peanut RAC samples were analysed for residues using Method 2253.01. The limit of quantification was 0.1 mg/kg.

Four peanut field trials were conducted in Brazil during the 2003/2004 growing season. The trials consisted of an untreated control plot and two (3 trials) or five (1 trial) treated plots. The treated plots received a single application of WG formulation of imazapic. In one trial, the plots were treated with 0.098 kg ai/ha, either 60, 65, 70, 75 or 80 days before harvest. In three trials, the plots were treated at a rate of either 0.098 kg ai/ha or 0.196 kg ai/ha, 70 days before harvest. The peanut samples were collected at 70 days after treatment. In one trial, samples were taken at 60, 65, 70, 75 and 80 days after treatment. Peanut RAC samples were analysed for residues using Method SOP-PA.0249. The limit of quantification was 0.05 mg/kg.

A total of six peanut field trial was conducted independently in the USA during the 1992 growing season. Each trial consisted of an untreated control plot and two treated plots. The treated plots received a single post-emergence application of an SL formulation of imazapic at a rate of either 70 or 210 g ai/ha, to the 10–15 cm high (vegetative stage) or 15–25 cm high (pre-bloom) peanut plants. The peanut nut and hull samples were taken 95, 102, 104, 105, 117 or 119 days after treatment. Peanut RAC samples were analysed for residues of imazapic and its metabolite CL 263284 using Method M 2253. The limit of quantification was 0.1 mg/kg.

A total of six peanut field trial was conducted in the USA during the 1993 growing season. Each trial consisted of an untreated control plot and one treated plot. The treated plots received a single post-emergence application of an SL formulation of imazapic at a rate of 70 g ai/ha, to the 5 cm high (seedling stage), 7.5–10 cm high (pre-bloom stage) 10–15 cm high (3 weeks post-emergence), or 15–20 cm high (early bloom stage) peanut plants. The peanut nutmeat and hull samples were taken at 75, 95, 105, 116 and 119 days after treatment. Peanut RAC samples were analysed for residues of imazapic and metabolites CL 263,284 and CL 189,215 using Method M 2379. The limit of quantification was 0.1 mg/kg.

Table 49 Residues of imazapic in peanut from supervised trials conducted in Brazil and the USA

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
GAP in Brazil	Spray	0.098	1	PHI 70						
GAP in USA	Spray	0.071	1	90						
# IA-740-019 Jaboticabal	Spray	0.07	1 11.11.96	70	nut	< 0.1	na	na		post- emerg.

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
Sao Paulo, BRA (Tatu vermelho)		0.14			nut	< 0.1	na	na		
# 2005/3001521 Santo Antonio de Posse Sao Paulo, BRA (CD/H/2003/539/BRU) (Tatu vermelho)		0.098 0.098 0.098 0.098 0.098	11/03/03 06/03/03 01/03/03 24/02/03 19/02/03	60 65 70 75 80	nut nut nut nut nut	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	na na na na na	na na na na na		n.r.
# 2005/3001521 Ponta Grossa Perugia, BRA (R/H/2003/537/BRT) (Tatu vermelho)		0.098 0.196	12/02/03	70 70	nut nut	< 0.05 < 0.05	na na	na na		n.r.
# 2005/3001521 Santo Antonio de Posse Sao Paulo, BRA (R/H/2003/538/BRU) (Tatu vermelho)		0.098 0.196	09/02/03	70 70	nut nut	< 0.05 < 0.05	na na	na na		n.r.
# 2005/3001521 Santo Antonio de Posse Sao Paulo, BRA (EC/R/H/2004/505/ BRU/A1) (Tatu vermelho)		0.098 0.196	15/12/03	70 70	nut nut	< 0.05 < 0.05	na na	na na		post- emerg.
# IA-740-001 Montezuma Macon County GA, USA (GK-7)		0.07 0.21	1 08.07.92	105 105 105 105	hull nutmeat hull nutmeat	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	na na na na		20-25 cm
# IA-740-002 Malone Jackson County FL, USA (Florunner)		0.07 0.21	1 09.06.92	119 119 119 119	hull nutmeat hull nutmeat	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	na na na na		10 cm
# IA-740-003 Grangeburg Houston County AL, USA (Florunner)		0.07 0.21	1 11.06.92	117 117 117 117	hull nutmeat hull nutmeat	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	na na na na		10 cm
# IA-740-004 Caddo County OK, USA (Spanco)		0.07 0.21	1 09.07.92	102 102 102	hull nutmeat hull	< 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1	na na na		bloom stage, 15-20 cm
# IA-740-005 Jamesville Martin County NC, USA (NC-9)		0.07 0.21	1 25.06.92	104 104 104 104	hull nutmeat hull nutmeat	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	na na na na		seedling stage, ca. 13 cm

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
# IA-740-006 Waller County TX, USA (Spanish)		0.07	1 02.07.92	95 95	hull nutmeat	< 0.1 < 0.1	< 0.1 < 0.1	na na		pre-bloom stage, 10-15 cm
		0.21		95 95	hull nutmeat	< 0.1 < 0.1	< 0.1 < 0.1	na na		
# IA-740-007 Waller County TX, USA (Spanish)		0.07	1 09.07.93	75 75	hull nutmeat	< 0.1 < 0.1	< 0.1 < 0.1	< 0.1 < 0.1	< 0.3 < 0.3	pre-bloom stage, 7.5-10 cm
# IA-740-008 Montezuma Macon County GA, USA (GK-7)		0.07	1 07.07.93	105 105	hull nutmeat	< 0.1 < 0.1	< 0.1 < 0.1	< 0.1 < 0.1	< 0.3 < 0.3	early bloom stage, 15-20 cm
		0.21		105 105	hull nutmeat	< 0.1 < 0.1	< 0.1 < 0.1	< 0.1 < 0.1	< 0.3 < 0.3	
# IA-740-009 Caddo County OK, USA (Spanco)		0.07	1 12.07.93	95 95	hull nutmeat	< 0.1 < 0.1	< 0.1 < 0.1	< 0.1 < 0.1	< 0.3 < 0.3	early bloom stage, 15 cm
# IA-740-010 Jamesville Martin County NC, USA (NC-9)		0.07	1 18.06.93	116 116	hull nutmeat	< 0.1 < 0.1	< 0.1 < 0.1	< 0.1 < 0.1	< 0.3 < 0.3	seedling stage, ca. 5 cm
# IA-740-011 Grangeburg Houston County AL, USA (Florunner)		0.07	1 16.06.93	119 119	hull nutmeat	< 0.1 < 0.1	< 0.1 < 0.1	< 0.1 < 0.1	< 0.3 < 0.3	10-15 cm
		0.21		119 119	hull nutmeat	< 0.1 < 0.1	< 0.1 < 0.1	< 0.1 < 0.1	< 0.3 < 0.3	
# IA-740-012 Malone Jackson County FL, USA (Florunner)		0.07	1 16.06.93	119 119	hull nutmeat	< 0.1 < 0.1	< 0.1 < 0.1	< 0.1 < 0.1	< 0.3 < 0.3	3 weeks post- emerg., 10-15 cm

Rapeseed

Six rape seed field trials were conducted in Australia during the 1997 and 1998 growing seasons. The trials consisted of an untreated control plot and two (four trials, 1998) or three (two trials, 1997) treated plots. The treated plots received a single application of a WG formulation of imazapic. In 1997, the plots were treated with either 35, 52.5 or 70 g ai/ha. In 1998, the plots were treated at a rate of either 21 or 35 g ai/ha. The rape seed forage samples were collected 1–5 times, 0–62 days after treatment. Samples of grain were taken once from three trials, 76–95 days after the application. Straw was taken once from two trials, 76–80 days after treatment. Rape seed RAC samples were analysed for residues of imazapic and CL 263222 using Method L741/1. The limit of quantification was 0.05 mg/kg.

Table 50 Residues of imazapic in rape seed from supervised trials conducted in Australia

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
GAP in Australia	Spray	0.0288	1	nr						
# 1998/1008955 # 1998/1008975 Galore New South Wales AUS (574/AU/97/01/SN01) (IT Canola)		0.035 0.0525 0.07	1 06.09.97	80 80 80	grain grain grain	< 0.05 < 0.05 < 0.05	na na na	na na na		early post- emerg. (PO01)
# 1998/1008955 # 1998/1008975 Beverley Western Australia AUS (574/AU/97/01/WA01) (Canadian IR variety)		0.035 0.0525 0.07	1 18.08.97	95 95 95	grain grain grain	< 0.05 < 0.05 < 0.05	na na na	na na na		post- emerg. (PO1)
# 1998/1008955 # 1998/1008975 Dookie Victoria AUS (574/AU/98/06/SV01) (IT Canola)		0.021 0.035	1 18.09.98	76 76	grain grain	< 0.05 < 0.05	na na	na na		post- emerg. (PO1)

Animal Feeds*Legume animal feed**Peanut hay*

A total of six peanut field trials were conducted in the USA during the 1995 growing season. Each trial consisted of an untreated control plot and one treated plot. The treated plots received a single post-emergence application of an SL formulation of imazapic at a rate of 70 g ai/ha except in one trial 84 g ai/ha. Peanut hay samples were taken 90, 95, 98, 100, 102 or 113 days after treatment. Peanut hay samples were analysed for residues of imazapic, CL 263284 and CL 189215 using Method M 2599. The limit of quantification was 0.1 mg/kg.

According to GAP in the USA, grazing and feeding of treated peanut hay to livestock is not allowed.

Table 51 Residues of imazapic in peanut hay from supervised trials conducted in the USA

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
GAP in USA		0.071	1	nr						
# 1A-740-013 Jamesville Martin County NC, USA (NC-9)		0.07	1 96.07.1995	98	hay	< 0.1	< 0.1	< 0.1	< 0.3	post- emerg.

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
# IA-740-014 Hawkinsville Pulaski County GA, USA (Andrew 93)		0.07	1 21.07.95	100	hay	< 0.1	< 0.1	< 0.1	< 0.3	post- emerg.
# IA-740-015 Montezuma Macon County GA, USA (GK07)		0.084	1 13.07.95	95	hay	< 0.1	< 0.1	< 0.1	< 0.3	post- emerg.
# IA-740-016 Lucama Wilson County NC, USA (NC-V11)		0.07	1 25.07.95	113	hay	< 0.1	< 0.1	< 0.1	< 0.3	post- emerg.
# IA-740-017 Groom Armstrong County TX, USA (Spanco)		0.07	1 31.07.95	90	hay	< 0.1	< 0.1	< 0.1	< 0.3	post- emerg.
# IA-740-018 Malone Jackson County FL, USA (GK-7)		0.07	1 29.06.95	102	hay	< 0.1	< 0.1	< 0.1	< 0.3	post- emerg., 20-30 cm

Straw, fodder and forage of cereal grains and grasses, except grasses for sugar production (including buckwheat fodder)

Wheat straw and fodder, dry

According to GAP in Australia, grazing and cutting for stock feed are not allowed for 4 weeks after the application.

Table 52 Residues of imazapic in wheat forage and straw from supervised trials conducted in Australia

Report-No. Location (trial no.)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks	
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum		
GAP in Australia	Spray	0.021	1	-							
# 2000/1023962 Galore New South Wales AUS (573/AU/97/01/SN01)		0.035	1	5	forage	0.10	na	na		post- emerg.	
				19	forage	< 0.05	na	na			
				33	forage	< 0.05	na	na			
				96	straw	< 0.05	na	na			
		0.0525		5	forage	0.17	na	na			
				19	forage	< 0.05	na	na			
				33	forage	< 0.05	na	na			
				96	straw	< 0.05	na	na			
		0.07		5	forage	0.24	na	na			
				19	forage	< 0.05	na	na			
				33	forage	< 0.05	na	na			
				96	straw	< 0.05	na	na			

Report-No. Location (trial no.)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
# 2000/1023962 Wongan Hills Western Australia AUS (573/AU/97/01/WA01)		0.035	1	32 113	forage straw	< 0.05 < 0.05	na na	na na		post- emerg.
		0.0525		32 113	forage straw	< 0.05 < 0.05	na na	na na		
		0.07		32 113	forage straw	< 0.05 < 0.05	na na	na na		
# 2000/1023962 Rannock New South Wales AUS (573/AU/98/08/SN01)		0.021	1	1 15 30	forage	0.27 < 0.05 < 0.05	na na na	na na na		post- emerg.
		0.035		1 15 30		0.97 < 0.05 < 0.05	na na na	na na na		
# 2000/1023962 Burabadji Western Australia AUS (573/AU/98/08/WA01)		0.021	1	0 14 28 42 93	forage forage forage forage straw	0.61 < 0.05 < 0.05 < 0.05 < 0.05	na na na na na	na na na na na		advanced tillering (Z25)
		0.035		0 14 28 42 93	forage forage forage forage straw	0.85 < 0.05 < 0.05 < 0.05 < 0.05	na na na na na	na na na na na		
# 2000/1023962 Manoora South Australia AUS (573/AU/98/08/SA01)		0.021	1	0 14 28 42 95	forage forage forage forage straw	0.37 < 0.05 < 0.05 < 0.05 < 0.05	na na na na na	na na na na na		stem elongation 1-2 nodes
		0.035		0 14 28 42 95	forage forage forage forage straw	0.57 0.06 < 0.05 < 0.05 < 0.05	na na na na na	na na na na na		

Hay or fodder (dry) of grasses

The registered use on grass in the USA allows one application at a maximum rate of 0.20 kg ai/ha after grass has reached full (100%) green-up for spring and summer application or grass is dormant before green-up or full green-up for winter application. According to GAP cutting treated area for hay is not allowed within 7 days after treatment. There are grazing restrictions on the US label.

One Bermuda grass (*Cynodon dactylon*) field trial was conducted in the United States during the 1996 growing season. The trial consisted of an untreated control plot and one treated plot. The treated plot received a single post-emergence application of an SL formulation of imazapic at a rate of 0.224 kg ai/ha. Prior to application, the field was observed to contain 85% Bermuda grass. Samples of forage and hay were harvested prior to application (control samples), immediately after application and 7, 14, 28 and 56 days after treatment (DALA). Hay samples were allowed to dry after cutting

before sampling. Bermuda grass forage and hay samples were analysed for residues of imazapic and metabolites CL263284 and CL189215 (CL 189215) using Method M 3114. The limit of quantification was 0.5 mg/kg.

One Bermuda grass field trial was conducted in the United States during the 1996 growing season. The trial consisted of an untreated control plot and one treated plot. The treated plot received a single post-emergence application of an SL formulation of imazapic at a rate of 0.235 kg ai/ha. Samples of forage and hay were cut prior to application (control samples), immediately after application and 7, 14, 28 and 54 days after treatment. Hay samples were allowed to dry for 5–7 days after cutting before sampling.

One Bermuda grass field trial was conducted in the United States during the 1997 growing season. The trial consisted of an untreated control plot and one treated plot. The treated plot received a single post-broadcast application of an SL formulation of imazapic at a rate of 0.224 kg ai/ha. Samples of forage and hay were harvested prior to application (control samples), immediately after application and 7, 14, 28 and 56 days after treatment. Hay samples were allowed to dry for 4–6 days after cutting before sampling.

One Big Bluestem (*Andropogon gerardii*) and Brome grass (*Bromus sp.*) field trial was conducted in the United States during the 1997 growing season. The trial consisted of an untreated control plot and one treated plot. The treated plot received a single post-broadcast application of an SL formulation of imazapic at a rate of 0.224 kg ai/ha. Samples of forage were harvested prior to application (control samples), immediately after application and 7, 14, 28 and 56 days after treatment (DALA). Hay samples were taken after being dried for 4–7 days after cutting.

One common Bermuda grass field trial was conducted in the United States during the 1997 growing season. The trial consisted of an untreated control plot and one treated plot. The treated plot received a single post-broadcast application of an SL formulation of imazapic at a rate of 0.224 kg ai/ha. Samples of forage and hay were harvested prior to application (control samples), immediately after application and 7, 14, 28 and 56 days after treatment. Hay samples were taken after being dried for 5–7 days after cutting.

One Bermuda grass field trial was conducted in the United States during the 1997 growing season. The trial consisted of an untreated control plot and one treated plot. The treated plot received a single post-broadcast application of SL formulation of imazapic at a rate of 0.224 kg ai/ha. Samples of forage and hay were harvested prior to application (control samples), immediately after application and 7, 14, 28 and 56 days after treatment (DALA). Hay samples were taken after being dried on plastic sheets for 1–4 days after cutting.

One Brome grass field trial was conducted in the United States during the 1997 growing season. The trial consisted of an untreated control plot and one treated plot. The treated plot received a single post-broadcast application of an SL formulation of imazapic at a rate of 0.224 kg ai/ha. Samples of forage were harvested prior to application (control samples), immediately after application and 7, 14, 28 and 56 days after treatment (DALA). Hay samples were taken after being dried.

One Little Bluestem and Bluegrass field trial was conducted in the United States during the 1997 growing season. The trial consisted of an untreated control plot and one treated plot. The treated plot received a single post-broadcast application of an SL formulation of imazapic at a rate of 0.224 kg ai/ha. Samples of forage were harvested prior to application (control samples), immediately after application and 7, 14, 28 and 56 days after treatment (DALA). Hay samples were taken after being dried after cutting.

One Little Bluestem (*Schizachyrium scoparium*) and Bluegrass (*Poa sp.*) field trial was conducted in the United States during the 1996/1997 growing season. The trial consisted of an untreated control plot and one treated plot. The treated plot received two post-broadcast applications of SL formulation of imazapic at rates of 0.157 kg ai/ha (1996) and 0.078 kg ai/ha (1997). Samples of forage were harvested prior to each application (control samples), immediately after each application and 7, 14, 28 and 56 days after the first and the last application (DAFA, DALA). Hay samples were taken after being dried after cutting.

One Big Bluestem grass field trial was conducted in the United States during the 1996/1997 growing season. The trial consisted of an untreated control plot and one treated plot. The treated plot received two post-broadcast applications of an SL formulation of imazapic at rates of 0.157 kg ai/ha (September 1996) and 0.078 kg ai/ha (July 1997). Samples of forage were harvested prior to each application (control samples), immediately after each application and 7 and 14 days after the first application (DAFA) and 7, 14, 28 and 56 days after the last application (DALA). Hay samples were taken after being dried after cutting.

In all the trials, hay samples were placed on a drying rack after harvest to dry. Residue concentrations were not adjusted for moisture content and expressed on as received basis.

Table 53 Residues of imazapic in grass forage and fodder from supervised trials conducted in the USA (* average of the two samples)

Report-No. Location (trial no.)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
GAP in USA	Spray	0.22	-	-						
# IA-731-008 Greenville Washington County Mississippi, USA	Spray	0.224	1 28.06.96	0 0 7 7 14 14 28 28 56 56	forage hay forage hay forage hay forage hay forage hay	15* 17* < 0.50* 0.68* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50*	< 0.50* 2.5* 0.60* 1.7* 0.96* 1.2* < 0.50* < 0.50* < 0.50* < 0.50*	< 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50*	16 20 1.6 2.88 1.96 2.2 < 1.5 < 1.5 < 1.5 < 1.5	post- emerg. Forage 0 DALA 15, 15 Hay 14 DALA < 0.5 (2)
# IA-731-010 Montezuma Macon County Georgia, USA		0.235	1 02.08.96	0 0 7 7 14 14 28 28 54 54	forage hay forage hay forage hay forage hay forage hay	15* 25* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50*	0.60* 10* 2.8* 3.0* 1.9* 4.1* 1.3* 1.9* 0.57* 0.50*	< 0.50* 0.59* < 0.50* < 0.50* < 0.50* 0.75* < 0.50* < 0.50* < 0.50* < 0.50*	16.1 35.59 3.8 4.0 2.9 5.35 2.3 2.9 1.57 1.50	post- emerg. Forage 0 DALA 15, 14 Hay 14 DALA < 0.5 (2)
# IA-731-011 Fort McCoy Marion County Florida, USA		0.224	1 21.06.97	0 0 7 7 14 14 28 28 56 56	forage hay forage hay forage hay forage hay forage hay	7.3* 13* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50*	< 0.50* 2.6* 1.6* 2.1* 1.2* 2.1* 0.69* 1.4* < 0.50* < 0.50*	< 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50*	8.3 16.1 2.6 3.1 2.2 3.1 1.69 2.4 < 1.5 < 1.5	post- emerg. Forage 0 DALA 7.2, 7.4 Hay 14 DALA < 0.5 (2)
# IA-731-013 Brookshire Waller County Texas, USA		0.224	1 19.06.97	0 0 7 7 14 14 28 28 56 56	forage hay forage hay forage hay forage hay forage hay	22* 36* 0.66* 0.54* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50*	< 0.50* 12* 2.5* 2.8* 2.2* 3.5* 1.5* 2.3* < 0.50* < 0.50*	< 0.50* 0.79* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50* < 0.50*	23 48.79 3.66 3.84 3.2 4.5 2.5 3.3 < 1.5 < 1.5	post- emerg. Forage 0 DALA 22, 21 Hay 14 DALA 0.57, < 0.5

Report-No. Location (trial no.)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
# IA-731-014 Hawkinsville Pulaski County Georgia, USA		0.224	1 26.06.97	0	forage	8.8*	< 0.50*	< 0.50*	9.8	post-emerg.
				0	hay	23*	3.2*	< 0.50*	26.7	Forage
				7	forage	< 0.50*	0.92*	< 0.50*	1.92	0 DALA
				7	hay	< 0.50*	1.8*	< 0.50*	2.8	10, 7.5
				14	forage	< 0.50*	0.88*	< 0.50*	1.88	Hay
				14	hay	< 0.50*	1.6*	< 0.50*	2.6	14 DALA
				28	forage	< 0.50*	0.71*	< 0.50*	1.71	< 0.5 (2)
				28	hay	< 0.50*	1.2*	< 0.50*	2.2	
				56	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				56	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
# IA-731-012 Webster City Hamilton County Iowa, USA (Bonilla (Big Bluestem)) (Brome)		0.224	1 03.06.97	0	forage	12*	< 0.50*	< 0.50*	13	post-emerg.
				0	hay	21*	3.2*	< 0.50*	24.7	Forage
				7	forage	0.53*	< 0.50*	< 0.50*	1.53	0 DALA
				7	hay	0.93*	0.98*	< 0.50*	2.41	10, 12
				14	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	Hay
				14	hay	< 0.50*	0.82*	< 0.50*	1.82	14 DALA
				28	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	< 0.5 (2)
				28	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				56	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				56	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
# IA-731-015 Read Delta County Colorado, USA (Brome)		0.224	1 15.07.97	0	forage	13*	< 0.50*	< 0.50*	14	post-emerg.
				0	hay	35*	5.2*	< 0.50*	40.7	Forage
				7	forage	1.8*	0.96*	< 0.50*	3.26	0 DALA
				7	hay	4.1*	3.2*	0.56*	7.86	14, 12
				14	forage	0.99*	1.1*	< 0.50*	2.59	Hay
				14	hay	2.3*	2.5*	0.60*	5.4	14 DALA
				28	forage	< 0.50*	0.61*	< 0.50*	1.61	2.2, 2.3
				28	hay	< 0.50*	1.2*	< 0.50*	2.2	
				56	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				56	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
# IA-731-016 Ephrata Grant County Washington, USA (VNS Bluestem)) (Kentucky (Blue))		0.224	1 02.06.97	0	forage	7.5*	< 0.50*	< 0.50*	8.5	post-emerg.
				0	hay	17*	0.87*	< 0.50*	18.37	Forage
				7	forage	< 0.50*	0.52*	< 0.50*	1.52	0 DALA
				7	hay	< 0.50*	1.4*	< 0.50*	2.4	8.5, 6.5
				14	forage	< 0.50*	0.55*	< 0.50*	1.55	Hay
				14	hay	< 0.50*	1.2*	< 0.50*	2.2	14 DALA
				28	forage	< 0.50*	0.59*	< 0.50*	1.59	< 0.5 (2)
				28	hay	< 0.50*	0.75*	< 0.50*	1.75	
				56	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				56	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
# IA-731-017 Ephrata Grant County Washington, USA (VNS (Little Bluestem)) (Kentucky (Blue))		0.157	1 21.08.96	0	forage	10*	< 0.50*	< 0.50*	11	post-emerg.
				0	hay	22*	1.7*	< 0.50*	24.2	Forage
				7	forage	< 0.50*	1.1*	< 0.50*	2.1	0 DALA
				7	hay	< 0.50*	1.9*	< 0.50*	2.9	11, 9.5
				14	forage	< 0.50*	0.99*	< 0.50*	1.99	Hay
				14	hay	< 0.50*	1.5*	< 0.50*	2.5	14 DALA
				28	forage	< 0.50*	0.56*	< 0.50*	1.56	< 0.5 (2)
				28	hay	< 0.50*	0.80*	< 0.50*	1.8	
				56	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				56	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
		0.157	2	0	forage	2.6*	< 0.50*	< 0.50*	3.6	post-emerg.
		0.078	02.06.97	0	hay	5.3*	< 0.50*	< 0.50*	6.3	

Report-No. Location (trial no.)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
				7	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				7	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				14	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				14	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				28	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				28	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				56	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				56	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
# IA-731-018 York York County Nebraska, USA (Champ (Big Bluestem)		0.157	1	0	forage	24*	0.56*	< 0.50*	25.06	post-
			24.09.96	0	hay	48*	3.2*	< 0.50*	51.7	emerg.
				7	forage	0.81*	2.9*	4.2*	7.91	Forage
				7	hay	1.4*	4.6*	< 0.50*	6.5	0 DALA
				14	forage	0.54*	1.8*	< 0.50*	2.84	24, 24
				14	hay	0.91*	3.4*	< 0.50*	4.81	Hay
										14 DALA
										0.89, 0.92
		0.157	2	0	forage	7.6*	< 0.50*	< 0.50*	8.6	post-
		0.078	03.07.97	0	hay	15*	4.7*	< 0.50*	20.2	emerg.
				7	forage	< 0.50*	0.57*	< 0.50*	1.57	
				7	hay	< 0.50*	1.6*	< 0.50*	2.6	
				14	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				14	hay	< 0.50*	0.75*	< 0.50*	1.75	
				28	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				28	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				55	forage	< 0.50*	< 0.50*	< 0.50*	< 1.5	
				55	hay	< 0.50*	< 0.50*	< 0.50*	< 1.5	

* average of two samples

*Miscellaneous fodder and forage crops**Rape seed forage*

Table 54 Residues of imazapic in rape seed forage straw from supervised trials conducted in Australia

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
GAP in Australia		0.0288	1	nr						
# 1998/1008955		0.035	1	5	forage	0.32	na	na		early
# 1998/1008975			06.09.97	19	forage	0.11	na	na		post-
Galore				33	forage	0.06	na	na		emerg.
New South Wales				80	straw	< 0.05	na	na		(PO01)
AUS										
(574/AU/97/01/SN01)		0.0525		5	forage	0.72	na	na		
(IT Canola)				19	forage	0.28	na	na		
				33	forage	0.13	na	na		
				80	straw	< 0.05	na	na		
		0.07		5	forage	0.67	na	na		
				19	forage	0.18	na	na		
				33	forage	0.17	na	na		
				80	straw	< 0.05	na	na		

Report-No. Location (trial no.) (variety)	Application rate			DALA (days)	Portion analysed	Residues (mg/kg)				Timing Remarks
	Method	Rate kg ai/ha	No.			Imazapic	CL263284	CL189215	Sum	
# 1998/1008955 # 1998/1008975 Beverley Western Australia AUS (574/AU/97/01/WA01) (Canadian IR variety)		0.035 0.0525 0.07	1 18.08.97	29 29 29	forage forage forage	0.10 0.20 0.20	na na na	na na na		post- emerg. (PO1)
# 1998/1008955 # 1998/1008975 Rannock New South Wales AUS (574/AU/98/06/SN01) (IT Canola)		0.021 0.035	1 05.08.98	19 33 47 62 19 33 47 62	forage forage forage forage forage forage forage forage	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	na na na na na na na na	na na na na na na na na		post- emerg. (PO1)
# 1998/1008955 # 1998/1008975 Burabadji Western Australia AUS (574/AU/98/06/WA01) (IT Canadian)		0.021 0.035	1 24.08.98	0 14 28 42 56 0 14 28 42 56	forage forage forage forage forage forage forage forage forage forage	0.46 0.05 < 0.05 < 0.05 < 0.05 1.80 0.13 0.07 < 0.05 < 0.05	na na na na na na na na na na	na na na na na na na na na na		post- emerg. (PO1) (C19-25)
# 1998/1008955 # 1998/1008975 Manoorra South Australia AUS (574/AU/98/06/SA01) (IT Canola)		0.021 0.035	1 24.09.98	9 20 35 49 9 20 35 49	forage forage forage forage forage forage forage forage	0.05 < 0.05 < 0.05 < 0.05 0.07 < 0.05 < 0.05 < 0.05	na na na na na na na na	na na na na na na na na		early flowering (PO1)
# 1998/1008955 # 1998/1008975 Dookie Victoria AUS (574/AU/98/06/SV01) (IT Canola)		0.021 0.035	1 18.09.98	0 12 27 42 76 0 12 27 42 76	forage forage forage forage straw forage forage forage forage straw	0.42 0.13 < 0.05 < 0.05 < 0.05 0.61 0.18 0.12 < 0.05 < 0.05	na na na na na na na na na na	na na na na na na na na na na		post- emerg. (PO1)

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

The Meeting received information on effects of heating in water and processing on imazapic residues in soya bean. An attempt was made to determine processing factors for processing of sugar cane into sugar and related commodities. However, even at the exaggerated rate (5× GAP rate), no residue was

detected in sugar cane samples above the LOQ of 0.01 mg/kg. For this reason no processing was performed.

High temperature hydrolysis

The hydrolysis of [^{14}C]-imazapic was investigated in sterile buffered aqueous solution under a range of hydrolysis conditions simulating processes such as pasteurization, baking/brewing/boiling and sterilization.

[Pyridine- ^{14}C]-imazapic was dissolved in the aqueous buffer solutions to give a final concentration of about 10 $\mu\text{g/ml}$ and incubated at 90 °C (pH 4) for 20 minutes, 100 °C (pH 5) for 60 minutes or 120 °C (pH 6) for 20 minutes. All test samples were prepared in sterile amber bottles to eliminate possible photolysis and all sterile buffers were bubbled with nitrogen to avoid effects of oxygen on the test systems. The samples were prepared in duplicates for each test system. For each of conditions, the total radioactivity present was determined at the end of the incubation period after cooling and compared to the theoretical radioactivity before incubation. The total radioactivity in each sample was determined by LSC. Radioactivity in the samples was analysed by HPLC immediately upon collection. Characterization of the radioactivity in the buffered samples after incubation was performed by HPLC-MS/MS.

After incubation at different pH, 101–102% of the applied radioactivity remained. At the end of the incubation periods, the detectable radioactive component was unchanged imazapic only. Imazapic was stable under conditions representing pasteurization and baking/brewing/boiling and sterilization.

Soya beans

Soya bean processing studies were conducted to determine the potential for concentration of residues of imazapic in the processed fractions of soya bean (Resende, 2009a and Leite, 2011a). During the 2008 growing season, two field trials were carried out in Brazil. Soya beans were treated with imazapic. Treated plot received one foliar post-emergence spray application at an exaggerated rate (same rates as the above study), 60 days before harvest. Samples of soya bean grain were taken 60 days after the application. The soya bean seed samples were separately processed using simulated commercial processing procedures into flaked soya bean, oil, meal and toasted meal. Soya bean samples were analysed for residues using Method SOP-PA.0288.

The analytical results indicate that imazapic slightly concentrated in meal. For all other analyte/commodity combinations, the processing factors showed residue decline.

Table 55 Residues of imazapic and its metabolites in processed commodities of soya bean seeds

Trial Location / Trial Number	Processed Commodity	Residues Found (mg/kg parent equiv.)				Processing Factor for Parent Imazapic	Processing Factor for Total Residue ^a
		Imazapic	CL263284	CL189215	Total ^a		
Santo Antonio de Posse, SP, Brazil (G080229) 2008	Seed	< 0.01	< 0.01	< 0.01	< 0.03	-	-
	Flaked soya bean	< 0.01	< 0.01	< 0.01	< 0.03	nd	nd
	Oil	< 0.01	< 0.01	< 0.01	< 0.03	nd	nd
	Meal	< 0.01	< 0.01	< 0.01	< 0.03	nd	nd
	Toasted meal	< 0.01	< 0.01	< 0.01	< 0.03	nd	nd
Londrina, PR, Brazil (G080230) 2008	Seed	0.08	< 0.01	0.03	0.12	-	-
	Flaked s.	0.04	< 0.01	0.01	0.06	0.50	0.50
	Oil	< 0.01	< 0.01	< 0.01	< 0.03	0.13	0.25
	Meal	0.09	< 0.01	0.03	0.13	1.13	1.08
	Toasted meal	0.07	< 0.01	0.02	0.10	0.88	0.83

^a sum of imazapic, CL263284 and CL189215

nd = not determined since residues in the RAC were below the LOQ

Another soya bean processing studies were conducted to determine the potential for concentration of residues of imazapic in the processed fractions of soya bean (Jones, 2011a). During the 2009 growing season, two field trials were carried out in Brazil. Soya beans were treated with imazapic. Treated plot received one foliar post-emergence spray application at an exaggerated rate of either 0.035 kg imazapic/ha (2×) or 0.0525 kg imazapic/ha (3×), 60 days before harvest. Samples of soya bean seed were taken 60 days after the application. The soya bean seed samples were separately processed using simulated commercial processing procedures into defatted meal, toasted defatted meal, laminated soya bean, oil, meal and hulls.

Soya bean samples were analysed for residues of imazapic and its metabolites using Method SOP-PA.0288.

The analytical results indicate that imazapic slightly concentrated in defatted and toasted defatted meal and CL189215 slightly concentrated in defatted meal. For all other analyte/commodity combinations, the processing factors showed a residue decline.

Table 56 Residues of imazapic and its metabolites in processed commodities of soya bean seeds

Trial Location / Trial Number	Processed Commodity	Residues Found (mg/kg parent equiv.)				Processing Factor for Imazapic	Processing Factor for Total Residue ^a
		Imazapic	CL263284	CL189215	Total ^a		
Santo Antonio de Posse, SP, Brazil (G090003) 2009	Seed	0.07	< 0.01	0.02	0.10	-	-
	Defatted meal	0.09	< 0.01	0.03	0.13	1.29	1.30
	Toasted defatted meal.	0.08	< 0.01	0.02	0.11	1.14	1.10
	Oil	< 0.01	< 0.01	< 0.01	< 0.03	0.14	0.30
	Laminated soya bean.	0.05	< 0.01	< 0.01	0.07	0.71	0.70
	Seed	0.07	< 0.01	0.03	0.11	-	-
	Hulls	0.07	< 0.01	0.01	0.09	1.00	0.81
	Meal	0.07	< 0.01	0.03	0.11	1.00	1.00
Londrina, PR, Brazil (G090004) 2009	Seed	< 0.01	< 0.01	< 0.01	< 0.03	-	-
	Defatted mal	< 0.01	< 0.01	na	(< 0.03)	nd	nd
	Toasted defatted meal.	< 0.01	< 0.01	na	(< 0.03) [#]	nd	nd
	Oil	< 0.01	< 0.01	na	(< 0.03)	nd	nd
	Laminated soya bean.	< 0.01	< 0.01	< 0.01	< 0.03	nd	nd
	Seed	0.02	< 0.01	< 0.01	0.04	-	-
	Hulls	0.02	< 0.01	< 0.01	0.04	1.00	1.00
	Meal	0.02	< 0.01	< 0.01	0.04	1.00	1.00

^a Sum of imazapic, CL263284 and CL189215

na = not analysed

nd = not determined since residues in the RAC were below the LOQ

Table 57 Summary of processing factors for soya bean processing

Processed commodity	N	Imazapic		Sum of imazapic, CL263284 and CL189215	
		Processing factor	Mean or best estimate	Processing factor	Mean or best estimate
Meal	3	1.00, 1.00, 1.13	1.04	1.00, 1.00, 1.08	1.03
Defatted meal	1	1.29	1.29	1.30	1.30

Processed commodity	N	Imazapic		Sum of imazapic, CL263284 and CL189215	
		Processing factor	Mean or best estimate	Processing factor	Mean or best estimate
Toasted Meal	1	0.88	0.88	0.83	0.83
Toasted Defatted Meal	1	1.14	1.14	1.10	1.10
Oil	2	0.13, 0.14	0.14	0.30, 0.25	0.28
Laminated Soya Bean	1	0.71	0.71	0.70	0.70
Flaked Soya Bean	1	0.50	0.50	0.50	0.50
Hulls	2	1.00, 1.00	1.00	0.81, 1.00	0.91

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

The Meeting received information on lactating cow feeding study.

Lactating cows

Four groups of lactating Holstein cows, each group containing three animals, were orally dosed with imazapic in gelatin capsules using a balling gun for 28 days following afternoon milking at levels equivalent to 0, 67, 223, and 676 ppm in feed (Leonard, 1999a). Milk samples were collected twice daily during dosing period and afternoon milk and morning milk were pooled. Within 24 hours after the last dose, cows were sacrificed. After sacrifice, loin muscle, omental fat, liver and kidney were collected. All samples were analysed for imazapic and CL 263284 using Methods M 3188 for milk, M 3222 for tissues, and M 3233 for fat.

In the lowest dose group (67 ppm), residues of imazapic in milk reached a plateau after Day 1 and averaged 0.025 mg/kg. In milk fat and kidney, average residues were 0.013 and 0.384 mg/kg, respectively. In muscle, liver and omental fat, average residues were < 0.050 mg/kg.

In the middle dose group (223 ppm), residues of imazapic in milk averaged 0.077 mg/kg. In milk fat and omental fat, average residues were 0.037 and 0.051 mg/kg, respectively. In loin muscle, kidney and liver, average residues were 0.054, 1.57 and 0.082 mg/kg, respectively.

In the highest dose group (676 ppm), residues of imazapic in milk averaged 0.274 mg/kg. In milk fat and omental fat, average residues were 0.127 and 0.051 mg/kg, respectively. In muscle, kidney and liver, average residues were 0.079, 2.71 and 0.192 mg/kg, respectively.

Levels of CL263284 was below the respective LOQ in all matrices and at all dosing levels.

Table 58 Residues of imazapic and CL263284 in whole milk during the feeding study

Day	Mean (mg/kg) (Maximum Individual Residues) (mg/kg)			
	Group A (Control)	Group B (67 ppm)	Group C (223 ppm)	Group D (676 ppm)
Imazapic				
-1	< 0.01	< 0.01 (< 0.01)*	< 0.01 (< 0.01)	< 0.01 (< 0.01)
1	< 0.01	0.025 (0.030)	0.067 (0.090)	0.308 (0.374)
2	< 0.01	0.027 (0.031)	0.081 (0.120)	0.267 (0.316)
3	na	0.027 (0.030)	0.076 (0.103)	0.284 (0.339)
6	< 0.01	0.018 (0.022)	0.076 (0.096)	0.247 (0.289)
10	< 0.01	0.025 (0.029)	0.074 (0.086)	0.244 (0.286)
15	< 0.01	0.030 (0.035)	0.082 (0.093)	0.271 (0.354)

Day	Mean (mg/kg) (Maximum Individual Residues) (mg/kg)			
	Group A (Control)	Group B (67 ppm)	Group C (223 ppm)	Group D (676 ppm)
20	< 0.01	0.025 (0.027)	0.071 (0.080)	0.286 (0.346)
24	< 0.01	0.029 (0.032)	0.089 (0.121)	0.280 (0.317)
27	< 0.01	0.023 (0.026)	0.079 (0.085)	0.281 (0.313)
CL 263284				
-1	< 0.01	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)
1	< 0.01	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)
2	< 0.01	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)
3	na	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)
6	< 0.01	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)
10	< 0.01	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)
15	< 0.01	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)
20	< 0.01	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)
24	< 0.01	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)
27	< 0.01	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)

na = not analysed

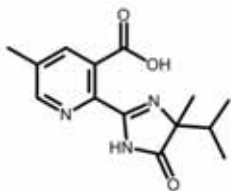
* maximum individual residues

Table 59 Residues of imazapic and CL263284 in tissues and milk fat

Tissue	Mean (mg/kg) Maximum Individual Residues (in parentheses) (mg/kg)			
	Group A (Control)	Group B (67 ppm)	Group C (223 ppm)	Group D (676 ppm)
Imazapic				
Muscle	< 0.05	< 0.05 (< 0.05)	0.054 (0.0626)	0.079 (0.081)
Kidney	< 0.05	0.384 (0.465)	1.567 (2.200)	2.708 (3.750)
Liver	< 0.05	< 0.05 (< 0.05)	0.082 (0.126)	0.192 (0.231)
Fat	< 0.05	< 0.05 (< 0.05)	0.051 (0.054)	0.051 (0.053)
Milk fat	< 0.01	0.013 (0.015)	0.037 (0.043)	0.127 (0.135)
CL 263284				
Muscle	< 0.05	< 0.05 (< 0.05)	< 0.05 (< 0.05)	< 0.05 (< 0.05)
Kidney	< 0.05	< 0.05 (< 0.05)	< 0.05 (< 0.05)	< 0.05 (< 0.05)
Liver	< 0.05	< 0.05 (< 0.05)	< 0.05 (< 0.05)	< 0.05 (< 0.05)
Fat	< 0.05	< 0.05 (< 0.05)	< 0.05 (< 0.05)	< 0.05 (< 0.05)
Milk fat	< 0.01	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)

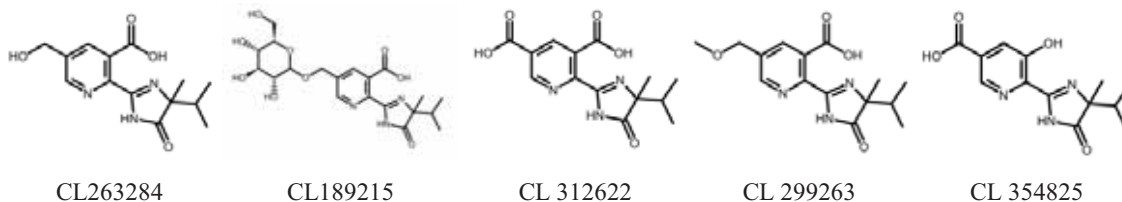
APPRAISAL

Imazapic is an imidazolinone herbicide developed for the control of grass and broadleaf weeds in a variety of crops and registered in a number of countries. It was considered for the first time by the present Meeting.



Information on the physical and chemical properties, animal and plant metabolism, environmental fate, analytical methods, storage stability, use patterns, supervised trials, processing and farm animal feeding was received by the present Meeting.

The following abbreviated names were used for the metabolites discussed below.



Animal metabolism

The Meeting received information on the fate of orally-dosed imazapic in rat, lactating goats and laying hens.

In metabolism studies, total radioactive residues are expressed in mg/kg imazapic acid equivalents unless otherwise stated.

Metabolism of imazapic in rat

Metabolism studies on laboratory animals including rats were reviewed in the framework of toxicological evaluation by the current JMPR.

Metabolism of imazapic in lactating goats

Imazapic

In two studies on lactating goats, [pyridine-6-¹⁴C]-imazapic was orally administered at three doses via capsule (equivalent to 2.0, 11.8 and 175 ppm in feed) for 5 or 7 consecutive days. The majority was eliminated in urine (67–94% of TAR) in the form of unchanged imazapic and faeces (7–10% of TAR). Milk contained up to 0.03% of TAR and edible tissues 0.01% of TAR at the highest dose.

The TRR of daily collected milk samples were lower than the LOQ of 0.01 mg eq/kg at the two lower doses.

The goats were sacrificed 20 or 23 hours after the last dose at which time tissue samples were obtained. The highest TRR (0.275 mg eq/kg) was observed in kidney from the highest dose regime, reflecting that urinary excretion was the predominant elimination route. At the two lower doses, except that the TRR of the kidney from goat dosed at 11.8 ppm was 0.05 mg eq/kg, the TRR in milk or tissues were below the respective LOQ of 0.01 (milk) or 0.02 mg eq/kg (muscle).

The analysis of acetonitrile+methanol extract of kidney from the highest dose indicates that imazapic was the major residue at 30% TRR (0.02 mg/kg) with CL263284 at 8% of TRR (< 0.01 mg/kg). As the TRRs in milk and tissues, other than kidney, from any dose levels were too low to characterize any of radioactive residues, extraction of radioactive residues was not attempted for these tissues or milk.

CL 263284

In a study on lactating goats with oral administration of [pyridine-6-¹⁴C]- CL 263284 in capsule at doses equivalent to 2.3 or 14.5 ppm in feed for 7 consecutive days, radioactivity was eliminated mostly via faeces (82% TAR for the low dose and 68% TAR for the high dose) and in a lesser amount from urine (15–18% TAR). The TRR of daily milk samples and tissues obtained 20 hours after the last dose were below the LOQ of 0.01 mg/kg except kidney from the high dose goat (0.03 mg eq/kg). About 91% of TRR in the kidney from high dose goat was extracted with methanol and CL 263284 was present at 9% (< 0.01 mg/kg) of the extracted TRR. Component M1 found at significant amounts (78% TRR, 0.02 mg eq/kg) may be an extraction artifact and was converted into CL 263284 on exposure to aqueous buffer.

Metabolism of imazapic in laying hens

In a hen study [Pyridine-6-¹⁴C]-imazapic orally administered in capsule to laying hens, at a dose equivalent to 2.1 or 11.4 ppm in feed for 7 consecutive days, was mostly eliminated into excreta (91–95% of TAR). The TRR in all egg and tissue samples were less than the LOQ of 0.01 mg eq/kg.

The [Pyridine-6-¹⁴C]-CL263284 orally administered to laying hens at 2.1 or 10.9 ppm in feed for 7 consecutive days was mostly eliminated into excreta and the TRR in all tissues, skin with adhering fat and eggs were below the LOQ of 0.01 mg/kg. No detectable radioactive residues were found in eggs or edible tissues obtained 22 hours after the last dose.

Metabolites of imazapic in goat were similar to those in rat. With rapid excretion, the radioactive residues in edible tissues, milk or eggs were mostly below the LOQ. In lactating goats, residues remaining in the kidney were mostly unchanged parent with a minor amount of CL263284.

Plant metabolism

The Meeting received information on the fate of imazapic in sugar cane, peanuts, Bermuda grass and transgenic soya bean.

When [pyridine-6-¹⁴C]-imazapic was applied to the soil surface as a pre-emergent treatment at a rate approximating 0.15 kg ai/ha (within GAP rates) in a small test plot, no radioactive residues were detected above the LOQ of 0.005 mg/kg in the stalk of sugar cane harvested 13 months after the treatment.

When [pyridine-6-¹⁴C]-imazapic was applied to the soil surface as a pre-emergent treatment at a rate approximating 0.25 kg ai/ha (within GAP rates) in a greenhouse, the TRR in the adult sugar cane stalk and leaves collected 236 DAT was 0.0039–0.048 mg eq/kg and 0.015–0.016 mg eq/kg respectively.

High percentages (63–84% TRR) of the radioactive residues in forage, leaves and stalks collected at various timings were extracted by methanol. Most of the extracted radioactive residues were water soluble.

Imazapic was found in all samples but declined with time, e.g., in stalks 0.003 mg/kg (41% TRR) at 151 DAT to 0.0005 mg/kg (11% TRR) at 236 DAT. CL263284 was found in all the samples collected at higher concentrations than the parent, but both the concentration and proportion to TRR also declined with time, e.g., in stalk 0.001 mg/kg (16% TRR) at 151 DAT to 0.0005 mg/kg (10% TRR) at 236 DAT. CL189215 was also found at lower concentrations in leaves (0.0005–0.002 mg/kg, 3–8% TRR), but not in stalks.

[Pyridine-6-¹⁴C]-imazapic was applied to peanut plants at a rate of 0.072 kg ai/ha (within GAP rates) 30 days post-emergence. The TRR declined significantly from 4.2 mg eq/kg at 0 DAT to 0.094 mg eq/kg at 61 DAT in green plants and 0.22 mg eq/kg in hay collected 131 DAT. The TRR in nutmeat at 131 DAT was low at 0.022 mg eq/kg. A mixture of methanol:water:acetone (1:1:1) extracted 76–96% of the TRR in peanut samples.

The concentration of imazapic sharply declined in plants to 0.006 mg/kg at 61 DAT (2% TRR). The concentration in nutmeat, hull and hay samples collected 131 DAT were even lower (< 0.001–0.006 mg/kg, 1–3% TRR). The concentration of CL263284 also decreased over time to 0.010 mg/kg (12% TRR) at 61 DAT in plants. The concentrations of CL189215 declined over time to 0.039 mg/kg at 61 DAT (46% TRR) in plants. The concentrations of these three compounds were all less than 0.01 mg/kg in nutmeat at 131 DAT. No other component in the extracts from immature or mature samples exceeded 10% of TRR or 0.01 mg/kg.

Bermuda grass was treated post-emergence with [pyridine-6-¹⁴C]-imazapic at a rate of 0.2 kg ai/ha (maximum GAP rate for grass in the USA). The TRR in plants decreased over time from 8.3 mg eq/kg at 0 DAT to 0.77 mg eq/kg at 47 DAT and was 0.92 mg eq/kg in hay (68 DAT). From forage and hay samples, 74–100% of radioactive residues were extracted by aqueous solutions with hay sample at the lowest 74%.

The concentration of imazapic declined sharply to 0.02 mg/kg (3% TRR) at 49 DAT. CL263284 concentration showed a sharp increase in the early period to the peak concentration of 1.7 mg/kg (30% TRR) at 15 DAT and then decrease to 0.16 mg/kg (21% TRR) at 49 DAT. It was found in hay at 0.08 mg/kg (8% TRR). CL189215 also increased in concentration in the early stage to the peak concentration of 0.17 mg/kg (4% TRR) at 15 DAT then to 0.08 mg/kg (9% TRR) at 49 DAT. In the hay sample collected 68 DAT, imazapic, CL263284 and CL189215 were present at 0.02, 0.08 and 0.08 mg/kg respectively but all below 10% of TRR.

There were many minor polar components but none exceeded 10% TRR individually.

[Pyridine-3-¹⁴C]-imazapic was applied to the above-ground portion of imidazolinone-tolerant soya bean plants (with mutated AtAHASL protein inserted to make the host tolerant to imidazolinone herbicide) at BBCH 65 at an application rate of 0.08 kg ai/ha. The TRR in soya bean seed and straw were 0.014 mg eq/kg and 0.092 mg eq/kg respectively. From forage, hay, seed, straw and pod samples, 78–98% of radioactive residues were extracted by aqueous solutions.

In seeds, imazapic was the most abundant residue at 20% TRR but only 0.003 mg/kg. Imazapic was the most abundant residue in straw and pods but at 0.00013 and 0.004 mg/kg respectively. CL189215 was the second most abundant compound individually but at < 0.01 mg/kg and less than 10% of TRR. CL263284 was also present but less than imazapic or CL189215. There were many minor polar components detected but none exceeded 0.01 mg/kg or 10% of TRR individually.

In the edible portions of treated food crops harvested at maturity, no or little residues of imazapic are expected to be found. In animal feed crops, such as grasses, imazapic, CL 263284 and CL 189215 are expected to be found above the LOQ.

Environmental fate

The Meeting received information on aerobic soil metabolism, photodegradation on the soil surface, hydrolysis and residues in succeeding crops.

Aerobic soil metabolism

About 70% of the applied imazapic (equivalent to 0.14 kg/ha) remained in sandy loam soils after one year of incubation in one study and about 80% remained in soil after 120 days of incubation in the other. Mineralization occurred but at very low percentage.

CL263284 applied to soil degraded to less than 1% of the applied dose in 3 days forming CL312622, CL354825 and carbon dioxide.

AC299263 and CL 312624 applied to soil degraded more gradually both transforming to CL354825 and carbon dioxide.

Degradation of these compounds was significantly less in soil under sterile conditions, indicating microbial action.

Imazapic was found to be persistent in sandy loam soils under anaerobic conditions. However, its metabolites/degradates were more readily degraded in soil.

Photodegradation

¹⁴C-Labelled imazapic was applied to a sandy loam soil at a rate equivalent to 0.08 kg/ha (within GAP rates). The total radioactivity in the aqueous sodium hydroxide extract (10% AR) and unextracted fraction (3% AR) was about 7% of the applied dose after 30 days of irradiation by a xenon-arc lamp comparable to mid-autumn sunlight in New Jersey, USA.

The imazapic concentration decreased from 94% of the extracted radioactivity on day 0 to 75% after the 30-day irradiation. A diacid degradate, CL 312622, formed up to 11% of the extracted radioactivity. The DT₅₀ was calculated to be 106 days.

Photolysis of imazapic (25 mg/kg) in sterilized water was rapid at pH 5, 7 and 9 under irradiation by a xenon-arc lamp comparable to mid-autumn sunlight in New Jersey, USA, with DT₅₀ in a range of 6.0–7.2 hours. Six degradation products, including carbon dioxide were formed, each of which accounted for around 10%.

Imazapic is photodegraded gradually with a half-life around 100 days on the surface of soil and rapidly with half-life of about 6–7 hours in sterilized water.

Hydrolysis

As imazapic can be used in rice production, ¹⁴C-Labelled imazapic was applied to water+soil at a nominal rate equivalent to about 0.14 kg/ha (within GAP rates) and kept under anaerobic conditions.

Only 0.5% of the applied dose was mineralized. No other radioactive volatile compounds were collected. No volatilization or degradation occurred.

The concentration of imazapic decreased from 92% (36% in the soil extract and 56% in water) on day 0 to 83% (54% in the soil extract and 29% in the water) of the applied dose after 366 days.

Imazapic was stable for 366 days at 25 °C in water+ soil.

Residues in succeeding crops

A confined study was conducted to examine the nature and level of residues of imazapic in succeeding crops. A single application of [pyridine-6-¹⁴C]-imazapic was made on soil in field plots at a nominal rate of 0.72 kg ai/ha, higher than any GAP rates.

At each rotational interval of 90, 120, 270 and 300 days after treatment, barley, maize cotton, lettuce and carrots were sown into the treated soil and harvested at maturity.

Following the application of imazapic to soil, uptake of radioactivity into rotational crops was low (< 0.004–0.070 mg eq/kg). However, the TRR in barley and maize samples show a tendency to be higher in samples obtained from longer plant back intervals. The TRR of lettuce and carrot (both with 20 day plant back intervals (PBI)) were 0.006 and < 0.004 mg eq/kg, respectively.

In barley grain, imazapic was the most abundant residue from the 120 day PBI at 23% TRR (0.007 mg/kg) followed by the sum of CL263284 and CL189215 at 18% TRR (0.006 mg/kg). In the 270 day PBI barley grain, the most abundant residue was the sum of CL263284 and CL189215 at 37% TRR (0.021 mg/kg) followed by imazapic at 10% (0.004 mg/kg). In straw the most abundant residue was the sum of CL263284 and CL189215 at 44% TRR (0.031 mg/kg) for 120 day PBI and

44% TRR (0.031 mg/kg) for 270 day PBI. Imazapic was present in straw at 5.4–5.5% TRR (0.003–0.004 mg/kg).

In the 300 day PBI maize forage and fodder, the sum of CL263284 and CL189215 was the most abundant residue at 28% (0.005 mg/kg) and 28% (0.008 mg/kg) TRR respectively.

Radioactive residues remained mostly in the 0–8 cm depth layer of soil. High percentage (57–91% TRR) of radioactive residues in soil were extracted with aqueous methanol/acetone mixture and 2% HCl. Nine to 43% TRR remained as unextracted residues.

Following the application of imazapic to soil, uptake of radioactivity into rotational crops was low (maximum at 0.070 mg eq/kg). Among registered uses related to the current review, the highest application rate was for sugar cane or grass. In comparison, the application rate used in this confined rotational crop study was about 3 times the GAP rate in Brazil and 7.5 times the GAP rate in Australia for sugar cane or 3.5 times the GAP rate for grass in the USA. This application rate was more than 7.5 times higher than the GAP rate for other crops used in crop rotation. Residues of imazapic in plant portions of rotational crops used as food or feed after approved application are expected to be less than one third of the residues observed in the confined rotational crop study, i.e., around or lower than the lowest LOQ of 0.01 mg/kg.

Methods of analysis

Analytical methods for the determination of residues of imazapic and its metabolites were developed for a wide range of matrices of plant and animal origin.

In general, the methods for data generation employ extraction by homogenization with a mixture of methanol:water:1M HCl (60:39:1) or, in the case of fat, acidic acetonitrile in hexane, clean-up with solid phase extraction or some other techniques, and determination of analytes using LC-MS/MS, HPLC-UV (245 nm) or capillary electrophoresis-UV (240 nm).

A number of specific methods for plant matrices were found suitable for analysis of imazapic, CL263284 and CL189215 with LOQ ranging 0.01–0.1 mg/kg for these analytes except that it was 0.5 mg/kg for grass.

Three methods for animal matrices were found suitable for analysis of imazapic and CL263284 with LOQ of 0.01 (milk and milk fat) and 0.05 (tissues) mg/kg.

No multi-residue methods were submitted.

Stability of residues in stored analytical samples

The stability of imazapic residues during storage of samples frozen at -25 to -5 °C was investigated in a range of plant and animal matrices for which supervised residue trials were submitted.

Compounds tested were imazapic, CL263284 and CL189215. Each compound was spiked to matrices at 0.5 mg/kg.

All of the compounds tested were found to be stable (> 70% remaining) at least during the storage periods tested: 2 years in wheat, sugar cane, peanut and grass matrices; 10 months in soya bean seeds; 3 months in processed soya bean products; 6 months in cattle milk; and 8 months in cattle tissues. These storage periods are longer than the longest storage conditions in trials on respective crops.

Definition of the residue

In animal metabolism, parent imazapic was the predominant residue with CL263284 a minor component at around 10% TRR in goat kidney. In other tissues, milk or eggs, TRR were below the respective LOQs. In a metabolism study in which CL 263284 was administered, TRR in milk and tissues were below the LOQ of 0.01 mg/kg. CL263284 found in goat kidney is also a metabolite in rats and, as such, is covered by the ADI. However, in the livestock feeding study using imazapic, CL 263284 was not detected above the LOQ of 0.01 mg/kg (milk and milk fat) or 0.05 mg/kg (tissues) at

the highest dose of 676 ppm in the feed. Therefore, the Meeting considered that parent imazapic is a suitable residue for enforcement of MRLs and for calculating dietary intake for commodities of animal origin.

With a low $\log P_{ow}$ of 0.054 and given the distribution of residues in animal tissues from the animal metabolism studies and animal feeding study, the Meeting considered imazapic residue not fat-soluble.

The plant metabolism studies indicate that no or little residues of imazapic or its metabolites are expected to be found in the edible portions of food crops harvested at maturity. In supervised trials on soya beans, CL 263284 and CL 189215 were found at lower concentrations than the parent, when measured.

In feed crop such as grass, imazapic, CL 263284 and CL 189215 (a glucoside of CL 263284 found in plants and in a very small amount in rats) are expected to be found above the LOQ of 0.5 mg/kg (in the residue trials) as demonstrated in the metabolism study and in residue trials.

The Meeting considered that the parent imazapic was a suitable residue for enforcement of MRLs and for calculating dietary intake for commodities of plant origin.

Based on the above, the Meeting recommended the following residue definition for plant and animal commodities:

Definition of the residue for plant and animal commodities (both for compliance with the MRL and for dietary intake): *Imazapic*.

Residue is not fat-soluble.

Results of supervised residue trials on crops

The Meeting received supervised trial data for imazapic on conventional and transgenic soya beans, maize, rice, wheat, sugar cane, peanut, grasses and transgenic rape seed.

Soya bean (dry)

A total of 16 supervised trials were conducted on imidazolinone-tolerant soya beans (conventionally bred or transgenic) in different years in Brazil. However, as no GAP for soya bean was available, it was not possible to estimate a maximum residue level.

Maize

A total of five trials were conducted on imidazolinone-tolerant maize in 2010 in Brazil.

The registered use on imidazolinone-tolerant maize in Brazil allows one application at a maximum rate of 0.0525 kg ai/ha with a PHI of 96 days.

Residues of imazapic from trials matching GAP in Brazil were: < 0.01 (4) and < 0.1 mg/kg.

Although the number of trials matching GAP is small, as the metabolism studies indicate that no residues are expected in edible portion of food crops harvested at maturity and the residue trial data on other cereal grains (rice and wheat) indicate that residues were below the respective LOQ at even exaggerated application rates, the Meeting considered that no residues would be expected in maize grain.

The Meeting therefore estimated a maximum residue level and STMR of 0.01* and 0 mg/kg, respectively, for maize.

Rice

A total of 11 trials were conducted on imidazolinone-tolerant rice in Brazil in different years.

The registered use on imidazolinone-tolerant rice in Brazil allows up to two applications at a maximum rate of 0.025 kg ai/ha with a PHI of 60 days.

Residues of imazapic from trials matching GAP in Brazil were: < 0.05 (10) mg/kg. In many trials, $2 \times$ GAP rate was used. In these trials, residues were all < 0.05 mg/kg (9).

The Meeting estimated a maximum residue level and STMR of 0.05 * and 0 mg/kg, respectively, for rice grain.

Wheat

Four trials were conducted for imidazolinone-tolerant wheat in Australia. The registered use of imazapic on wheat in Australia allows one application at a maximum rate of 0.021 kg ai/ha (only for imidazolinone-tolerant wheat) at 4 leaf (Z14) to the commencement of the flag leaf (Z37) stage. No PHI is required. Grazing and cutting for animal feed are not allowed for 4 weeks after application.

Residues of imazapic from trials matching GAP in Australia were: < 0.05 (2) mg/kg.

Although the number of trials matching GAP is small, as residues from trials using higher rate (up to $3.5 \times$ GAP rate) were all < 0.05 mg/kg (total of 4), and the metabolism studies indicate that no residues are expected in edible portions of food crops harvested at maturity, the Meeting considered that no residues would be expected in wheat grain.

The Meeting therefore estimated a maximum residue level and STMR of 0.05* and 0 mg/kg, respectively for wheat.

Sugar cane

A total of 14 trials were conducted on sugar cane in Argentina, Australia, Brazil, Costa Rica and Guatemala.

The registered uses on sugar cane in these countries allow one application at a maximum rate of: 0.35 kg ai/ha with a PHI of 392 days in Argentina, 0.096 kg ai/ha in Australia, 0.245 kg ai/ha with a PHI of 283 days, 0.175 kg ai/ha with a PHI of 85 days in Costa Rica and Guatemala respectively.

The trial data were evaluated against GAP in Brazil. Residues of imazapic in sugar cane from trials matching GAP in Brazil were: < 0.01 (8) and < 0.05 (5) mg/kg. With shorter PHI or at $5 \times$ GAP rate (two trials), residues were < 0.01 mg/kg.

The Meeting estimated a maximum residue level and STMR of 0.01* and 0 mg/kg, respectively, for sugar cane.

Peanut

A total of 17 trials were conducted on peanuts in Brazil (5) and in the USA (12) in different years.

The registered uses on peanut in these countries allow one application at a maximum rate of 0.098 kg ai/ha with a PHI of 70 days in Brazil; and 0.071 kg ai/ha with a PHI of 90 days in the USA.

Residues in peanuts from trials in Brazil matching Brazilian GAP were: < 0.05 (4) and < 0.1 mg/kg. Residues in peanut nutmeat from trials in the USA matching the GAP in the USA were: < 0.1 mg/kg (7). In the 12 trials using exaggerated rates ($2 \times$ or $3 \times$ GAP rate), residues in nut, hull or nutmeat were all below the LOQ (0.05 or 0.1 mg/kg) (10).

The Meeting estimated a maximum residue level and STMR of 0.05* and 0 mg/kg, respectively for peanut.

The Meeting also estimated a median residue of 0 mg/kg for peanut hulls.

Rape seed

Three trials were conducted on imidazolinone-tolerant rape seed in Australia in 1997 and 1998.

The registered use on imidazolinone-tolerant rape seed in Australia allows one application at a maximum application rate of 0.0288 kg ai/ha at the 2–6 leaf stage of the crop. No PHI is required.

Residues of imazapic in rape seed from trials within

25% of GAP in Australia were: < 0.05 mg/kg (3). Residues from trials using exaggerated application rates (up to 2.4× GAP rate) were all < 0.05 mg/kg (2).

The Meeting estimated a maximum residue level and STMR of 0.05* and 0 mg/kg, respectively for rape seed.

Animal feed

Peanut fodder

Six trials involving peanut fodder were conducted in the USA in 1995. However, according to the GAP in the USA, grazing and feeding of treated peanut hay to livestock is not allowed. Therefore, there is no need to evaluate residues in peanut hay.

Wheat straw and fodder, dry, and forage

Five trials were conducted in Australia for wheat forage (four for straw).

According to GAP in Australia, grazing and cutting for stock feed are not allowed for 4 weeks after the application.

Residues of imazapic in wheat forage from trials matching GAP in Australia 4 weeks after application were: < 0.05 (3) mg/kg. Residues in forage from trials with exaggerated rates (up to 3.5× GAP rate; five trials) were < 0.05 mg/kg and residues in forage collected 15–19 days after application at any application rate were also < 0.05 mg/kg.

A median residue and highest residue were estimated for wheat forage at 0.05 and 0.05 mg/kg, respectively.

Residues of imazapic in wheat straw from trials matching GAP in Australia were: < 0.05 mg/kg (2). Residues in wheat straw from trials with exaggerated rates (up to 3.5× GAP rate) were all < 0.05 mg/kg (4).

The Meeting estimated a maximum residue level of 0.05* mg/kg for wheat straw and fodder, dry.

A median residue and highest residue for wheat straw and fodder, dry were 0 mg/kg.

Hay or fodder (dry) of grasses

A total of 10 trials were conducted on grasses in the USA.

The registered use on grasses in the USA allows one application at a maximum rate of 0.20 kg ai/ha after grass is full (100%) green-up for spring and summer application, or grass is dormant before green-up or full green-up for winter application. According to GAP cutting treated area for hay is not allowed within 7 days after treatment. There is no restriction on grazing on the label.

Residues of imazapic in forage from trials matching GAP in the USA were: 7.3, 7.5, 8.8, 10, 12, 13, 15, 15, 22 and 24 mg/kg.

The Meeting estimated a median residue and highest residue at 12.5 and 24 mg/kg respectively for grass forage on an "as received" basis.

Residues of imazapic in hay (> 7 DALA) from trials matching GAP in the USA were: < 0.50 (8), 0.91 and 2.3 mg/kg.

The Meeting estimated a maximum residue level, median residue and highest residue at 3, 0.5 and 2.3 mg/kg for hay or fodder (dry) of grasses, respectively.

Rape seed forage

Five trials were conducted in Australia for rape seed forage.

The approved uses in Australia do not allow grazing or cutting for stock feed for 6 weeks after application. Residues in rape seed forage 42 days after application at application rates within $\pm 25\%$ of the GAP rate were: < 0.05 (4) mg/kg.

The Meeting estimated a median residue and highest residue of 0.05 mg/kg.

Fate of residues during processing

High temperature hydrolysis

The hydrolysis of [^{14}C]-imazapic was investigated in sterile buffered aqueous solution.

After incubation at 90 °C (pH 4) for 20 minutes, 100 °C (pH 5) for 60 minutes or 120 °C (pH 6) for 20 minutes, 101–102% of the applied radioactivity remained. At the end of the incubation periods, the detectable radioactive component was unchanged imazapic only. Imazapic was stable under conditions representing pasteurization and baking/brewing/boiling and sterilization.

Processing

The Meeting received information on processing of soya beans.

A processing factor was calculated for the processing of soya beans to oil to be 0.14.

Processing factors for meal and hulls which can be fed to animals were also calculated but not reported here as no maximum residue level was recommended for soya beans, dry.

Residues in animal commodities

Estimation of dietary burdens

The maximum and mean dietary burdens were calculated using the highest residues or median residues of imazapic estimated at the current Meeting on a basis of the OECD Animal Feeding Table.

Summary of livestock dietary burdens (ppm of dry matter diet)

	US-Canada		EU		Australia		Japan	
	max	mean	max	Mean	max	mean	Max	mean
Beef cattle	0.401	0.094	48.0	25.0	96.0	50.0	5.72	2.71
Dairy cattle	43.2	22.5	57.6	30.0	96.0 ^a	50.0 ^b	11.2	5.34
Broilers	0.009	0.009	0.008	0.008	0	0	0.008	0.008
Layers	0.009	0.009	9.63 ^c	5.03 ^d	0	0	0.009	0.009

^a Suitable for estimating maximum residue levels for milk, meat, fat and edible offal of cattle.

^b Suitable for estimating STMRs for meat, fat and edible offal of cattle.

^c Suitable for estimating maximum residue levels for meat, fat and edible offal of poultry and eggs.

^d Suitable for estimating STMRs for meat, fat and edible offal of poultry and eggs.

Residues in milk and cattle tissues

Four groups of lactating Holstein cows, each group containing three animals, were orally dosed with imazapic in gelatine capsules using a balling gun for 28 days following afternoon milking at levels equivalent to 0, 67, 223, and 676 ppm in the feed. Milk samples were collected twice daily during the dosing period with afternoon and morning milk pooled. Within 24 hours after the last dose, the cows were sacrificed. After sacrifice, loin muscle, omental fat, liver and kidney were collected and analysed.

In the lowest dose group (67 ppm), residues of imazapic in milk reached a plateau after Day 1 and averaged 0.025 mg/kg. In milk fat and kidney, average residues were 0.013 and 0.384 mg/kg, respectively. In muscle, liver and omental fat, average residues were < 0.050 mg/kg.

In the middle dose group (223 ppm), residues of imazapic in milk averaged 0.077 mg/kg. In milk fat and omental fat, average residues were 0.037 and 0.051 mg/kg, respectively. In loin muscle, kidney and liver, average residues were 0.054, 1.57 and 0.082 mg/kg, respectively.

In the highest dose group (676 ppm), residues of imazapic in milk averaged 0.274 mg/kg. In milk fat and omental fat, average residues were 0.127 and 0.051 mg/kg, respectively. In muscle, kidney and liver, average residues were 0.079, 2.71 and 0.192 mg/kg, respectively.

Levels of CL263284 were below the respective LOQ in all matrices and at all dosing levels.

The maximum and mean dietary burdens in cattle were 96 and 50 ppm of dry matter diet respectively for estimating a maximum residue level and STMR for milk and edible tissues. The maximum residue levels, STMRs and HRs for relevant commodities of animal origin were estimated using the residue levels in tissues and milk at 67 and 223 ppm feeding group.

	Feed level (ppm) for milk residues	Imazapic (mg/kg) in	Feed level (ppm) for tissue residues	Imazapic (mg/kg) in			
		milk		Muscle	Liver	Kidney	Fat
Maximum residue level beef or dairy cattle							
Feeding study ^a	67	0.025	67	< 0.05	< 0.05	0.465	< 0.05
	223	0.274	223	0.063	0.126	2.20	0.054
Dietary burden and highest residue	96	0.071	96	0.052	0.064	0.788	0.051
STMR beef or dairy cattle							
Feeding study ^b	67	0.025	67	< 0.05	< 0.05	0.384	< 0.05
Dietary burden and mean residue	50	0.019	50	< 0.05	< 0.05	0.287	< 0.05

^a highest residues for tissues and mean residue for milk

^b mean residues for tissues and mean residue for milk

The Meeting estimated STMRs of 0.019, 0.05, 0.05, 0.287 and 0.05 mg/kg for milk, meat, liver, kidney and fat, respectively.

Based on the above, the Meeting estimated maximum residue levels of 0.1, 0.1, 1 and 0.1 mg/kg respectively for milks, meat (from mammals other than marine mammals), edible offal (mammalian) and Mammalian fats (other than milk fat).

Residues in eggs and poultry tissues

No feeding study on laying hens was conducted as expected dietary burdens for hen were low and the metabolism studies showed extremely low residues remaining in hen tissues.

In the metabolism study, the TRR in all edible tissues and eggs from hens fed orally radiolabelled imazapic at doses equivalent to 2.1 and 10.9 ppm in feed for 7 days were below the LOQ of 0.01 mg/kg.

At the maximum calculated dietary burden of 9.63 ppm in feed, the residues in eggs and edible tissues were estimated to be < 0.01 mg/kg. The Meeting therefore estimated a maximum residue level, STMR and HR at 0.01*, 0 and 0 mg/kg respectively applicable to poultry meat, poultry offal, poultry fat and eggs.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue for plant and animal commodities (for compliance with the MRL and for estimation of dietary intake): *Imazapic*.

Residue is not fat-soluble.

Commodity		Recommended MRL, mg/kg		STMR/STMR-P mg/kg
CCN	Name	New	Previous	
MO 0105	Edible offal (mammalian)	1	-	Liver, 0.05 Kidney, 0.287
PE 0112	Eggs	0.01*	-	0
AS 0162	Hay or fodder (dry) of grasses	3		(see table below)
GC 0645	Maize	0.01*	-	0
MF 0100	Mammalian fats (except milk fats)	0.1		0.05
MM 0095	Meat (from mammals other than marine mammals)	0.1		0.05
ML 0106	Milks	0.1		0.019
SO 0697	Peanut	0.05*	-	0
PF 0111	Poultry fats	0.01*	-	0
PM 0110	Poultry meat	0.01*	-	0
PO 0111	Poultry, edible offal of	0.01*	-	0
SO 0495	Rape seed	0.05*	-	0
GC 0649	Rice	0.05*	-	0
GS 0659	Sugar cane	0.01*	-	0
GC 0654	Wheat	0.05*	-	0
AS 0654	Wheat straw and fodder, dry	0.05*		(see table below)

For calculating animal dietary burdens.

Commodity		Median residue mg/kg	Highest mg/kg
CCN	Name		
	Grass forage	12.5	24
	Hay or fodder (dry) f grasses	0.5	2.3
	Peanut hull	0	-
	Rape seed forage	0.05	0.05
	Wheat forage	0.05	0.05
	Wheat straw and fodder, dry	0	0

Expressed on an “as received” basis.

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Dietary Intakes (IEDIs) of imazapic were calculated for the 13 GEMS/Food cluster diets using STMRs estimated by the current Meeting (Annex 3 of the 2013 JMPR Report). The ADI is 0–0.7 mg/kg bw and the calculated IEDIs were 0% of the maximum ADI. The Meeting concluded that the long-term intake of residues of imazapic resulting from the uses considered by the current JMPR is unlikely to present a public health concern.

Short-term intake

The 2013 JMPR decided that an ARfD is unnecessary. The Meeting therefore concluded that the short-term intake of residues of imazapic is unlikely to present a public health concern.

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Doc. ID	Author(s)	Year	Title, Source, published or not
9			processed fractions (meal, oil and flaked soya bean) after treatment with BAS 714 01 H, under field conditions in Brazil BASF SA, Guaratingueta, Brazil, Unpublished
2010/107921 2	Resende G.	2010 a	Amendment 01 - Final report 1273-07 - Study of residues of Imazapyr and Imazapic in soya bean cultivance (grains) after treatment with BAS 714 01 H under field conditions in Brazil for import tolerance, BASF SA, Guaratingueta, Brazil, Unpublished
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2012/700035 9	Robaugh D.A.	2012 a	Independent laboratory validation of analytical method number SOP-PA.0288: Determination of Imidazolinones residues and its metabolites in several matrices and processed fractions by LC/MS/MS Pyxant Labs Inc., Colorado Springs CO, USA, Unpublished
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IA-790-011	Steling C.	1998 a	CL 263,222: Determination of CL 263,222 residues in sugar cane samples from Argentina LAADL - Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil Unpublished
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2001/300170 5	Steling C.	2001 b	Estudo de residuos de Imazapic (CL 263,222) em arroz (grao com casca) do Brasil LAADL - Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil Unpublished
2001/300170 6	Steling C.	2001 c	Estudo de residuo de Imazapic (CL 263,222) em arroz (grao com casca) do Brasil LAADL - Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil Unpublished
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IA-245-002	Sweeney R.A.,	1998 b	CL 263222 (Imazapic): Independent laboratory validation of capillary electrophoresis (CE) determinative and LC/MS confirmatory method for CL

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			American Cyanamid Co., Princeton NJ, USA, Unpublished
IA-620-001	Ta C.	1994	AC 263,222: Photodegradation on soil
US		b	American Cyanamid Co., Princeton NJ, USA, Unpublished
IA-620-009	Ta C.T.	1997 a	Aerobic soil metabolism of AC 263222 and its metabolites CL 263284 and CL 312622 (non GLP), American Cyanamid Co., Ewing NJ, USA, Unpublished
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			Unpublished
2000/102396 2	Thomas G.	2000 a	Residues evaluation report - Midas herbicide
			National Registration Authority for Agricultural & Veterinary Chemicals, Kingston Australian Capital Territory 2604, Australia, No, not subject to GLP regulations
			Unpublished
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			BIOAGRI Laboratorios Ltda., Piracicaba, Brazil, Unpublished
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			American Cyanamid Co., Princeton NJ, USA, Unpublished

IMAZAPYR (267)

First draft prepared by Mr Makoto Irie, Ministry of Agriculture, Forestry and Fisheries, Tokyo, Japan

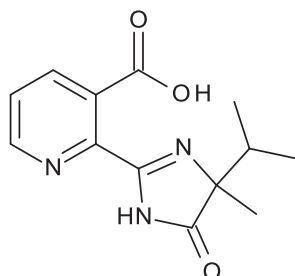
EXPLANATION

Residue and analytical aspects of imazapyr were considered for the first time by the present Meeting. The residue evaluation was scheduled for the 2013 JMPR by the Forty-fourth Session of the CCPR.

Imazapyr is a broad-spectrum herbicide in the imidazolinone family. Its primary use is as a post-emergence herbicide which is particularly effective on hard-to-control perennial grasses. It is non-selective, absorbed by foliage and rapidly translocated. The mode of action of imidazolinone herbicides is the inhibition of the enzyme acetohydroxy acid synthase (AHAS) which is a critical enzyme for the biosynthesis of branched chain amino acids necessary for cell growth and protein synthesis. The Meeting received information on identity, animal and plant metabolism, environmental fates in soil, rotational crops, analytical methods, storage stability, use patterns, supervised trials, farm animal feeding studies and fates of residues in processing.

IDENTITY

Common name	Imazapyr
Chemical name	
IUPAC:	2-[(<i>RS</i>)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl] nicotinic acid
CAS:	2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-pyridinecarboxylic acid
CAS Registry No:	81334-34-1
CIPAC No:	530
Synonyms:	BAS 693 H, CL 243,997
Structural formula:	



Molecular formula:	C ₁₃ H ₁₅ N ₃ O ₃
Molecular weight:	261.3

PHYSICAL AND CHEMICAL PROPERTIES*Pure active ingredient*

Property	Results	Reference
Appearance (colour, physical state, odour)	Dirty white/ egg-shell white powder with a faint non-specific odour (99.6% purity)	Werle <i>et al.</i> , 2001 2001/1024893
Vapour pressure	< 2.7 × 10 ⁻⁵ Pa at 45 °C	Anonymous 1985

Property	Results	Reference
		IZ-301-016
Melting point	170.2–172.0 °C (99.6% purity)	Werle <i>et al.</i> , 2001
Boiling point	Imazapyr decomposes prior to boiling (99.6% purity)	2001/1024893
Octanol/water partition coefficient	log Pow = 0.11 at 22 °C (99% purity)	Reichert, 1983 IZ-315-001
	log P _{OW} = 0.04 deionized water at 20 °C	Daum, 2001
	log P _{OW} = -0.39 at pH 4 at 20 °C	IZ-315-002
	log P _{OW} = -3.96 at pH 7 at 20 °C	
	log P _{OW} = -3.97 at pH 10 at 20 °C (99.6% purity)	
Solubility in water	9.74 g/L in distilled water at 15 °C 11.3 g/L in distilled water at 25 °C 13.5 g/L in distilled water at 35 °C (99% purity)	Anonymous 1985 IZ-311-001
Relative density	1.36 g/cm ³ at 20 °C (99.6% purity)	Werle <i>et al.</i> , 2001 2001/1024893
Hydrolysis	In distilled water, pH 5, pH 7 buffers there was no detectable degradation, thus a half-life could not be calculated because of the stability of the compound. At pH 9 the half-life was calculated to be 325 days.	Mangels, 1990 1990/7001950
Photolysis	DT ₅₀ = 2.7 days in distilled water DT ₅₀ = 2.7 days at pH 5 DT ₅₀ = 1.3 days at pH 9	Mangels, 1990 1990/7001949
Dissociation constant	pKa = 3.8 (99.9% purity)	Anonymous 1985 IZ-301-016
	pKa1 = 1.7, pKa2 = 3.5, pKa3 = 11.1 at 20 °C (99.6% purity)	Daum, 2001 IZ-390-005

Technical material

Property	Results	Reference
Appearance (colour, physical state, odour)	White to tan solid with a slightly pungent odour	Anonymous 1985 IZ-301-016
Vapour pressure	< 1.3 × 10 ⁻⁵ Pa at 60 °C (97.6% purity)	Mangels, 1986 IZ-306-001
Melting point	168–172 °C	Anonymous 1985 IZ-301-016
Solubility in water	11.1 g/L in distilled water at 25 °C	Anonymous 1985 IZ-301-016
Solubility in organic solvents	Hexane 0.0095 g/L at 25 °C	Teeter, 1990

Property	Results	Reference
(98.6% purity)	Toluene	1.80 g/L at 25 °C
	Acetone	33.9 g/L at 25 °C
	Dichloromethane	87.2 g/L at 25 °C
	Methanol	105 g/L at 25 °C
	Dimethyl sulfoxide	471 g/L at 25 °C
Stability	Imazapyr is physically stable for 2 years. (95% purity)	Peevey, 1989 1989/7002428

Formulations

- Water soluble liquid (SL)
- Water dispersible granule (WG)
- Water soluble granule (SG)
- Emulsifiable concentrate (EC)
- Dustable powder (DP)

METABOLISM AND ENVIRONMENTAL FATE

The metabolism, distribution of imazapyr has been investigated in animals and plants. The fate and behaviour of imazapyr in animals, plants and the environment was investigated using the [^{14}C] labelled test materials shown in Figure 1.

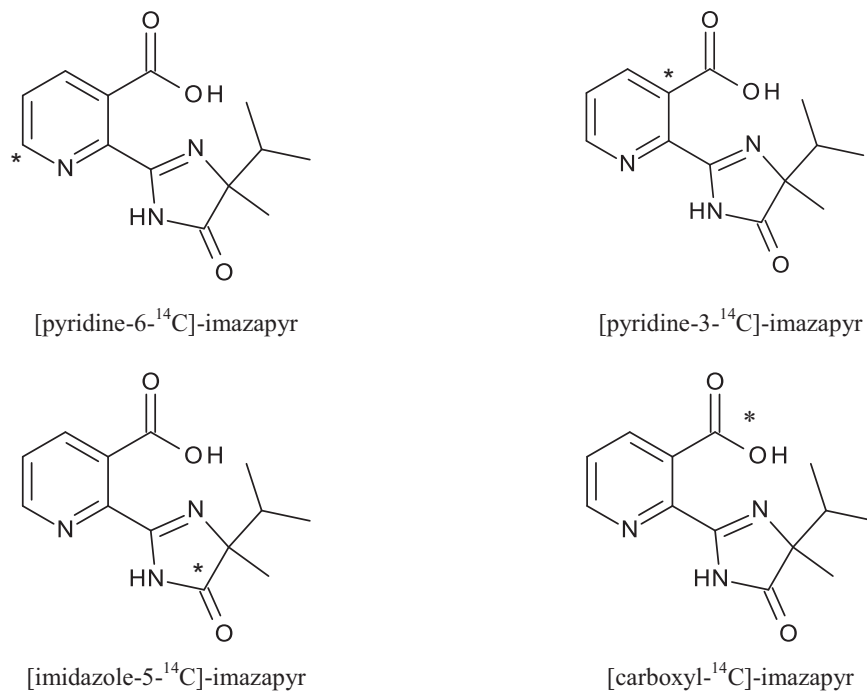
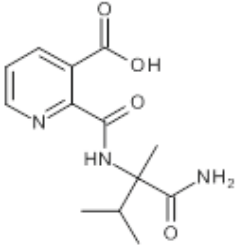
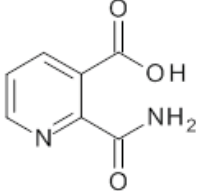
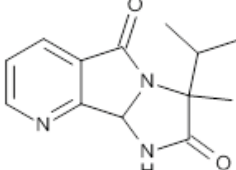
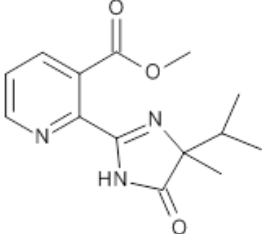
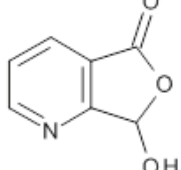
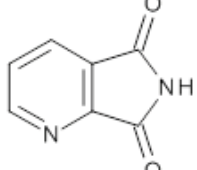
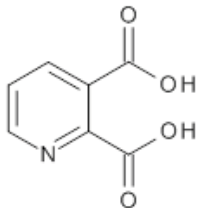
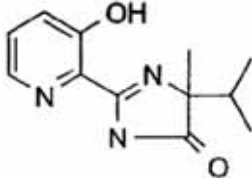


Figure 1 [^{14}C]-Labelled test materials used in animals, plants metabolism studies, and the environmental fate studies

The chemical structures of the major degradation compounds from the metabolism of imazapyr are provided below.

Compound name	Structure	Found in metabolism studies
CL 252,974 2-[(1-carbamoyl-1,2- dimethylpropyl) carbamoyl] nicotinic acid		Rat, Plants, Soil, Water
CL 60,032 2-carbamoyl-nicotinic acid		Rat, Soil
CL 247,087 5 <i>H</i> -imidazo [1',2':1,2] pyrrolo [3,4- <i>b</i>] pyridine -2(3 <i>H</i>),5-dione, 1.9 <i>b</i> α(β)-dihydro-3α- isopropyl-3-ethyl-		Plants, Soil
240,000 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3 -carboxymethyl pyridine		Plants, Soil
CL 119,060 Furo[3,4- <i>h</i>]pyridine-5(7 <i>H</i>)-one, 7-hydroxy-		Plants
CL 17,226 Pyridine 2,3-dicarboximide		Plants

Compound name	Structure	Found in metabolism studies
PDC Pyridine 2,3-dicarboxylic acid		Plants, Soil
CL 288,247 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-hydroxy pyridine		Soil

Animal metabolism

The Meeting received studies on the metabolism of imazapyr in rats, lactating goat and laying hens. The study on rats was evaluated by the WHO Core Assessment Group of the 2013 JMPR. A summary of the rat metabolism is given in this section.

Rats

The metabolism studies performed on rats indicated that imazapyr was quickly and extensively absorbed following administration. There were no substantial sex differences in the absorption, elimination or distribution of radioactivity in rats receiving an oral dose of radiolabelled imazapyr. The majority of the administered doses were excreted in urine (68–95%) and, to a lesser degree, in faeces (5.5–33%). Most elimination occurred within the first 24 hours after dosing (57–91% in urine; 3–24% in faeces). The half-life of imazapyr in the rat was less than 1 day. Imazapyr was excreted mostly unchanged. Trace levels of polar and nonpolar metabolites were formed and excreted in urine and faeces. Only trace amount of tissue residues were detected in the liver and kidneys on the high dose group, indicating no bioaccumulation.

Lactating goat

Study 1

The metabolism of imazapyr by the lactating dairy goats was studied by Zdybak (1992: IZ-440-002). [pyridine-6-¹⁴C]-imazapyr was orally administered in gelatin capsules to lactating goats. Three lactating goats, each weighing from 44 to 67 kg, were used as model ruminants in the study. Each goat received a single daily oral dosage equivalent to a dietary level of 0 ppm (control), 17.7 ppm, or 42.5 ppm, respectively, for seven consecutive days. Based on actual mean feed consumption of 0.859 kg and 1.08 kg per day for low and high dosed goats during the test period, the mean actual daily dietary dosages of imazapyr were 17.7 ppm and 42.5 ppm for low and high dose goats, respectively.

Urine and faeces were collected daily and analysed for radioactivity content. During the treatment period, blood and milk samples were also collected and analysed for total radioactive residues (TRR). Goats were sacrificed ca. 22 hours after the seventh and final doses. Blood and edible tissues (liver, kidneys, leg muscle, loin muscle and omental fat) were collected.

Orally-administered radioactivity was mainly excreted in the urine (65.3% and 60.4% of the doses in the 17.7 ppm and 42.5 ppm dosed goats, respectively). Faecal elimination accounted for 16.1% and 19.0% of the doses in the 17.7 ppm and the 42.5 ppm dosed goats, respectively.

At both treatment levels, radiocarbon content in blood was less than the validated detection limit of 0.05 mg/kg. The TRR levels were < 0.01–0.01 mg/kg and 0.01–0.02 mg/kg in the milk samples of the 17.7 ppm and 42.5 ppm dosed goats, respectively. TRR levels for leg and loin muscles, liver, and fat were all less than the validated limit of detection of 0.05 mg/kg. Detectable residues were found in the kidneys namely 0.08 mg/kg (17.7 ppm dose) and 0.11 mg/kg (42.5 ppm dose).

Milk (day-7) and kidney samples from the 42.5 ppm dosed goat were subjected to solvent extraction followed by chromatographic analysis. Organosoluble milk residues distributed in hexane and ethyl acetate amounted to 17.7% and 6.4% of the TRR (or < 0.01 mg/kg), respectively. Water soluble residues accounted for approximately 49% (0.01 mg/kg) of the TRR, whereas the remainder was unextractable (26.6%, 0.01 mg/kg). Kidney residues were quantitatively extractable, with the majority (95.5%) isolated in a methanol/water fraction.

Table 1 Total radioactive residue (TRR) in goat milk and tissues

Sample	TRR (mg imazapyr equivalent/kg)		
	Control	Low dose (17.7 ppm)	High dose (42.5 ppm)
Milk (Day 1)	< 0.01	< 0.01	0.01
Milk (Day 2)	< 0.01	0.01	0.02
Milk (day 3)	< 0.01	< 0.01	0.01
Milk (Day 4)	< 0.01	< 0.01	0.01
Milk (Day 5)	< 0.01	0.01	0.01
Milk (Day 6)	< 0.01	0.01	0.02
Milk (Day 7)	< 0.01	0.01	0.02
Leg Muscle	< 0.05	< 0.05	< 0.05
Loin Muscle	< 0.05	< 0.05	< 0.05
Fat	< 0.05	< 0.05	< 0.05
Liver	< 0.05	< 0.05	< 0.05
Kidney	< 0.05	0.08	0.11
Blood (Day 0)	< 0.05	< 0.05	< 0.05
Blood (Day 1)	< 0.05	< 0.05	< 0.05
Blood (Day 3)	< 0.05	< 0.05	< 0.05
Blood (Day 7)	< 0.05	< 0.05	< 0.05

The extracted ^{14}C residue in the milk (0.01 mg/kg) was identified as unchanged parent compound by thin layer chromatography (TLC) and high performance liquid chromatography (HPLC) analyses. Similarly, the ^{14}C residue in the kidney was identified as unchanged parent compound. Chromatographic analyses of the urine showed a single radioactive residue component identical to that found in the kidney and milk.

Study 2

The purpose of this study was to determine the concentration of the total ^{14}C residues and the nature of these residues in kidneys and milk of the lactating goats following administration of daily oral doses of [imidazole-5- ^{14}C]-imazapyr (Tsalta, 2000: IZ-440-005). [^{14}C] imazapyr or blank gelatin capsules were administered orally to lactating goats weighing between 49 and 50 kg (at treatment) that were less than 5 years of age. The two goats were dosed orally by capsule for seven consecutive days with the actual dietary equivalent of 0 ppm and 47 ppm [^{14}C] imazapyr as groups A (control) and B (treated), respectively, to determine total [^{14}C] imazapyr derived residues in daily milk, urine and faeces, and in the kidneys at sacrifice. The dose rate of 47 ppm for the treated goat was slightly higher than the rate of 42.5 ppm used for a goat study (IZ-440-002). That study showed that kidney and milk were the edible matrices that contained detectable residues following oral dosing of 42.5 ppm for 7 days. The study was to provide tissues (kidney and milk) with high enough residues so that they could be used to conduct an extraction efficiency/accountability study.

The TRR in the milk and the urine samples were determined by direct scintillation counting (LSC). The TRR in the kidneys and faeces were determined by combustion followed by LSC. Radioactivity in the extracts of the kidney and in liquid chromatographic fractions was determined by LSC. Radioactivity in the post extraction solids (PES) generated after kidney and milk extraction was determined by combustion followed by LSC. The specific radioactivity afforded a theoretical detection limit of 0.006 mg/kg imazapyr equivalents in the kidney, milk, urine and faeces when 0.5 g or 0.5 mL (nominal) sample aliquots were analysed by combustion and LSC or by direct LSC. The validated detection limit was 0.006 mg/kg for the milk and urine and 0.007 mg/kg for kidney and faeces.

During this study, milk, urine and faeces samples were collected daily. At sacrifice (approximately 22 hours after the last dose) only kidney samples were collected. The TRR levels in all control samples and pre-treatment samples were non-detectable (< 0.006 mg/kg). The TRR levels for the dosed goat were 0.014–0.015 mg/kg for milk and 0.074 mg/kg for kidney. The rate of elimination for the goat treated daily for 7 days with an oral dose of [^{14}C] imazapyr was determined by analysing the daily samples of urine and faeces. After seven days, 58.7% and 34.4% of the administered radioactive doses were excreted in the urine and faeces, respectively.

Radioactive residues were extracted from kidneys using acetone: water (3:1, v/v) as solvent. The overall recovery in the extractable portion was 93.5% and the unextractable (PES) was 6.5%. The concentrated extract was analysed by HPLC to determine the nature of the radioactive residue. The parent compound (imazapyr) was the predominant radioactive residue (81.9% of TRR, 0.061 mg/kg) in the kidney. Minor polar unknowns (total 11.6% of TRR) were also present in the kidney extract. Since these fractions contained multiple components (at least three), each less than 0.004 mg/kg, no further characterization was attempted.

The Day-7 treated goat milk was extracted by a procedure involving sequential extractions with acetonitrile: water, ethyl acetate and hexane. The extractable radioactivity was 82% and the unextractable (PES) was 18% of the TRR. The major component in the milk extract (65.6% of TRR, 0.01 mg/kg) was the parent compound (imazapyr). Minor polar unknowns (total 14.7% of TRR) were also present in the milk extract. Since these fractions were equivalent to 0.002 mg/kg and contained multiple components, no further characterization was attempted.

Table 2 Characterization and identification of radioactive residues in kidney and milk

Compound	Kidney		Milk, Day 7			
	% TRR	mg/kg ^a	% TRR		mg/kg ^a	
			Aqueous	Ethyl acetate	Aqueous	Ethyl acetate
Extract	93.5	0.07	46.3	35.8	0.006	0.005
Imazapyr	81.9	0.061	33.4	32.2	0.005	0.005
Polar unknowns	11.6	0.009	11.3	3.35	0.002	< 0.001
Unextracted	6.5	0.005	18.0			
TRR		0.074			0.014	

^a mg imazapyr equivalent/kg

The results of this lactating goat study showed that orally administered [^{14}C] imazapyr was rapidly absorbed and eliminated in urine and faeces. At the end of the 7-day dosing period, 93.1% of the administered cumulative dose was recovered in the urine and faeces of the treated goat. The kidney and the milk of the treated goat contained 0.074 and 0.014–0.016 mg/kg, respectively, of TRR following seven days of oral treatment at approximately 47 ppm. The parent compound (imazapyr) was the predominant radioactive residue in the kidney (81.9% of TRR or 0.061 mg/kg) and in the milk (65.6% of TRR or 0.01 mg/kg). The concentration of the remaining radioactive components in the kidney and the milk were below 0.01 mg/kg.

Laying hens

The elimination, distribution and metabolic fate of imazapyr by egg laying hens were studied by Tsalta (1995: IZ-440-003). Three groups consisting of eight Dekalb XL white leghorn hens, each hen about 20 weeks old and weighing approximately 2.0 kg were used as test animals in this metabolism study. The three groups of hens were dosed orally by capsule for seven consecutive days with the nominal dietary equivalent of 0 ppm, 2 ppm, and 10 ppm [^{14}C]-labelled imazapyr as groups A (control), B (low dose), and C (high dose), respectively. The hens were used to determine total imazapyr-derived residues in the eggs (daily), in the excreta and in the blood and edible tissues at sacrifice. [pyridine-6- ^{14}C]-imazapyr was used in the study. The specific radioactivity afforded a validated detection limit of 0.01 mg/kg imazapyr equivalents in the egg and hen tissues when 0.5 g sample aliquots were analysed.

The TRR in the daily egg samples were determined by LSC. The TRR in the blood, tissues and excreta were determined by combustion followed by LSC. Radioactivity in the extracts of excreta and in liquid chromatographic fractions was determined by combustion and by LSC; radioactivity in the post extraction solids of excreta was determined by combustion followed by LSC. The metabolite profile of imazapyr was defined by analysing acetone extracts of the excreta using high performance liquid chromatography. The identity of the main residue component imazapyr was determined by GC-MS.

Elimination of ^{14}C via the excreta accounted for 90.5 and 91.7% of the total doses for the low and high doses, respectively. During treatment, TRR in the egg samples was less than the validated detection limit of 0.01 mg/kg. The only significant component of the excreted ^{14}C residue was defined as imazapyr by HPLC analysis and by mass spectrometry.

Residues in blood, skin with adhering fat, muscle, liver and kidney tissues taken at 22 hours after the last dose were all less than the validated detection limit of 0.01 mg/kg. The results of this study clearly show that orally administered imazapyr was rapidly eliminated by the hen as unchanged parent compound and that imazapyr-related residues do not accumulate in eggs or the edible tissues of poultry at 108× the potential maximal dietary exposure level. These data demonstrate that there is no reasonable expectation of finite residues of imazapyr occurring in poultry tissue or eggs as a result of the herbicide use on corn.

Table 3 Total radioactive residues (TRR) in egg and tissues of hens

Sample	TRR (mg imazapyr equivalent/kg) ^a		
	Control	Low dose (1.98 ppm)	High dose (9.72 ppm)
Excreta (Day 1)	< 0.01	1.98	9.52
Excreta (Day 2)	< 0.01	1.57	9.85
Excreta (day 3)	< 0.01	1.62	9.90
Excreta (Day 4)	< 0.01	1.70	8.66
Excreta (Day 5)	< 0.01	1.78	9.73
Excreta (Day 6)	< 0.01	1.54	9.91
Excreta (Day 7)	< 0.01	1.77	9.45
Eggs (Day 1)	< 0.01	< 0.01	< 0.01
Eggs (Day 2)	< 0.01	< 0.01	< 0.01
Eggs (day 3)	< 0.01	< 0.01	< 0.01
Eggs (Day 4)	< 0.01	< 0.01	< 0.01
Eggs (Day 5)	< 0.01	< 0.01	< 0.01
Eggs (Day 6)	< 0.01	< 0.01	< 0.01
Eggs (Day 7)	< 0.01	< 0.01	< 0.01
Blood	< 0.01	< 0.01	< 0.01
Muscle	< 0.01	< 0.01	< 0.01
Skin with adhering fat	< 0.01	< 0.01	< 0.01
Liver	< 0.01	< 0.01	< 0.01
Kidney	< 0.01	< 0.01	< 0.01

^a Excreta: mg/kg calculated on a fresh weight basis. Excreta sample from all hens (eight) from each group were combined for each day and analysed.

Blood and tissues: Values are the average of eight laying hens

The results of this laying hen study conducted at the actual dose levels of 1.98 and 9.72 ppm feed equivalents of imazapyr, showed that the parent compound or derived residues are excreted without retention or accumulation in eggs and edible poultry tissues. Thus, poultry exposed to diets of agricultural commodities containing even highly exaggerated levels of imazapyr residues would not contain or accumulate imazapyr-derived residues in the edible tissues and eggs.

Summary of animal metabolism

The metabolism of ^{14}C -labelled imazapyr has been studied in lactating goat and laying hens. In both studies, imazapyr was mainly eliminated and metabolised to several polar compounds. Imazapyr was the most important component in milk and kidney for lactating goat.

Plant metabolism

Plant metabolism studies were performed on soya bean, maize, sugarcane, oil palm, clover and Bermuda grass with imazapyr ^{14}C -labelled at the 3 or 6-position pyridine ring to track metabolites. Metabolites were identified using multiple chromatographic systems and authentic standards.

Soya beans

A metabolism study was conducted with [pyridine-3- ^{14}C]-imazapyr in transgenic soya bean variety BPS-CV127-9 in which the *csr1-2* gene encoding an altered AtAHS1 protein was inserted to make the host tolerant to imidazolinone herbicide (Dohn, 2012: 2012/7000103). [^{14}C] imazapyr was formulated (a soluble liquid (SL)) and applied once to the above ground portion of soya beans plants at BBCH growth stage 65 with a hand operated pump sprayer. The application rate was 107 g/ha which was 149% of the maximum anticipate use rate of 72 g/ha. The test plots were located outdoors, and consisted of two plots, one control and one treated. The forage was harvested approximately one hour after application and the hay was harvested 35 days after application. Soya bean straw, pods and seeds were harvested when mature at 98 days after treatment.

All crop samples were processed, subjected to combustion analysis, extracted and analysed by reverse phase HPLC. The TRR of soya bean forage from combustion was 0.655 mg/kg, soya bean hay was 0.247 mg/kg, soya bean seed was 0.062 mg/kg, soya bean straw was 0.079 mg/kg and soya bean pod was 0.146 mg/kg. The extraction procedure released 72.5% to 98.7% of the TRR. The unextracted residues were small, 0.008 mg/kg (1.3% TRR) in forage, 0.028 mg/kg (11.1% TRR) in hay, 0.011 mg/kg (15.9% TRR) in seeds, 0.016 mg/kg (21.6% TRR) in straw, and 0.039 mg/kg (27.5% TRR) in pods (see Table 4).

The parent compound imazapyr was identified by co-chromatography with a reference standard and by LC-MS analysis of an isolated fraction from hay. Imazapyr was detected in all matrices and was the most abundant component of the residue in soya bean forage (0.599 mg/kg, 93.6% TRR), hay (0.094 mg/kg, 37.3% TRR), and seed (0.0236 mg/kg, 34.2% TRR). Imazapyr was present in straw at 0.006 mg/kg (8.1% TRR) and pods at 0.018 mg/kg (12.7% TRR).

Table 4 Extractability of Soya bean matrices and Total Radioactive Residues

Matrix	DAT	Distribution of radioactive residues						Total extracted		Unextracted		TRR (calculated)	TRR (combustion)
		Methanol extract		Aqueous extract		Acidic methanol							
		mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	mg/kg
Forage	0	0.591	92.3	0.035	5.5	0.006	0.9	0.632	98.7	0.008	1.3	0.640	0.655
Hay	35	0.182	72.2	0.036	14.3	0.006	2.4	0.224	88.9	0.028	11.1	0.252	0.247
Seeds	98	0.022	31.9	0.014	20.3	0.022	31.9	0.058	84.1	0.011	15.9	0.069	0.062
Straw	98	0.040	54.1	0.014	18.9	0.004	5.4	0.058	78.4	0.016	21.6	0.074	0.079
Pods	98	0.031	21.8	0.036	25.4	0.036	25.4	0.103	72.5	0.039	27.5	0.142	0.146

A polar component M3 (not retained on reverse phase HPLC) was the most abundant component in the pods (0.041 mg/kg, 28.9% TRR). This component was also present in hay

(0.028 mg/kg, 11.1% TRR), straw (0.009 mg/kg, 12.2% TRR) and seeds (0.0161 mg/kg, 23.3% TRR), but was not detected in forage. The polar peak was isolated from the soya bean seeds, and shown to consist of multiple components, present at ≤ 0.004 mg/kg. A polar component was observed in seed, hay, straw and pod and shown to be comprised of multiple components. Imazapyr was degraded in soya bean to multiple products present in relatively small concentrations.

The remainder of the residues consisted of multiple components individually present in small concentrations. No metabolites were present at levels exceeding 10% TRR in any crop matrices except for M19 in the straw. M19 was present in the straw at 0.013 mg/kg (17.6% TRR) and was also found in hay at 0.022 mg/kg (8.7% TRR).

Table 5 Nature of the radioactive residues in soya bean matrices

Components	Forage		Hay		Seeds		Straw		Pods	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Extract	0.632	98.7	0.224	88.9	0.058	84.1	0.058	78.4	0.103	72.5
Imazapyr	0.599	93.6	0.094	37.3	0.0236	34.2	0.006	8.1	0.018	12.7
M3 ^a	ND		0.028	11.1	0.0161	23.3	0.009	12.2	0.041	28.9
M4-5	ND		0.013	5.2	0.0008	1.2	0.002	2.7	0.010	7.0
M8	ND		0.008	3.2	ND		ND		0.006	4.2
M19	ND		0.022	8.7	ND		0.013	17.6	0.003	2.1
M28	ND		ND		ND		0.003	4.1	ND	
M31	ND		0.011	4.4	0.0026	3.8	0.005	6.8	0.011	7.7
M45.5	ND		0.024	9.5	0.0016	2.3	0.004	5.4	0.004	2.8
M52	0.027	4.2	0.004	1.6	ND		ND		ND	
Unknowns	0.006	0.9	0.020	8.0	0.0136	19.7	0.016	21.6	0.010	7.0
Unextracted	0.008	1.3	0.028	11.1	0.011	15.9	0.016	21.6	0.039	27.5
Total	0.640	100	0.252	100	0.069	100	0.074	100	0.142	100

^a Components code with a retention time of LC-MS

Imazapyr underwent significant metabolism, however, the parent molecule was the most abundant component of the residue in all matrices except straw and pods. The concentration of imazapyr declined from 0.599 mg/kg (93.6% TRR) in forage collected approximately 1 hour after application to 0.094 mg/kg in the hay sample (37.3% TRR) collected 35 days after application, and then 0.006 mg/kg (8.1% of the TRR) in the straw sample collected 97 days after application. The imazapyr concentrations were 0.0236 mg/kg (34.2% TRR) in seed, and 0.018 mg/kg (12.7% TRR) in pods (see Table 5).

Imazapyr was degraded to a number of components in soya bean commodities. In seed, multiple metabolites are present with concentrations at ≤ 0.004 mg/kg (5.8% TRR), and parent was the main component. The very polar peak M3 that was not retained on reverse phase HPLC was isolated from the seed extract. Analysis using a Hypercarb column showed the peak to be comprised of multiple components, each present at ≤ 0.004 mg/kg (5.8%TRR). In straw, component M19, a component of intermediate polarity with a retention time of about 19 minutes, was present at amounts > 10% TRR with concentration of 0.013 mg/kg (17.6% TRR). The component was also present in hay but at levels < 10% TRR. Due to the presence over 10% TRR in only straw which is an animal feed item, the component M19 was not further analysed. In addition to minor components such as M31 and M45.5, a large number of components that did not exceed 0.002 mg/kg were present in the matrices of hay, straw and pod. As was demonstrated with the polar peak isolated from the seed extract, the polar peak in the hay, straw and pod was assumed to be comprised of a large number of low-level components.

Maize

A metabolism study was conducted in imidazolinone-resistant maize (Pioneer hybrid 3245 IR) to determine the total ¹⁴C residues following a post-emergence treatment of maize plants at the 3 to 4 leaf growth stage with [pyridine-6-¹⁴C]-imazapyr at treatment rates of 0.028 kg ai/ha (plot A) and 0.080 kg ai/ha (plot B), and to determine the nature of any significant imazapyr-derived residues in

the green plants, forage, fodder (stalks/husks/cobs), and grain (Zulalian, 1995: IZ-640-003). The treatment rates used in this study correspond to 1× and 2.8× the maximum label rate (0.027 kg ai/ha) for the use of imazapyr on imidazolinone-resistant maize. Soil core samples were taken prior to application of the test substance (−1 DAT), within two hours following application of the test substance (0 DAT), and one day after final harvest (115 DAT) of the mature maize plants. Samples of maize plants were harvested at 0 DAT (green plant), 14 DAT (green plant), 30 DAT (early forage), and 62 DAT (late forage). At maturity (114 DAT), the stalks, husks, and cobs with grain were collected.

The TRR in all plant and soil samples were determined by combustion and liquid scintillation counting (LSC). The TRR in soil (0–3 inches) at 0 DAT was 0.012 mg/kg and 0.047 mg/kg from plots A and B, respectively. At 115 DAT (1 day after maize harvest), the TRR in the soil (0–3 inches) was 0.006 mg/kg and 0.016 mg/kg from plots A and B, respectively. Residues were 0.002 to 0.007 mg/kg in soil at 7.6–15 cm, < 0.002 to 0.003 mg/kg at 15–30 cm and < 0.002 at 30–46 cm.

The green plant and forage samples were extracted with methanol. The fodder was extracted with methanol: water: hydrochloric acid and the grain were extracted with hexane followed by methanol: water: hydrochloric acid.

For the 0 DAT maize plant from plot A, 96.3% (2.37 mg/kg) of the TRR was extracted and 3.7% (0.093 mg/kg) remained in the post extracted solids (PES). The 0 DAT maize plant from plot B was not extracted. For the 14 DAT maize plants from plot A and B, 78.6 to 81.9% (0.046 to 0.126 mg/kg) was extracted and 18.1 to 21.4% (0.012 to 0.028 mg/kg) remained in the PES. For the 30 DAT samples (early forage) from plots A and B, 84.2 to 85.8% (0.008 to 0.022 mg/kg) of the TRR was extracted and 14.2 to 15.7% (0.002 to 0.004 mg/kg) remained in the PES. For the 62 DAT samples (late forage) from plot B, 86.8% (0.022 mg/kg) of the TRR was extracted and 13.3% (0.003 mg/kg) remained in the PES. For the 114 DAT fodder from plot B, 69.9% (0.020 mg/kg) of the TRR was extracted and 30.1% (0.008 mg/kg) remained in the PES. The late forage and fodder samples from plot A were not extracted because the TRR was < 0.01 mg/kg. For the 114 DAT maize grain from plots A and B, 0.8 to 1.5% (< 0.002 mg/kg) was extracted with hexane, 80.0 to 88.8% (0.023 to 0.076 mg/kg) was extracted with methanol: water: hydrochloric acid, and 10.3 to 18.5% (0.005 to 0.009 mg/kg) remained in the PES (see Table 6).

Table 6 Extractability of residues from maize matrices and Total Radioactive Residues

Matrix	DAT	1× Treatment rate (0.028 kg ai/ha: Plot A)						2.8× Treatment rate (0.080 kg ai/ha: Plot B)					
		TRR		Extracted		Unextracted		TRR		Extracted		Unextracted	
		mg/kg		mg/kg	%TRR	mg/kg	%TRR	mg/kg		mg/kg	%TRR	mg/kg	%TRR
Green plant	0	2.471		2.379	96.3	0.093	3.7	8.711		n.p.			
Green plant	14	0.058		0.046	78.6	0.012	21.4	0.153		0.126	81.9	0.028	18.1
Early forage	30	0.010		0.008	84.2	0.002	15.7	0.026		0.022	85.8	0.004	14.2
Late forage	62	0.004		n.p.				0.025		0.022	86.8	0.003	13.3
Fodder ^a	114	0.009		n.p.				0.028		0.020	69.9	0.008	30.1
Grain	114	0.029		0.023	81.5	0.005	18.5	0.086		0.077	89.6	0.009	10.3

n.p. = not performed

^a Stalks/husks/cobs, combined

The imazapyr-derived residues in the grain did not concentrate in the maize oil since no residues (< 0.002 mg/kg) were detected in the hexane extract of the maize grain from the 1× and 2.8× treatments.

HPLC analyses of the radioactivity extracted with methanol and methanol: water: hydrochloric acid was conducted on a C18 reverse phase column. The radioactivity profiles of the extracts of the green plant, forage, fodder, and grain were similar qualitatively. There was one major component and a minimum of sixteen minor radiolabelled components that were separated and detected by C18 reverse-phase HPLC and LSC. Parent imazapyr constituted the major component of the extractable residue in the green plant, forage, fodder, and grain (12.0 to 80.8% TRR, 0.003 to 1.997 mg/kg). The residue levels of the minor components in the 30 DAT to 114 DAT samples were

all < 0.01 mg/kg. A number of minor components of the TRR exhibited the same HPLC retention times as PDC, CL 60,032, CL 263,078, CL 252,974, CL 252,663 and CL 271,045 (see Table 7).

Table 7 Distribution of extracted ^{14}C residue in the maize matrices following foliar application of [^{14}C] imazapyr

	1× Treatment rate (0.028 kg ai/ha)						2.8× Treatment rate (0.080 kg ai/ha)									
	0 DAT (green plant)		14 DAT (green plant)		114 DAT (grain)		14 DAT (green plant)		30 DAT (early forage)		62 DAT (late forage)		114 DAT (fodder)		114 DAT (grain)	
	mg/kg ^a	% ^b	mg/kg ^a	% ^b	mg/kg ^a	% ^b	mg/kg ^a	% ^b	mg/kg ^a	% ^b	mg/kg ^a	% ^b	mg/kg ^a	% ^b	mg/kg ^a	% ^b
Imazapyr	1.997	84.0	0.029	63.7	0.012	51.0	0.082	64.8	0.014	65.0	0.013	61.5	0.003	16.8	0.055	71.9
PDC	< 0.001	< 0.1	0.001	2.5	0.001	2.4	0.001	0.8	< 0.001	1.3	< 0.001	1.4	0.002	9.6	< 0.001	0.5
CL60,032	0.002	0.1	0.001	1.4	< 0.001	1.1	0.001	1.1	< 0.001	0.9	< 0.001	0.7	< 0.001	1.1	0.0	0.0
CL263,078	0.025	1.1	0.001	2.7	0.001	4.0	0.004	2.8	0.001	2.5	0.001	3.8	0.002	8.9	0.003	3.7
CL252,974	0.026	1.1	0.002	3.7	0.001	3.6	0.004	2.8	0.001	3.6	0.001	2.9	0.001	4.6	0.003	3.7
CL252,663	0.078	3.3	0.001	2.1	0.001	6.3	0.004	3.3	0.001	3.0	0.001	2.9	0.001	3.2	0.006	8.1
CL271,045	0.042	1.8	0.001	2.2	0.001	2.2	0.002	1.7	< 0.001	1.6	< 0.001	1.3	< 0.001	1.1	0.001	1.0
Unknowns	0.209	8.8	0.011	21.9	0.007	29.5	0.028	22.9	0.005	22.0	0.006	25.6	0.011	54.6	0.009	11.2
Total extracted	2.379	100	0.046	100	0.021	100	0.126	100	0.020	100	0.020	100	0.018	100	0.075	100

^a mg/kg TRR

^b Relative percent of extracted TRR

Imazapyr was isolated from the extracts of the 62 DAT forage and 114 DAT grain from plot B by affinity chromatography using an anti-imidazolinone antibody and identified by GC-MS analysis.

Imazapyr is the only significant component of the residue in imidazolinone-resistant maize after application of imazapyr at the maximum intended label rate. All components of the residue in the raw agricultural commodities were < 0.01 mg/kg with the exception of the grain in which imazapyr accounted for only 0.012 mg/kg.

Sugarcane

The metabolism of [^{14}C] imazapyr in sugarcane variety CP 65-357 was investigated (Mangels and Lucas, 1987: IZ-640-001). [pyridine-6- ^{14}C]-imazapyr was formulated and applied to the soil surface once as a pre-emergence application at a rate equivalent to 0.28 kg ai/ha using a hand-sprayer. Stalk samples were taken at maturity approximately 14 months after the pre-emergence treatment. The sugarcanes (without outer leaves) were homogenized and subjected to combustion analysis.

There were no detectable residues in the treated samples, which gave counts that were equivalent to both the control samples and the background levels of the cocktails and the equipment. The TRR of the samples was below the sensitivity of the method (< 0.005 mg/kg). No further investigations and storage stability analyses were carried out.

Oil palm

A metabolism study was conducted with [pyridine-6- ^{14}C]-imazapyr in oil palm (Mallipudi, Taylor and Paniagua, 1986: IZ-640-002). [^{14}C] imazapyr was formulated as the isopropylamine salt and applied to the ground beneath an actively fruiting oil palm. The application rate was 1.0 kg ai/ha. Out of three palms selected as test plots, two were treated with [^{14}C] imazapyr and one was used as control. Fruit samples were collected from the oil palm as they ripened at 0 hour, 7, 30 and 62 days after treatment.

Ripe fruits were collected from untreated palms on the same day as from the treated palms. Palm oil was extracted from the fruits using a hexane: water mixture (3:1, v/v).

Residual radioactivity levels expressed as mg/kg equivalents of imazapyr were below the validated sensitivity of the method (< 0.03 mg/kg) at any given time in the palm oil, aqueous phase, fruit marc, kernel shell and kernel nut. There was no detectable radiocarbon in palm oil and other fruit fractions from the control palm.

The radioactive residues derived from [^{14}C] imazapyr were present in the soil samples (0.30–1.70 mg/kg in the 0–7.6 cm depth) at each sampling interval of oil palm fruits. The results indicate that imazapyr derived residues will not accumulate in the palm oil of an actively fruiting oil palm after application to the ground beneath the palm.

Clover

A metabolism study was conducted with [pyridine-6- ^{14}C]-imazapyr (Wu, 1997: IZ-640-007). [^{14}C] imazapyr was applied to clover at a rate of 1.68 kg ai/ha (acid equivalents) as a 240 g/L water soluble formulation. Soil cores were collected to a depth of 45.7 cm before application (–1 day), after application (0 day), and at final sampling (21 day). Clover foliage was collected at 0, 4, 10, 15 and 21 days after treatment (DAT) and analysed for metabolite identification. The field study was conducted outdoors in two separate plots; plot A received the test material spray treatment, and plot B (control) received the blank spray treatment. Phytotoxic effects were apparent four days after application of the test material to the clover in the test plot. The clover in the untreated control plot appeared healthy. The phytotoxicity remained apparent until the final collection 21 days after treatment.

The soil cores and clover foliage from the control and treated plots were analysed for total radioactive residue (TRR) content. The clover foliage from the treated plot at each sampling interval also was extracted with acidified methanol and analysed for metabolites.

The TRR levels (expressed as mg/kg imazapyr equivalent) in soil were low. For example, levels were 0.084 mg/kg at 0–7.62 cm, 0.017 mg/kg at 7.62–15.2 cm at 0 DAT and < 0.01 to 0.144 mg/kg at different depths at 21 DAT. The level of radioactivity in soil increased due to wash-off by water and release of radioactivity by dying plants. Soil cores at all other sampling times and depths had only background levels (< 0.01 mg/kg).

TRR levels in foliage were 43.0 mg/kg (0 DAT), 37.4 mg/kg (4 DAT), 23.4 mg/kg (10 DAT), 41.6 mg/kg (15 DAT) and 49.2 mg/kg (21 DAT). The high radioactive residues in foliage at 0 DAT resulted from direct application of [^{14}C] imazapyr to clover. The TRR in foliage declined from the time of application to 10 DAT. The increased TRR in 15 and 21 DAT samples was probably attributed to the loss of water from plants as the plants died. TRR values in control soil and plant samples were all less than the minimum quantifiable limit of detection (< 0.01 mg/kg). Control clover from 10 DAT, however, was 0.011 mg/kg.

Each clover sample was extracted by blending with methanol/hydrochloric acid (100/0.75, v/v). The acidified methanol extracted 97.6%, 98.9%, 96.9%, 93.7% and 89.4% of TRR from the 0, 4, 10, 15 and 21 DAT samples, respectively. Post extraction solids (PES-1) were hydrolysed with protease in a phosphate buffer (pH approximately 7.5), followed by cellulase in an acetate buffer (pH approximately 5). The enzyme hydrolysates were combined and concentrated for metabolite analysis. The PES-3 fractions (PES after protease and cellulase hydrolyses of PES-1) from 0, 10, 15 and 21 DAT samples were further hydrolysed using 6 N HCl (Aqueous-3).

The acidified methanol extracts were analysed by HPLC and TLC. The majority of the radioactivity was unchanged imazapyr, ranging from approximately 66% to 99% of TRR. The other major metabolites were CL 247,087 plus CL 240,000 (approximately 0–18% of TRR, 80–90% of the total was estimated to be contributed by CL 247,087) and PDC (approximately 0–5% of TRR). There also appeared to be trace amounts of CL 252,974 (0–3% of TRR) and several other unknown metabolites.

Analysis of the enzyme hydrolysate from PES indicated that parent imazapyr was still the major component identified (28.5–44.2%), other metabolites detected were CL 240,000/CL 247,087 (2.74–12.5%) and PDC (0–17.6%), unknown A (R_t approximately 20–21 min, 0–20.7%), unknown B (R_t approximately 32 min, 5.63–58.3%), and CL 252,974 (0–13.9%). The AQ-3 fractions of the 15 and 21 DAT samples (i.e., hydrolysates after 6 N HCl hydrolysis of PES-3) were analysed by HPLC. The 15 and 21 DAT samples showed a major peak at R_t approximately 8 min, this retention time was very close to that of PDC. In addition, two-dimensional TLC analysis indicated that this peak was very likely PDC.

Table 8 Distribution of metabolites in clover after application of [^{14}C] imazapyr

Components	0 DAT		4 DAT		10 DAT		15 DAT		21 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Imazapyr	42.23	98.2	37.06	99.2	20.17	86.1	31.81	76.4	33.23	67.5
PDC	0.09	0.21	nd		0.11	0.48	2.73	6.56	1.20	2.43
CL 240000 + CL 247087 ^a	0.03	0.07	0.007	0.02	1.86	7.93	2.97	7.14	9.05	18.4
CL 252974	0.05	0.12	nd		0.045	0.19	0.60	1.45	1.77	3.60
Unknown A	0.07	0.17	nd		0.81	3.47	1.20	2.89	0.39	0.79
Unknown B	0.06	0.14	0.18	0.47	0.023	0.10	0.14	0.34	0.12	0.25
Other Unknowns	nd		nd		0.068	0.29	1.27	3.05	1.63	3.32
Precipitate	0.28	0.64	0.08	0.22	0.18	0.77	0.73	1.77	1.52	3.09
Aqueous-3	0.19	0.43	n.a.	n.a.	0.13	0.54	n.a.	n.a.	n.a.	n.a.
Unextracted (PES)	0.01	0.02	0.03	0.08	0.04	0.94	0.15	0.37	0.31	0.62
Total	43.01	100	37.35	100	23.44	100	41.62	100	49.22	100

DAT = days after treatment

nd = not detected

n.a. = not applicable

^a Majority of the total (80 to 90%) was estimated to be contributed by CL 247087.

In conclusion, imazapyr remained mostly unchanged when applied to clover at 1.68 kg ai/ha. Overall, approximately 91.6–99.2% of the incurred residue had been defined in the study. The unchanged imazapyr accounted for 67.5–99.2% of the total residue. A number of minor metabolites, including CL 240,000/CL 247,087, CL 252,974 and PDC were present at 0.02–18.4% (the estimated ratio of CL 240,000/CL 247,087 was in the range of 1:5 to 1:10), 0–3.60% and 0–6.56% of TRR, respectively.

Bermuda grass

A metabolism study was conducted with [pyridine-6- ^{14}C]-imazapyr (Wu, 1997: IZ-640-006). [^{14}C] imazapyr was applied to Bermuda grass at a rate of 1.68 kg ai/ha (acid equivalents) as a 240 g/L water soluble formulation. Soil cores were collected to a depth of 45.7 cm before application (-1 day), after application (0 day), and at the final sampling (21 day). Bermuda grass foliage was collected at 0, 4, 10, 15 and 21 days after treatment (DAT) and analysed for metabolite identification. The field study was conducted outdoors in two separate plots; plot A received the test material spray treatment, and plot B (control) received the blank spray treatment. Phytotoxic effects were apparent four days after application of the test material to the Bermuda grass in the test plot. The Bermuda grass in the untreated control plot appeared healthy. The phytotoxicity remained apparent until the final collection 21 days after treatment.

The soil cores and grass foliage from the control and treated plots were analysed for total radioactive residue (TRR) content. The grass foliage from the treated plot at each sampling interval also was extracted with acidified methanol and analysed for metabolites.

The TRR levels (expressed as mg/kg imazapyr equivalent) in soil were low. For example, levels were 0.041 mg/kg (0 day) at 0–7.62 cm and ranged from 0.048 to 0.131 mg/kg (21 day) at different depths (up to 30.5 cm). The level of radioactivity in soil increased due to wash-off by water

and release of radioactivity by dying plant. Soil cores at all other sampling times and depths had only background levels.

TRR levels in foliage were the highest at 0 DAT (64.3 mg/kg); they then decreased to 17.5 mg/kg at 4 DAT; 22.0 mg/kg at 10 DAT, 24.9 mg/kg at 15 DAT and 47.7 mg/kg at 21 DAT. The high radioactive residues in foliage at 0 DAT resulted from direct application of [^{14}C] imazapyr to Bermuda grass. The increased TRR in 21 DAT compared to the 15 DAT samples was probably attributed to the loss of water as the plants died. TRR values in control soil and plant samples were all less than the minimum quantifiable limit of detection (< 0.01 mg/kg).

Each grass sample was extracted by blending with methanol/hydrochloric acid (100/0.75, v/v). The acidified methanol extracted 97.3%, 97.1%, 94.5%, 88.1% and 85.8% of TRR from the 0, 4, 10, 15 and 21 DAT samples, respectively. Post extraction solids (PES) were hydrolysed with protease in a phosphate buffer (pH approximately 7.5), followed by cellulase in an acetate buffer (pH approximately 5). The enzyme hydrolysates were combined and concentrated for metabolite analysis. The PES-3 fractions from 0, 4, 10, 15 and 21 DAT samples were further hydrolysed using 6 N HCl, yielding AQ-3 and PES-4 fractions. The PES-4 fractions from the 10 and 15 DAT samples were further hydrolysed by 1 N NaOH.

The acidified methanol extracts were analysed by HPLC and TLC. The majority of the radioactivity was unchanged imazapyr, ranging from 74.4% to 94.7% of TRR. Three other identified radio components were PDC, CL 247,087 cyclized product and CL 240,000. The amount of PDC in the acidified methanol fraction increased with time from 0% at 0 DAT to 7.23% of TRR at 21 DAT. The amount of CL 247,087 and CL 240,000 in the acidified methanol fraction was highly variable, ranging from 0% to 10.1% of TRR.

It is known that imazapyr forms methyl ester (CL 240,000) in methanol. Additional experiments were conducted to find out whether the CL 240,000 detected was formed metabolically or as a result of chemical reaction. Extraction of a separate subsample of 0 and 21 DAT grass samples with methanol/HCl or acetone followed by chromatographic analysis showed that CL 240,000 was present in both acetone and acidified methanol extract. The acidified methanol fraction showed higher amounts of CL 240,000; however, acetone had much lower extraction efficiency for the radioactivity. The peak height of CL 240,000 increased after one month storage of acidified methanol extract in the refrigerator. The results indicate that small amounts of CL 240,000 are metabolite generated by the grass; the variability may be a result of the storage stability property.

Analysis of the enzyme hydrolysate from PES indicated that parent imazapyr was still the major component identified (1.10–4.55% of TRR), other metabolites detected were CL 240,000 and/or CL 247,087 (0–0.54% of TRR), PDC (0.08–1.79% of TRR) and unknown C (R_t approximately 20–20.5 min, 0–0.45%). The PES-3 fractions from the 0, 4, 10, 15 and 21 DAT samples were further hydrolysed by 6 N HCl. The hydrolysates were analysed by HPLC. All of the samples showed a single peak at R_t approximately 5 min; this retention time was very close to that of PDC. In addition, two-dimensional TLC analysis indicated that this peak was very likely PDC. The PES-4 samples from the 10 and 15 DAT grass were again hydrolysed with 1 N NaOH, however, the hydrolysates (AQ-4) were not further analysed due to the presence of low radioactive residue levels.

Table 9 Distribution of metabolites in Bermuda grass after application of [^{14}C] imazapyr

Components	0 DAT		4 DAT		10 DAT		15 DAT		21 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Imazapyr	62.19	96.7	16.52	94.4	20.01	90.8	19.45	78.1	38.15	80.0
PDC	0.21	0.32	0.23	1.32	0.91	4.12	1.22	4.91	6.12	12.8
CL 240000 + CL 247087 ^a	0.19	0.30	nd		0.044	0.20	2.62	10.5	1.44	3.01
Unknown A	nd		nd		0.093	0.42	nd		nd	
Unknown B	nd		0.38	2.18	nd		0.12	0.48	nd	
Unknown C	0.45	0.70	0.28	1.60	0.007	0.03	0.27	1.07	0.50	1.04
Unknown D	nd		nd		0.19	0.87	0.22	0.88	nd	
Unknown E	0.41	0.64	nd		0.079	0.36	nd		nd	
Unknown F	0.78	1.22	nd		0.34	1.54	nd		nd	

Components	0 DAT		4 DAT		10 DAT		15 DAT		21 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Precipitate	0.045	0.07	0.039	0.22	0.12	0.56	0.24	0.95	0.76	1.60
Aqueous-4	n.a.	n.a.	n.a.	n.a.	0.22	1.00	0.70	2.81	n.a.	n.a.
Unextracted (PES)	0.019	0.03	0.047	0.27	0.013	0.06	0.065	0.26	0.72	1.50
Total	64.30	100	17.50	100	22.02	100	24.89	100	47.68	100

DAT = days after treatment

^a The estimated contribution of CL 247087 was about 50% of the total. The estimation was based on extraction of new 0 DAT and 21 DAT subsamples using acetone.

nd = not detected

n.a. = not applicable

In conclusion, imazapyr remained mostly unchanged when applied to Bermuda grass at 1.68 kg ai/ha. Overall, approximately 94–97% of the incurred residue had been defined in the study. The unchanged imazapyr accounted for 78–97% of the total residue. A number of metabolites, including PDC and CL 247,087 plus CL 240,000 were present at 0.32–12.8% and 0–10.5% of TRR, respectively.

Summary of plant metabolism

Metabolism of [¹⁴C] imazapyr labelled in pyridine ring has been studied in soya bean (imidazolinone-resistant), maize (imidazolinone-resistant), sugarcane, oil palm, clover and Bermuda grass, which are suitable to cover the crop groups of pulses, cereals, oilseeds and animal feed. Imazapyr is the major component of the residues found in soya bean, maize, clover, and Bermuda grass. PDC is also the major components of the residues in clover and Bermuda grass. The following metabolic pathways were speculated in the plant metabolism studies available.

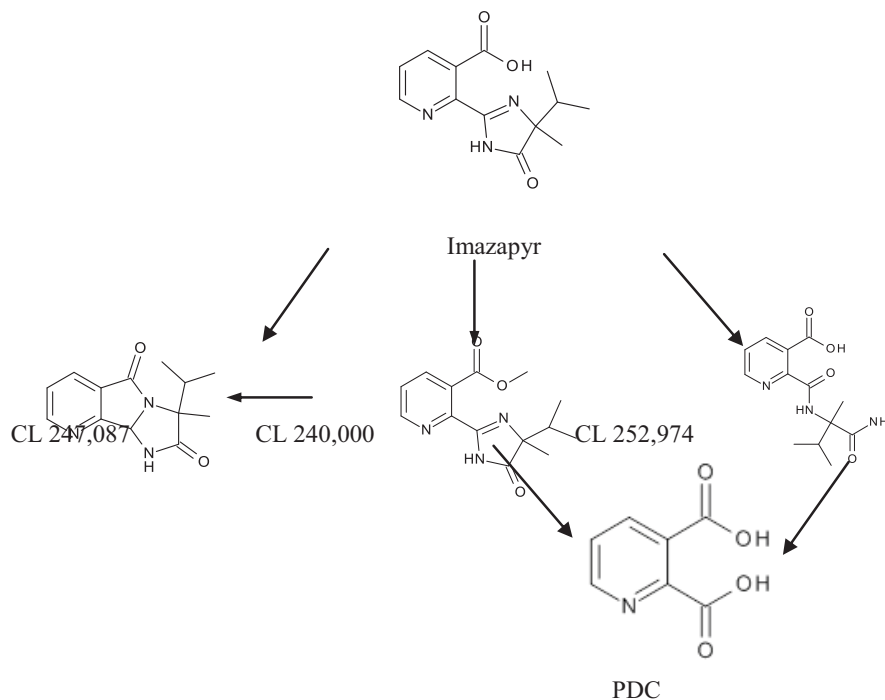


Figure 2 Metabolic Pathway of Imazapyr in Plants (clover and Bermuda grass)

Environmental fate in soil

The Meeting received information on aerobic degradation in soil, photolysis on soil surface, rotational crop and hydrolytic degradation study. Because imazapyr is intended for use as foliar and soil treatment, aerobic degradation, soil photolysis, rotational crop and hydrolytic degradation study relevant to the current evaluations were reported below (FAO Manual 2009).

The fate and behaviour of imazapyr in soils were investigated using [^{14}C -carboxyl] and [^{14}C -pyridine] labelled compounds.

Aerobic degradation

Study 1

The aerobic soil metabolism of [carboxyl- ^{14}C]-imazapyr was studied in Princeton sandy loam soil. Imazapyr was applied to the soil at the rate of 1.12 kg ai/ha and kept under aerobic conditions in the dark (Mallipudi, 1983: IZ-620-001). At sampling intervals of 1, 2, 4, 6, 9 and 12 months, [^{14}C] carbon dioxide collected was 2.0, 4.0, 7.2, 9.8, 11.2 and 13.6% of the applied dose, respectively. Aerobic microbes present in the soil slowly decarboxylated the compound imazapyr. No other ^{14}C volatile materials were collected at any given interval during the course of the experiment, indicating volatilization of the parent compound or metabolites had not occurred.

Table 10 Soil characteristics

Parameters	Soil (Princeton)
pH (water)	5.3
Organic matter (%)	1.8
Cation exchange capacity (meq/100 g soil)	8.5
Soil type (USDA)	Sandy loam
Clay (%)	10.4
Silt (%)	30.8
Sand (%)	58.8
Moisture at 1/3 bar (%)	14.4
Bulk density on dry soil (g/cc)	1.3

At sampling intervals of 1, 2, 4, 6, 9 and 12 months, the ^{14}C residues remaining in the soil were 96.4, 95.8, 95.2, 90.8, 89.3 and 86.0% of the applied dose, respectively. The rate constant and the half-life of imazapyr under laboratory conditions were calculated as 0.041/month and 17 months, respectively. The extractable soil ^{14}C residue at 1 to 12 months intervals was characterized as imazapyr by TLC and mass spectrometry. The unextractable soil-bound radioactive residues varied from 6.6 to 14.0% of the total soil radioactive residue during the 12-month period. ^{14}C labelled CO_2 was the only major metabolite detected using [carboxyl- ^{14}C]-imazapyr. No marked changes were found in the total bacterial and mould counts on untreated and treated soil with imazapyr, indicating that soil aerobic microflora was active throughout the experimental period and imazapyr has no lethal effects on soil aerobic microflora.

Study 2

The aerobic soil metabolism of [carboxyl- ^{14}C]-imazapyr was studied in North Dakota clay loam soil. Imazapyr was applied to the soil at the rate of 1.12 kg ai/ha and kept under aerobic conditions at 22 to 24 °C in the dark (Mallipudi, 1985: IZ-620-002). At sampling intervals of 1, 2, 4, 6, 9 and 12 months, the ^{14}C residues remaining in the soil were 95.1, 91.3, 94.5, 79.0, 83.8 and 79.8%, while [^{14}C] carbon dioxide collected was 2.8, 3.2, 7.3, 13.4, 14.5 and 15.4% of the applied dose, respectively. No other ^{14}C volatile materials were collected at any given interval during the course of the experiment, indicating volatilization of the parent compound or metabolites had not occurred.

Table 11 Soil characteristics

Parameters	Soil (North Dakota)
pH (water)	7.5
Organic matter (%)	2.2
Cation exchange capacity (meq/100 g soil)	50.7
Soil type (USDA)	Clay loam
Clay (%)	34.0
Silt (%)	42.8
Sand (%)	23.2
Moisture at 1/3 bar (%)	46.6
Bulk density on dry soil (g/cc)	1.01

The carboxyl [^{14}C] imazapyr found in soil at the end of the 12-month interval was 60.5% of the applied radioactive dose. At the same time interval, some minor metabolites were identified as PDC (0.3%), CL 60,032 (0.6%) and CL 252,974 (5.4%). There were about six other unknowns comprising 3.0% of the applied dose. No attempt was made to identify these minor unknowns. The unextractable soil-bound radioactive residues varied from 6.0 to 11.2% of the total applied dose during the 12-month period. The amount of ^{14}C residues remaining in the aqueous phase and humic acid were very small at all time intervals. Based on the recovered imazapyr in the soil extract, the rate constant and the half-life of imazapyr under laboratory conditions were calculated as 0.019/month and 37.2 months, respectively, which is longer than the sandy loam soil half-life of 17 months.

Table 12 Distribution of radioactivity in the NaOH trap and in the soil fraction

Time (months)	% of Total Applied Dose		
	NaOH trap	Soil	Total
1	2.8	95.1	97.9
2	3.2	91.3	94.5
4	7.3	94.5	101.8
6	13.4	79.0	92.4
9	14.5	83.8	98.3
12	15.4	79.8	95.2

Table 13 Distribution of [^{14}C] Imazapyr and Metabolites in the soil extracts

Time (months)	% of Total Applied Radioactivity				
	Imazapyr	CL 252,974	CL 60,032	PDC	Others
1	77.6	4.9	0.4	–	2.1 (4) ^a
2	71.8	4.6	0.3	–	1.7 (3)
4	73.9	5.0	0.7	–	1.9 (3)
6	64.4	3.4	0.4	–	1.6 (4)
9	69.0	4.4	0.3	0.2	1.1 (3)
12	60.5	5.4	0.6	0.3	3.0 (6)

^a number of unknowns metabolites

– = Not detected

Study 3

The aerobic soil metabolism of [^{14}C] imazapyr was studied in Princeton sandy loam soil. The [^{14}C] imazapyr labelled at the pyridine ring was dissolved in acetonitrile and applied to the soil at the rate of 1.68 kg ai/ha and kept under aerobic conditions at 35 °C in the dark (Mangles, 1988: IZ-620-036). Water was added to the soil to bring the moisture of the soil to 75% of field capacity. At intervals of 0, 30, 60, 122, 181, 272 and 365 days after treatment of soil aerobically with [^{14}C] Imazapyr were extracted. At the same intervals, the ethylene glycol, sulphuric acid and potassium hydroxide traps were assayed for the ^{14}C -volatile materials. The soil was extracted with 0.1–0.5 N aqueous sodium hydroxide and the humic acid was removed by acid precipitation. The [^{14}C] imazapyr from the

aqueous phase was extracted with dichloromethane. The solvent was concentrated and analysed by TLC. The soil was combusted to determine the bound residues.

Table 14 Soil characteristics

Parameters	Soil (Princeton)
pH (water)	5.3
Organic matter (%)	2.0
Cation exchange capacity (meq/100 g soil)	7.3
Soil type (USDA)	Sandy loam
Clay (%)	10.0
Silt (%)	22.0
Sand (%)	68.0
Moisture at 1/3 bar (%)	9.5
Bulk density on dry soil (g/cc)	1.49

After 12 months of aerobic incubation 89.3% of the initial dose applied remained as parent compound. Two unknown degradates, none of which accounted for greater than 0.8% of the applied dose, were observed intermittently during the study. None of these intermittent products co-chromatographed with the five reference standards used (PDC, CL 60,032, CL 247,087, CL 247,271 and CL 252,974). A half-life of 7.5 years was calculated.

Table 15 Characterization of Non-volatile [^{14}C] Imazapyr

Time (days)	% of Total Applied Radioactivity						
	Imazapyr	UK 1	UK 2	UK 3	UK 4	UK 5	Remainder
0	98.0	–	–	–	–	–	0.4
30	98.7	–	–	–	–	–	0.9
60	95.8	–	–	0.3	0.6	–	2.7
122	94.6	–	–	–	0.8	–	2.7
181	93.9	–	–	–	–	–	2.5
272	92.2	–	–	–	–	–	2.3
365	89.3	–	–	–	–	–	3.0

UK = unknown compound

– = Not detected

Study 4

The aerobic soil metabolism of [^{14}C] imazapyr was studied in Princeton sandy loam soil. The [^{14}C] imazapyr labelled at the pyridine ring was dissolved in acetonitrile and applied to the soil at the rate of 1.68 kg ai/ha and kept under aerobic conditions at 25 °C in the dark (Mangels, 1987: IZ-620-037). Water was added to the soil to bring the moisture of the soil to 75% of field capacity. At intervals of 0, 30, 60, 122, 181, 272 and 365 days after treatment of soil aerobically with [^{14}C] imazapyr were extracted. At the same intervals, the ethylene glycol, sulphuric acid and potassium hydroxide traps were assayed for the [^{14}C] volatile materials. The soil was extracted with 0.1–0.5 N aqueous sodium hydroxide and the humic acid was removed by acid precipitation. The [^{14}C] imazapyr from the aqueous phase was extracted with dichloromethane. The solvent was concentrated and analysed by TLC. The extracted soil was combusted to determine the bound residues.

Table 16 Soil characteristics

Parameters	Soil (Princeton)
pH (water)	5.3
Organic matter (%)	2.0
Cation exchange capacity (meq/100 g soil)	7.3
Soil type (USDA)	Sandy loam
Clay (%)	10.0
Silt (%)	22.0
Sand (%)	68.0
Moisture at 1/3 bar (%)	9.5

Parameters	Soil (Princeton)
Bulk density on dry soil (g/cc)	1.49

After 12 months of aerobic incubation 87.6% of the initial dose applied remained as parent compound. Five unknown degradates, none of which accounted for greater than 1.3% of the applied dose, were observed intermittently during the study. None of these intermittent products co-chromatographed with the five reference standards used (PDC, CL 60,032, CL 247,087, CL 247,271 and CL 252,974). A half-life of 5.9 years was calculated.

Table 17 Characterization of Non-volatile [^{14}C] Imazapyr

Time (days)	% of Total Applied Radioactivity						
	Imazapyr	UK 1	UK 2	UK 3	UK 4	UK 5	Remainder
0	99.2	0.2	0.1	—	—	—	0.5
30	98.8	0.2	0.1	—	—	—	0.6
60	96.7	—	—	—	—	—	3.0
122	93.3	—	—	0.4	0.3	1.3	3.3
181	93.5	—	—	—	—	—	3.6
272	91.8	—	—	—	—	—	3.1
365	87.6	—	—	—	—	—	5.4

UK = unknown compound

— = Not detected

Study 5

The aerobic soil metabolism of [^{14}C] imazapyr was studied in Princeton Sassafras sandy loam soil. [pyridine-6- ^{14}C]-imazapyr was dissolved in water and applied to the soil at the rate of 0.25 kg ai/ha and kept under aerobic conditions at 25 °C in the dark (Ta, 1999: IZ-620-053). Water was added to the soil to bring the moisture of the soil to 75% of 1/3 bar. At intervals of 0, 7, 14, 21, 28, 62, 94 and 121 days after treatment of soil aerobically with [^{14}C] imazapyr were extracted. At the same intervals, the ethylene glycol and sodium hydroxide traps were assayed for the ^{14}C -volatile materials. The soil was extracted once with water and three times with 0.5 N aqueous sodium hydroxide. After extraction, the soils were washed with 100 mL of water, followed by 100 mL of methanol. The water and NaOH extracts were cleaned up and concentrated by C_{18} and SCX solid phase extraction then analysed by TLC, HPLC and HPLC-MS. The extracted soil was combusted to determine the bound residues.

Table 18 Soil characteristics

Parameters	Soil (Princeton)
pH (water)	6.0
Organic matter (%)	2.0
Cation exchange capacity (meq/100 g soil)	7.3
Soil type (USDA)	Sandy loam
Clay (%)	10.0
Silt (%)	22.0
Sand (%)	68.0
Moisture at 1/3 bar (%)	14.9

Approximately 26% of the imazapyr was degraded after 121 days of aerobic incubation. The first-order degradation half-life was calculated to be 313 days. The rate of degradation of imazapyr decreased after 1 month of incubation and appeared to be a biphasic pattern with transition point at approximately 28 days. Using the first month degradation data only, the half-life of imazapyr in soil was calculated to be 117 days. The half-life in the second phase was 438 days. Degradation of imazapyr proceeded via the opening of the imidazolinone ring to yield the metabolite CL 252,974 which accounted for approximately 2% of the applied dose at 4 months of incubation. Degradation of imazapyr can also proceed via the conversion of the carboxylic acid group at the 3 position in the

pyridine ring to form the hydroxyl metabolite (CL 288,247) which reached approximately 6% of the applied dose at 4 months of incubation. The metabolites were identified by co-chromatography (TLC and HPLC) with authentic standard and by mass spectrometry analysis.

Table 19 Distribution of Imazapyr and metabolites in soil (analysed by HPLC)

Time (days)	% of Total Applied Radioactivity							
	Imazapyr	CL288,247	CL252,974	CL240,000	CO ₂	Others ^a	Bound Residue	Total
0	94.4	0.5	1.6	1.1	0.0	2.7	0.1	100.4
7	86.4	1.3	3.1	2.1	0.8	3.5	2.1	99.3
14	83.9	1.2	2.4	1.5	1.5	5.2	2.9	98.6
21	81.3	1.7	2.8	1.5	2.1	6.4	3.2	99.0
28	78.9	1.9	2.8	1.3	2.5	6.8	3.8	98.0
62	75.1	4.5	1.5	1.6	4.0	6.7	4.8	98.2
94	70.5	5.7	2.0	1.9	4.9	6.2	5.9	97.1
121	67.6	6.4	2.1	2.3	5.6	6.6	6.1	96.7

^a Consist of several unknown components

Approximately 5.6% of the total applied radioactivity was evolved as ¹⁴CO₂ over the 4 months of incubation indicating that the pyridine ring was mineralized. No organic volatiles were detected in the glycol traps. Results showed that imazapyr is aerobically degraded in soil and is ultimately mineralized to CO₂.

Soil photolysis

The photolysis of ¹⁴C labelled imazapyr was studied on sandy loam soil. [pyridine-6-¹⁴C]-imazapyr was dissolved in acetonitrile and applied to the soil surface at a rate equivalent to 1.68 kg ai/ha, then exposed continuously for 28 days to light from a borosilicate-filtered Xenon-arc lamp in a custom-made environmental chamber (Mangels, 1986: IZ-620-010). The soils were irradiated approximately 80 cm from the light, which was operated continuously at 6000 watts and 25 °C. The light produced by the lamp is comparable to summer sunlight in Chicago, Illinois.

Table 20 Recoveries of radioactivity (% of total applied dose)

Time (days)	Sample	% Recovery ^a
0		100.0
7	Irradiated	98.7
	Control	101.0
14	Irradiated	104.5
	Control	106.5
21	Irradiated	106.4
	Control	105.5
28	Irradiated	99.5
	Control	105.2

^a Mean of two replicates

Table 21 Distribution of radioactivity (% of total applied dose)

Time (days)	sample	% of total applied dose ^a		
		Imazapyr (organic phase)	Imazapyr (aqueous phase)	Total
0		95.3	2.5	97.6
7	Irradiated	92.1	2.4	94.3
	Control	93.3	2.5	95.3
14	Irradiated	86.3	2.1	87.9
	Control	93.8	1.7	95.2

Time (days)	sample	% of total applied dose ^a		
		Imazapyr (organic phase)	Imazapyr (aqueous phase)	Total
21	Irradiated	85.1	2.0	86.7
	Control	93.5	1.8	94.9
28	Irradiated	84.7	2.4	86.5
	Control	94.7	2.2	96.5

^a Mean of two replicates

There was 11% degradation of imazapyr over the 28 days of continuous irradiation. There were at least five degradation products formed, none of which accounted for > 10% of the applied dose. The photodegradation half-life of imazapyr under the conditions of this test was calculated to be 149 days.

Residues in rotational crops

Confined rotational crop studies

Study 1

The field phase of the confined rotational crop study was conducted in North Carolina and initiated in the summer of 1993 (Zulalian, 1995: IZ-640-004). The study consisted of one treated and one control plot. For the treated plot, pyridine-6-¹⁴C-labeled imazapyr was mixed with [pyridine-6-¹³C]-imazapyr to afford a final specific activity of 20.8 μ Ci/mg. The radioactive test substance, formulated as an aqueous ammonium salt solution, was applied as a post-emergence application to IMI-Maize plants (Pioneer hybrid 3245 IR) at the 6-leaf stage at a rate of 0.028 kg ai/ha. The IMI-Maize plants in the control plot were treated with the blank formulation. The final specific activity of the radiolabelled imazapyr afforded a detection limit of 0.002 mg/kg in the radio-assay of soil and plant samples. Soil core samples were taken prior to application (–1 DAT), within two hours following application (0 DAT) and at final harvest (86 DAT) of the mature maize plants.

Winter wheat (cereal grain) was planted 120 DAT. Soya beans (legume), lettuce (leafy vegetable), and radishes (root crop) were planted 271 DAT. Lettuce and radishes were also planted 420 DAT. Samples were collected from the respective plots at immature and mature stages of crop development. The total radioactive residues (TRR) were determined by combustion and liquid scintillation counting. The TRR in winter wheat forage, straw and grain; lettuce; radish foliage and root; and soya bean forage, hay, and seed were all < 0.002 mg/kg, the limit of detection of the radioassay.

Table 22 Total radioactive residues (TRRs) found in crops for confined rotational crop study

Sample		Planting Interval (DAT)	Harvest Interval (DAT)	TRR (mg/kg)
Wheat (Pioneer 2548)	Mid Harvest Forage	120	278	< 0.002
	Final Harvest Straw		337	< 0.002
	Final Harvest Grain		337	< 0.002
Lettuce (Black Seeded Simpson)	Mid Harvest	271	316	< 0.002
	Final Harvest		328	< 0.002
Lettuce (Buttercrunch)	Mid Harvest	420	457	< 0.002
	Final Harvest		474	< 0.002
Radish (White Icicle)	Mid Harvest Foliage	271	306	< 0.002
	Mid Harvest Root		306	< 0.002
	Final Harvest Foliage		321	< 0.002
	Final Harvest Root		321	< 0.002
Radish (White Icicle)	Mid Harvest Foliage	420	449	< 0.002
	Mid Harvest Root		449	< 0.002
	Final Harvest Foliage		461	< 0.002
	Final Harvest Root		461	< 0.002
Soya bean	Mid Harvest Forage	271	356	< 0.002

Sample		Planting Interval (DAT)	Harvest Interval (DAT)	TRR (mg/kg)
(Hartz 6686)	Final Harvest Hay		484	< 0.002
	Final Harvest Seed		484	< 0.002

DAT = days after treatment

The TRRs in soil (0–8 cm) at 0 DAT was 0.013 mg/kg. At the time of maize harvest (86 DAT) the residue in the soil (0–8 cm) was 0.004 mg/kg. Residues were < 0.002 mg/kg in deeper soil layers (8–15 cm, 15–30 cm and 15–46 cm).

In summary, the results of this study indicate that residues in rotational crops would be expected to be < 0.01 mg/kg at the recommended planting intervals following a post-emergence application of imazapyr on IMI-Maize at a maximum label rate of approximately 0.028 kg ai/ha.

Study 2

An outdoor confined rotational crop study with ^{14}C -labelled imazapyr was conducted at Lucama, North Carolina during the year 1997–1999 (Mallipudi, 2000: IZ-640-008). The study was designed to determine the nature and amount of imazapyr-related residue uptake in rotational crops. A leafy vegetable, root crop and small grain were planted at various time intervals after a single application of [^{14}C] imazapyr to the soil at a rate of 0.885 kg ai/ha. [pyridine-6- ^{14}C]-imazapyr was used in the study. The position of the ^{14}C label was considered metabolically stable to allow determination of the metabolic profile in the confined rotational crops. The radiolabelled imazapyr-spray mixture was formulated as a liquid end-use product in water. The control plot was treated with a blank formulation and water mixture without test substance.

Five months after treatment with the test substance, the test and control plots were planted with annual weeds and maintained the plots with weeds until the designated rotational crop planting time. The treated test plot and control plot were planted with a series of rotational crops, namely carrot and lettuce were planted at 330 and 540 days after treatment (DAT), winter wheat planted at 359 DAT, spring wheat at 520 DAT. Confined rotational crop samples were collected from the respective plants at immature and mature stages of crop development. Soil core samples were taken to a depth of approximately 30 to 46 cm prior to test substance application, immediately following application, and at each rotational crop replant and harvest. No soil samples were taken for carrot and lettuce planted at 330 DAT.

Before analysis, individual crop samples were homogenized by grinding with dry ice. Soil samples were air dried and homogenized by grinding. Total radioactive residues (TRR) in all plant parts and in soil were determined by combustion of aliquots to yield $^{14}\text{CO}_2$. LSC counting was used to analyse trapped $^{14}\text{CO}_2$. The LSC techniques were used to analyse fractions from HPLC. The identity of the extractable residue component was determined by chromatography with unknown reference compounds using HPLC.

TRR levels were less than 0.01 to 0.02 mg/kg in different crop samples at various plant-back intervals. TRR values in control samples were all less than the validated minimum quantifiable limit of detection of 0.005 mg/kg. A summary of the TRR values in the treated crop samples is shown below.

Table 23 Total radioactive residues (TRRs) found in crops for confined rotational crop study

Sample		Planting Interval (DAT)	Harvest Interval (DAT)	TRR (mg/kg)
Winter wheat	forage	359	514	< 0.005
	hay		582	0.005
	straw		596	0.006
	grain		596	0.007
Spring wheat	forage	520	574	< 0.005
	hay		590	0.018
	straw		623	0.015

Sample		Planting Interval (DAT)	Harvest Interval (DAT)	TRR (mg/kg)
	grain		623	0.016
Carrot	mature top	330	427	< 0.005
	mature root			< 0.005
Carrot	mature top	540	646	0.007
	mature root			< 0.005
Lettuce	mature	330	391	< 0.005
Lettuce	mature	540	623	0.009

Significant levels of soil radioactive residues were present throughout the experiment period. TRR in the top zero to 8 cm soil layer were 0.472 mg/kg at 0 days after treatment (0 DAT). Residues in the top 8 cm of soil ranged from 0.022 to 0.028 mg/kg up to 646 DAT during which time various crops were grown. The soil TRR ranged between 0.016 to 0.023 mg/kg in the 8 to 15 cm soil core during the same period. During the same time interval, the soil TRRs were 0.029 to 0.051 mg/kg in 15 to 30 cm soil layer and 0.018 to 0.036 mg/kg in 15 to 46 cm soil layer. TRR levels in the control (untreated) soil core samples were all less than the validated limit of detection (0.005 mg/kg).

The radioactivity in the various rotational crop matrices was moderately extractable (ranging from about 23.6% for the winter wheat hay to 51.1% for lettuce) by aqueous acetone. An additional amount of radioactivity (about 5.0% for the spring wheat grain to 15.0% for the winter wheat grain) was extracted with 2% acidified aqueous acetone. Exhaustive extraction and digestion procedure using acetone: water: HCl (3%), 6 N aqueous HCl and 6 N aqueous NaOH yielded additional 3.1% to 18.7% of TRR (< 0.001 to 0.002 mg/kg) in various fractions from different crops. The unextractable radiocarbon in various solids after solvent extraction of crop samples ranged from 12.7% to 71.2% of TRR (0.001 to 0.004 mg/kg).

Table 24 Extraction efficiency of residues of imazapyr in rotational crops

Sample		Harvest DAT	TRR (mg/kg)	Extractable (%TRR)			Unextracted (PES)	
				Aqueous Acetone ^a	Acetone: H ₂ O:HCl ^b	Total	mg/kg	%TRR
Winter wheat	hay	582	0.005	23.6	7.0	30.6	0.004	71.2
	grain	596	0.007	31.0	15.0	46.0	0.006	80.1
Spring wheat	hay	590	0.018	37.8	10.9	48.7	0.009	51.1
	straw	623	0.015	28.0	5.5	33.5	0.010	67.2
	grain	623	0.016	47.9	5.0	52.9	0.007	46.2
Carrot	mature top	646	0.007	49.8	7.7	57.5	0.003	45.2
Lettuce	mature	623	0.009	51.1	9.9	61.0	0.004	48.1

DAT = days after treatment

^a: extracted with acetone:H₂O (1:1)

^b: extracted with 2% HCl (acetone:H₂O:HCl 49:49:2)

Table 25 Distribution of radioactivity in fractions extracted from post extraction solid (PES) of rotational crops

Sample	Harvest DAT	TRR (mg/kg)	Residue in crop PES		Residue Fraction	Residue in crop	
			mg/kg	%TRR		mg/kg	%TRR
Winter wheat grain	596	0.007	0.006	80.1	6 N aqueous HCl	0.001	12.7
					6 N aqueous NaOH	0.001	18.7
					PES (unextractable)	0.001	19.3
Spring wheat straw	623	0.015	0.010	67.2	Aqueous:Acetone:HCl (3%)	0.002	15.0
					6 N aqueous HCl	0.002	15.1
					6 N aqueous NaOH	0.002	12.1
					PES (unextractable)	0.003	19.2
Spring wheat grain	623	0.016	0.007	46.2	Aqueous:Acetone:HCl (3%)	0.002	9.8
					6 N aqueous HCl	0.002	13.2
					6 N aqueous NaOH	0.001	8.4

Sample	Harvest DAT	TRR (mg/kg)	Residue in crop PES		Residue Fraction	Residue in crop	
			mg/kg	%TRR		mg/kg	%TRR
Lettuce	623	0.009	0.004	48.1	PES (unextractable)	0.002	12.7
					Aqueous:Acetone:HCl (3%)	0.001	7.6
					6 N aqueous HCl	0.001	13.2
					6 N aqueous NaOH	< 0.001	3.1
					PES (unextractable)	0.002	22.4

DAT = days after treatment

Analysis of the aqueous acetone and aqueous acetone: HCl (2%) fractions from various crop parts by HPLC was possible. The results showed that the major fraction comprised of unchanged imazapyr, which ranged from < 0.001 to 0.003 mg/kg in various crops. Chromatographic region of interests corresponded to CL 247,087, CL 252,974, CL 17,226 and CL 119,060 were each at less than 0.001 mg/kg by calculations.

When [pyridine-6-¹⁴C]-imazapyr was applied to bare sandy loam soil at a use rate of 0.885 kg ai/ha (acid equivalents) radioactivity in soil was present throughout the experiment period. A trace amount of imazapyr-related residue in soil was transported into leafy vegetable, root crop and small grain. Total radioactive residues in follow crops were at < 0.01 to 0.02 mg/kg at the various plant back intervals: Winter wheat at 359 days, spring wheat at 520 days, and carrot and lettuce at 330 and 540 days.

Attempts to elucidate the metabolic profile of imazapyr in rotational crops showed terminal residue in the rotational crops included the unchanged imazapyr which ranged from < 0.001 to 0.003 mg/kg. Metabolites CL 247,087, CL 252,974, CL 17,226, and CL 119,060, each at 0.001 mg/kg or less were present. Thus, it appeared that imazapyr was metabolized in the rotational crops by hydrolysis of imidazolinone ring and cyclization of the carboxyl group and imidazolinyl nitrogen.

Environmental fate in water systems

Hydrolysis

Study 1

The [pyridine-6-¹⁴C]-imazapyr was dissolved in water and applied in to the water layer at an application rate of 1.5 mg/kg (Mangels, 1990: 1990/7001955). Samples were incubated at 25 °C under aerobic conditions in the dark. After various time intervals (0, 1, 2, 3 and 4 weeks), the water samples were directly, analysed by LSC and by TLC two-dimensional TLC upon comparison with authentic standards. Since there was less than 2% of the radioactivity presented in the sediment, no extraction was performed and the radioactivity in the sediment was determined by combustion.

Greater than 98% of the applied radioactivity (AR) was recovered. A total of 1.12% AR mineralized to ¹⁴CO₂ during four weeks of aging and no volatile organic compounds were detected. Greater than 95% of the applied imazapyr remained in the water layer. Less than 2% of the applied radioactivity was detected in the sediment. No measurable degradation occurred during the 1 month experiment indicating imazapyr is stable under aerobic aquatic conditions. In conclusion, imazapyr is stable under aerobic aquatic conditions.

Study 2

The [carboxyl-¹⁴C]-imazapyr was dissolved in water to give stock solutions containing 50 mg/L of [¹⁴C] imazapyr (Mangels, 1990: 1990/7001950). Aliquots were placed into flasks and diluted in aqueous buffer solutions of pH 5 (0.01 M citrate), pH 5.2 (Distilled water), pH 7 (0.01 M phosphate) and pH 9 (0.01 M borate). Thereafter, aliquots duplicate samples containing each approximately 50 µg/mL were placed into test tubes and incubated in the dark at a controlled temperature of at 25 °C for 30 days. After various time intervals (0, 2, 12, 19, 26 and 30 days), the samples were directly, analysed by LSC and by TLC two-dimensional TLC upon comparison with authentic standards.

The recovery of radioactivity in all samples was between 92.3% and 107.0% of the total applied radioactivity. There was no detectable degradation of imazapyr in distilled water, pH 5 or pH 7 buffers. In pH 9 buffer, there was a slow degradation to a single product which reached a maximum level of 6.9% of the applied dose 30 days after treatment. The degradate was identified as CL 252,974.

Half-life =	pH 5	pH 7	pH 9	Distilled water
	NDD	NDD	325 days	NDD

NDD = No Detectable Degradation after 30 days

In conclusion, imazapyr is hydrolytically stable in distilled water (pH 5.2) pH 5, 7 and 9.

RESIDUE ANALYSIS

Analytical methods

Descriptions of analytical methods together with validation data for residues of imazapyr in plant and animal matrices were submitted to the Meeting. The methods rely on an initial extraction, usually with acetonitrile/water. After solvent partition and column cleanup, the imazapyr and metabolites residues are prepared for LC analysis. Imazapyr residues can be measured either by UV detector or mass selective detector (MS), typically to an LOQ of 0.01 mg/kg. Determinations for the metabolites were conducted using HPLC with mass spectrometric detector (MS/MS). The LOQ for the metabolites were typically 0.01 mg/kg. Since the methods use standard extraction solvents and standard detection techniques, they have the potential to be incorporated into existing multi-residue methods.

Brief descriptions of all these analytical methods are presented below.

Plant matrices

Imidazolinone-tolerant sunflower and rape (seeds, meal and refined oil) (2008/7019225, 2008/7019227)

Analyte:	Imazapyr	LC-MS/MS	M 3519 modified
	(m/z 262→217 for quantification, 262→149 for confirmation)		
LOQ:	0.05 mg/kg		
Description	Samples are extracted with acidic aqueous methanol. An aliquot of the extract is diluted with methanol then passed through a SCX cartridge, which retains the analyte. The SCX cartridge is washed with methanol to remove co-extractives then the residues are selectively eluted with a water-methanol solution. The eluate is evaporated to dryness and the residues are dissolved in acidic water for analysis. Residue of imazapyr is determined by LC-MS/MS.		

Soya bean (grain, flaked, meal, toasted meal and oil) (2010/1033332)

Analyte:	Imazapyr	LC-MS/MS	SOP-PA.0288
	(m/z 262→217 for quantification, 262→149 for confirmation)		
LOQ:	0.01 mg/kg		

Description 5 g $\pm$ 0.1 of sample are weighed and 50 mL of extraction solution (methanol/water/HCl 1 mol/L, 60/39/1, v/v/v) is added. A mechanical shaker is used for 10 minutes to extract the analytes. The extract is centrifuged for 5 minutes at 3000 rpm and an aliquot of 1 mL is taken into a 5 mL volumetric flask. The volume is filled to the mark with solution 1. The solution is filtered, when necessary, and injected in the liquid chromatographic system, mass/mass spectrometer (LC-MS/MS).

Solution 1: 0.1% formic acid in water/0.1% formic acid in methanol (1/1, v/v)

Soya bean (grain, flaked, meal, toasted meal and oil) (2010/1090461)

Analyte: Imazapyr LC-MS/MS SOP-PA-0288_E
(m/z 262 $\rightarrow$ 217 for quantification, 262 $\rightarrow$ 149 for confirmation)

LOQ: 0.01 mg/kg

Description The residues of imidazolinones and its metabolites are extracted from samples using extraction solution (methanol/water/1 M HCl 60/39/1, v/v/v) in a homogenizer for 5 minutes. The addition of HCl provides additional extraction capability for the analytes with acidic properties. Centrifugation is done whenever it is necessary for 5 minutes at 2000 rpm. For sunflower (seed or oil) shaking is to be done in a mechanical shaker for 10 minutes. A 1 mL aliquot is taken and complete to the mark with solution 1 in a 5 mL volumetric flask. Filter it in a filter unit, when necessary. The residues of imidazolinones and its metabolites are performed by LC-MS/MS and quantified by directive comparison with external standards.

Solution 1: 0.1% formic acid in water/0.1% formic acid in methanol (1/1, v/v)

Sunflower (seed, meal and refined oil) (2002/5004111)

Analyte: Imazapyr LC-MS

LOQ: 0.05 mg/kg

Description Residues of imazapyr are extracted from sunflower seed and meal samples with an acidified methanol/water solution, filtered, and concentrated. The residues are purified on a C₁₈ solid phase extraction (SPE) column eluted with 25% MeOH in 0.05 M aqueous ammonium acetate and brought to final volume with water. Residues in refined oil samples are diluted in hexane and extracted by shaking with acidified acetonitrile/water solution. Following phase separation, the lower aqueous ACN layer is collected and adjusted to final volume with water. The final chromatography analysis of imazapyr residues is performed using LC-MS.

Sunflower (seed, flower) (2002/3000641)

Analyte: Imazapyr LC-UV (254 nm) SOP-PA.0200, Rev.02-RE.01

LOQ: 0.05 mg/kg

Description: Residues of imazapyr are extracted from sunflower seed and flower samples with acidic aqueous methanol. The extract is filtered, and an aliquot is taken and concentrated. After adding water and acetate, the pH is adjusted to 6.2 with 1 N NaOH solution. Following centrifugation, an aliquot of the upper layer is taken and the pH is then adjusted to 2.1 with 1 N HCl solution. The sample is then partitioned four times with dichloromethane (DCM). The DCM layers are combined and concentrated to dryness. The residue is re-dissolved in methanol-water and passed through an SCX cartridge. The SCX cartridge is washed with methanol to remove co-extractives, and then the residue is selectively eluted with KCl in methanol. The residue is then evaporated to dryness and re-dissolved in acidic water (pH 2.5). The samples are partitioned again four times with DCM and concentrated to dryness. The final extract is dissolved in water for HPLC analysis. A liquid chromatograph (HPLC) equipped with a diode array detector (DAD) set at 254 nm is used for detection.

Soya bean (seed) (2010/1149746), Rice (grain) (2010/1141978)

Analyte: Imazapyr LC-MS/MS SOP-PA.0249
(m/z 262→217 for quantification, 262→149 for confirmation)

LOQ: 0.05 mg/kg

Description: The sample is weighed into an extraction container. 100 mL of 1 N methanol/water/HCl (60:39:1 v/v/v) are added and extracted in the homogenizer for 5 minutes or in the extraction bath for 20 minutes. The extract is centrifuged for 20 minutes at 2000 rpm and an aliquot of 20 mL is transferred to a concentration flask. The volume is reduced to approximately 7 mL. The extract is transferred to a volumetric flask and filled up to the mark with Milli-Q water. The pH is adjusted to 2.1 with HCl 1 N solution. An aliquot of 2 mL is transferred to a centrifuge tube. 10 mL of dichloromethane are added. Partitioning is performed for 1 minute, followed by centrifugation for 5 minutes to separate the phases. An aliquot of 4 mL of the organic phase (lower phase) is evaporated to dryness. The residue is dissolved in 2 mL of mobile phase A / mobile phase B (1/1, v/v) and injected into the chromatographic system, MS/MS detector.
Mobile phase A: 0.1% formic acid in water, Mobile phase B: 0.1% formic acid in methanol

Maize (grain, forage and fodder) (IZ-731-001, IZ-244-006, IZ-244-005)

Analyte: Imazapyr GC-MS M 2468

LOQ: 0.05 mg/kg

Description: The sample is weighed into an extraction flask and 200 mL of acidic acetone/water (1:3 v/v) is added. The extract solution is allowed to soak for 15 minutes, and then blended at medium speed for approximately 5 minutes using an Omni mixer. After mixing, 10 g Celite 545AW are added to the extract and the solution is swirled. The extract is then vacuum-filtered using a glass fibre filter on a Buchner funnel. A 2 mL aliquot of the extract is transferred into a flask and evaporated to near dryness on a rotary evaporator. The extract is then cleaned-up by solid-phase extraction on a Varian Bond Elut C18 cartridge using Milli-Q water, hexane and methylene chloride as wash solvents. After evaporation to dryness, the residue is re-dissolved in 1 mL methanol and sonicated, then transferred to an auto-injector vial for GC-MS analysis. Determination is done at m/z 289 in the negative ion monitoring mode.

Maize (grain) (IZ-731-021, 1997/7004635 and 1999/7004025)

Analyte: Imazapyr LC-UV (254 nm) M-LAADL R0001

LOQ: 0.05 mg/kg

Description: Residues are extracted with acidic aqueous methanol using a Polytron ultrasonic extractor. Residues are partitioned with methylene chloride from concentrated aqueous acid solution. The methylene chloride is evaporated and the remaining material is reconstituted in 50% methanol in pH 2.5 for SPE SCX—Benzenesulfonic acid (Strong Cation Exchange) clean-up. The residue is eluted from the SCX with a saturated KCl in methanol, partitioned with methylene chloride, evaporated to dryness and diluted in 2 mL of Milli-Q water for HPLC analysis.

Sugarcane (juice and bagasse) (IZ-790-015 and IZ-790-017)

Analyte: Imazapyr LC-UV (254 nm) M-LAADL R0002

LOQ: 0.05 mg/kg

Description: Residues are extracted from sugar cane or sugar cane juice with acetone/methanol/water (1/1/1, v/v/v). The extracts are subjected to suitable clean-up involving solid phase extraction (Ag 1-X8 and SCX cartridge). The determination of imazapyr residues in the final extracts is performed by HPLC-UV (juice) or HPLC-DAD (cane) at 254 nm. Residue concentrations are calculated by direct comparison to external standards.

Rape (seed) (1998/1008995)

Analyte: Imazapyr LC-UV (254 nm) L741/1

LOQ: 0.05 mg/kg

Description: Residues are extracted from samples with methanol/HCl/water (60:1:39, v/v/v). The extract is partitioned with dichloromethane after adjusting the pH to 2 with HCl. Subsequently, the extract is evaporated to dryness and the residue dissolved in methanol/water (1:1, v/v). Following SCX cartridge clean-up, separation and quantitation of imazapyr is accomplished by reverse phase high performance liquid chromatography (HPLC).

Maize (grain, forage, fodder) (IZ-244-009)

Analyte: Imazapyr GC-MS

LOQ: 0.05 mg/kg

Description: After soaking for 15 minutes imazapyr is extracted from the sample with 200 mL of acetone/water/HCl (25:74:1 v/v/v) at medium speed in an Omni-Mixer for 5 minutes. The extract is mixed with 10 g of Celite 545 AW and filtered. A 2 mL aliquot of the filtrate is taken, the acetone is evaporated and the remaining extract is transferred to a C18-cartridge. Imazapyr is eluted from the cartridge with CH₂Cl₂. Subsequently, CH₂Cl₂ is evaporated and the residue is dissolved in 1 mL CH₃OH and sonicated for 30 seconds. Of the final extract 0.5 mL are mixed with 50 µL of 0.1 M trimethyl anilinium hydroxide. The determination is performed by GC-MS using ion m/z 289.

Maize (grain, forage, fodder) (IZ-244-008)

Analyte: Imazapyr Capillary Electrophoresis M 2657

LOQ: 0.05 mg/kg

Description: The sample is weighed into an extraction flask and 200 mL of acidic acetone/water (1:4 v/v) are added. The extract solution is allowed to soak for 15 minutes, and then blended using an Omni mixer. After mixing, 10 g Celite 545AW are added to the extract and the solution is swirled. The extract is then vacuum-filtered. An aliquot of the extract is transferred into a separatory funnel. Methylene chloride is added and shaken for 15 seconds. The lower, methylene chloride, layer is drained into a beaker. The aqueous, upper, fraction is partitioned with another 25 mL of methylene chloride, which is added to the previously drained fraction. Solid-phase extraction is done using an Isolute SCX cartridge, the extract allowed to drain through the cartridge by gravity. The cartridge is then washed with acetone, followed by methanol and saturated KCl/methanol. After evaporation to dryness using a rotary evaporator, the residue is re-dissolved in 1% formic acid, then subjected to further clean-up using Spe-ed RP 102 cartridge and washing with methanol and water. After evaporation to dryness, the sample is re-dissolved in 1 mM Tris/1 mM NaH₂PO₄ solution, sonicated for 15 seconds, then transferred to a sample vial for capillary electrophoresis (CE) analysis. The CE system is equipped with a high sensitivity optical flow cell and a UV detector set at 240 nm.

Maize (1999/7004026)

Analyte: Imazapyr LC-UV (254 nm) M 2020

LOQ: 0.05 mg/kg

Description: The sample is weighed into an extraction container. Then, the extraction solution of methanol/water/1 N HCl (60:39:1, v/v/v) is added and blended using an Omni mixer. The extract is filtered, and then Celite 545AW is added. The extraction jar is washed and filtered with extraction solvent. The filtrate is poured into a mixing cylinder, diluted to 250 mL with methanol, mixed and an aliquot is taken. The methanol is evaporated to approx. 50 mL using a flash evaporator. The sample solution is extracted and filtered again, using acetone and Celite, then evaporated to a volume of 10 mL. 1 N HCl is added, the solution filtered and the filter rinsed using methanol and 0.05 N HCl. The solution is partitioned twice, using methylene chloride, before evaporating to dryness. Further partitioning is done using methanol, acetonitrile and hexane. The hexane layer is discarded, the acetonitrile solution evaporated to dryness and the residue dissolved in methanol and 0.05 N HCl. The extract is cleaned-up by solid-phase extraction on a Bond Elut C18 cartridge with deionized water, 0.05 N and 1 N HCl, hexane and methanol as wash solvents. The eluate is discarded, and the system eluted with saturated KCl in methanol. After evaporation to dryness, the residue is re-dissolved in methanol and 0.05 N HCl, and poured into a separatory funnel with methylene chloride. Three more portions of methylene chloride are added for partitioning, then the solution is evaporated to dryness, and partitioning is repeated with methylating reagent and methanol. After re-evaporation to dryness, the residue is dissolved in methanol in preparation for analysis by LC with a UV detector set at 254 nm.

Validation data for methods on plant matrices are summarized in Table 26.

Table 26 Summary of Recovery Data for imazapyr fortified into plant matrices

Commodity		Fortification mg/kg	N	Range Recovery (%)	Mean recovery (%)	% RSD	Reference Method
Sunflower, seed (CR)		0.05	4	59–86	73	15.3	2008/7019225 M 3519 modified
		0.50	3	71–94	81	14.4	
		5.0	5	75–78	76	1.8	
Sunflower, meal (CR)		0.05	1	79	—		
		0.50	1	88			
Sunflower, refined oil (CR)		0.05	1	112	—		2008/7019226 M 3519 modified
		0.50	1	109			
Lentil, seed (CR)		0.05	3	71–77	74	4.1	2008/7019227 M 3519 modified
		5.0	3	68–75	71	5.1	
Rape, seed (MV) Dilution solution: water/methanol/formic acid	Mass transition 262→217	0.05	5	80–94	89	6.2	
		0.50	5	74–98	86	10.8	
	Mass transition 262→149	0.05	5	74–100	87	11.6	
		0.50	5	79–102	89	11.1	
Rape, seed (MV) Dilution solution: water/formic/acid	Mass transition 262→217	0.05	5	73–85	78	5.6	
		0.50	5	76–88	84	5.5	
	Mass transition 262→149	0.05	5	73–90	81	9.4	
		0.50	5	78–91	87	6.1	
Rape, refined oil (MV) Dilution solution: water/formic acid	Mass transition 262→217	0.05	6	91–102	96	4.5	
		0.50	5	96–101	99	1.9	
	Mass transition 262→149	0.05	6	92–106	98	5.9	
		0.50	5	93–105	101	4.9	
Rape, seed (CR) Dilution solution: water/methanol/formic acid		0.05	4	70–89	79	10.6	
		0.50	4	74–86	80	6.6	
Rape, seed (CR) Dilution solution: water/formic acid		0.05	2	68, 71	69		
Rape, meal (CR) Dilution solution: water/formic acid		0.05	2	81, 83	82		
		0.50	2	79, 83	81		
Rape, refined oil (CR) Dilution solution: water/formic acid		0.05	2	103, 109	106		
		0.50	2	103, 106	104		
Soya bean, seed (MV)	Mass transition 262→217	0.01	5	111–119	114	2.8	2010/1033332 SOP-PA.0288
		1.0	5	98–104	102	2.5	
	Mass transition 262→149	0.01	5	108–119	114	4.1	
		1.0	5	96–102	100	2.5	

Commodity		Fortification mg/kg	N	Range Recovery (%)	Mean recovery (%)	% RSD	Reference Method
Soya bean, oil (MV)	Mass transition 262→217	0.01	5	81–90	86	4.2	
		1.0	5	94–102	97	3.4	
	Mass transition 262→149	0.01	5	86–89	87	1.5	
		1.0	5	91–104	99	5.3	
Soya bean, flaked (MV)	Mass transition 262→217	0.01	5	107–115	112	2.9	
		1.0	5	95–102	98	2.7	
	Mass transition 262→149	0.01	5	110–119	116	3.0	
		1.0	5	97–106	100	3.8	
Soya bean, meal (MV)	Mass transition 262→217	0.01	5	110–120	113	3.4	
		1.0	5	88–92	90	1.7	
	Mass transition 262→149	0.01	5	93–106	99	4.9	
		1.0	5	78–89	86	5.1	
Soya bean, toasted meal (MV)	Mass transition 262→217	0.01	5	113–120	116	2.8	
		1.0	5	82–89	86	3.2	
	Mass transition 262→149	0.01	5	85–111	98	10.3	
		1.0	5	78–90	83	5.4	
Soya bean, seed (ILV)		0.01	5	76–99	84	11.1	2010/1090461 2012/7000359 SOP-PA.0288
		0.50	5	83–96	91	5.9	
Soya bean, oil (ILV)		0.01	5	91–99	94	3.4	
		0.10	5	79–91	88	5.8	
Soya bean, hulls (ILV)		0.01	5	72–91	79	10.1	
		2.0	5	92–99	95	2.9	
Soya bean, seed (CR)		0.01	2	98, 100	99		
		0.10	1	105	–		
		1.0	2	98, 102	100		2012/3000423 SOP-PA.0288
		4.0	2	98, 109	104		
Sunflower, seed (MV)		0.05	3	74.3–91.1	81.3	10.8	
		0.10	3	76.9–79.3	78.2	1.56	
		0.50	3	84.9–85.6	85.3	0.44	2002/5004111
Sunflower, refined oil (MV)		0.05	3	95.2–98.2	96.7	1.55	
		0.10	3	96.8–99.6	97.8	1.57	
		0.50	3	105–108	106	1.44	
Sunflower, meal (MV)		0.05	3	70.9–77.8	75.0	4.82	
		0.10	3	70.8–78.6	75.8	5.70	
		0.50	3	77.4–78.9	78.0	1.00	
Sunflower, seed (CR)		0.05	1	96	–		
		0.50	1	86	–		2002/3000641 SOP-PA.0200, Rev.02-RE.01
Sunflower, flower (CR)		0.05	1	92	–		
		0.50	1	88	–		
Soya bean, seed (MV)	Mass transition 262→217	0.05	5	88–100	94	4.6	2010/1149746 SOP-PA.0249
		5.0	5	84–98	91	6.3	
	Mass transition 262→149	0.05	5	88–102	94	5.9	
		5.0	5	82–100	91	8.0	
Rice, grain (MV)	Mass transition 262→217	0.05	5	76–92	85	7.6	2010/1141978 SOP-PA.0249
		0.05	9	90–100	95	3.7	
		0.05	1	96	–		
		5.0	1	82	–		
		5.0	14	92–108	102	4.8	
	Mass transition 262→149	0.05	5	76–92	85	7.0	
		0.05	9	88–98	94	4.0	
		0.05	1	96	–		
		5.0	1	82	–		
		5.0	14	90–108	101	4.8	
Maize, grain		0.05	4	89–101	96	5.8	IZ-731-001 M 2468
		0.50	1	99			
		1.0	1	80			
Maize, grain		0.05	2	119, 119	119		IZ-244-005 M 2468
		0.10	2	93, 105	99		
		1.0	2	93, 99	96		

Commodity	Fortification mg/kg	N	Range Recovery (%)	Mean recovery (%)	% RSD	Reference Method
Maize, forage	0.05	2	87, 96	92		
	0.10	2	113, 119	116		
	1.0	2	99, 102	101		
Maize, fodder	0.05	2	114, 114	114		
	0.10	2	103, 110	107		
	1.0	2	103, 105	104		
Rape, seed	0.5	2	78, 91	85		1998/1008995 L 741/1
Rape, straw	0.05	2	93, 97	95		
	0.5	2	81, 82	82		
Maize, grain	0.05	5		106		IZ-244-009 (Stout S.J. <i>et al.</i> , 1996
	0.10	3		97		
	1.0	2		96		
Maize, forage	0.05	10		96		
	0.10	3		106		
	1.0	2		101		
Maize, fodder	0.05	3		108		IZ-244-008 M 2657
	0.10	2		107		
	1.0	2		104		
Maize, grain	0.05	2	88, 102	95		
	0.10	2	79, 93	86		
	1.0	2	90, 95	93		
Maize, forage	0.05	2	64, 73	69		
	0.10	2	75, 80	78		
	1.0	2	83, 84	84		
Maize, fodder	0.05	2	79, 91	85		
	0.10	2	83, 84	84		
	1.0	2	80, 85	83		
Maize, plant	0.05	3	78–80	79	1.3	1999/7004026 M 2020

CR: Concurrent Recovery, MV: Method Validation, ILV: Independent Laboratory Validation

Animal matrices

Milk (IZ-245-003, IZ-245-009 and IZ-245-010)

Analyte: Imazapyr Capillary Electrophoresis M 3075

LOQ: 0.01 mg/kg

Description Residues are extracted from milk with 1 M hydrochloric acid. The imazapyr residues are subjected to suitable clean-up involving solvent partitioning (methylene chloride and acetone) and solid phase extraction (SCX and C18 cartridge). Measurement of imazapyr is accomplished by capillary electrophoresis (CE) with UV detection (240 nm) and results are calculated using external standards.

Muscle, Liver, Kidney and Fat (IZ-245-004)

Analyte: Imazapyr Capillary Electrophoresis M 3184

LOQ: 0.05 mg/kg

Description Residues are extracted from bovine tissues with an acidic water/acetone solution (3:1, v/v). The mixture is centrifuged and then filtered through celite. An aliquot of the filtrate containing the imazapyr residues is subjected to partitioning with methylene chloride. The extract is purified by solid phase extraction. Quantitation of imazapyr is accomplished by capillary electrophoresis (CE) using UV detection (265 nm). The results are calculated by direct comparison to external standards.

Milk fat (IZ-245-007)

Analyte: Imazapyr Capillary Electrophoresis M 3223

LOQ: 0.01 mg/kg

Description: Residues are extracted from milk fat (5 g) with water (19 mL), acetonitrile (50 mL) and hexane (100 mL). The mixture is filtered and the filtrate containing the imazapyr residues is subjected to solvent partitioning (dichloromethane) and solid phase extraction (SCX and C18 cartridge). Quantitation of imazapyr is accomplished by capillary electrophoresis (CE) using UV detection (265 nm), results are calculated by direct comparison to external standards.

Validation data for methods on animal matrices are summarized in Table 27.

Table 27 Summary of Recovery Data for imazapyr fortified into animal matrices

Commodity	Fortification mg/kg	N	Range of Recovery (%)	Mean recovery (%)	% RSD	Reference
Bovine milk (ILV)	0.01	2	81, 85	83		IZ-245-009 M 3075
	0.10	2	92, 96	94		
	0.50	2	92, 93	93		
Bovine muscle (ILV)	0.05	2	71, 78	75		IZ-245-004 M 3184
	0.25	2	80, 81	81		
	0.50	2	82, 85	84		
Bovine liver (ILV)	0.05	2	72, 78	75		
	0.25	2	79, 85	82		
	0.50	2	81, 82	82		
Bovine kidney (ILV)	0.05	2	71, 77	74		
	0.25	2	78, 86	82		
	0.50	2	80, 84	82		
Bovine fat (ILV)	0.05	2	71, 78	75		
	0.25	2	87, 87	87		
	0.50	2	84, 84	84		
Bovine milk fat (ILV)	0.01	2	67, 81	74		IZ-245-007 M 3223
	0.05	2	73, 86	80		
	0.10	2	70, 91	81		

Stability of pesticide residues in stored analytical samples

The Meeting received data on the stability of imazapyr residues in maize (grain, forage and fodder) and soya bean (seeds and processed fractions) samples for plant and animal commodities stored frozen.

The freezer stability study of imazapyr was conducted on maize grain, forage and fodder (Fletcher, 1997: IZ-326-004). Samples of control maize grain, forage and fodder were fortified with imazapyr at 1.0 mg/kg and stored frozen at -5 to -26 °C. Samples were analysed after storage using GC/MS Method M 2468. The LOQ was 0.05 mg/kg.

Table 28 Recovery of imazapyr from stored fortified samples of maize

Storage interval	Recovery (%) [1.0 mg/kg fortification]		
	Procedural	% remaining	Mean
Grain			
9 months	92	81, 93	87
12 months	105	95, 104	100
18 months	92	95, 102	99
27 months	88	87, 90	89
Forage			
9 months	98	76, 79	78
12 months	89	94, 97	96

Storage interval	Recovery (%) [1.0 mg/kg fortification]		
	Procedural	% remaining	Mean
18 months	96	88, 94	91
27 months	96	87, 87	87
Fodder			
9 months	106	73, 79	76
12 months	91	83, 101	92
18 months	96	77, 92	85
27 months	106	78, 81	80

The storage stability of imazapyr was investigated under deep frozen conditions over a time period of about 10 months for soya bean (seeds) and over a time period of about 3 months for soya bean processed fractions (oil, laminated soya bean, meal and toasted meal), all at -20°C or lower (Leite, 2011: 2011/1207286). Soya bean samples were spiked with the test items at a concentration level of 0.10 mg/kg. The storage conditions correspond to the usual storage conditions for field samples. The samples were analysed using Method SOP-PA.0288.

Table 29 Recovery of imazapyr from stored fortified samples of soya bean

Storage interval	Recovery (%) [0.10 mg/kg fortification]		
	Procedural	% remaining	Mean
Seed			
0 month	109, 109		
1 month	100, 108	100, 102	101
2 months	91, 97	92, 104	98
3 months	98, 100	88, 97	93
7 months	89, 90	62, 69	66
10 months	141, 145	133, 135	134
Laminated soya bean			
0 month	95, 96		
1 month	109, 113	101, 107	104
3 months	98, 101	101, 101	101
Meal			
0 month	100, 106		
1 month	100, 104	97, 99	98
3 months	100, 101	97, 101	99
Toasted meal			
0 month	101, 110		
1 month	108, 110	111, 113	112
3 months	97, 98	93, 94	94
Oil			
0 month	100, 104		
1 month	95, 102	91, 97	94
3 months	101, 105	99, 105	102

The stability of imazapyr was investigated in bovine milk during freezer storage (Khunachak, 1999: IZ-326-010). The storage conditions chosen were equivalent to the storage conditions used for residue samples awaiting analysis. Milk samples were spiked with the test items at a concentration level of 0.1 mg/kg. The samples were analysed using Method M 3075.

Table 30 Recovery of imazapyr from stored fortified samples of bovine milk

Storage interval	Recovery (%) [0.1 mg/kg fortification]		
	Procedural	% remaining	Mean
0 months	86	85, 87	86
3 months	76	73, 75	74
6 months	95	79, 84	82

The stability of imazapyr was investigated in bovine tissues (muscle and liver) during freezer storage (Khunachak, 1999: IZ-326-011). The storage conditions chosen were equivalent to the storage conditions used for residue samples awaiting analysis. Samples were spiked with the test items at a concentration level of 0.1 mg/kg. The samples were analysed using Method M 3184.

Table 31 Recovery of imazapyr from stored fortified samples of bovine tissues

Storage interval	Recovery (%) [0.1 mg/kg fortification]		
	Procedural	% remaining	Mean
Muscle			
0 month	86	84, 84	84
3 month	84	80, 83	82
8 months	76	80, 82	81
Liver			
0 month	83	81, 81	81
3 month	80	81, 82	82
8 months	75	77, 77	77

USE PATTERN

Imazapyr is registered for the control of broad leaf and grassy weeds on pulses, cereals and oilseed etc. The Meeting received labels from Argentina, Australia, Brazil and the USA. The information available to the Meeting on registered uses of imazapyr is summarized in the table below.

Table 32 Registered uses of imazapyr for crops

Crop	Country	Formulation		Application				PHI, days or Application timing
		Type	Conc. of imazapyr	Method	Rate kg ai/ha	Volume L/ha	No. max	
Grasses for sugar or syrup production								
Sugarcane	Argentina	SL	250 g/L	Spray onto weeds	0.5	150–200	2	30–45 days before planting
Sugar cane	Brazil	SL	266.3 g/L	Spray onto weeds	0.125–0.5	100–400	1	not required when used as directed

Table 33 Registered uses of imazapyr for imidazolinone tolerant crops

Crop	Country	Formulation		Application				PHI, days and/or Application timing
		Type	Conc. of imazapyr	Method	Rate kg ai/ha	Volume L/ha	No. max	
Pulses								
Lentil	Canada	SL	15 g/L	Foliar	0.00906	50–100	1	60
Cereals								
Maize	Argentina	WG	175 g/kg	Foliar	0.025	150–200 (ground)	1	before reaching 6 th fully developed leaf status
Maize	Argentina	WG	175 g/kg	Foliar	0.0252	100–150 (ground)	1	before reaching 6 th fully developed leaf status
Maize	Australia	WG	175 g/kg	Foliar	0.0175–0.0219	> 50	1	crops in the 2–6 leaf stage ^a
Maize	Brazil	WG	175 g/kg	Foliar	0.0175	100–250 (ground) 40–50 (aerial)	1	96
Maize	USA	WG	175 g/kg	Foliar	0.0157	> 94 (ground) > 47 (aerial)	1	45
Maize	USA		40 g/kg	Foliar	0.0157	> 94 (ground) > 47 (aerial)	1	45 before crop height is 20 inches or crop has 6 leaf collars

Crop	Country	Formulation		Application				PHI, days and/or Application timing
		Type	Conc. of imazapyr	Method	Rate kg ai/ha	Volume L/ha	No. max	
Rice	Brazil	WG	175 g/kg	Foliar	0.0735	100–200 (ground) 40–50 (aerial)	2	60
Wheat	Australia	WG	175 g/kg	Foliar	0.0035–0.0070	> 70	1	crops in the 2–6 leaf stage ^a
Wheat	Australia	EC	7.3 g/L	Foliar	0.0066	> 50	1	crops in the 4 leaf to commencement of flag leaf stage (BBCH 14–37) ^a
Oilseeds								
Rape	Australia	SL	15 g/L	Foliar	0.0045–0.0113	> 70	1	^b
Rape	Australia	WG	175 g/kg	Foliar	0.0035–0.0096	> 70	1	^c
Rape	Canada	SL	15 g/L	Foliar	0.00906	50–100	1	60
Sunflower	Argentina	WG	175 g/kg	Foliar	0.025	150–200 (ground)	1	before reaching 6 th fully developed leaf status
Sunflower	Argentina	SL	240 g/L	Foliar	0.080	120–150	1	early post emergence
Sunflower	Argentina	WG	800 g/kg	Foliar	0.080	120–150	1	early post emergence
Sunflower	Argentina	SL	15 g/L	Foliar	0.0225–0.030	150–200	1	early post emergence
Sunflower	Uruguay	SL	240 g/L	Foliar	0.080	120–150	1	

^a Do not graze or cut for stock food for 4 weeks after application, not required to harvest for grains when used directed.

^b Do not graze or cut for stock food for 5 weeks, not required for grains when used as directed

^c Do not graze or cut for stock food for 6 weeks, not required for grains when used as directed

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on imazapyr supervised field trials for the following crops.

Group	Commodity	Table
Pulses	Lentil (dry)	Table 34
	Soya bean (dry)	Table 35
Cereal grains	Maize	Table 36
	Rice	Table 37
	Wheat	Table 38
Grasses for sugar or syrup production	Sugar cane	Table 39
Oilseed	Rape seed	Table 40, 41
	Sunflower seed	Table 42
Straw, fodder and forage of cereals	Maize fodder and forage	Table 43
	Wheat straw and forage	Table 44
Miscellaneous fodder and forage crops	Rape straw and forage	Table 45

Imazapyr formulation was applied for foliar treatment. Each of the field trial sites generally consisted of an untreated control plot and a treated plot. Application rates and spray concentrations have generally been rounded to two significant figures.

Residue values from the trials, which have been used for the estimation of maximum residue levels, STMRs and HRs, are underlined.

Laboratory reports included method validation with procedural recoveries from spiking at residue levels similar to those occurring in samples from the supervised trials. Date of analyses and duration of residue sample storage were also provided. Although trials included control plots, no control data are recorded in the tables except when residues were found in samples from control plots. Residue data are not corrected for percent recovery.

Conditions of the supervised residue trials were generally well reported in detailed field reports. Most field reports provided data on the sprayers used, plot size, field sample size and sampling date.

Pulses

Lentil (dry)

The Meeting received five trials on imidazolinone-tolerant lentil which were conducted in Canada (Norris, 2009: 2008/7019226). In each trial, a single broadcast foliar application of a SL formulation (15 g/L imazapyr) was made to lentil targeting 0.009 kg ai/ha of imazapyr. The application was made 58–60 days prior to the normal harvest of mature (dry) seed.

The lentil seed samples were analysed for residues of imazapyr using Method M3519 (modified). The maximum storage interval for field-treated samples was 166 days (5.5 months).

Table 34 Imazapyr residues on imidazolinone-tolerant lentil from supervised trials in Canada

Lentil, seed country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	GS	no			
GAP, Canada	SL	0.00906	50–100		1	60		
Canada, 2008 Dundurn/SK (Impact)	SL	0.009	100	Stem elongation (7–8 nodes)	1	58	0.06, 0.06 mean 0.06	2008/7019226 Norris, 2009 Sampling to analysis: 125–166 days
Canada, 2008 Dundurn/SK (Imperial)	SL	0.009	100	Stem elongation (7–8 nodes)	1	58	0.06, 0.10 mean 0.08	
Canada, 2008 Portage la Prairie/MB (CDC Impact)	SL	0.009	99	Early flower	1	40	0.08, 0.08 mean 0.08	
						50	0.07, 0.08 mean 0.08	
						60	0.07, 0.07 mean 0.07	
						70	0.07, 0.08 mean 0.08	
						81	0.07, 0.07 mean 0.07	
Canada, 2008 Wellwood/MB (CDC Imperial)	SL	0.009	103	Early bud	1	59	0.06, 0.06 mean 0.06	
Canada, 2008 Alvena/MB (Impact)	SL	0.009	100	Stem elongation (6–8 nodes)	1	59	0.06, 0.06 mean 0.06	

Soya bean (dry)

Eight residue trials in soya beans were conducted in different representative growing areas in Brazil (Resende, 2008: 2008/1097472). The 480 g/L SL formulation was applied once at a rate equivalent to 0.072 kg ai/ha in a spray volume of 200 L/ha. Method SOP-PA.0249 rev.03 was used to analyse soya bean seed samples for the residues of imazapyr. Imazapyr was quantified by LC-MS/MS with a LOQ of 0.05 mg/kg.

Eight residue trials in soya beans were conducted in different representative growing areas in Brazil (Resende, 2008: 2008/1097470). The WG formulation containing 525 g/kg imazapyr was applied once at a rate equivalent to 0.0525 kg ai/ha in a spray volume of 200 L/ha. Method SOP-

PA.0249 rev.04 was used to analyse soya bean seed samples for the residues of imazapyr. Imazapyr was quantified by LC-MS/MS with a LOQ of 0.05 mg/kg.

One trial (with five plots) in soya bean was conducted in Brazil (Resende, 2010: 2010/1079212, 2010/1010261). The WG formulation containing 525 g/kg imazapyr was applied once at a rate equivalent to 0.0525 kg ai/ha in a spray volume of 200 L/ha. Method SOP-PA.0288 was used for analysis of imazapyr residues in soya bean quantifying the analyte by LC-MS/MS with a LOQ of 0.01 mg/kg.

Two trials in soya beans were conducted in Brazil (Jones, 2011: 2010/1127505). The WG formulation containing 525 g/kg imazapyr was applied once at a rate equivalent to 0.0525 kg ai/ha in a spray volume of 200 L/ha. Each trial consisted of four plots. Method SOP-PA.0288 was used for analysis of imazapyr residues in soya beans quantifying the analyte by LC-MS/MS with a LOQ of 0.01 mg/kg.

Five trials in soya beans were conducted in Brazil (Jones, 2012: 2012/3000423). The WG formulation containing 525 g/kg imazapyr was applied once at a rate equivalent to 0.0525 kg ai/ha in a spray volume of 200 L/ha. Method SOP-PA.0288 was used for analysis of imazapyr residues in soya beans quantifying the analyte by LC-MS/MS with a LOQ of 0.01 mg/kg.

Table 35 Imazapyr residues on imidazolinone-tolerant soya bean seeds from supervised trials in Brazil

Soya bean, seed country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	kg ai/hL	water, L/ha	GS	no .			
GAP, Brazil	SL	0.072		100–200 (ground) 40–50 (aerial)		1	60		
Brazil, 2007 Santo Antônio de Goiás/GO (CV 603)	SL	0.072		200	77 71 66 59 39	1	40 60 80 100 120	1.8 1.7 2.0 < 0.05 < 0.05	2008/1097472 Resende, 2008 Sampling to analysis: 46–87 days
Brazil, 2007 Santo Antônio de Goiás/GO (CV 603)	SL	0.072		200	67	1	60	1.4	
Brazil, 2007 Uberaba/MG (CV 603)	SL	0.072		200	78 73 51 29 19	1	40 60 80 100 120	1.7 1.3 1.5 0.05 < 0.05	
Brazil, 2007 Uberaba/MG (CV 603)	SL	0.072		200	73	1	60	2.0	
Brazil, 2007 Brasília/DF (CV 603)	SL	0.072		200	75	1	60	1.9	
Brazil, 2007 Santo Antônio de Posse/SP (CV 603)	SL	0.072		200	72	1	60	0.92	
Brazil, 2007 Santo Antônio de Posse/SP (CV 603)	SL	0.072		200	29 24 18 15 12	1	40 60 80 100 120	0.06 0.41 0.08 < 0.05 < 0.05	
Brazil, 2007 Londrina/PR (CV 603)	SL	0.072		200	71	1	60	< 0.05	
Brazil, 2007 Uberaba/MG (CV 603)	WG	0.053		200	77 73 51	1	40 60 80	2.3 2.5 0.09	2008/1097470 Resende, 2008

Soya bean, seed country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	kg ai/hL	water, L/ha	GS	no .			
					29 19		100 120	< 0.05 < 0.05	Sampling to analysis: 49–65 days
Brazil, 2007 Uberaba/MG (CV 603)	WG	0.053		200	73	1	60	3.0	
Brazil, 2007 Brasília/DF (CV 603)	WG	0.053		200	75	1	60	1.3	
Brazil, 2007 Santo Antônio de Posse/SP (CV 603)	WG	0.053		200	78 72 65 53 38	1	40 60 80 100 120	0.85 0.48 0.08 < 0.05 < 0.05	
Brazil, 2007 Santo Antônio de Goiás/GO (CV 603)	WG	0.053		200	77 71 66 59 39	1	40 60 80 100 120	1.4 0.45 0.30 0.07 < 0.05	
Brazil, 2007 Santo Antônio de Goiás/GO (CV 603)	WG	0.053		200	71	1	60	1.3	
Brazil, 2007 Santo Antônio de Posse/SP (CV 603)	WG	0.053		200	24	1	60	0.27	
Brazil, 2007 Londrina/PR (CV 603)	WG	0.053		200	67	1	60	< 0.05	
Brazil, 2008 Santo Antônio de Posse/SP (CV 127)	WG	0.053	0.026	200	79– 83 75 66 51 13	1	40 60 80 100 120	0.10 0.07 0.01 < 0.01 < 0.01	2010/1010261 2010/1079212 Sampling to analysis: 613 days
Brazil, 2010 Ponta Grossa /PR (L 08)	WG	0.053	0.026	200	83 75 68 66	1	20 40 60 80	< 0.01 0.07 0.90 1.0	2010/1127505 Jones, 2011
Brazil, 2010 Santo Antônio de Posse/SP (CV 127)	WG	0.053	0.026	200	89 87 77 73	1	20 40 60 80	< 0.01 < 0.01 0.35 0.20	Sampling to analysis: 27–78 days
Brazil, 2011 Ponta Grossa /PR (BRZ 08-200151)	WG	0.053	0.026	200	79 75 73 64 62	1	20 40 60 80 100	< 0.01 < 0.01 0.26 0.83 0.25	2012/3000423 Jones, 2012
Brazil, 2011 Senador Canedo/PR (BRZ 5384)	WG	0.053	0.026	200	66	1	60	0.11	Sampling to analysis: 162–273 days
Brazil, 2011 Anápolis/GO (BRZ 5384)	WG	0.053	0.026	200	69	1	60	0.07	
Brazil, 2011 Santo Antônio de Posse/SP (BRZ 5384))	WG	0.053	0.026	200	73	1	60	1.3	
Brazil, 2011 Castro/PR (BRZ 08-200151)	WG	0.053	0.026	200	71	1	60	0.55	

*Cereal grains**Maize*

Residue data have been collected from 19 field trials located in the USA. At each trial, one broadcast application was made to the treated plot. The formulations used in the trials were 240 g/kg ASU and 240 g/kg WP formulation. Method M 2468 was used for analysis of imazapyr residues in maize grains quantifying the analyte by gas chromatography/negative ion chemical ionization mass spectrometry (GC/ECNICI) with a limit of quantitation of 0.05 mg/kg.

Six trials in maize were conducted in Australia to determine the residue level of imazapyr in/on maize grains. The SL formulations containing 250 g/L imazapyr was applied once as broadcast foliar application. The applications were made in half of the trials post sowing—pre-emergence and in the second half of the trials at early post-emergence. Imazapyr was analysed in the maize grains using method L 741/1. Separation and quantitation were accomplished with reverse phase high performance liquid chromatography using a UV-VIS detector with a limit of quantitation of 0.05 mg/kg.

Seven trials in maize were conducted in the Argentina to determine the residue level of imazapyr on maize. Method LAADL R0001 was used for analysis of imazapyr residues in maize grains quantifying the analyte by HPLC/UV with a limit of quantitation of 0.05 mg/kg.

Three trials in maize were conducted in Brazil to determine the residue level of imazapyr in/on maize. The WG formulation was applied to the plots as broadcast foliar application in spray volumes of 200 L/ha. Method SOP-PA.0200 rev.02-re.01, based on methods MR0001.01, M-2020 and M-1928, was used for analysis of imazapyr residues in maize grains. Imazapyr was determined by LC-MS/MS (mass transition 262/217). The limit of quantitation for this method in maize grains was 0.05 mg/kg.

Table 36 Imazapyr residues on imidazolinone-tolerant maize grains from supervised trials

Maize grain country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage (BBCH)	no .			
GAP, USA		0.0157			1	45		
USA, 1993 Conklin/MI (Pioneer Hybrid 3417 IR)	ASU	0.027	188	14	1	126	< 0.05	IZ-731-001 Mahl, 1995 Sampling to analysis: 456–581 days
USA, 1993 Webster/IA (Pioneer Hybrid 3377 IR)	ASU	0.027	187	14	1	131	< 0.05	IZ-731-002 Mahl, 1995 Sampling to analysis: 513–642 days
USA, 1993 Verona/WI (Pioneer Hybrid 3417 IR)	ASU	0.027	186	14	1	125	< 0.05	IZ-731-003 Mahl, 1995 Sampling to analysis: 520–644 days
USA, 1993 Jamesville/ NC (Pioneer Hybrid 3245 IR)	ASU	0.027	202	14–15	1	103	< 0.05	IZ-731-004 Mahl, 1995 Sampling to analysis: 538–638 days
USA, 1994 Conklin/MI (Pioneer Hybrid 3751 IR)	WP	0.027	191	14	1	124	< 0.05	IZ-731-005 Mahl, 1995 Sampling to analysis: 191–314 days
USA, 1994 New Holland/ OH (Pioneer Hybrid 3245 IR)	WP	0.027	171	14	1	123	< 0.05	IZ-731-006 Mahl, 1995 Sampling to analysis: 209–332 days
USA, 1993 Gary/SD	ASU	0.027	181	14	1	134	< 0.05	IZ-731-007 Mahl, 1995

Maize grain country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage (BBCH)	no .			
(Pioneer Hybrid 3417 IR)								Sampling to analysis: 476–609 days
USA, 1994 Snock/TX (Pioneer Hybrid 3162 IR)	WP	0.027	199	15	1	110	< 0.05	IZ-731-008 Mahl, 1995 Sampling to analysis: 244–353 days
USA, 1994 Noblesville /IN (Pioneer Hybrid 3395 IR)	WP	0.027	181	14	1	132	< 0.05	IZ-731-009 Mahl, 1995 Sampling to analysis: 224–354 days
USA, 1994 Carman/IL (Pioneer Hybrid 3417 IR)	WP	0.027	187	14–15	1	126	< 0.05	IZ-731-010 Mahl, 1995 Sampling to analysis: 210–335 days
USA, 1993 York/NE (Pioneer Hybrid 3417 IR)	ASU	0.027	187	14–15	1	116	< 0.05	IZ-731-011 Mahl, 1995
		0.27	187	14–15	1	116	< 0.05	Sampling to analysis: 666–802 days
USA, 1993 Carman/IL (Pioneer Hybrid 3417 IR)	ASU	0.027	187	14–15	1	117	< 0.05	IZ-731-012 Mahl, 1995 Sampling to analysis: 561–677 days
USA, 1993 Clarence/MO (Pioneer Hybrid 3245 IR)	ASU	0.027	187	14	1	112	< 0.05	IZ-731-013 Mahl, 1995 Sampling to analysis: 490–733 days
USA, 1994 Fisher/MN (Pioneer Hybrid 3751 IR)	WP	0.027	187	14–15	1	146	< 0.05	IZ-731-014 Mahl, 1995 Sampling to analysis: 201–425 days
USA, 1994 Webster City/ IA (Pioneer Hybrid 3417 IR)	WP	0.027	191	14	1	131	< 0.05	IZ-731-015 Mahl, 1995 Sampling to analysis: 212–419 days
USA, 1993 Noblesville/ IN (Pioneer Hybrid 3417 IR)	ASU	0.027	187	14	1	149	< 0.05	IZ-731-016 Mahl, 1995 Sampling to analysis: 581–730 days
USA, 1993 New Holland/ OH (Pioneer Hybrid 3417 IR)	ASU	0.027	187	14	1	127	< 0.05	IZ-731-017 Mahl, 1995
		0.27	187	14	1	127	0.088	Sampling to analysis: 484–779 days
USA, 1994 York/NE (Pioneer Hybrid 3417 IR)	WP	0.027	189	14	1	122	< 0.05	IZ-731-018 Mahl, 1995 Sampling to analysis: 234–355 days
USA, 1993 Hamburg/PA (Pioneer Hybrid 3245 IR)	ASU	0.027	189	14	1	141	< 0.05	1995/7004189 Mahl, 1995 Sampling to analysis: 488–630 days
GAP, Australia	WG	0.018-0.022	> 50		1	not required		
Australia, 1997 Darlington Point/NSW (62 IT)	SL	0.016	112	Early post emergent	1	109	< 0.05	2000/1023965 Mooney, 2000 Sampling to analysis: 138 days
		0.032	112	Early post emergent	1	109	< 0.05	
		0.048	112	Early post emergent	1	109	< 0.05	
	SL	0.016	112	Post sowing pre- emergent	1	152	< 0.05	Sampling to analysis:

Maize grain country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage (BBCH)	no .			
			0.032	112	Post sowing pre- emergent	1	152	< 0.05
		0.048	112	Post sowing pre- emergent	1	152	< 0.05	
GAP, Argentina GAP, Brazil	WG WG	0.025 0.0175			1 1	before reaching 6 th fully developed leaf status 96 day PHI		
Argentina, 1996–1997 Santa Fe (Pioneer 3162 IR)	SL	0.040	170	12–13	1	117	< 0.05	IZ-731-021 Steling, 1998 Sampling to analysis: 530 days
		0.080	170	12–13	1	117	< 0.05	
	WG	0.020	170	12–13	1	117	< 0.05	
		0.030	170	12–13	1	117	< 0.05	
Argentina, 1995–1996 Santa Fe (IR)	SL	0.020		17	1	110	< 0.05	1997/7004635 Steling, 1997 Sampling to analysis: 345 days
		0.040		17	1	110	< 0.05	
Argentina, 1997–1998 San Jeronimo (Pioneer 3162 IR)	SC	0.025	166	14	1	140	< 0.05	1999/7004025 Steling, 1999 Sampling to analysis: 48–395 days
		0.040	166	14	1	140	< 0.05	
		0.050	166	14	1	140	< 0.05	
Argentina, 1997–1998 Santos Unzue (Pioneer 3162 IR)	SC	0.025	195	14	1	121	< 0.05	
		0.040	195	14	1	121	< 0.05	
		0.050	195	14	1	121	< 0.05	
Argentina, 1997–1998 Fauzon (Pioneer 3162 IR)	SC	0.025	195	12	1	141	< 0.05	
		0.040	195	12	1	141	< 0.05	
		0.050	195	12	1	141	< 0.05	
Argentina, 1998–1999 San Jeronimo (Asgrow AX 888 IT)	WG	0.020	180	16	1	116	< 0.05	
		0.040	180	16	1	116	< 0.05	
Argentina, 1995–1996 Fauzon (Funks Capitan IT)	SL	0.040	190	14	1	135	< 0.05	1998/3002021 Steling, 1998 Sampling to analysis: 665 days
		0.080	190	14	1	135	< 0.05	
		0.020	190	14	1	135	< 0.05	
		0.040	190	14	1	135	< 0.05	
Brazil, 2002 Londrina/PR (Clearfield)	WG	0.021	200	83	1	30	< 0.05	2002/3001461 Borges, 2002 Sampling to analysis: 118 days
		0.042	200	83	1	30	0.05	
Brazil, 2002 Santo Antônio de Posse/SP (Clearfield)	WG	0.021	200	89	1	30	< 0.05	2002/3001462 Borges, 2002 Sampling to analysis: 36 days
		0.042	200	89	1	30	< 0.05	
Brazil, 2002 São Gotardo/ MG (Clearfield)	WG	0.021	200	73	1	30	< 0.05	2002/3001463 Borges, 2002 Sampling to analysis: 77 days
		0.042	200	73	1	30	< 0.05	

ASU: Aqueous Solution with urea

NA: not analysed

Rice

Four trials with 11 plots in rice were conducted in Brazil (Dantas, 2003: 2003/3001441). The WG formulation containing 525 g/kg imazapyr was applied twice to each trial with rate equivalents of 0.12 kg ai/ha or 0.24 kg ai/ha for each application. Method SOP-PA.0231 was used for analysis of

residues in rice. Imazapyr was measured by liquid chromatography with a UV detector. The limit of quantitation for this method in rice grain samples was 0.05 mg/kg.

Table 37 Imazapyr residues on imidazolinone-tolerant rice grains from supervised trials in Brazil

Rice grain country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	For m	kg ai/ha	water, L/ha	Growth stage	no .			
GAP, Brazil	WG	0.074	100–200		2	60		
Brazil, 2003 São Vicente do Sul/RS (IRGA 422 CL)	WG	0.12	200	5 leaf stage + Stem elongation Booting Booting Inflorescence emergence flowering	2	50 55 60 65 70	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	2003/300144 1 Dantas, 2003 Sampling to analysis: 132–139 days
Brazil, 2003 São Vicente do Sul/RS (XP 701 CL)	WG	0.12	200	4 leaf stage + Booting	2	60	0.05	
		0.24	200	4 leaf stage + Booting	2	60	0.05	
Brazil, 2003 Cachoeirinha/RS (XP 701 CL)	WG	0.12	200	3–4 leaf stage + Booting	2	60	< 0.05	
		0.24	200	3–4 leaf stage + Booting	2	60	< 0.05	
Brazil, 2003 Uruguaiana/ RS (Irga 422 CL)	WG	0.12	200	1–2 leaf stage + tillering	2	60	< 0.05	
		0.24	200	1–2 leaf stage + tillering	2	60	< 0.05	

Wheat

The trials were conducted at six locations in Australia (Mooney, 1999: 1999/1013037). The SL formulation containing 250 g/L imazapyr or the WG formulation containing 750 g/kg imazapyr were applied once as broadcast foliar or band application. Samples were collected 83–104 days after application and stored frozen at or below –18°C until analysis. Imazapyr was analysed in the wheat grains using method L 741/1. In principle the active substance is extracted from the matrix using several extraction and separation steps involving HCl:water (1:39) and DCM (dichloromethane). The extract is then cleaned-up by elution through a SCX cartridge and further extractions with DCM. Separation and quantitation are accomplished with reverse phase high performance liquid chromatography using a UV-VIS detector and external standard calibration procedures. The limit of quantitation for this method in wheat grain samples was 0.05 mg/kg.

Table 38 Imazapyr residues on imidazolinone-tolerant wheat from supervised trials in Australia

Wheat grain country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage	no .			
GAP, Australia	WG	0.004–0.007	> 70		1	not required		
Australia, 1997–1998 Winulta, Yorke Peninsula/SA (IT)	SL	0.007	110	2 node stage	1	88	< 0.05	11999/1013037 Mooney, 1999 Sampling to analysis: 182 days
		0.014	110	2 node stage	1	88	< 0.05	
		0.028	110	2 node stage	1	88	< 0.05	
Australia, 1997–1998 Osbourne/ NSW (IT)	SL	0.007	112	Early post emergent	1	83	< 0.05	Sampling to analysis: 193 days
		0.014	112	Early post emergent	1	83	< 0.05	
		0.028	112	Early post emergent	1	83	< 0.05	
Australia, 1997–1998 Gnarwarre/ Vic (IT)	SL	0.007	50	Early post emergent	1	104	< 0.05	Sampling to analysis: 46 days
		0.015	50	Early post emergent	1	104	< 0.05	

Wheat grain country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage	no .			
		0.028	50	Early post emergent	1	104	< 0.05	
Australia, 1998 Manoorra/SA (IT)	SL	0.014	117	Stem elongation stage (1–2 node stage)	1	95	< 0.05	Sampling to analysis: 67 days
		0.028	117	Stem elongation stage (1–2 node stage)	1	95	< 0.05	
Australia, 1998–1999 Burabadji/WA (IT)	WG	0.014	110	Advanced tillering	1	94	< 0.05	Sampling to analysis: 54–148 days
		0.028	110	Advanced tillering	1	94	< 0.05	

Grasses for sugar or syrup production

Sugar cane

The trials were conducted at two locations in Argentina and Brazil to determine the residue level of imazapyr in/on sugar cane. The SL formulation containing 250 or 500 g/L imazapyr, were applied once at a rate equivalent to 0.18, 0.35 and 0.50 kg ai/ha in a spray volume of 168 and 400 L/ha. Method LAADL R0002 was used for analysis of imazapyr residues in sugar cane. Imazapyr was extracted from the sugar cane with acetone:methanol:water (1:1:1) and then subjugated the extract to suitable cleanup involving solid phase extraction techniques. Measurement of imazapyr was accomplished by high performance liquid chromatography (HPLC). Results were calculated by direct comparison of the sample peak heights to those of external standards. The limit of quantitation of the method is 0.05 mg/kg for sugar cane.

Table 39 Imazapyr residues on sugar cane from supervised trials in Argentina and Brazil

Sugar cane country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage/ Timing	no .			
GAP, Argentina	SL	0.5	150–200		2	30–45 days before planting		
GAP, Brazil	SL	0.125–0.5	100–400		1	Not required when used as directed		
Argentina, 1996–1998 Lules/Tucumán (Famaillá 8116)	SL	0.50	168	38 days before plantation	1	392	< 0.05	IZ-790-015 Steling, 1998 Sampling to analysis: 354 days
Brazil, 1996–1998 Piracicaba/SP (RB-72454)	SL	0.18	400	Pre-emergent	1	243	< 0.05	IZ-790-017 Steling, 1998 Sampling to analysis: 216 days
		0.35	400	Pre-emergent	1	243	< 0.05	

Oilseed

Rape seed

A total of 12 trials were conducted on rape in Canada (Norris, 2009: 2008/7019227). At each test location, a single broadcast foliar application of a SL formulation containing 15 g ai/L was made to rape seed targeting 0.009 kg ai/ha. The applications were made in 98–102 L/ha of water using ground equipment, and an adjuvant (0.5% v/v) was added to the spray mixture for all applications. The rape seed RAC (seed) samples were analysed for residues of imazapyr using Method M 3519, modified. Imazapyr was quantified by liquid chromatography, mass/mass detector (LC-MS/MS) with a limit of quantitation (LOQ) of 0.05 mg/kg.

In the growing seasons 1997/1998, trials were conducted at three locations in Australia to determine the residue level of imazapyr in/on rape seed. The WG formulation containing 175 g/kg imazapyr was applied once as broadcast foliar application. The application was generally made post-emergence. Imazapyr was analysed in the rape matrices using method L 741/1. Quantitation was accomplished with reverse phase high performance liquid chromatography using a UV-VIS detector and external standard calibration procedures. The LOQ of the method is 0.05 mg/kg for rape matrices.

Table 40 Imazapyr residues on imidazolinone-tolerant rape seed from supervised trials in Canada

Rape seed country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	Water, L/ha	GS (BBCH)	no .			
GAP, Canada	SL	0.009			1	60		
Canada, 2008 Portage la Prairie/MB (Clearfield 45H73)	SL	0.009	101	65	1	70	< 0.05, < 0.05 Mean < 0.05	2008/7019227 Norris, 2009 Sampling to analysis: 126-184 days
Canada, 2008 Josephberg/AB (Clearfield 45H73)	SL	0.009	101	14	1	49 60 70 80 90	< 0.05, < 0.05 < 0.05, < 0.05 Mean < 0.05 < 0.05, < 0.05 < 0.05, < 0.05 < 0.05, < 0.05	
Canada, 2008 Waldheim/SK (Clearfield 45H72)	SL	0.009	100	16–33	1	70	< 0.05, < 0.05 Mean < 0.05	
Canada, 2008 Wellwood/MB (Clearfield 45H72)	SL	0.009	101	65	1	70	< 0.05, < 0.05 Mean < 0.05	
Canada, 2008 Wellwood/MB (Clearfield 45H72)	SL	0.009	101	65	1	70	< 0.05, < 0.05 Mean < 0.05	
Canada, 2008 Dundern/SK (Clearfield 45H72)	SL	0.009	100	13	1	72	< 0.05, < 0.05 Mean < 0.05	
Canada, 2008 Alvena/SK (Clearfield 45H72)	SL	0.009	100	25–33	1	68	< 0.05, < 0.05 Mean < 0.05	
Canada, 2008 Alvena/SK (Clearfield 45H73)	SL	0.009	99	25–33	1	68	< 0.05, < 0.05 Mean < 0.05	
Canada, 2008 Waldheim/SK (Clearfield 45H73)	SL	0.009	102	16–33	1	70	< 0.05, < 0.05 Mean < 0.05	
Canada, 2008 Josephberg/AB (Clearfield 45H72)	SL	0.009	100	15–16	1	70	< 0.05, < 0.05 Mean < 0.05	
Canada, 2008 Lamont/AB (Clearfield 45H72)	SL	0.009	98	> 30	1	70	< 0.05, < 0.05 Mean < 0.05	
Canada, 2008 Lamont/AB (Clearfield 45H73)	SL	0.010	102	> 30	1	70	< 0.05, < 0.05 Mean < 0.05	

Table 41 Imazapyr residues on imidazolinone-tolerant rape seed from supervised trials in Australia

Rape seed country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage	no .			
GAP, Australia	SL	0.005-0.011	> 70		1	not required		
Australia, 1997 Winula, Yorke Peninsula/SA (IT)	WG	0.007	110	Post emergence	1	66	< 0.05	1998/1008955 Anonymous, 2003
		0.014	110	Post emergence	1	66	< 0.05	
		0.028	110	Post emergence	1	66	< 0.05	

Rape seed country, year (variety)	Application					DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage	no .			
Australia, 1997 Gnarwarre/Vic (IT)	WG	0.007	50	Post emergence	1	106	< 0.05	Sampling to analysis: not specified
		0.015	50	Post emergence	1	106	< 0.05	
		0.028	50	Post emergence	1	106	< 0.05	

Sunflower seed

During the two growing seasons 2007/2008 and 2008/2009, trials were conducted for imidazolinone-resistant sunflower at three locations in Argentina to determine the residue level of imazapyr. The WG formulation containing 800 g/kg imazapyr were applied once at rates of 0.06 and 0.12 kg ai/ha. Method SOP-PA.0288 was used to analyse sunflower seed samples for the residues of imazapyr by liquid chromatography using a mass/mass detector (LC-MS/MS) with a limit of quantitation (LOQ) of 0.01 mg/kg.

During the growing season 2010/2011, four trials were conducted in sunflower in Argentina to determine the residue level of imazapyr. The SL formulation containing 15 g/L imazapyr was applied once at a rate of 0.030 kg ai/ha while on the other 4 plots 0.060 kg ai/ha were applied. Method SOP-PA.0288 was used to analyse sunflower seed samples for the residues of imazapyr by liquid chromatography and mass/mass detector (LC-MS/MS) with a limit of quantitation (LOQ) of 0.01 mg/kg.

Table 42 Imazapyr residues on imidazolinone-tolerant sunflower seed from supervised trials

Sunflower seed country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref	
	Form	kg ai/ha	water, L/ha	kg ai/hL	Growth stage	no .				
GAP, Argentina	WG	0.080	120–150			1	Early post emergent			
Argentina, 2007–2008 Balcarce	WG	0.060	120	0.050	13–14	1	106	< 0.01	2010/1057139 Guimarães, 2010	
		0.12	120	0.10	13–14	1	106	< 0.01		
Argentina, 2008–2009 Balcarce	WG	0.060	120	0.050	13–14	1	105	< 0.01	Sampling to analysis: 381–751 days	
		0.12	120	0.10	13–14	1	105	< 0.01		
Argentina, 2007–2008 Tandil	WG	0.060	120	0.050	13–14	1	105	0.03		
		0.12	120	0.10	13–14	1	105	0.01		
Argentina, 2008–2009 Tandil	WG	0.060	120	0.050	13–14	1	104	0.01		
		0.12	120	0.10	13–14	1	104	0.02		
Argentina, 2007–2008 Realicó	WG	0.060	120	0.050	13–14	1	98	< 0.01		
		0.12	120	0.10	13–14	1	98	0.02		
Argentina, 2008–2009 Realicó	WG	0.060	120	0.050	13–14	1	109	< 0.01		
Argentina, 2010–2011 Gonzalez Moreno	SL	0.030				1	81	< 0.01		2012/3000521 Jones, 2012
		0.060				1	81	0.03		
Argentina, 2010–2011 Venado Tuerto	SL	0.030				1	98	< 0.01	Sampling to analysis: 380–746 days	
		0.060				1	98	< 0.01		
Argentina, 2010–2011 Balcarce	SL	0.030				1	103	< 0.01		
		0.060				1	103	< 0.01		
Argentina, 2010–2011 Yuto	SL	0.030				1	143	< 0.01		
		0.060				1	143	< 0.01		
Argentina, 2001–2002	SL	0.080	170		12–14	1	90	< 0.05		2002/3000641 Borges, 2002

Sunflower seed country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	kg ai/hL	Growth stage	no .			
Balcarce (Clearfield)		0.16	170			1	90	< 0.05	Sampling to analysis: 89–458 days
Argentina, 2002 Miramar (Clearfield)	SL	0.10	170		12–14	1	100	< 0.05	
Uruguay, 2010–2011 Ciudad Del Plata (Neo G-09 CL)	SL	0.080	148.4		14	1	102	< 0.01, < 0.01 Mean ≤ 0.01	
Uruguay, 2010–2011 Canelones (Neo G-09 CL)	SL	0.080	148.3		14	1	103	< 0.01, < 0.01 Mean ≤ 0.01	Sampling to analysis: 321–339 days
Argentina, 2010–2011 Gahan (Paraiso 103 CL)	SL	0.076	142.4		15	1	111	< 0.01, < 0.01 Mean ≤ 0.01	

Straw, fodder and forage of cereals

Maize fodder and forage

Residue data have been collected from 19 field trials located in the USA. Method M 2468 was used for analysis of imazapyr residues in maize samples quantifying the analyte by gas chromatography/negative ion chemical ionization mass spectrometry (GC/ECNICI) with a limit of quantitation of 0.05 mg/kg.

Six trials in maize were conducted in Australia to determine the residue level of imazapyr in/on maize. The SL formulation was applied once as broadcast foliar application. The applications were made in half of the trials post sowing—pre-emergence and in the second half of the trials at early post-emergence. Imazapyr was analysed in the maize matrices using method L 741/1. Separation and quantitation were accomplished with reverse phase high performance liquid chromatography using a UV-VIS detector with a limit of quantitation of 0.05 mg/kg.

Seven trials in maize were conducted in the Argentina. Method LAADL R0001 was used for analysis of imazapyr residues in maize quantifying the analyte by HPLC/UV with a limit of quantitation of 0.05 mg/kg.

Three trials in maize were conducted in Brazil. The WG formulation was applied to the plots as broadcast foliar application in spray volumes of 200 L/ha. Method SOP-PA.0200 rev.02-re.01, based on methods MR0001.01, M-2020 and M-1928, was used for analysis of imazapyr residues in maize samples. Imazapyr was determined by LC-MS/MS (mass transition 262/217). The limit of quantitation for this method in maize samples was 0.05 mg/kg.

Table 43 Imazapyr residues on imidazolinone-tolerant maize from supervised trials

Maize country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage (BBCH)	Analytical portion	no .			
GAP, USA		0.016				1	45		
USA, 1993 Conklin/MI (Pioneer Hybrid 3417 IR)	ASU	0.027	188	14	Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 30 45 60 80 90 126	3.1 0.11 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-001 Mahl, 1995 Sampling to analysis: 456–581 days

Maize country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage (BBCH)	Analytical portion	no.			
USA, 1993 Webster/IA (Pioneer Hybrid 3377 IR)	ASU	0.027	187	14	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 31 46 60 80 90 131	2.6 0.087 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-002 Mahl, 1995 Sampling to analysis: 513–642 days
USA, 1993 Verona/WI (Pioneer Hybrid 3417 IR)	ASU	0.027	186	14	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 30 45 60 82 105 125	1.6 0.13 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-003 Mahl, 1995 Sampling to analysis: 520–644 days
USA, 1993 Jamesville/NC (Pioneer Hybrid 3245 IR)	ASU	0.027	202	14–15	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 29 43 60 81 90 103	1.9 0.14 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-004 Mahl, 1995 Sampling to analysis: 538–638 days
USA, 1994 Conklin/MI (Pioneer Hybrid 3751 IR)	WP	0.027	191	14	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 30 45 60 80 98 124	1.8 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-005 Mahl, 1995 Sampling to analysis: 191–314 days
USA, 1994 New Holland/ OH (Pioneer Hybrid 3245 IR)	WP	0.027	171	14	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 32 45 60 80 89 123	5.4 0.057 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-006 Mahl, 1995 Sampling to analysis: 209–332 days
USA, 1993 Gary/SD (Pioneer Hybrid 3417 IR)	ASU	0.027	181	14	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 30 44 61 80 92 134	2.7 0.17 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-007 Mahl, 1995 Sampling to analysis: 476–609 days
USA, 1994 Snock/TX (Pioneer Hybrid 3162 IR)	WP	0.027	199	15	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 8 30 45 60 80 90 110	2.4 0.13 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-008 Mahl, 1995 Sampling to analysis: 244–353 days

Maize country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage (BBCH)	Analytical portion	no .			
USA, 1994 Noblesville /IN (Pioneer Hybrid 3395 IR)	WP	0.027	181	14	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 6 31 48 60 80 90 132	1.7 0.10 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-009 Mahl, 1995 Sampling to analysis: 224–354 days
USA, 1994 Carman/IL (Pioneer Hybrid 3417 IR)	WP	0.027	187	14–15	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 30 44 61 79 91 126	3.8 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-010 Mahl, 1995 Sampling to analysis: 210–335 days
USA, 1993 York/NE (Pioneer Hybrid 3417 IR)	ASU	0.027	187	14–15	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 31 45 60 80 90 116	4.7 0.095 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-011 Mahl, 1995 Sampling to analysis: 666–802 days
USA, 1993 Carman/IL (Pioneer Hybrid 3417 IR)	ASU	0.027	187	14–15	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 29 46 60 81 91 117	3.2 0.11 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-012 Mahl, 1995 Sampling to analysis: 561–677 days
USA, 1993 Clarence/MO (Pioneer Hybrid 3245 IR)	ASU	0.027	187	14	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 31 44 62 80 92 112	3.1 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-013 Mahl, 1995 Sampling to analysis: 490–733 days
USA, 1994 Fisher/MN (Pioneer Hybrid 3751 IR)	WP	0.027	187	14–15	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 30 45 60 80 93 146	3.0 0.073 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-014 Mahl, 1995 Sampling to analysis: 201–425 days
USA, 1994 Webster City/IA (Pioneer Hybrid 3417 IR)	WP	0.027	191	14	Forage Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 31 45 60 81 90 131	2.4 0.087 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-015 Mahl, 1995 Sampling to analysis: 212–419 days

Maize country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage (BBCH)	Analytical portion	no.			
USA, 1993 Noblesville/IN (Pioneer Hybrid 3417 IR)	ASU	0.027	187	14	Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 31 44 59 80 90 149	4.2 < 0.05 < 0.05 NA < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-016 Mahl, 1995 Sampling to analysis: 581–730 days
USA, 1993 New Holland/ OH (Pioneer Hybrid 3417 IR)	ASU	0.027	187	14	Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 8 30 45 59 80 90 127	2.1 0.16 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-017 Mahl, 1995 Sampling to analysis: 484–779 days
USA, 1994 York/NE (Pioneer Hybrid 3417 IR)	WP	0.027	189	14	Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 30 45 60 80 90 122	2.7 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	IZ-731-018 Mahl, 1995 Sampling to analysis: 234–355 days
USA, 1993 Hamburg/PA (Pioneer Hybrid 3245 IR)	ASU	0.027	189	14	Forage Forage Forage Forage Early Silage Late Silage Fodder	1	0 7 30 46 60 81 91 141	3.3 0.16 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	1995/700418 9 Mahl, 1995 Sampling to analysis: 488–630 days
GAP, Australia	WG	0.018 – 0.022	> 50			1	Do not graze and cut for 4 weeks after application		
Australia, 1997 Darlington Point/NSW (62 IT)	SL	0.016	112	Early post emergent	Forage	1	7 21 37 50	0.08 < 0.05 < 0.05 < 0.05	2000/102396 5 Mooney, 2000 Sampling to analysis: 197–240 days
		0.032	112	Early post emergent	Forage	1	7 21 37 50	0.09 < 0.05 < 0.05 < 0.05	
		0.048	112	Early post emergent	Forage	1	7 21 37 50	0.19 < 0.05 < 0.05 < 0.05	
	SL	0.016	112	Post sowing pre- emergent	Forage	1	29 43 67	< 0.05 < 0.05 < 0.05	Sampling to analysis: 179–216 days
		0.032	112	Post sowing pre- emergent	Forage	1	29 43 67	< 0.05 < 0.05 < 0.05	
		0.048	112	Post sowing pre- emergent	Forage	1	29 43 67	< 0.05 < 0.05 < 0.05	
GAP, Argentina	WG	0.025				1	before reaching 6 th fully developed leaf status		

Maize country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage (BBCH)	Analytical portion	no.			
Argentina, 1997–1998 San Jeronimo (Pioneer 3162 IR)	SC	0.025	166	14	Forage	1	90	< 0.05	1999/7004026 Steling, 1999
		0.040	166	14	Forage	1	90	< 0.05	
		0.050	166	14	Forage	1	90	< 0.05	
Argentina, 1997–1998 Santos Unzue (Pioneer 3162 IR)	SC	0.025	195	14	Forage	1	80	< 0.05	Sampling to analysis: 109–461 days
		0.040	195	14	Forage	1	80	< 0.05	
		0.050	195	14	Forage	1	80	< 0.05	
Argentina, 1997–1998 Fauzon (Pioneer 3162 IR)	SC	0.025	195	12	Forage	1	96	< 0.05	
		0.040	195	12	Forage	1	96	< 0.05	
		0.050	195	12	Forage	1	96	< 0.05	
Argentina, 1998–1999 San Jeronimo (Asgrow AX 888 IT)	WG	0.020	180	16	Forage	1	56	< 0.05	
		0.040	180	16	Forage	1	56	< 0.05	

ASU: Aqueous Solution with urea

Wheat straw and forage

The trials were conducted at six locations in Australia. The SL formulation or the WG formulation were applied once as broadcast foliar or band application. Imazapyr was analysed in the wheat matrices using method L 741/1. Quantitation was accomplished with reverse phase high performance liquid chromatography using a UV-VIS detector and external standard calibration procedures. The limit of quantitation for this method in wheat samples was 0.05 mg/kg.

Table 44 Imazapyr residues on imidazolinone-tolerant wheat from supervised trials in Australia

Wheat country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage	Analytical portion	no.			
GAP, Australia	WG	0.004–0.007	> 70			1	Do not gaze and cut for 4 weeks after application		
Australia, 1997–1998 Winulta, Yorke Peninsula/SA (IT)	SL	0.007	110	2 node stage	Straw	1	88	< 0.05	1999/1013037 Mooney, 1999 Sampling to analysis: 182 days
		0.014	110	2 node stage		1	88	< 0.05	
		0.028	110	2 node stage		1	88	< 0.05	
		0.007	110	2 node stage	Forage	1	0 13 25	0.12 < 0.05 < 0.05	Sampling to analysis: 245–273 days
		0.014	110	2 node stage		1	0 13 25	0.12 < 0.05 < 0.05	
		0.028	110	2 node stage		1	0 13 25	0.22 0.05 < 0.05	
Australia, 1997–1998 Osbourne/NSW (IT)	SL	0.007	112	Early post emergent	Straw	1	83	< 0.05	Sampling to analysis: 193 days
		0.014	112	Early post emergent		1	83	< 0.05	
		0.028	112	Early post emergent		1	83	< 0.05	
		0.007	112	Early post emergent	Forage	1	0 14 28	0.40 < 0.05 < 0.05	Sampling to analysis: 217–

Wheat country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage	Analytical portion	no.			
		0.014	112	Early post emergent		1	0 14 28	0.73 0.08 < 0.05	245 days
		0.028	112	Early post emergent		1	0 14 28	1.5 0.10 0.05	
Australia, 1997–1998 Gnarwarre/ Vic (IT)	SL	0.007	50	Early post emergent	Straw	1	104	< 0.05	Sampling to analysis: 46 days
		0.015	50	Early post emergent		1	104	< 0.05	
		0.028	50	Early post emergent		1	104	< 0.05	
		0.007	50	Early post emergent	Forage	1	14 29	0.051 < 0.05	Sampling to analysis: 107– 122 days
		0.015	50	Early post emergent		1	14 29	0.090 0.087	
		0.028	50	Early post emergent		1	14 29	< 0.05 < 0.05	
Australia, 1998 Rannock/ NSW (IT)	SL	0.014	84	Early to late tillering	Forage	0 1	– 1 15 30	< 0.05 0.11 < 0.05 < 0.05	Sampling to analysis: 21– 48 days
		0.028	84	Early to late tillering	Forage	1	1 15 30	0.65 0.05 < 0.05	
Australia, 1998 Manoora/SA (IT)	SL	0.014	117	Stem elongation stage (1–2 node stage)	Straw	1	95	< 0.05	Sampling to analysis: 67 days
		0.028	117	Stem elongation stage (1–2 node stage)		1	95	< 0.05	
		0.014	117	Stem elongation stage (1–2 node stage)	Forage	1	0 13 26 42	0.10 0.08 < 0.05 < 0.05	Sampling to analysis: 91– 133 days
		0.028	117	Stem elongation stage (1–2 node stage)	Forage	1	0 13 26 42	0.33 0.11 0.11 < 0.05	
Australia, 1998–1999 Burabadji/WA (IT)	WG	0.014	110	Advanced tillering	Straw	1	94	< 0.05	Sampling to analysis: 54– 148 days
		0.028	110	Advanced tillering		1	94	< 0.05	
		0.014	110	Advanced tillering	Forage	1	0 14 28 42	0.37 < 0.05 < 0.05 < 0.05	
		0.028	110	Advanced tillering	Forage	1	0 14 28 42	0.62 0.10 < 0.05 < 0.05	

Miscellaneous fodder and forage crops

Rape straw and forage

In the growing seasons 1997/1998, trials were conducted at 3 locations in Australia. The WG formulation was applied once as broadcast foliar application. Imazapyr was analysed in the rape matrices using method L 741/1. Quantitation was accomplished with reverse phase high performance

liquid chromatography using a UV-VIS detector and external standard calibration procedures. The LOQ of the method is 0.05 mg/kg for rape matrices.

Table 45 Imazapyr residues on imidazolinone-tolerant rape from supervised trials in Australia

Rape country, year (variety)	Application						DALA Days	Residues, mg/kg	Ref
	Form	kg ai/ha	water, L/ha	Growth stage	Analytica l portion	no .			
GAP, Australia	SL	0.005 – 0.012	> 70			1	Do not gaze and cut for 5 weeks after application		
Australia, 1997 Winula, Yorke Peninsula/SA (IT)	WG	0.007	110	Post emergence	Forage	1	0 13 25	0.12 < 0.05 < 0.05	1998/100895 5 Anonymous, 2003 Sampling to analysis: not specified
		0.014	110	Post emergence	Forage	1	0 13 25	0.14 < 0.05 < 0.05	
		0.028	110	Post emergence	Forage	1	0 13 25	0.22 0.11 < 0.05	
		0.007 0.014 0.028	110	Post emergence	Straw	1 1 1	66 66 66	< 0.05 < 0.05 < 0.05	
Australia, 1997 Gnarwarre/Vic (IT)	WG	0.007 0.015 0.028	50	Post emergence	Forage	1 1 1	29 29 29	< 0.05 < 0.05 < 0.05	
		0.007 0.015 0.028	50	Post emergence	Straw (fodder)	1 1 1	106 106 106	< 0.05 < 0.05 < 0.05	
Australia, 1998 Rannock/NSW (IT)	WG	0.014	84	Post emergence	Forage	1	19 33 47	< 0.05 < 0.05 < 0.05	
		0.028	84	Post emergence	Forage	1	19 33 47	0.05 < 0.05 < 0.05	

FATE OF RESIDUES IN STORAGE AND PROCESSING

In Processing

The Meeting received information on high temperature hydrolysis of imazapyr and the fate of imazapyr residues during the processing of soya bean seeds, maize grains, rape seeds and sunflower seeds.

Soya bean, maize, rape and sunflower of the crops that the Meeting received information on supervised field trials may be processed prior to consumption. Processing factors have been calculated for imazapyr residues in soya bean seeds, maize grains, rape seeds and sunflower seeds.

High temperature hydrolysis

The degradation of [¹⁴C] imazapyr was studied under hydrolytic conditions at high temperatures in sterile aqueous buffers at pH 4, 5 and 6 for periods of up to 60 minutes so as to simulate common processing practices (pasteurization, baking/brewing/boiling/, and sterilization) (Osterman, 2012: 2012/7000341). All test samples were prepared in sterile amber bottles to eliminate possible photolysis and all sterile buffers were bubbled with nitrogen to avoid the effects of oxygen on the test systems. The concentration of imazapyr was approximately 10 mg/L. The hydrolysis tests were conducted with [¹⁴C] imazapyr in sterile 0.1 M aqueous solutions buffered at pH 4, 5 and 6. The samples were prepared in duplicates for each test system. Samples were analysed immediately at time zero (these samples were not heated). Two additional samples at pH 4 ± 0.1 were placed in an oven and maintained at 90 °C ± 5 °C for 20 minutes, another two samples at pH 5 ± 0.1 were placed in an

oven and maintained at $100\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ for 60 minutes, and two more samples at $\text{pH } 6 \pm 0.1$ were placed in an autoclave and maintained at sterilizing conditions ($121\text{ }^{\circ}\text{C}$) for 20 minutes.

Radiocarbon recoveries ranged from 99.7 to 101.5% for all samples. The test solutions were analysed by reverse phase HPLC. The experiments showed that imazapyr was stable under hydrolytic conditions at high temperatures. No degradates were detected at any of the investigated pH and temperature ranges.

Table 46 Hydrolysis recovery under the conditions for processing simulation

Temperature	Time	pH	Representative process	Recovery (%) [10 mg/L]	
				% remaining	Mean
$90\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$	20 minutes	4 ± 0.1	Pasteurization	100.2, 99.7	100
$100\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$	60 minutes	5 ± 0.1	Baking/brewing/boiling	101.5, 101.2	101
$121\text{ }^{\circ}\text{C}$ (actual)	20 minutes	6 ± 0.1	Sterilization	100.1, 100.5	100

Soya bean seeds

Processing studies for soya bean were conducted in Brazil to determine the potential for concentration of residues of imazapyr in the processed fractions of soya bean. The SC formulation containing 480 g/L imazapyr was applied once at exaggerated rates of 0.22 kg ai/ha ($3\times$) or 0.14 kg ai/ha ($2\times$), respectively. The WG formulation containing 525 g/kg imazapyr was applied once at exaggerated rates of 0.16 kg ai/ha or 0.11 kg ai/ha, respectively. Samples of soya bean seeds (RAC) were processed according to simulated commercial procedures into flaked soya bean, oil, meal, toasted meal, defatted meal, toasted defatted meal, laminated soya bean fractions and hulls. For one trial, The WG formulation containing 525 g/kg imazapyr was applied once at a rate equivalent to 0.053 kg ai/ha in a spray volume of 200 L/ha. Soya bean seeds were used for processing and aspirated grain fractions (AGF) were produced. Method SOP-PA.0288 was used for analysis of imazapyr residues in soya bean quantifying the analyte by LC-MS/MS with a LOQ of 0.01 mg/kg.

The soya bean grains were initially dried in a ventilated oven at $60\text{ }^{\circ}\text{C}$, for approximately 5 hours and after drying they were cleaned. The soya bean grains were rolled in an “expeller” press type. The layers of soya bean presented an average thickness of 2 mm (flaked/laminated). Part of rolled material was submitted to the extraction of the oil in “batch” type equipment, using indirect vapor for heating the solvent n-hexane between $45\text{--}50\text{ }^{\circ}\text{C}$. The extractors were heated with indirect vapour during 20 min to evaporate the residual solvent from the meal. The material was heated with direct vapour for 5 min (defatted meal). The material was submitted under pressure of 0.4 kg/cm^2 during 2 min to finish the toasting process (toasted meal). The first part (oil mixture and solvent), produced after the extraction was collected in the tank and the solvent was removed under indirect heating at $60\text{ }^{\circ}\text{C}$ (oil). The humidity of the meals was reduced by a ventilated oven at $60\text{ }^{\circ}\text{C}$ for 12 hours (meal).

Table 47 Imazapyr residues in processed commodities of soya bean seeds from supervised trials

country, year (variety)	Application				DALA Days	Commodity	Residues, mg/kg		Ref.
	kg ai/ha	water, L/ha	GS (BBCH)	no .			mg/kg	PF	
Brazil, 2007– 2008 Santo Antônio de Posse/SP (CV 127)	0.22	200	75	1	60	seed flaked oil meal toasted meal	0.18 0.28 < 0.01 0.33 0.25	1.6 < 0.06 1.8 1.4	2009/7000088 Resende, 2009 Processing to analysis: 70–85 days
Brazil, 2007– 2008 Londorina/P R (CV 127)	0.14	200	72	1	60	seed flaked oil meal toasted meal	1.56 1.41 < 0.01 1.90 2.14	0.90 < 0.006 1.2 1.4	

country, year (variety)	Application				DALA Days	Commodity	Residues, mg/kg		Ref.
	kg ai/ha	water, L/ha	GS (BBCH)	no .			mg/kg	PF	
Brazil, 2007– 2008 Santo Antônio de Posse/SP (CV 127)	0.16	200	75	1	60	seed flaked oil meal toasted meal	0.14 0.13 < 0.01 0.21 0.20	0.93 < 0.07 1.5 1.4	2009/7000089 Resende, 2009 Processing to analysis: 70–87 days
Brazil, 2007– 2008 Londorina/P R (CV 127)	0.11	200	72	1	60	seed flaked oil meal toasted meal	1.04 0.60 < 0.01 1.23 0.91	0.58 < 0.01 1.2 0.88	
Brazil, 2008– 2009 Santo Antônio de Posse/SP (CV 127)	0.16	200	67	1	60	seed defatted meal toasted defatted meal oil laminated	2.22 2.79 2.42 < 0.01 0.85	1.3 1.1 < 0.005 0.38	2012/1044747 Jones, 2012 Sampling to analysis: max. 16 months
						seed meal hulls	1.81 1.65 0.97	0.91 0.54	
Brazil, 2008– 2009 Londorina/P R (CV 127)	0.11	200	69	1	60	seed defatted meal toasted defatted meal oil laminated	1.22 1.63 1.54 < 0.01 0.39	1.3 1.3 < 0.008 0.32	
						seed meal hulls	0.98 1.01 0.77	1.0 0.79	
Brazil, 2011 Santo Antônio de Posse/SP (BRZ 5384))	0.053	200	73	1	60	seed AGF	1.27 0.04	0.031	2012/3000423 Jones, 2012 Sampling to analysis: 169 days

Maize grains

A processing study was conducted on maize in the USA during the 1993 growing season to determine the potential for concentration of residues of imazapyr in maize processed fractions. At the test location, a single broadcast foliar application of the ASU formulation containing 240 g/L imazapyr was made to maize targeting 0.27 kg ai/ha (10×) of imazapyr. Grains for processing were harvested at 136 days after application and were later processed according to simulated commercial procedures into maize processed commodities meal and oil. The maize grain RAC and processed commodity samples (meal and oil) were analysed for residues of imazapyr using Method M 2468 with a LOQ of 0.05 mg/kg. Measurement of imazapyr was accomplished by gas chromatography/negative ion chemical ionization mass spectrometry.

Table 48 Imazapyr residues in processed commodities of maize grains from supervised trials

country, year (variety)	Application				DALA Days	Commodity	Residues, mg/kg		Ref.
	kg ai/ha	water, L/ha	GS (BBCH)	no .			mg/kg	PF	
USA, 1993 York/NE (Pioneer Hybrid 3417 IR)	0.27	187	14–15	1	136	grain meal oil	0.0995 0.116 < 0.05	1.2 < 0.50	IZ-731-011 Mahl, 1995 Sampling to analysis: 667 days

Rape seeds

A processing study for rape seed was conducted to determine the potential for concentration of residues of imazapyr in the processed fractions of rape seed. The study was conducted in Canada during the 2008 growing season to determine the potential for concentration of residues of imazapyr in rape seed processed fractions. At the test location, a single broadcast foliar application of a SL formulation containing 15 g/L imazapyr was made to rape targeting 0.045 kg ai/ha. Rape seed bulk samples harvested from the plot treated at an exaggerated rate (5×) were harvested 70 days after treatment and were later processed according to simulated commercial procedures into rape seed meal and refined oil. Method M 3519 was used to analyse rape seed samples for the residues of imazapyr. Imazapyr was quantified by liquid chromatography and mass/mass detector (LC-MS/MS) with a LOQ of 0.05 mg/kg.

Table 49 Imazapyr residues in processed commodities of rape seeds from supervised trials

country, year (variety)	Application				DALAD ays	Commodity	Residues, mg/kg		Ref.
	kg ai/ha	water, L/ha	GS (BBCH)	no .			mg/kg	PF	
Canada, 2008 Waldheim/SK (Clearfield 45H72)	0.045	100	16–33	1	70	grain meal refined oil	0.07 0.10 < 0.05	1.4 < 0.71	2008/701922 7 Norris, 2009 Sampling to analysis: 126- 184 days

Sunflower seed

A processing study for sunflower seed was conducted in the USA in the year 2000 to determine the potential for concentration of residues of imazapyr in the processed fractions of sunflower seeds. The applications were made as broadcast, post-emergence sprays targeting when the plants were 18–30 cm tall. Replicate sunflower seed RAC samples were harvested at normal crop maturity, 88 days after treatment. The whole sunflower seed samples were processed into meal and refined oil according to simulated commercial procedures.

The method used for analysis determines residues of imazapyr using HPLC with MS detection. Residues of imazapyr were extracted from sunflower seed and meal samples with an acidified methanol: water solution, filtered, and concentrated. The residues are then purified on a C18 solid phase extraction (SPE) column and eluted with 25% MeOH in 0.05 M aqueous ammonium acetate. Residues in refined oil samples are diluted in hexane and extracted by shaking with acidified acetonitrile: water solution. Following phase separation, the lower aqueous ACN layer is collected and imazapyr residues are detected by LC-MS with a LOQ of 0.05 mg/kg.

Table 50 Imazapyr residues in processed commodities of sunflower seeds from supervised trials

country, year (variety)	Application				DALA Days	Commodity	Residues, mg/kg		Ref.
	kg ai/ha	water, L/ha	Growth stage	no.			mg/kg	PF	
USA/ND, 2000 (CMS HA425/ RHA 426)	0.022	95	18–30 cm height	1	88	seed meal refined oil	< 0.05 < 0.05 < 0.05		2002/5004111 Johnston, 2003
	0.045	94	18–30 cm height	1	88	seed meal refined oil	< 0.05 0.07 < 0.05	> 1.4	Processing to analysis: max. 5 months

RESIDUES IN ANIMAL COMMODITIES*Farm animal feeding studies*

The Meeting received lactating dairy cow feeding studies.

Lactating dairy cow

The study was designed to determine the residues of imazapyr found in milk and tissues following oral administration to dairy cow (Khunachak, 1999: IZ-705-001). Five groups of cows, each group containing three animals, were orally dosed with imazapyr for 28–29 days at dosages of approximately 1.2, 3.6, 12 and 36 g imazapyr per animal per day. This would be equivalent to total dietary residues of approximately 58, 157, 607 and 1680 ppm feed. Dose levels were based on a nominal feed intake of 20 kg (dry matter equivalent) per day for a cow. Gelatin capsules containing imazapyr were used for administration.

Milk samples (composites of the pm and am milking of the following day) were collected from all cows. Milk fat samples were prepared from composite milk samples of all cows in each group at 8, 15 and 22 days of treatment. Within 24 hours of the last dosing, all cows were sacrificed and the edible tissues (muscle, fat, liver and kidney) from each animal were collected. All samples were analysed for imazapyr using Methods M 3075 (milk), M 3184 (tissues, fat) and M 3223 (milk fat). Quantitation in milk, muscle, fat, liver, and kidney was performed using capillary electrophoresis with UV detection, and quantitation in milk fat was performed using LC-MS with single ion monitoring (SIM). The LOQ of the individual methods for imazapyr detection in milk and milk fat was 0.01 mg/kg and for tissues and fat 0.05 mg/kg.

Imazapyr residues in milk samples from cows in group A (control) were less than LOQ. The pre-treatment milk samples from all cows from the treated groups showed imazapyr residues of < 0.01 mg/L. In the three highest dose groups (157, 607, 1.680 ppm feed), residues of imazapyr in milk reached a plateau after about 2–3 days

Table 51 Residues of imazapyr in whole milk

Day	Residues, mg/L		
	Group A (control)	Group B (58 ppm feed)	Group C (157 ppm feed)
-1	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)
2	< 0.01 (3)	< 0.01, < 0.01, 0.013 mean 0.011	0.030, 0.039, 0.036 mean 0.035
3	< 0.01 (3)	< 0.01, < 0.01, 0.012 mean 0.011	0.029, 0.021, 0.024 mean 0.024
6	< 0.01 (3)	< 0.01 (3)	0.022, 0.029, 0.027 mean 0.026
8	< 0.01 (3)	< 0.01 (3)	0.028, 0.028, 0.024 mean 0.027
10	< 0.01 (3)	< 0.01 (3)	0.023, 0.036, 0.028 mean 0.029
13	< 0.01 (3)	< 0.01 (3)	0.023, 0.025, 0.025 mean 0.024
15	< 0.01 (3)	na	na
17	< 0.01 (3)	< 0.01 (3)	0.031, 0.033, 0.023 mean 0.029
20	< 0.01 (3)	na	na
22	< 0.01 (3)	na	na
24	< 0.01 (3)	< 0.01, < 0.01, 0.013 mean 0.011	0.024, 0.025, 0.034 mean 0.028
27	< 0.01 (3)	< 0.01, < 0.01, 0.012 mean 0.011	0.021, 0.031, 0.027 mean 0.026
Day	Residues, mg/L		
	Group D (607 ppm feed)	Group E (1680 ppm feed)	
-1	< 0.01 (3)	< 0.01 (3)	
2	0.073, 0.072, 0.12 mean 0.087	0.24, 0.35, 0.35 mean 0.31	
3	0.11, 0.094, 0.12 mean 0.11	0.24, 0.27, 0.30 mean 0.27	
6	0.090, 0.075, 0.11 mean 0.092	0.21, 0.25, 0.27 mean 0.24	
8	0.083, 0.080, 0.13 mean 0.096	0.19, 0.25, 0.23 mean 0.22	
10	0.067, 0.057, 0.12 mean 0.082	0.21, 0.29, 0.32 mean 0.27	
13	0.077, 0.081, 0.13 mean 0.095	0.18, 0.33, 0.30 mean 0.27	
15	na	na	
17	0.11, 0.076, 0.10 mean 0.096	0.17, 0.27, 0.23 mean 0.22	
20	na	na	
22	na	na	
24	0.11, 0.071, 0.099 mean 0.094	0.25, 0.30, 0.25 mean 0.27	
27	0.083, 0.057, 0.086 mean 0.075	0.18, 0.26, 0.29 mean 0.24	

na: not analysed

Imazapyr residues in milk fat samples from cows in group A (control) were < 0.01 mg/kg. Averages imazapyr residues in milk fat samples from cows in treated groups B, C, D and E were < 0.01, 0.013, 0.037 and 0.10 mg/kg, respectively.

Table 52 Residues of imazapyr in milk fat

Group	Residue, mg/kg		
	Day 8	Day 15	Day 22
A (control)	< 0.01	< 0.01	< 0.01
B (58 ppm)	< 0.01	< 0.01	< 0.01
C (157 ppm)	0.012	0.011	0.015
D (607 ppm)	0.039	0.041	0.032
E (1680 ppm)	0.10	0.093	0.11

Imazapyr residues in muscle, fat, kidney and liver samples from cows in group A (control) were all < 0.05 mg/kg. In kidney, imazapyr was detected as predominant residue in all treated groups.

Table 53 Residues of imazapyr in tissues

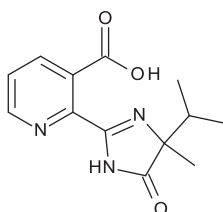
Group	Residues, mg/kg			
	Muscle	Fat	Kidney	Liver
A (control)	< 0.05 (3)	< 0.05 (3)	< 0.05 (3)	< 0.05 (3)
B (58 ppm)	< 0.05 (3)	< 0.05 (3)	0.11, 0.36, 0.28 mean 0.25	< 0.05 (3)
C (157 ppm)	< 0.05 (3)	< 0.05 (3)	0.32, 0.90, 0.34 mean 0.52	< 0.05, 0.070, < 0.05 mean 0.057
D (607 ppm)	0.15, 0.083, 0.064 mean 0.097	0.15, < 0.05, < 0.05 mean 0.083	7.0, 3.9, 2.1 mean 4.4	0.32, 0.39, 0.20 mean 0.30
E (1680 ppm)	0.19, 0.25, 0.27 mean 0.23	0.086, 0.11, 0.080 mean 0.092	7.3, 7.2, 8.0 mean 7.5	0.55, 0.70, 1.2 mean 0.81

APPRAISAL

Residue and analytical aspects of imazapyr were considered for the first time by the present Meeting. The residue evaluation was scheduled for the 2013 JMPR by the Forty-fourth Session of the CCPR.

Imazapyr is a broad-spectrum herbicide in the imidazolinone family. Its primary use is as a post-emergence herbicide which is particularly effective on hard-to-control perennial grasses. It is non-selective, absorbed by foliage and rapidly translocated. The mode of action of imidazolinone herbicides is the inhibition of the enzyme acetohydroxy acid synthase (AHAS) which is a critical enzyme for the biosynthesis of branched chain amino acids necessary for cell growth and protein synthesis. The Meeting received information on identity, animal and plant metabolism, environmental fates in soil, rotational crops, analytical methods, storage stability, use patterns, supervised trials, farm animal feeding studies and fates of residues in processing.

2-[(*RS*)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl] nicotinic acid



Imazapyr is a 1:1 mixture of the enantiomers.

In this appraisal, the following abbreviated names were used for metabolites.

CL 247, 087	CL 240,000	CL 60,032	PDC
5 <i>H</i> -imidazo [1',2':1,2] pyrrolo [3,4- <i>b</i>] pyridine - 2(3 <i>H</i>),5-dione, 1.9 <i>b</i> α(β)-dihydro-3α- isopropyl-3-ethyl-	2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-carboxymethyl pyridine	2-carbamoyl-nicotinic acid	Pyridine 2,3-dicarboxylic acid

Animal metabolism

The Meeting received animal metabolism studies with imazapyr in rats, lactating goats and laying hens. The metabolism and distribution of imazapyr in animals were investigated using the [^{14}C -carboxyl], [^{14}C -6-pyridine] and [^{14}C -5-imidazole]-labelled imazapyr.

Metabolism in rats was summarized and evaluated by the WHO panel of the JMPR in 2013.

Lactating goats were dosed with [pyridine-6- ^{14}C]-imazapyr as a single daily oral dosage equivalent to a dietary level of 17.7 or 42.5 ppm for 7 consecutive days. Radioactivity was mainly excreted in the urine (65.3% and 60.4%) and faeces (16.1% and 19.0%) of the dose in the 17.7 ppm and 42.5 ppm dosed goats, respectively).

The TRR levels were <0.01–0.01 mg equiv/kg and 0.01–0.02 mg equiv/kg in the milk samples of the 17.7 and 42.5 ppm dose goats, respectively. TRR levels for leg and loin muscles, liver, and fat were all less than the LOQ (0.05 mg equiv/kg) and these tissues were not analysed further. Detectable residues were found in the kidneys at 0.08 mg equiv/kg (17.7 ppm dose) and 0.11 mg equiv/kg (42.5 ppm dose).

Kidney residues were quantitatively extractable, with the majority (95.5%) isolated in a methanol/water fraction. The extracted ^{14}C residue in the milk and kidney was identified as unchanged imazapyr.

Lactating goats received [imidazole-5- ^{14}C]-imazapyr at a dose equivalent to 47 ppm in the diet once daily for 7 consecutive days. After seven days, 58.7% and 34.4% of the administered radioactive dose were excreted in the urine and faeces, respectively. The TRR levels for the dosed goat were 0.014–0.015 mg equiv/kg for milk and 0.074 mg equiv/kg for kidney.

The major component in the milk (day-7) extract (65.6% of TRR, 0.01 mg/kg) was the parent compound (imazapyr). Polar unknowns (total 14.7% of TRR) were also present in the milk extract. Since these fractions were 0.002 mg equiv/kg and contained multiple components, no further characterization was attempted. Imazapyr was the predominant radioactive residue (81.9% of TRR,

0.061 mg/kg) in the kidney. Polar unknowns (total 11.6% of TRR) were also present in the kidney extract. The concentration of the remaining radioactive components in the kidney and the milk was below 0.01 mg equiv/kg individually.

Laying hens were orally dosed with [pyridine-6-¹⁴C]-imazapyr at the actual dietary dose equivalent to 2.0 or 9.7 ppm in the feed for 7 consecutive days. The majority of the dose was rapidly eliminated in the excreta. Elimination of ¹⁴C via the excreta accounted for 90.5 and 91.7% of the total dose for the low and high dose, respectively.

During treatment, TRR in the egg samples was less than the LOQ (0.01 mg equiv/kg). Residues in skin with adhering fat, muscle, liver and kidney tissues were all less than the LOQ (0.01 mg equiv/kg). Parent compound or derived residues are excreted without retention or accumulation in eggs and edible poultry tissues.

In animal metabolism studies, imazapyr was the major component in milk and kidney of lactating goat, but no residue was found in eggs and all tissues of laying hens.

Plant metabolism

Imazapyr is used in three different situations:

- Directed sprays for weed control (crop not intentionally treated)
- Use for weed control with a crop (crop treated)
- Selective use in genetically modified imidazolinone-resistant crops (crop treated)

Plant metabolism studies were conducted with imazapyr to investigate these three situations.

The Meeting received plant metabolism studies performed on soya bean, maize, sugarcane, oil palm, clover and Bermuda grass with imazapyr [¹⁴C] labelled in two positions ([¹⁴C-3-pyridine] and [¹⁴C-6-pyridine]).

Directed sprays to weeds

In a sugar cane metabolism study, [pyridine-6-¹⁴C]-imazapyr was applied to the soil surface once as a pre-emergence application at a rate equivalent to 0.28 kg ai/ha. Stalk samples were taken at maturity approximately 14 months after the pre-emergence treatment. There were no detectable residues in the treated samples.

In an oil palm metabolism study, [pyridine-6-¹⁴C]-imazapyr was applied to the ground beneath an actively fruiting oil palm at an application rate of 1.0 kg ai/ha. Fruit samples were collected from the oil palm as they ripened at 0 hour, 7, 30 and 62 days after treatment. Palm oil was extracted from the fruits using a hexane: water mixture (3:1, v/v). Residual radioactivity levels were below the LOQ (0.03 mg equiv/kg) at any given time in the palm oil, aqueous phase, fruit marc, kernel shell and kernel nut. The results indicate that imazapyr derived residues will not accumulate in the palm oil of an actively fruiting oil palm after application to the ground beneath the palm.

Weed control

In a clover metabolism study, [pyridine-6-¹⁴C]-imazapyr was applied to clover at a rate of 1.68 kg ai/ha. Clover foliage was collected at 0, 4, 10, 15 and 21 days after treatment (DAT). Phytotoxic effects were apparent four days after application of the test material to the clover in the test plot. The phytotoxicity remained apparent until the final collection 21 days after treatment. The TRR levels in foliage ranged from 23–49 mg equiv/kg. The majority of the radioactivity was unchanged imazapyr ranging from 68–99% of TRR. The major metabolite was CL 247,087 with CL 240,000 as a minor metabolite (their sum accounting for 0.02–18% of TRR).

In a Bermuda grass metabolism study, [pyridine-6-¹⁴C]-imazapyr was applied to Bermuda grass at a rate of 1.68 kg ai/ha. Bermuda grass foliage was collected 0, 4, 10, 15 and 21 days after treatment (DAT). Phytotoxic effects were apparent four days after application of the test material to

the Bermuda grass in the test plot. The phytotoxicity remained apparent until the final collection 21 days after treatment. TRR levels in foliage were the highest at 0 DAT (64 mg equiv/kg), and then were 18 mg equiv/kg (4 DAT), 22 mg equiv/kg (10 DAT), 25 mg equiv/kg (15 DAT) and 48 mg equiv/kg (21 DAT). The majority of the radioactivity was unchanged imazapyr ranging from 78–97% of TRR. Three other identified radio-components were PDC, CL 247,087 and CL 240,000. The amount of PDC increased with time to 13% of TRR at 21 DAT. The amount of CL 247,087 plus CL 240,000 ranged from 0% to 10.5% of TRR between 4 DAT and 21 DAT.

Imidazolinone-resistant crops

In a soya bean metabolism study, [pyridine-3-¹⁴C]-imazapyr (SL formulation) was applied once to the above ground portion of transgenic soya bean plants at BBCH growth stage 65 at an application rate of 0.11 kg ai/ha. The forage was harvested approximately one hour after application and the hay was harvested 35 days after application. Soya bean straw, pods and seeds were harvested when mature at 98 days after treatment.

The TRR of soya bean forage was 0.66 mg equiv/kg, soya bean hay was 0.25 mg equiv/kg, soya bean seed was 0.062 mg equiv/kg, soya bean straw was 0.079 mg equiv/kg and soya bean pod was 0.15 mg equiv/kg. Imazapyr was detected in all matrices and was the most abundant component of the residue in soya bean forage (0.60 mg/kg, 93.6% TRR), hay (0.094 mg/kg, 37.3% TRR), and seed (0.024 mg/kg, 34.2% TRR). Imazapyr was present in straw at 0.006 mg/kg (8.1% TRR) and pods at 0.018 mg/kg (12.7% TRR). A polar component M3 was the most abundant component in the pods (0.041 mg equiv/kg, 28.9% TRR). This component was also present in hay (0.028 mg equiv/kg, 11.1% TRR), straw (0.009 mg equiv/kg, 12.2% TRR) and seeds (0.0161 mg equiv/kg, 23.3% TRR), but was not detected in forage. This polar peak was isolated from the soya bean seeds, and shown to consist of multiple components, each present at ≤ 0.004 mg equiv/kg. M19 was present in the straw at 0.013 mg equiv/kg (17.6% TRR) and was also found in hay at 0.022 mg equiv/kg (8.7% TRR). This component had an intermediate polarity with a retention time of about 19 minutes and was not identified.

In a maize metabolism study, [pyridine-6-¹⁴C]-imazapyr was applied to imidazolinone-resistant maize at the 3 to 4 leaf growth stage at treatment rates of 0.028 and 0.080 kg ai/ha. Samples of maize plants were harvested at 0 DAT (green plant), 14 DAT (green plant), 30 DAT (early forage), and 62 DAT (late forage). At maturity (114 DAT), the stalks, husks, and cobs with grain were collected.

For the 0 DAT, 96.3% (2.37 mg equiv/kg) of the TRR was extracted. For the 114 DAT fodder, 69.9% (0.020 mg equiv/kg) of the TRR was extracted and 30.1% (0.008 mg equiv/kg) remained in the PES. For the 114 DAT grain, 0.8 to 1.5% (< 0.002 mg equiv/kg) was extracted with hexane, 80.0 to 88.8% (0.023 to 0.076 mg equiv/kg) was extracted with methanol:water:hydrochloric acid (80:18:2, v/v/v), and 10.3 to 18.5% (0.005 to 0.009 mg equiv/kg) remained in the PES. Parent imazapyr constituted the major component of the extractable residue in the green plant, forage, fodder and grain (16.8 to 84.0% of extracted TRR, 0.003 to 2.0 mg/kg). The residue levels of the minor components in the 30 DAT to 114 DAT samples were all < 0.01 mg equiv/kg.

In the plant metabolism studies on soya bean (imidazolinone-resistant), maize (imidazolinone-resistant), sugarcane, oil palm, clover and Bermuda grass, Imazapyr is the major component of the residues found in soya bean, maize, clover, and Bermuda grass. CL 247,087 and PDC were also significant components of the residues in clover and Bermuda grass.

Environmental fate

The Meeting received information on aerobic soil metabolism, soil photolysis, rotational crop and hydrolysis.

In soil under the aerobic conditions, the DT_{50} ranged from 15 months to 7.5 years at 20 °C–35 °C. At 12 months after application, imazapyr remained in soil was 60.5–89.3% of the applied radioactivity. Minor degradates were identified as PDC, CL 60,032 and CL 240,000.

In soil photolysis study, there was 11% degradation of imazapyr over the 28 days of continuous irradiation. There were at least five degradation products formed, none of which accounted for > 10% of the applied dose. The photodegradation half-life of imazapyr was 149 days at 25 °C.

In confined rotational crop study, rotational crops (wheat, radish, lettuce and soya bean) were planted at 120 days after treatment (DAT) for wheat, 271 DAT for radish, lettuce and soya bean, 420 DAT for radish and lettuce. The test substance was applied as a post-emergence application to imidazolinone-resistant maize plants at the 6-leaf stage at a rate of 0.028 kg ai/ha.

The TRR in wheat forage, straw and grain; lettuce; radish foliage and root; and soya bean forage, hay, and seed were all < 0.002 mg/kg, the limit of detection of the radio assay.

A series of rotational crops, namely carrot and lettuce were planted at 330 and 540 DAT, winter wheat planted at 359 DAT, spring wheat at 520 DAT. A single application of [¹⁴C] imazapyr was made to the soil at a rate of 0.885 kg ai/ha which is 10 times the highest GAP rate for crops used in rotation.

The TRR in follow crops were at < 0.01 to 0.02 mg equiv/kg at the various plant back intervals. Residue in the rotational crops included the unchanged imazapyr which ranged from < 0.001 to 0.003 mg/kg. Metabolites were not detected (< 0.001 mg/kg). The Meeting noted that residues are not expected on rotational crops.

Imazapyr is used for paddy rice. In a hydrolysis study, imazapyr was stable in water (pH 5, 7 and 9) at 25 °C.

Methods of analysis

The Meeting received description and validation data for analytical methods for residues of imazapyr in plant and animal commodities.

In most of the methods for determination of imazapyr in plants, homogenized samples were extracted with acidic aqueous methanol or acidic aqueous acetone, and the extract was cleaned up with column chromatography using solid phase extraction and/or strong cation exchange cartridges. Residues were determined by HPLC with UV or MS/MS detection. The methods of analysis for a range of substrates were validated with LOQs of the 0.05 mg/kg for imazapyr.

In the methods for animal commodities, homogenized samples were extracted with acidic solvent, and the extract was cleaned up by solvent partition and solid phase extraction. Residue of imazapyr was determined by capillary electrophoresis with UV detection. The methods of analysis were validated with the LOQ of 0.01 mg/kg for milk and milk fat, and 0.05 mg/kg for tissues of cattle.

No multi-residue method was submitted.

Stability of residues in stored analytical samples

The Meeting received information on the freezer storage stability of imazapyr in plant (maize grain, forage and fodder and soya bean seed), their processed (soya bean meal and oil) commodities and animal products.

Storage stability results indicate that imazapyr residue was stable for at least 3 months in soya bean (seed, laminated soya bean, meal and oil), at least 6 months in milk, at least 8 months in muscle and liver, and at least 27 months in maize (grain, forage and fodder).

The periods of storage stability studies generally cover the sample storage intervals of residue trials.

Definition of the residue

In the lactating goat metabolism studies, TRRs in kidney (0.074–0.11 mg equiv/kg) was higher than those in milk (< 0.01–0.02 mg equiv/kg), liver (< 0.05 mg equiv/kg), muscle (< 0.05 mg equiv/kg) and fat (< 0.05 mg equiv/kg). Imazapyr is the major component of the residue in kidney (82% TRR)

and milk (67% TRR). The concentration of the remaining radioactive components in the kidney and milk were below 0.01 mg/kg.

The Meeting decided that imazapyr is suitable analytes for enforcement purposes and dietary risk assessment in animal commodities.

The octanol/water coefficient ($\log P_{ow}$) of imazapyr is -3.96 at $20\text{ }^{\circ}\text{C}$ (pH 7). The Meeting considered the residue of imazapyr is not fat soluble.

In plant metabolism studies, parent imazapyr was a major component (8.1–99% TRR) in soya bean (forage, hay, seed, straw and pods), maize (forage, grain and fodder), clover and Bermuda grass. Imazapyr was a major compound in conventional and tolerant crops. Though PDC was found as a significant compound in Bermuda grass (13% TRR) which is a feed commodity, it may not be necessary to consider this compound for the definition of residue for food commodities.

The Meeting decided that parent imazapyr is a suitable analyte for enforcement purposes and dietary risk assessment in plant commodities.

The Meeting recommended the following residue definition:

For plants and animals the definition of the residue (for compliance with the MRL and for estimation of dietary intake): *Imazapyr*

The residue is not fat soluble

Results of supervised residue trials on crops

The Meeting received supervised trial data for the foliar application of imazapyr on lentil, soya bean, maize, rice, wheat, sugar cane, rape and sunflower. Residue trial data was made available from Argentina, Australia, Brazil, Canada, Uruguay and the USA.

Labels were available from Australia, Canada, Latin American countries and the USA describing the registered uses of imazapyr.

Pulses

Lentil (dry)

Data were available from supervised trials on imidazolinone-tolerant lentils in Canada.

The GAP on imidazolinone-tolerant lentil of Canada is a foliar application at a maximum rate of 0.0091 kg ai/ha with a PHI of 60 days.

Imazapyr residues in lentil seeds from independent trials in Canada matching GAP were (n=4): 0.06 (2) and 0.08 (2) mg/kg.

Based on the trials for lentils in Canada, the Meeting estimated a maximum residue level and an STMR value for imazapyr in lentil seeds of 0.3 and 0.07 mg/kg respectively.

Soya bean (dry)

Data were available from supervised trials on imidazolinone-tolerant soya beans in Brazil.

No GAP of Brazil was available for imidazolinone-tolerant soya beans.

The Meeting agreed that no recommendation could be made for soya beans.

Cereal grains

Maize

Data were available from supervised trials on imidazolinone-tolerant maize in Argentina, Brazil, Australia and the USA.

The GAP on imidazolinone-tolerant maize of Argentina is a foliar application at a maximum rate of 0.025 kg ai/ha with the application timing before reaching 6th fully developed leaf status.

Imazapyr residues in maize grains from trials in Argentina matching GAP were (n=7): < 0.05 (7) mg/kg.

Trials from Australia on maize were reported for a foliar application of a SL formulation (GAP: a foliar application at a rate of 0.018–0.022 kg ai/ha with a PHI not required when used as directed at the application timing of 2–6 leaf stage for crop). Imazapyr residue in maize grains from data in Australia at exaggerated rate of 0.032 kg ai/ha ($1.5 \times$ GAP rate) were < 0.05 (2) mg/kg and 0.048 kg ai/ha ($2.2 \times$ GAP rate) were < 0.05 (2) mg/kg.

The GAP on imidazolinone-tolerant maize of the USA is a foliar application at a maximum rate of 0.016 kg ai/ha with a PHI of 45 days at the application timing of before 6 leaf stage for crop. However, imazapyr residue trials on maize in the USA did not match the GAP of the USA.

The Meeting decided to use the data of imazapyr residues in maize grain from the trials in Argentina.

Based on the trials for maize in Argentina, the Meeting estimated a maximum residue level, an STMR value for imazapyr in maize of 0.05 (*) and 0.05 mg/kg respectively.

Rice

Data were available from supervised trials on imidazolinone-tolerant paddy rice in Brazil.

The GAP on imidazolinone-tolerant rice of Brazil is two foliar applications at a maximum rate of 0.074 kg ai/ha with a PHI of 60 days.

Trials from Brazil on rice were reported for two foliar applications at a rate of 0.12 kg ai/ha with a PHI of 60 days. Imazapyr residues in rice grains from trials at a rate of 0.12 kg ai/ha in Brazil were (n=4): < 0.05 (3) and 0.05 mg/kg. However, the trials for rice in Brazil were insufficient to estimate a maximum residue level for the commodity.

The Meeting could not estimate a maximum residue level for imazapyr in rice.

Wheat

Data were available from supervised trials on imidazolinone-tolerant wheat in Australia.

The GAP on imidazolinone-tolerant wheat of Australia is a foliar application at a rate of 0.004–0.007 kg ai/ha with a PHI not required for wheat grains when used as directed.

Imazapyr residues in wheat grains from trials in Australia matching GAP were (n=3): < 0.05 (3) mg/kg. Imazapyr residues in wheat grains from data in Australia at exaggerated rate of 0.014 kg ai/ha ($2 \times$ GAP rate) were < 0.05 (5) mg/kg and 0.028 kg ai/ha ($4 \times$ GAP rate) were < 0.05 (5) mg/kg.

Based on the trials for wheat in Australia, the Meeting estimated a maximum residue level and an STMR value for imazapyr in wheat grains of 0.05 (*) and 0 mg/kg respectively.

Grasses for sugar or syrup production

Sugar cane

Data were available from supervised trials on sugar cane in Argentina and Brazil.

The GAP on sugar cane of Argentina is two applications with spray to weeds at a maximum rate of 0.5 kg ai/ha with 30–45 days before planting. The GAP on sugar cane of Brazil is an application with spray to weeds of a rate of 0.13–0.5 kg ai/ha with a PHI not required when used as directed.

Imazapyr residue in sugar cane from trials in Argentina matching GAP was (n=1): < 0.05 mg/kg. However, the trial for sugar cane in Argentina was insufficient to estimate a maximum residue level for the commodity.

The Meeting could not estimate a maximum residue level for imazapyr in sugar cane.

Oilseed

Rape seed

Data were available from supervised trials on imidazolinone-tolerant rape in Australia and Canada.

The GAP on imidazolinone-tolerant rape of Canada is a foliar application at a maximum rate of 0.0091 kg ai/ha with a PHI of 60 days.

Imazapyr residues in rape seeds from independent trials in Canada matching GAP were (n=10): < 0.05 (10) mg/kg.

Trials from Australia on rape were reported for a foliar application of a WG formulation (GAP: a foliar application at a rate of 0.0045–0.011 kg ai/ha with a PHI not required when used as directed).

Imazapyr residues in rape seeds from trials in Australia matching GAP were (n=2): < 0.05 (2) mg/kg. Imazapyr residues in rape seeds from data in Australia at an exaggerated rate of 0.028 kg ai/ha ($2.3 \times$ GAP rate) were < 0.05 (2) mg/kg.

Based on the trials for rape seeds in Canada and Australia, the Meeting estimated a maximum residue level, an STMR value for imazapyr in rape seed of 0.05 (*) and 0 mg/kg respectively.

Sunflower seed

Data were available from supervised trials on imidazolinone-tolerant sunflower in Argentina and Uruguay.

The GAP on imidazolinone-tolerant sunflower of Argentina and Uruguay is a foliar application at a maximum rate of 0.080 kg ai/ha with the application timing of early post emergence.

Imazapyr residues in sunflower seeds from trials in Argentina and Uruguay approximating GAP were (n=15): < 0.01 (10), 0.01, 0.03 (2) and < 0.05 (2) mg/kg.

Based on the trials for sunflower in Argentina and Uruguay, the Meeting estimated a maximum residue level and an STMR value for imazapyr in sunflower seed of 0.08 and 0.01 mg/kg respectively.

Animal feedstuffs

Maize fodder and forage

Data were available from supervised trials on imidazolinone-tolerant maize in Argentina, Australia and the USA.

Trials from Argentina on maize forage were reported for the foliar application of SC or WG formulation (GAP: a foliar application of a maximum rate of 0.025 kg ai/ha, the application timing before reaching 6th fully developed leaf status).

Trials from Australia on maize forage were reported for the foliar application of a SL formulation (GAP: a foliar application of a rate of 0.018–0.022 kg ai/ha at the application timing of 2–6 leaf stage for crop, do not graze or cut for stock food for 4 weeks after application and not required to harvest for grains when used directed).

Trials from the USA on maize fodder and forage were reported for the foliar application of ASU or WP formulation at a rate of 0.027 kg ai/ha (GAP: a foliar application of a maximum rate of 0.016 kg ai/ha, PHI of 45 days at the application timing of before 6 leaf stage for crop).

Maize fodder

In the residue trials for imazapyr on maize fodder in the USA, no samples were collected on 45 days after application. The Meeting could not estimate a maximum residue level for imazapyr in maize fodder.

Maize forage

Imazapyr residues in maize forage from trials in Argentina matching GAP were (n=4): < 0.05 (4) mg/kg as received basis. Imazapyr residues in maize forage from data in Argentina at exaggerated rate of 0.040 kg ai/ha ($1.6 \times$ GAP rate) were < 0.05 (4) mg/kg and 0.050 kg ai/ha ($2 \times$ GAP rate) were < 0.05 (4) mg/kg.

Imazapyr residues in maize forage from data in Australia at exaggerated rate of 0.032 kg ai/ha ($1.5 \times$ GAP rate) were < 0.05 (2) mg/kg and 0.048 kg ai/ha ($2.2 \times$ GAP rate) were < 0.05 (2) mg/kg.

Imazapyr residues in maize forage from trials in the USA at exaggerated rate of 0.027 kg ai/ha ($1.7 \times$ GAP rate) were < 0.05 (18) mg/kg as received basis.

Based on the residues in maize forage from trials in Argentina, Australia and the USA, the Meeting estimated a median residue value and a highest residue value for imazapyr in maize forage both at 0 mg/kg.

Wheat straw and forage

Data were available from supervised trials on imidazolinone-tolerant wheat in Australia.

Trials from Australia on wheat were reported for the foliar application of a SL formulation (GAP: a foliar application of a rate of 0.004–0.007 kg ai/ha, do not graze or cut for stock food for 4 weeks after application and not required to harvest for grains when used directed).

Wheat straw

Imazapyr residues in wheat straw from trials in Australia matching GAP were (n=3): < 0.05 (3) mg/kg as received basis. Imazapyr residues in wheat straw from data in Australia at exaggerated rate of 0.014 kg ai/ha ($2 \times$ GAP rate) were < 0.05 (5) mg/kg and 0.028 kg ai/ha ($4 \times$ GAP rate) were < 0.05 (5) mg/kg.

Based on the residues in wheat straw from trials in Australia, the Meeting estimated a maximum residue level, a median residue value and a highest residue value for imazapyr in wheat straw and fodder of 0.05 (*), 0 and 0 mg/kg respectively.

Wheat forage

Imazapyr residues in wheat forage from trials in Australia matching GAP were (n=3): < 0.05 (3) mg/kg as received basis. Imazapyr residues in wheat forage from data in Australia at exaggerated rates of 0.014 kg ai/ha ($2 \times$ GAP rate) were < 0.05 (5) and 0.087 mg/kg, and 0.028 kg ai/ha ($4 \times$ GAP rate) were < 0.05 (5) and 0.11 mg/kg as received basis.

Based on the residues in wheat forage from trials in Australia, the Meeting estimated a median residue value and a highest residue value for imazapyr in wheat forage both at 0.05 mg/kg.

Rape forage

Data were available from supervised residue trials on imidazolinone-tolerant rape in Australia.

Trials from Australia on rape were reported for the foliar application of a WG formulation (GAP: a foliar application of a rate of 0.005–0.012 kg ai/ha, do not graze or cut for 5 weeks).

Imazapyr residues in rape forage from trials in Australia matching GAP were (n=1): < 0.05 mg/kg. Imazapyr residues in rape forage from data in Australia at an exaggerated rate of 0.028 kg ai/ha ($2.3 \times$ GAP rate) or at DALA 25–29 days were < 0.05 (4) mg/kg.

Based on the residues in rape forage from trials in Australia, the Meeting estimated a median residue value and a highest residue value for imazapyr in rape forage both at 0 mg/kg.

Fate of residues during processing

High temperature hydrolysis

The degradation of [¹⁴C] imazapyr was studied under hydrolytic conditions at high temperatures in sterile aqueous buffers at pH 4, 5 and 6 for periods of up to 60 minutes so as to simulate common processing practice (pasteurization, baking/brewing/boiling, and sterilization). No degradates were detected at any of the investigated pH and temperature ranges. Imazapyr is stable under hydrolytic conditions at high temperatures.

Residues in processed commodities

The fate of imazapyr residues has been examined in maize grains, rape seeds and sunflower seeds processing studies. Based on the results of processing studies conducted in Canada and the USA in combination with the residues from supervised trials, the Meeting concluded that no residues are expected in processed rape and sunflower commodities. Estimated processing factors and the derived STMR-Ps are summarized in the Table below.

Processing factors, STMR-P and HR-P for food and feed

Raw agricultural commodity (RAC)	Processed commodity	Calculated processing factors*	PF (Mean or best estimate)	RAC STMR (mg/kg)	STMR-P (mg/kg)
Maize grain	Meal	1.2	1.2	0.05	0.06
	Crude oil	< 0.50	< 0.50		0.025

* Each value represents a separate study. The factor is the ratio of the residue in processed commodity divided by the residue in the RAC.

Residue in animal commodities

Farm animal dietary burden

The Meeting estimated the dietary burden of imazapyr in farm animals on the basis of the diets listed in Appendix IX of the FAO Manual 2009. Calculation from highest residue, STMR (some bulk commodities) and STMR-P values provides levels in feed suitable for estimating MRLs, while calculation from STMR and STMR-P values for feed is suitable for estimating STMR values for animal commodities. The percentage dry matter is taken as 100% when the highest residue levels and STMRs are already expressed in a dry weight basis.

Estimated maximum and mean dietary burdens of farm animals

Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are provided in Appendix IX of the FAO manual. The calculations were made according to the animal diets from US-Canada, EU, Australia and Japan in the Table (Appendix IX of the FAO manual).

Livestock dietary burden, imazapyr, ppm of dry matter diet								
	US-Canada		EU		Australia		Japan	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	0.063	0.063	0.085	0.085	0.20 ^a	0.20 ^b	0.061	0.061
Dairy cattle	0.083	0.083	0.057	0.057	0.15	0.15 ^c	0.045	0.045
Poultry—broiler	0.056d	0.056e	0.040	0.040	0.014	0.014	0.040	0.040
Poultry—layer	0.056	0.056	0.073 ^d	0.073 ^c	0.014	0.014	0.045	0.045

^a Highest maximum beef cattle dietary burden suitable for MRL estimates for mammalian meat, fat, edible offal and milk

^b Highest mean beef cattle dietary burden suitable for STMR estimates for mammalian meat, fat and edible offal

^c Highest mean dairy cattle dietary burden suitable for STMR estimates for milk

^d Highest maximum broiler poultry dietary burden suitable for MRL estimates for poultry meat, fat, edible offal and eggs

^c Highest mean broiler poultry dietary burden suitable for STMR estimates for poultry meat, fat, edible offal and eggs

Farm animal feeding studies

The Meeting received a lactating dairy cow feeding studies using imazapyr, which provided information on likely residues resulting in animal commodities and milk from imazapyr residues in the animal diet.

A poultry feeding study was not submitted as the expected residues of imazapyr in poultry feed were extremely low. A poultry metabolism study at a dose rate of 9.7 ppm imazapyr in feed demonstrated that there was very low transfer to eggs and tissues with all residues of imazapyr less than 0.01 mg/kg.

Lactating dairy cows

Lactating dairy cows were dosed with imazapyr for 28–29 days at the dose equivalent to 58, 157, 607 and 1680 ppm in the diet. Residues of imazapyr were at or less than the LOQ (0.01 mg/kg) in whole milk at 58 ppm of feeding level. In the three higher dose groups (157, 607 and 1680 ppm feed), imazapyr residues in milk reached a plateau after 2–3 days. In kidney, imazapyr was detected as the highest concentrations among all tissues and milk in all treated groups.

Animal commodities maximum residue levels

For MRL estimation, the residue in the animal commodities is imazapyr.

The maximum dietary burden for beef and dairy cattle is 0.20 and is lower than the dose level in the lactating goat metabolism study of 18 ppm and the lactating cow feeding study of 58 ppm. In the metabolism study, in which imazapyr equivalent to 18 ppm in the diet was dosed to lactating goats for 7 consecutive days, residues of imazapyr were detected at 0.01 mg/kg in milk and 0.08 mg/kg in kidney. The maximum dietary burden for beef and dairy cattle is 1% of the dose rate in feed of the metabolism study.

The Meeting estimated a maximum residue level of 0.01 (*) mg/kg and an STMR value of 0 mg/kg in milk.

The Meeting estimated a maximum residue level of 0.05 (*) mg/kg, an STMR value of 0 mg/kg and an HR value of 0 mg/kg in mammalian meat and fat.

The Meeting estimated a maximum residue level of 0.05 (*) mg/kg, an STMR value and an HR value of 0.0008 in mammalian edible offal.

The maximum dietary burden for broiler and layer poultry is 0.073 and is lower than the dose level in the laying hen metabolism study of 9.7 ppm. In the metabolism study, in which imazapyr equivalent to 9.7 ppm in the diet was dosed to laying hens for 7 consecutive days, no residues of imazapyr exceed 0.01 mg/kg were detected in tissues and eggs.

The Meeting estimated a maximum residue level of 0.01 (*) mg/kg, an STMR value of 0 mg/kg and an HR value of 0 mg/kg in poultry meat, fat, edible offal and eggs.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue levels listed below are suitable for estimating maximum residue limits and for IEDI and IESTI assessment.

Plant and animal commodities:

Definition of the residue for plant commodities (for compliance with the MRL and for estimation of dietary intake): *Imazapyr*

The residue is not fat soluble.

Commodity		Recommended MRL, mg/kg	STMR or STMR-P, mg/kg	HR or HR-P, mg/kg
CCN	Name	New		
MO 0105	Edible offal (Mammalian)	0.05*	0.0008	
PE 0112	Eggs	0.01*	0	
VD 0533	Lentil (dry)	0.3	0.07	
GC 0645	Maize	0.05*	0.05	
MF 0100	Mammalian fats (except milk fats)	0.05*	0	
MM 0095	Meat (from mammals other than marine mammals)	0.05*	0	
ML 0106	Milks	0.01*	0	
PO 0111	Poultry, Edible offal of	0.01*	0	
PF 0111	Poultry fats	0.01*	0	
PM 0110	Poultry meat	0.01*	0	
SO 0495	Rape seed	0.05*	0	
SO 0702	Sunflower seed	0.08	0.01	
GC 0654	Wheat	0.05*	0	
AS 0654	Wheat straw and fodder, dry	0.05*	0	0

* At or about the LOQ.

Commodity Name	STMR or STMR-P, mg/kg	HR or HR-P, mg/kg
Maize forage	0	0
Maize meal	0.06	
Maize oil	0.025	
Rape forage	0	0
Wheat forage	0.05	0.05

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDIs) of imazapyr were calculated for the 13 GEMS/Food cluster diets using STMRs/STMR-Ps estimated by the current Meeting (Annex 3). The ADI is 0–3 mg/kg bw and the calculated IEDIs were 0% of the maximum ADI (3 mg/kg bw). The Meeting concluded that the long-term intakes of residues of imazapyr, resulting from the uses considered by current JMPR, are unlikely to present a public health concern.

Short-term intake

The 2013 JMPR decided that an ARfD is unnecessary. The Meeting therefore concluded that the short-term intake of residues of imazapyr is unlikely to present a public health concern.

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2010/1127505	Jones, B & Takahashi, J	2011	Study of residues of Imazapyr and Imazapic in cultivance soya bean (grains) after treatment with BAS 714 01 H under field conditions in Brazil, BASF SA, Guaratingueta, Brazil, GLP, Unpublished
2012/3000423	Jones, B & Cardoso, B	2012	Residue study of Imazapyr and Imazapic in GMO soya bean grains and aspirated grain fraction (AGF) after treatment with BAS 714 01 H under

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IZ-731-001	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Michigan 1993, American Cyanamid Co., Princeton NJ, USA. IZ-731-001, GLP, Unpublished
IZ-731-002	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Iowa 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-003	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Wisconsin 1993. American Cyanamid Co., Princeton NJ, USA. IZ-731-003, GLP, Unpublished
IZ-731-004	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in North Carolina 1993. American Cyanamid Co., Princeton NJ, USA. IZ-731-004, GLP, Unpublished
IZ-731-005	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Michigan 1994. American Cyanamid Co., Princeton NJ, USA. IZ-731-005, GLP, Unpublished
IZ-731-006	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Ohio 1994, American Cyanamid Co., Princeton NJ, USA. IZ-731-006, GLP, Unpublished
IZ-731-007	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in South Dakota 1993, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-008	Mahl, T.	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Texas 1994, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-009	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Indiana 1994., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-010	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Illinois 1994., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-011	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Nebraska processing study 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-012	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Illinois 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-013	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue with AC 243,997 on field corn in Missouri 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-014	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Minnesota 1994., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-015	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Iowa 1994., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-016	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Indiana 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-017	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Ohio 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-018	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Nebraska 1994., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-021	Steling, C	1998	CL 243,997: Determination of CL 243,997 residues in corn samples from Argentina, LAADL—Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished
1995/7004189	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 in field corn in Pennsylvania 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
2000/1023965	Anonymous	2000	Application for registration of the new combination end-use product, Lightning herbicide—Part 5A—Residue studies, Cyanamid Agriculture Pty. Ltd., Baulkham Hills New South Wales 2153, Australia, Unpublished

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1999/7004026	Steling, C	1999	CL 243,997: Determination of CL 243,997 residues in corn plant from Argentina, LAADL—Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished
2002/3001461	Borges, Z	2002	Estudo de residuo de Imazapyr (BAS 693 H) em milho (grao) do Brasil. LARAL - Laboratorio Agro de Residuos da America Latina, Resende, Brazil, GLP, Unpublished
2002/3001462	Borges, Z	2002	Estudo de residuo de Imazapyr (BAS 693 H) em milho do Brasil. LARAL—Laboratorio Agro de Residuos da America Latina, Resende, Brazil, GLP, Unpublished
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1998/3002021	Steling, C	1998	CL 243,997: Determination of CL243,997 (Imazapyr) in corn samples from Argentina, Cyanamid Quimica do Brasil Ltda., Rio de Janeiro, Brazil, GLP, Unpublished
2003/3001441	Dantas, C	2003	Estudo de residuo de Imazapyr em arroz (grao) apos tratamento com Kifix (BAS 714 01 H) no Brasil, LARAL—Laboratorio Agro de Residuos da America Latina, Resende, Brazil, GLP, Unpublished
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IZ-790-015	Steling, C	1998	CL 243,997: Determination of CL 243,997 residues in sugar cane samples from Argentina, LAADL—Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished
IZ-790-017	Steling, C	1998	CL 243,997: Determination of CL 243,997 (Imazapyr) in sugar cane samples from Brazil, LAADL—Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished
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2010/1057139	Freitas Guimaraes, S	2010	Study of Imazapyr and Imazamox residues in sunflower (seed), after treatment with Sweeper 70 DG and Clearsol DF, under field conditions in Argentina, BASF SA, Guaratingueta, Brazil, GLP, Unpublished
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2002/3000641	Borges, Z	2002	Determination of Imazapyr (BAS 693 H) residues in sunflower (seed and flower) samples from Argentina, LARAL - Laboratorio Agro de Residuos da America Latina, Resende, Brazil, GLP, Unpublished
2012/7000183	Carringer, SJ	2012	Magnitude of the residues of Imazapyr and Imazamox in or on sunflower raw agricultural commodities following one foliar application of BAS 723 00 H, The Carringers Inc., Apex NC, United States of America, GLP, Unpublished
2012/7000341	Osterman, B & Chu, J	2012	High temperature hydrolysis of 14C-BAS 693 H (Imazapyr) at 90 °C, 100 °C, and 120 °C, PTRL West Inc., Hercules CA, USA, GLP, Unpublished
2009/7000088	Resende, G	2009	Study of residues of Imazapyr in soya bean cultivance (grain) and processed fractions (meal, oil, and flaked soya bean) after treatment with BAS 693 02 H, under field conditions in Brazil, BASF SA, Guaratingueta, Brazil, GLP, Unpublished
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2002/5004111	Johnston, R	2003	Study of residues of Imazapyr and Imazapic in soya bean cultivance (grains) and processed fractions (meal, oil, laminated soya bean and hulls), after treatment with BAS 714 01 H under field conditions in Brazil, BASF SA, Guaratingueta, Brazil, GLP, Unpublished
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IZ-705-001	Khunachak, A	1999	The magnitude of Imazamox and Imazapyr residues in Clearfield canola and Clearfield canola processed fractions following application of BAS 723 00 H, BASF Agricultural Research Center, Research Triangle Park NC, USA, GLP, Unpublished
1989/7002428	Peevey, R	1989	Arsenal (Imazapyr-CL 243997): Magnitude of CL 243997 in milk, milk fat, and edible tissues from dairy cattle after oral administration for at least 28 days, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
1990/7001949	Mangels, G	1990	Storage stability analysis of Imazapyr (AC 243,997) and Imazethapyr (AC 263,499) in Event AS plant growth regulator. American Cyanamid Co., Princeton NJ, USA, Unpublished
1990/7001950	Mangels, G	1990	Phase 3 summary of MRID 00131617 (ACC. #251505)—Arsenal herbicide (AC 243,997): Photolysis of ¹⁴ C-labeled CL 243,997 in aqueous media, American Cyanamid Co., Princeton NJ, USA, Unpublished
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1999/7004025	Steling, C	1999	CL 243,997: Determination of CL 243,997 in corn samples from Argentina, LAADL—Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished

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2001/1024893	Werle, H <i>et al.</i>	2001	AC 243997: BAS 693 H: Imazapyr. (BioChem): Determination of physico-chemical properties: appearance (color, physical state, odor), melting point, boiling point, density. (Siemens): Determination of thermal stability, BASF Agro Research, Research Triangle Park NC, USA, GLP, Unpublished
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2003/3001441	Dantas, C	2003	Estudo de residuo de Imazapyr em arroz (grao) apos tratamento com Kifix (BAS 714 01 H) no Brasil, LARAL—Laboratorio Agro de Residuos da America Latina, Resende, Brazil, GLP, Unpublished
2003/3001441	Dantas, C	2003	Estudo de residuo de Imazapyr em arroz (grao) apos tratamento com Kifix (BAS 714 01 H) no Brasil, LARAL—Laboratorio Agro de Residuos da America Latina, Resende, Brazil, GLP, Unpublished
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2007/1065864	Jones, B	2007	Estudo de residuos de Imazapyr em soja cultivance (graos) apos tratamento com BAS 693 02 H, em condicoes de campo no Brasil. BASF SA, Guaratingueta, Brazil, GLP, Unpublished
2008/1097470	Resende, G & Souza C	2008	Amendment report 01 RF-1088-06—Study of residues of Imazapyr and Imazapic in soya bean cultivance (grains) after treatment with BAS 714 01 H, under field conditions in Brazil, BASF SA, Guaratingueta, Brazil, GLP, Unpublished
2008/1097471	Resende, G	2008	Amendment report 02 RF-1088-06—Study of residues of Imazapyr and Imazapic in soya bean cultivance (grains) after treatment with BAS 714 01 H, under field conditions in Brazil, BASF SA, Guaratingueta, Brazil, GLP, Unpublished

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2008/1097473	Dantas, C	2008	Adendo 01 RF-1089-06—Estudo de residuos de Imazapyr em soja cultivance (graos) apos tratamento com BAS 693 02 H, em condicoes de campo no Brasil, BASF SA, Guaratingueta, Brazil, GLP, Unpublished
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2008/7019225	Norris, FA	2009	The magnitude of Imazamox and Imazapyr residues in Clearfield sunflower and Clearfield sunflower processed fractions following application of BAS 723 00 H, BASF Agricultural Research Center, Research Triangle Park NC, USA, GLP, Unpublished
2008/7019226	Norris, F	2009	The magnitude of Imazamox and Imazapyr residues in Clearfield lentils following application of BAS 723 00 H, BASF Agricultural Research Center, Research Triangle Park NC, USA, GLP, Unpublished
2008/7019227	Norris, FA	2009	The magnitude of Imazamox and Imazapyr residues in Clearfield canola and Clearfield canola processed fractions following application of BAS 723 00 H, BASF Agricultural Research Center, Research Triangle Park NC, USA, GLP, Unpublished
2008/7019227	Norris, FA	2009	The magnitude of Imazamox and Imazapyr residues in Clearfield canola and Clearfield canola processed fractions following application of BAS 723 00 H, BASF Agricultural Research Center, Research Triangle Park NC, USA, GLP, Unpublished
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2009/7000088	Resende, G	2009	Study of residues of Imazapyr in soya bean cultivance (grain) and processed fractions (meal, oil, and flaked soya bean) after treatment with BAS 693 02 H, under field conditions in Brazil, BASF SA, Guaratingueta, Brazil, GLP, Unpublished
2009/7000089	Resende, G	2009	Study of residues of Imazapyr and Imazapic in soya bean cultivance (grains) and processed fractions (meal, oil and flaked soya bean) after treatment with BAS 714 01 H, under field conditions in Brazil. BASF SA, Guaratingueta, Brazil, GLP, Unpublished
2010/1010261	Resende, G & Marinho, E	2010	Study of residues of Imazapyr and Imazapic in soya bean cultivance (grains) after treatment with BAS 714 01 H under field conditions in Brazil for import tolerance, BASF SA, Guaratingueta, Brazil, GLP, Unpublished
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2011/3005983	Leite, R	2011	Amendment 01: Study of residues of Imazapyr and Imazapic in soya bean cultivance (grains) and processed fractions (meal, oil and flaked soya bean) after treatment with BAS 714 01 H, under field conditions in Brazil, BASF SA, Guaratingueta, Brazil, GLP, Unpublished
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2012/7000183	Carringer, SJ	2012	Magnitude of the residues of Imazapyr and Imazamox in or on sunflower raw agricultural commodities following one foliar application of BAS 723 00 H, The Carringers Inc., Apex NC, United States of America, GLP, Unpublished
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IZ-244-005	Fletcher, JS	1995	CL 243,997: Independent laboratory validation of GC/MS method M 2468 for the determination of CL 243,997 residues in corn grain, forage and fodder. American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-244-006	Fletcher, JS & Khunachak, A	1995	CL 243,997: Extractability and accountability of CL 243,997 residues in corn grain and plant, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-244-008	Fletcher, JS	1996	CL 243,997: Independent laboratory validation of CE method M 2657 for the determination of CL 243,997 residues in corn grain, forage and fodder, American Cyanamid Co., Princeton NJ, United States of America, GLP, Unpublished
IZ-244-009	Stout, SJ <i>et al.</i>	1996	Rapid determination of Imazapyr in corn by gas chromatography/mass spectrometry with electron capture negative ion chemical ionization, JAOAC International 1966.
IZ-245-003	Fletcher, JS	1997	Imazapyr (CL 243997): Capillary electrophoresis (CE) determinative and LC/MS confirmatory method for CL 243997 residues in milk. American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-245-004	Bixler, TA & Khunachak, A	1999	CL243997 (Imazapyr): Independent laboratory validation of capillary electrophoresis (CE) determinative and LC/MS confirmatory method M 3184 for CL 243997 residues in cattle tissues (muscle, liver, kidney and fat), American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-245-007	Bixler, TA & Khunachak, A	1999	CL 243997 (Imazapyr): Independent laboratory validation of capillary electrophoresis (CE) determinative and LC/MS confirmatory method M 3223 for CL 243997 residues in bovine milk fat, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-245-009	Sweeney, RA. &	1999	CL 243997 (Imazapyr): Independent laboratory validation of CE

Code	Author	Year	Title, Institution, Report reference
	Fletcher, JS		method M 3075 for the determination of residues of CL 243997 in milk. American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-245-010	Fletcher, JS	1999	CL 243997 (Imazapyr): Independent laboratory validation of CE method M 3075 for the determination of residues of CL 243997 in milk (Report Amendment #1), American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-301-016	Anonymous	1985	Summary of Arsenal herbicide technical - Physical and chemical properties, Unpublished
IZ-306-001	Mangels, G	1986	Arsenal herbicide (AC 243,997): Determination of the vapor pressure. American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-311-001	Mangels, G	1986	AC 243,997: The determination of the water solubility. American Cyanamid Co., Princeton NJ, USA, Unpublished
IZ-312-001	Teeter, D	1990	Imazapyr (CL 243,997): Determination of the solubility in organic solvents, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-315-001	Reichert, B	1983	Herbicide AC 243,997: Determination of the partition coefficient in n-Octanol/water. American Cyanamid Co., Princeton NJ, USA, Unpublished
IZ-315-002,	Daum, A	2001	Determination of the partition coefficient (n-octanol/water) of Imazapyr (BAS 693 H, Reg.No. 172267 identical with CL# 243997) at 20 °C by flask shaking method, BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany, GLP, Unpublished
IZ-326-004	Fletcher, JS	1997	CL 243,997: Freezer stability of residues of CL 243,997 in corn commodities (grain, forage and fodder). American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-326-010	Khunachak, A & Naumann, LN	1999	Freezer storage stability of CL 243997 residues in bovine milk. American Cyanamid Co., Princeton NJ, USA. IZ-326-010, GLP, Unpublished
IZ-326-011	Bixler, TA & Khunachak, A	1999	CL 243997 (Imazapyr): Freezer storage stability of CL 243997 residues in cattle tissues (muscle and liver), American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-390-005	Daum, A	2001	Determination of the dissociation constant of Imazapyr (BAS 693 H, Reg.No. 172267 identical with CL 243997) in water 20 °C by UV spectrophotometric method, BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany, GLP, Unpublished
IZ-440-001	Mallipudi, NM	1983	Herbicide AC 243,997: The absorption, excretion, tissue residues and metabolism of Carboxyl Carbon-14 labeled AC 243,997 [Nicotinic acid, 2-(4-Isopropyl-4-methyl-5-oxo-imadazolin-2-yl)-] in the rat. American Cyanamid Co., Princeton NJ, USA, Unpublished
IZ-440-002	Mallipudi, NM	1992	CL 243,997: Carbon-14 CL 243,997-derived residues in blood, milk and edible tissues of lactating goats. XenoBiotic Laboratories Inc., Princeton NJ, USA, GLP, Unpublished
IZ-440-003	Tsalta, C	1995	CL 243,997: Metabolic fate of (¹⁴ C) CL 243,997 in tissues and eggs of the laying hen, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-440-004	Wu, D	1994	CL 243,997: Rat metabolism study. XenoBiotic Laboratories Inc., Plainsboro NJ, USA, GLP, Unpublished
IZ-440-005	Tsalta, C	2000	CL 243997: Metabolism of [14C]-CL 243997 in the lactating goat. American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-620-001	Mallipudi, M	1983	Arsenal herbicide (AC 243,997): Aerobic soil metabolism of carboxyl carbon-14 labeled AC 243,997 [Nicotinic acid, 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-] in sandy loam soil. American Cyanamid Co., Princeton NJ, USA. IZ-620-001, Unpublished
IZ-620-002	Mallipudi, M	1985	Arsenal herbicide (AC 243,997): A laboratory aerobic soil metabolism of Carboxyl carbon-14 labeled AC 243,997 [Nicotinic acid, 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-] in clay loam soil. American Cyanamid Co., Princeton NJ, USA. IZ-620-002, Unpublished
IZ-620-010	Mangels, G	1986	AC 243,997: Soil photolysis. American Cyanamid Co., Princeton NJ, USA. IZ-620-010, Unpublished
IZ-620-036	Tollackson, LG	1988	Aerobic soil metabolism of 13C-14C-AC 243,997 in sandy loam soil at 1.50 ppm concentration at 35 °C. ABC—Analytical Bio-Chemistry Laboratories Inc., Columbia MO, USA, IZ-620-036, GLP, Unpublished
IZ-620-037	Tollackson, LG	1988	Aerobic soil metabolism of 13C-14C-AC 243,997 in sandy loam soil at 1.50 ppm ppm concentration at 25°C, ABC—Analytical Bio-Chemistry Laboratories Inc., Columbia MO, USA, , GLP, Unpublished
IZ-620-053	Ta, CT	1999	AC 243997: Aerobic soil metabolism, American Cyanamid Co.,

Code	Author	Year	Title, Institution, Report reference
			Princeton NJ, USA, GLP, Unpublished
IZ-640-001	Mangels, G & Lucas, L	1987	Arsenal herbicide: Metabolism in sugarcane. American Cyanamid Co., Princeton NJ, USA. IZ-640-001, Unpublished
IZ-640-002	Mallipudi, M <i>et al.</i>	1986	Imazapyr herbicide (AC 243,997): Metabolism of carbon-14 Imazapyr [Nicotinic acid, 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl-)] in oil palm. American Cyanamid Co., Princeton NJ, USA. IZ-640-002, Unpublished
IZ-640-003	Zulalian, J	1995	CL 243,997: Metabolism of carbon-14 labeled CL 243,997 in Imidazolinone resistant corn under field conditions. American Agricultural Services Inc., Lucama NC, USA. IZ-640-003, GLP, Unpublished
IZ-640-004	Zulalian, J	1995	Imazapyr (CL 243,997): Metabolism of Carbon-14 CL 243,997 using radishes, soya beans, lettuce and winter wheat as rotational crops. American Agricultural Services Inc., Lucama NC, USA, GLP, Unpublished
IZ-640-006	Wu, D	1997	AC 243,997: Metabolism in bermuda grass under field conditions. XenoBiotic Laboratories Inc., Plainsboro NJ, United States of America. IZ-640-006, GLP, Unpublished
IZ-640-007	Wu, D	1997	AC 243,997: Metabolism in clover under field conditions. XenoBiotic Laboratories Inc., Plainsboro NJ, United States of America. IZ-640-007, GLP, Unpublished
IZ-640-008	Mallipudi, NM	2000	Imazapyr (AC 243997): Confined rotational crop study with carbon-14 labeled AC 243997, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-705-001	Khunachak, A	1999	Arsenal (Imazapyr-CL 243997): Magnitude of CL 243997 in milk, milk fat, and edible tissues from dairy cattle after oral administration for at least 28 days, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-001	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Michigan 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-001	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Michigan 1993, American Cyanamid Co., Princeton NJ, USA. IZ-731-001, GLP, Unpublished
IZ-731-002	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Iowa 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-003	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Wisconsin 1993. American Cyanamid Co., Princeton NJ, USA. IZ-731-003, GLP, Unpublished
IZ-731-004	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in North Carolina 1993. American Cyanamid Co., Princeton NJ, USA. IZ-731-004, GLP, Unpublished
IZ-731-005	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Michigan 1994. American Cyanamid Co., Princeton NJ, USA. IZ-731-005, GLP, Unpublished
IZ-731-006	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Ohio 1994., American Cyanamid Co., Princeton NJ, USA IZ-731-006, GLP, Unpublished
IZ-731-007	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in South Dakota 1993, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-008	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Texas 1994, American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-009	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Indiana 1994., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-010	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Illinois 1994., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-011	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Nebraska processing study 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-011	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Nebraska processing study 1993., American Cyanamid Co.,

Code	Author	Year	Title, Institution, Report reference
			Princeton NJ, USA, GLP, Unpublished
IZ-731-012	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Illinois 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-013	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue with AC 243,997 on field corn in Missouri 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-014	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Minnesota 1994., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-015	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Iowa 1994., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-016	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Indiana 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-017	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Ohio 1993., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-018	Mahl, T	1995	CL 243,997 (Imazapyr): Crop residue study with AC 243,997 on field corn in Nebraska 1994., American Cyanamid Co., Princeton NJ, USA, GLP, Unpublished
IZ-731-021	Steling, C	1998	CL 243,997: Determination of CL 243,997 residues in corn samples from Argentina, LAADL—Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished
IZ-731-021	Steling, C	1998	CL 243,997: Determination of CL 243,997 residues in corn samples from Argentina, LAADL—Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished
IZ-790-015	Steling, C	1998	CL 243,997: Determination of CL 243,997 residues in sugar cane samples from Argentina, LAADL—Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished
IZ-790-015	Steling, C	1998	CL 243,997: Determination of CL 243,997 residues in sugar cane samples from Argentina, LAADL—Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished
IZ-790-017	Steling, C	1998	CL 243,997: Determination of CL 243,997 (Imazapyr) in sugar cane samples from Brazil, LAADL - Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished
IZ-790-017	Steling, C	1998	CL 243,997: Determination of CL 243,997 (Imazapyr) in sugar cane samples from Brazil, LAADL—Latin America Agricultural Development Laboratory, Rio de Janeiro, Brazil, GLP, Unpublished

INDOXACARB (216)*First draft prepared by Dr. Yibing He,**Department of Science and Education, Ministry of Agriculture, China***EXPLANATION**

Indoxacarb is an indeno-oxadiazine insecticide that is used for control of lepidopteran and other insect pests. It was first evaluated by the 2005 JMPR when an ADI of 0–0.01 mg/kg bw and an ARfD of 0.1 mg/kg bw were established. It has been re-evaluated for residues in 2007 and 2009. At the Forty-fifth Session of the CCPR, indoxacarb was scheduled for the evaluation by the current Meeting for additional uses on tea (REP13/PR-Appendix XIV). The present Meeting received information on the residue analysis, storage stability, use pattern, supervised field trials and processing study. The supervised trial information included data on tea.

RESIDUE ANALYSIS*Analytical methods*

The Meeting received descriptions and validation data for analytical methods for residues of indoxacarb in tea. Methods rely on HPLC-MS-MS for analysis of indoxacarb in tea and infusion.

Fresh tea leaves and tea. Fresh tea leaf or tea leaf sample was extracted with water, acetonitrile and ammonia, with the addition of NaCl before centrifugation. Supernatant was cleaned up with SPE cartridge, and centrifuged again. The supernatant was filtered and analysed by UPLC-MS/MS.

Tea infusion. Crushed and blended tea leaves were added into boiling water, and filtered. Cool tea infusion was cleaned up with SPE cartridge and analysed with UPLC-MS/MS. Both recoveries from tea leaf and tea infusion were shown in Table 1.

Table 1 Recoveries of indoxacarb in fresh tea leaves, tea and tea infusion.

Samples	Spiked concentration (mg/kg)	Recoveries (%)						mean. (%)	RSD (%)
		1	2	3	4	5	6		
Tea	0.020	111.4	107.0	111.3	112.6	92.6	---	107.0	7.8
	0.200	110.2	102.2	93.2	95.9	104.6	105.7	102.0	6.3
	4.000	110.8	103.8	107.8	106.3	100.6	98.6	104.6	4.4
Fresh tea leaves	0.010	108.0	102.1	106.1	102.0	101.5	95.0	102.5	4.4
	0.100	104.3	97.8	101.3	103.1	100.8	103.8	101.9	2.3
	2.000	103.0	104.9	103.9	102.1	100.4	101.0	102.5	1.7
Tea infusion	0.0004	101.1	110.1	99.0	102.7	103.7	100.4	102.8	3.8
	0.0040	97.9	93.5	102.4	95.2	94.4	91.0	95.7	4.1
	0.0400	102.6	101.0	103.5	103.4	103.1	100.3	102.3	1.3

RSD-relative standard deviation

Stability of residues in stored analytical samples

The Meeting received information on the stability of residues of indoxacarb in tea.

The storage stability of indoxacarb residue in tea was conducted under freeze storage conditions (-18 °C). The samples were analysed after 30 days, 60 days and 180 days with the above method. The results are listed in Table 2.

Table 2 The storage stability of indoxacarb residue in tea during storage under -18 °C

Tea sample	Residue levels (mg/kg)	Residues (mg/kg)			Remaining (%)		
		30 days	60 days	180 days	30 days	60 days	180 days
1	28.969	28.485	28.198	27.369	1.7	2.7	5.5
2	1.197	1.188	1.178	1.136	0.8	1.6	5.1
3	0.698	0.688	0.682	0.679	1.4	2.3	2.7
4	0.457	0.446	0.440	0.432	2.5	3.8	5.5

USE PATTERN

Indoxacarb is an indeno-oxadiazine insecticide that is registered for use against a large number of insect pests on a wide range of crops in many countries. It is used to control lepidopteran insect (e.g., budworm, armyworm, diamondback moth, loopers, codling moth, grape berry moth, and certain leaf rollers) and a range of other insect pests, including Colorado potato beetle, cranberry weevil, leafhoppers, sawflies, and tarnished plant bug. The Meeting received a copy of the official label providing information on registered uses of indoxacarb on tea in China relevant to the supervised trial data.

Table 3 Registered field uses of indoxacarb in China. Labels for the following use on tea were available to the Meeting.

Crop	Country or Region	End use product	F/G/I ^a	Application					PHI [days]
				Method	No. per crop season min. max.	Growth stage	Max. Rate (g ai/ha per application)	Max. Water Volume (L/ha)	
Tea	China	EC, 15%	F	spraying	1-2	Shoots with one bud and two leaves	38-49.5	900	10

F = field use, G = glasshouse application, I = indoor application.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised field trials for indoxacarb uses on tea plant from China.

Crop	commodity	Country	Table No.
Tea		China	Table 4

A total of eight residue trials were carried out according to GAP ($\pm 30\%$) in China in 2010, 2011 and 2012. In all trials, indoxacarb was applied 1–2 times as an EC formulation containing 50–75 g ai/ha as a foliar application to tea. The water rate was about 900 L/ha. The PHI was 10 days. One-bud and two or three-leaf shoot of tea plant were plucked about 2 kg at PHI. Fresh tea leaves were spreaded under room temperature to leaves surface dry and processed into commercial products of tea such as green tea and black tea etc. The residue data from the supervised trials were summarised in Table 4.

Table 4 Results of residue trials with indoxacarb conducted as a foliar application to tea in China in 2010 to 2012.

TEA	Application					PHI	Crop part	Residues mg/kg, indoxacarb
Products, location, year (variety)	Form. (g /L)	g ai/ha	water, L/ha	Growth stage	no.	days		
Green tea Hang zhou, Zhejiang, 2010 (Longjing 43)	15% EC	50	900	na	1	3	leaves	2.11
						5		1.12
						7		1.19
						10		0.10
						14		0.02
					2	3	leaves	2.32
						5		1.76
						7		1.23
						10		0.14
						14		<0.01
	75	900	na	1	3	leaves	2.58	
					5		2.02	
7					1.24			
10					0.13			
14					0.02			
2				3	leaves	3.87		
				5		1.71		
				7		1.66		
				10		0.09		
				14		0.04		
Black tea Zhangjiajie, Hunan, 2010 (Xiangbolv)	15% EC	50	900	na	1	3	leaves	9.24
						5		1.83
						7		0.85
						10		0.18
						14		0.04
					2	3	leaves	15.3
						5		6.88
						7		2.61
						10		1.97
						14		0.02
		75	900	na	1	3	leaves	8.45
						5		3.00
						7		1.49
						10		0.56
						14		0.06
					2	3	leaves	14.9
						5		3.02
						7		2.91
						10		2.24
						14		0.39
Black tea Songxi, Fujian, 2010 (Maoxie)	15% EC	50	900	na	1	3	leaves	2.68
						5		1.39
						7		1.17
						10		0.03
						14		0.02
					2	3	leaves	2.04
						5		1.81
						7		0.61
						10		0.33
						14		0.01
		75	900	na	1	3	leaves	3.21
						5		1.80
						7		0.75
						10		0.19
						14		0.04
					2	3	leaves	4.82
						5		3.48
						7		0.73
						10		0.10
						14		0.01

TEA Products, location, year (variety)	Application					PHI days	Crop part	Residues mg/kg, indoxacarb
	Form. (g /L)	g ai/ha	water, L/ha	Growth stage	no.			
Black tea Zhangjiajie, Hunan, 2011 (Xiangbolv)	15% EC	50	900	na	1	3	leaves	4.75
						5		2.52
						7		0.76
						10		0.32
						14		0.10
					2	3	leaves	7.12
						5		3.80
						7		1.27
						10		0.40
						14		0.08
		75	900	na	1	3	leaves	4.82
						5		3.19
						7		0.86
						10		0.41
						14		0.17
					2	3	leaves	8.41
						5		5.00
						7		1.83
						10		0.60
						14		0.19
Black tea Songxi, Fujian, 2011 (Maoxie)	15% EC	50	900	na	1	3	leaves	0.94
						5		0.92
						7		0.39
						10		0.13
						14		0.05
					2	3	leaves	0.86
						5		0.96
						7		0.45
						10		0.07
						14		0.01
		75	900	na	1	3	leaves	0.81
						5		0.87
						7		0.52
						10		0.15
						14		0.01
					2	3	leaves	0.70
						5		0.80
						7		0.42
						10		0.15
						14		0.01
Green tea Hang zhou, Zhejiang, 2012 (Longjing 43)	15% EC	50	900	na	1	3	leaves	6.58
						5		4.39
						7		1.95
						10		1.24
						14		0.78
						18		0.30
					2	3	leaves	10.6
						5		7.61
						7		3.25
						10		2.60
						14		0.97
						18		0.64
		75	900	na	1	3	leaves	10.7
						5		5.74
						7		3.84
						10		1.82
						14		1.04
						18		0.56
					2	3	leaves	12.7
						5		8.71
						7		5.03
						10		2.67
						14		1.09

TEA Products, location, year (variety)	Application					PHI days	Crop part	Residues mg/kg, indoxacarb
	Form. (g /L)	g ai/ha	water, L/ha	Growth stage	no.			
						18		0.97
Black tea Zhangjiajie, Hunan, 2012 (Xiangbolv)	15% EC	50	900	na	1	3	leaves	1.53
						5		0.86
						7		0.61
						10		0.42
						14		0.14
						18		0.07
					2	3	leaves	1.50
						5		1.21
						7		0.58
						10		0.30
						14		0.22
						18		0.11
	75	900	na	1	1	3	leaves	2.03
						5		1.02
						7		0.69
						10		0.40
						14		0.20
						18		0.10
					2	3	leaves	2.73
						5		1.55
						7		0.93
						10		0.40
						14		0.34
						18		0.17
	15% EC	50	900	na	1	3	leaves	8.15
						5		2.89
						7		1.38
						10		0.45
						14		0.11
						18		0.03
					2	3	leaves	9.50
						5		2.33
						7		0.81
						10		0.26
						14		0.10
						18		0.03
	75	900	na	1	1	3	leaves	8.98
						5		2.71
						7		1.47
						10		0.45
						14		0.14
						18		0.04
					2	3	leaves	12.4
						5		3.68
						7		1.73
						10		0.12
						14		0.17
						18		0.05

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

The Meeting received information on the fate of indoxacarb residues during the storing and processing of tea.

Table 5 The storage stability of indoxacarb residue in tea during storage under 25 °C

Tea sample	Remaining in tea (mg/kg)	Residues(mg/kg) of indoxacarb in tea during storage (days)			Remaining (%)		
		30	60	180	30	60	180
1	28.969	28.362	28.023	27.054	97.9	96.7	93.4
2	1.197	1.180	1.166	1.116	98.6	97.4	93.2
3	0.698	0.681	0.674	0.662	97.6	96.4	94.8
4	0.457	0.442	0.432	0.426	96.7	94.5	93.2

In Processing

The brewing rate of indoxacarb pesticide residue from tea to tea infusion has been carried out for 16 samples. Weighs up 3.0 g crushed and blended tea sample (supervised trials) in the 250 mL round beaker, add 150 mL boiling water and wait for 20 minutes, remove the infusion in 1000mL separator funnel, repeat two more times and combine all infusion together. The brewing rates of indoxacarb from tea to tea infusion were summarized in Table 6.

Table 6 Processing factors of indoxacarb from tea to tea infusion

Sample No.	Residue mg/kg	First tea infusion		Second tea infusion		Third tea infusion		Total Processing factor %
		Residue mg/kg	Brewing rate %	Residue mg/kg	Brewing rate %	Residue mg/kg	Brewing rate %	
1	0.8574	0.0227	2.65	0.0142	1.66	0.0107	1.24	5.55
2	0.8600	0.0159	1.85	0.0122	1.42	0.0086	1.00	4.27
3	0.5163	0.0127	2.46	0.0087	1.69	0.0081	1.57	5.72
4	0.6412	0.0169	2.63	0.0111	1.74	0.0111	1.74	6.10
5	0.9688	0.0188	1.94	0.0240	2.48	0.0440	4.54	8.95
6	2.5978	0.0705	2.71	0.0481	1.85	0.0565	2.17	6.74
7	3.2492	0.1398	4.30	0.0690	2.12	0.0868	2.67	9.10
8	7.6057	0.1411	1.86	0.1503	1.98	0.0893	1.17	5.00
9	10.5763	0.2379	2.25	0.1965	1.86	0.1559	1.47	5.58
10	0.3038	0.0056	1.86	0.0041	1.36	0.0038	1.23	4.45
11	0.784	0.0200	2.55	0.0230	2.93	0.0079	1.00	6.49
12	1.2355	0.0246	1.99	0.0208	1.68	0.0138	1.11	4.78
13	1.9523	0.0589	3.02	0.0395	2.02	0.0313	1.60	6.64
14	4.3927	0.0885	2.01	0.1269	2.89	0.0655	1.49	6.39
15	6.584	0.1975	3.00	0.1600	2.43	0.1136	1.73	7.16
16	0.5552	0.0171	3.08	0.0121	2.18	0.0080	1.44	6.71
Average value			2.51		2.02		1.70	6.23

APPRAISAL

Indoxacarb was previously evaluated by the JMPR in 2005 (T, R), 2007 (R), 2009 (R) and 2012 (R), the Meeting established an ADI of 0–0.01 mg/kg bw and an ARfD of 0.1 mg/kg bw. At the Forty-fifth Session of the CCPR, indoxacarb was scheduled for the evaluation by the current Meeting for the additional use on tea (REP13/PR-Appendix XIV).

Definition of the residue for compliance with the MRL for all commodities and for estimation of dietary intake for plant commodities is sum of indoxacarb and its R enantiomer. Definition of the residue for estimation of dietary intake for animal commodities is sum of indoxacarb, its R enantiomer and methyl 7-chloro-2,5-dihydro-2-[[[4-(trifluoromethoxy)phenyl]amino]carbonyl]indeno[1,2-e][1,3,4]oxadiazine-4a(3H)-carboxylate, expressed as indoxacarb. The residue is fat soluble.

Methods of analysis

The Meeting received descriptions and validation data for analytical methods for residues of indoxacarb in tea and tea infusion samples.

Fresh tea leaf or tea leaf sample was extracted with water, acetonitrile and ammonia, with the addition of NaCl before centrifugation. The supernatant underwent clean-up with SPE cartridge, and centrifuged again. The supernatant was filtered and analysed by UPLC-MS/MS.

Crushed and blended tea leaves were added into boiling water, and filtered. Cool tea infusion was cleaned up with SPE cartridge and analysed with UPLC-MS/MS.

Recoveries ranged from 95.7% to 107% and validated LOQs were 0.0004 mg/kg for tea infusions, 0.01 mg/kg for fresh tea leaves and 0.02 mg/kg for tea.

Stability of residues in stored analytical samples

The Meeting received information on the stability of residues in tea.

The storage test showed that residues of indoxacarb in tea sample under -18 °C were stable for at least 6 months.

Results of supervised residue trials on tea

The Meeting received supervised trials data for indoxacarb uses on tea plants.

Eight trials were conducted on tea in China (maximum GAP: 0.050kg ai/ha, 2 applications, 10-day PHI) in 2010, 2011 and 2012. Two green tea trials and six black tea trials were available from Zhejiang, Hunan and Fujian, respectively. In the total of eight trials conducted at the maximum Chinese GAP, residues in tea leaves, median underlined, were: 0.13, 0.14, 0.33, 0.40, 0.42, 0.45, 1.97 and 2.60 mg/kg. The Meeting estimated a maximum residue level and an STMR value for indoxacarb in Tea, green, black (black, fermented and dried) of 5 and 0.41 mg/kg.

Fate of residues during storage and processing

The Meeting received information on the fate of indoxacarb residues during the storing and processing of tea.

Residues of indoxacarb stored under -25 °C were stable for at least 6 months.

The processing factor for tea infusion (0.062) was applied to the STMR of tea (0.41 mg/kg) to estimate an STMR-P value for tea infusion of 0.025 mg/kg.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue concentrations listed below are suitable for establishing MRLs and for assessing IEDIs.

Definition of the residue for compliance with the MRL for all commodities and for estimation of dietary intake for plant commodities: *sum of indoxacarb and its R enantiomer*.

Definition of the residue for estimation of dietary intake for animal commodities: *sum of indoxacarb, its R enantiomer and methyl 7-chloro-2,5-dihydro-2-[[[4-(trifluoromethoxy)phenyl]amino]carbonyl]indeno[1,2-e][1,3,4]oxadiazine-4a(3H)-carboxylate, expressed as indoxacarb*.

The residue is fat soluble.

CCN	Commodity	MRL, mg/kg	STMR or STMR-P, mg/kg
DT 1114	Tea, green, black (black, fermented and dried)	5	0.41
-	Tea infusion	-	0.025

DIETARY RISK ASSESSMENT

Long-term intake

The Meeting noted that the new estimation for tea did not result in a significant change in long-term dietary intake and concluded that the long-term intake of residues of indoxacarb resulting from the uses of indoxacarb considered by the present JMPR is unlikely to present a public health concern.

Short-term intake

The IESTI of indoxacarb calculated on the basis of the recommendations of tea made by the JMPR 1% of the ARfD (0.1 mg/kg bw) for child and general population.

The Meeting therefore concluded that the short-term intake of indoxacarb residues in tea, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

REFERENCES

Code	Author	Year	Title, Institute, Report reference
-	Chen, Z. D., etc.	2013	Indoxacarb: The Report of Indoxacarb Residues in Tea, Tea Research Institute Chinese Academy of Agricultural Sciences (CAAS), Hangzhou 310008, Zhejiang Province, China. Unpublished.

ISOXAFLUTOLE (268)

First draft prepared by Ms T. van der Velde-Koerts and K.M. Mahieu, Centre for Food, Prevention and Health Services, National Institute of Public Health and the Environment, The Netherlands

EXPLANATION

Isoxaflutole was scheduled for evaluation as a new compound by 2013 JMPR at the 44th session of the CCPR (2012).

Isoxaflutole is a synthetic compound of the isoxazole group of chemicals used as an herbicide. The mode of action of isoxaflutole is the inhibition of the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD), thereby inhibiting pigment formation, and causing bleaching of the developing tissues of the target plants. Isoxaflutole controls a wide spectrum of grasses and broadleaf weeds by bleaching emerging or emerged weeds following herbicide uptake via the root system.

The Meeting received information from the manufacturer on identity, metabolism, storage stability, residue analysis, use pattern, residues resulting from supervised trials on sweet corn, chickpeas, glyphosate/HPPD tolerant soya beans, maize, sugar cane and poppy seed, fate of residue during processing, and livestock feeding studies.

IDENTITY

ISO common name: isoxaflutole

Chemical name

IUPAC: 5-cyclopropyl-4-(2-methylsulfonyl-4-trifluoromethylbenzoyl)-isoxazole

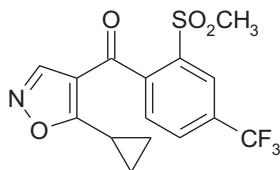
CAS: (5-cyclopropyl-4-isoxazolyl)[2-(methylsulfonyl)-4-(trifluoromethyl)phenyl]-methanone

CAS Registry No: 141112-29-0

CIPAC No: 575

Synonyms and trade names: RPA 201772; AE B197278; AE B197278; RPA 591428; 94 BCS-AH21981 IFT

Structural formula:



Molecular formula: C₁₅H₁₂F₃NO₄S

Relative Molecular weight: 359.3

Structure confirmed by: UV-VIS (aq MeOH), IR (KBr pellet), ¹H-NMR (250 MHz, CDCl₃), ¹³C-NMR (62.9 MHz, CDCl₃), EI-MS [Guesnet *et al.*, 1994, M-189749-01-1]

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient, purity at least 99.7% w/w

Parameter	Result	References	Guidelines/ method
Appearance:	White granular powder	[Cousin, 1994b,	visual

Parameter	Result	References	Guidelines/ method
	the pure active substance.		
Specific gravity	specific gravity 1.593 (20 °C/20 °C)	[Cousin, 1994b,	OECD 109
Density:	density 1.590 g/cm ³ at 20 °C	M-213139-02-1]	EC A3
	Batch JYG 708, 99.7% w/w		pycnometer
Hydrolysis in water:	at 25 ± 1 °C, in the dark, under sterile conditions, at an initial concentration of 3 mg ai/L	[Corgier <i>et al.</i> , 1994, M-162558-01-1]	EPA 161-1
	Duplicate samples were removed at: pH 5: 0, 3, 5, 7,10,12 and 14 days pH 7: 0, 3, 5, 7,16,19 and 24 hours pH 9: 0,1,1.5,2,2.5,3,4 and 24 hours.		
	The radioactivity balance ranged from 98.2 to 101.3% of the initial radioactivity. No volatile compounds were formed at any pH studied.		
	Isoxaflutole was hydrolysed following a pseudo-first order kinetics, with half-life DT ₅₀ 11.1 days at pH 5 20.1 hours at pH 7 3.2 hours at pH 9 [U- ¹⁴ C-phenyl]-Isoxaflutole (batch JKS 473, radiochem purity > 98% w/w)		
	The only hydrolysis-product is IFT-DKN pH 5: 1.2–55% TAR at 0–14 days pH 7: 1.7–54% TAR at 0–24 hours pH 9: 2.2–95% TAR at 0–24 hours		
Photolysis in water:	at 25 ± 1 °C, under sterile conditions, at an initial concentration of 3.0 mg ai/L in pH 5 buffer with 1% v/v ACN, as a co-solvent. Duplicate samples were removed after 0, 16, 30, 40 and 54 hours of irradiation using a Xenon lamp at wavelengths > 290 nm at 612 W/m ² .	[Corgier and Plewa, 1995, M-162794-01-1]	EPA 161-2
	The radioactivity balance ranged from 97.3 to 99.9% of the initial radioactivity. A maximum of 0.11% of the initial radioactivity was recovered as volatile compounds at 54 hours.		
	Isoxaflutole was photodegraded following pseudo-first order kinetics with half-life DT ₅₀ 40 hrs [U- ¹⁴ C-phenyl]-isoxaflutole (batch JKS 473, radiochemical purity > 98% w/w)		

Parameter	Result	References	Guidelines/ method
	Several degradates were observed: IFT-BA, 0.9–2.8% TAR at 0–54 hrs, IFT-DKN, 0.0–2.7% TAR at 0–54 hrs RPA 205834, 0.0–1.7% TAR at 0–54 hrs Met 20 (MW 359), 0.0–16.8% TAR at 0–54 hrs Met 14 (MW 377), 0.0–9.3% TAR at 0–54 hrs		
Dissociation constant:	pH 4.6 at 25 °C, 1% w/v aqueous suspension in water containing 2% (v/v) ACN	[Cousin, 1993b, M-162129-01-2]	OECD 112 EPA 63-10 EPA 63-12
	No dissociation constant could be determined. The solubility of isoxaflutole in water containing 3% (v/v) ACN or MeOH was too low to use the potentiometric method. The UV spectra of isoxaflutole did not differ significantly with the pH and did not allow the determination of pKa using the spectrophotometric method.		
	Technical materials Batch 21ADM93, 98.7% w/w Batch FP1308, 98.3% w/w		

Technical material, purity at least 97.5% w/w

Parameter	Result	References	Guidelines/ method
Appearance:	Yellow granular powder slight characteristic odour, acetic acid-like Batch 21ADM93, 98.7% w/w	[Cousin, 1993a, M-162115-01-1]	EPA 63-2 EPA 63-3 EPA 63-4 visual
	Yellow granular powder slight characteristic odour, acetic acid-like Batch FP1308 98.3% w/w	[Cousin, 1993a, M-162115-01-1]	EPA 63-2 EPA 63-3 EPA 63-4 visual
Specific gravity Density:	Specific gravity 1.416 (20 °C/20 °C) Density: 1.413 g/cm ³ at 20.1 ± 0.1 °C Batch 21ADM93, 98.7% w/w	[Cousin, 1993a, M-162115-01-1]	OECD 109 EPA 63-7 EC A3 pycnometer
	Specific gravity 1.421 (20 °C/20 °C) Density 1.418 g/cm ³ at 20.1 ± 0.1 °C Batch FP1308 98.3% w/w	[Cousin, 1993a, M-162115-01-1]	OECD 109 EPA 63-7 EC A3 pycnometer
Melting range:	136 ± 1 °C Batch 21ADM93, 98.7% w/w	[Cousin, 1993a, M-162115-01-1]	EPA 63-5 EC A1 Differential

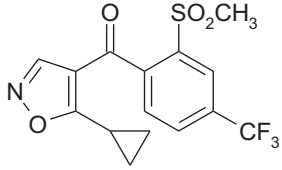
Parameter	Result	References	Guidelines/ method
	135 ± 1 °C Batch FP1308, 98.3% w/w	[Cousin,1993a, M-162115-01-1]	Calorimetric Analysis EPA 63-5 EC A1 Differential Calorimetric Analysis
Thermal stability	Thermal decomposition above 160 °C Batch 21ADM93, 98.7% w/w	[Cousin,1993a, M-162115-01-1]	EC A2, Differential Calorimetric Analysis
	Thermal decomposition above 160 °C Batch FP1308, 98.3% w/w	[Cousin,1993a, M-162115-01-1]	EC A2, Differential Calorimetric Analysis
Stability in air:	Stable for at least 2 weeks at 54 °C. Stable for at least 2 years at ambient temperature Batch 21ADM93, 98.7% w/w	[Cousin, 1995b, M-162149-02-1]	OECD 113, EPA 63-13

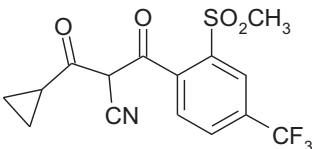
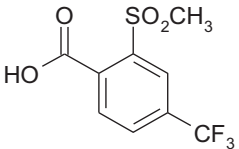
Formulations

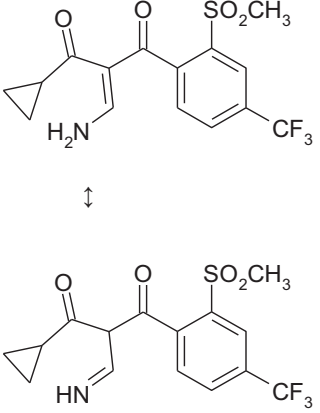
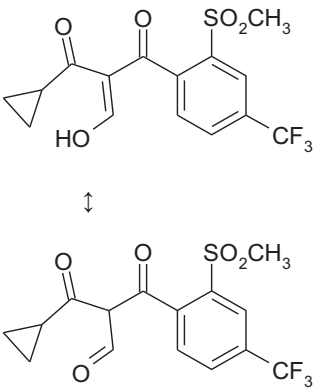
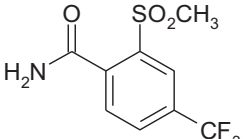
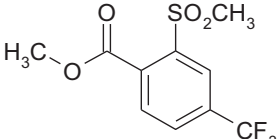
Isoxaflutole has not been evaluated by JMPS and therefore no FAO specifications for technical and formulated isoxaflutole have been published.

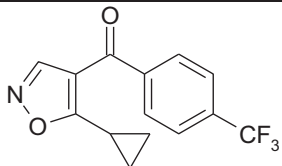
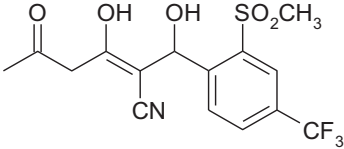
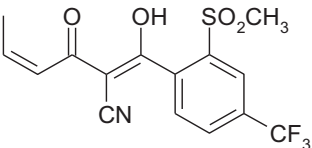
The following formulations with isoxaflutole are commercially available: SL formulations (479 g ai/L), WG formulations (750 g ai/kg), SC formulations (240 g ai/L, 479 g ai/L and 480 g ai/L), SC formulations (44 g ai/L and 240 g ai/L) in combination with a safener cyprosulfamide, SC formulations (50 g ai/L and 225 g ai/L) in combination with a safener cyprosulfamide and a herbicide thien carbazon-methyl.

Table 1 List of reference compounds used in various study reports

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
parent, IFT MW=359.3	Isoxaflutole, RPA 201772, AE B197278; RPA 591428; 94 BCS-AH21981 IFT; 4-(2-methanesulfonyl-4-trifluoromethylbenzoyl)-5-cyclopropyl isoxazole; 5-cyclopropyl-4-(2-methanesulfonyl-4-trifluoromethylbenzoyl)- isoxazole IUPAC: 5-cyclopropyl-1,2-oxazol-4-yl α,α,α -trifluoro-2-mesyl-p-tolyl ketone CAS: (5-cyclopropyl-4-isoxazolyl)[2-(methylsulfonyl)-4-(trifluoromethyl)phenyl] methanone CAS No.: 141112-29-0 	Glyphosate/HPPD-tolerant soya bean forage and hay (only in post emergent application), wheat hay, sugar cane plants (only after post emergence application). Rat (high dose animals only): urine (< 0.22%) and faeces (< 8.2%). Soil compound
IFT-DKN	Isoxaflutole diketone nitrile;	Rat: major metabolite in urine

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
MW = 359.3	RPA 202248, DKN; Diketonitrile metabolite of isoxaflutole; AE 0540092; 14733 BCS-AB59005; 2-cyano-3-cyclopropyl-1-(2-methylsulfonyl-4-trifluoromethylphenyl)propane-1,3-dione; 2-cyclopropylcarbonyl-3-(2-methylsulfonyl-4-trifluoromethylphenyl)-3-oxopropanenitrile; IUPAC: 3-cyclopropyl-2-[2-mesyl-4-(trifluoromethyl)benzoyl]-3-oxopropanenitrile; CAS: α-(cyclopropyl-carbonyl)-2-(methylsulfonyl)-β-oxo-4-trifluoromethyl-benzenepropanenitrile; CAS No.: 143701-75-1 	(28–64%), faeces (21–44%) and liver. Hen: major metabolite in egg yolk, muscle, fat, skin, liver and kidney. Goat: major metabolite in milk, liver, kidney, muscle, renal and omental fat. Maize: minor metabolite in sweet corn, forage, fodder and grain. Glyphosate/HPPD-tolerant soya bean: (major) metabolite in forage, hay and seed. Wheat: minor metabolite in hay and straw. Sugar cane: minor metabolite in whole plant. Poppies: minor metabolite in seed bolls and upper stem and straw. Soil aerobic degradation product Soil photolysis product Rotational crop metabolite: radish leaf, sorghum grain Hydrolysis product Photodegradation product
IFT-BA MW = 268.2	Isoxaflutole benzoic acid IFT Benzoic acid, BA, RPA 203328, IFT-acid benzoic acid metabolite of isoxaflutole AE B197555; 10069 BCS-AB49990 Pyrasulfotole benzoic acid; IUPAC: 2-mesyl-4-trifluoromethylbenzoic acid; CAS: 2-(methylsulfonyl)-4-trifluoromethyl-benzoic acid CAS No.: 142994-06-7 	Rat: minor metabolite in urine and faeces (0.58–3.6%). Hen: minor metabolite in muscle and possibly kidney. Maize: major metabolite in forage, sweet corn, forage, fodder and grain. Glyphosate/HPPD-tolerant soya bean: (major) metabolite in forage, hay and seed. Wheat: major metabolite in hay, grain and straw. Sugar cane: major metabolite in whole plant. Poppies: major metabolite in seeds, seed bolls and upper stem and straw. Soil aerobic degradation product Soil photolysis product Rotational crop metabolite: radish leaf, lettuce leaf, sorghum forage, sorghum fodder, sorghum grain, wheat forage, wheat straw, wheat grain Photodegradation product
RPA 205834 MW = 361.3	AE 0692291; 10361 BCS-BY16134; 2-aminomethylene-1-cyclopropyl-3-(2-methylsulfonyl-4-trifluoromethylphenyl)propane 1,3-dione; 2-aminomethylene-1-cyclopropyl-3-(2-methylsulfonyl α, α-trifluoro-p-tolyl)propane-1,3-dione; IUPAC: 2-aminomethylene-1-cyclopropyl-3-(2-mesyl-4-trifluoromethylphenyl)-propane-1,3-dione	Rat: minor metabolite in urine (< 2.3%) and faeces (< 1.5%). Hen: minor metabolite detected in yolk. Goat: minor metabolite detected in milk, renal and omental fat. Photodegradation product

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
		
RPA 207048 MW = 360.3	AE 0893029; 10054 IUPAC: 1-cyclopropyl-2-hydroxymethylene-3-(2-methyl-4-trifluoromethylphenyl)-propane-1,3-dione 	Rat: minor metabolite in faeces (< 1.9%). Hen: minor metabolite in muscle and fat. Goat: minor metabolite in milk, liver, kidney, muscle, renal and omental fat.
IFT-amide MW= 267.2	Isoxaflutole benzamide IUPAC: 2-methyl-4-(trifluoromethyl)benzamide CAS: 2-(methylsulfonyl)-4-(trifluoromethyl)benzamide 	Glyphosate/HPPD-tolerant soya bean: (major) metabolite in forage, hay and seed after pre-plant applications. Minor metabolite in post emergent applications (hay and seeds).
RPA 204497 MW = 282.2	methyl-2-methyl-4-trifluoromethylbenzoate 	–
RPA 205568 MW=281.2	5-cyclopropyl-1,2-oxazol-4-yl- α,α -trifluoro-p-tolyl ketone	Rat: minor metabolite in urine and faeces.

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
		
Met 14 MW= 377	IUPAC: (2Z)-3-hydroxy-2-{hydroxy[2-(methylsulfonyl)-4-(trifluoromethyl)phenyl]methyl}-5-oxohex-2-enitrile 	Photodegradation product
Met 20 MW = 359	IUPAC : (2Z,4Z)-2-{hydroxy[2-(methylsulfonyl)-4-(trifluoromethyl)phenyl]methylene}-3-oxohex-4-enitrile 	Photodegradation product

METABOLISM AND ENVIRONMENTAL FATE

The Meeting received information on the fate of isoxaflutole in livestock, plant commodities, soil and rotational crops. In all these studies isoxaflutole was uniformly labelled with ^{14}C in the phenyl ring (Figure 1).

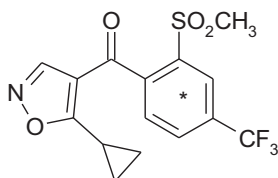


Figure 1 Position of [^{14}C]- radiolabel in isoxaflutole

Animal metabolism

The Meeting received information on the fate of isoxaflutole in ruminants (lactating goat) and poultry (laying hens). The metabolism in laboratory animals was summarized and evaluated by the WHO panel of the JMPR in 2013.

Lactating goats

Radiolabelled [$\text{U-}^{14}\text{C}$ -phenyl]-isoxaflutole was administered orally by gavage to four lactating goats (British Saanen) twice daily for 7 consecutive days at a nominal dose of 1 (goat 001F), 10 (goat 002F and goat 003F) or 50 (goat 004F) mg/kg feed assuming a daily intake of 2 kg dry matter [Lappin, 1995b, M-166744-01-2]. Animals were dosed in the morning and afternoon prior to feeding and after milk and excreta collections. The mean actual concentrations were 1.084, 10.04, 12.98 and 63.92 mg ai/kg dry feed for goat 001F, 002F, 003F and 004F, respectively. In terms of mg ai/animal, the corresponding daily means were 2.00, 20.1, 20.1 and 100 mg ai/animal. Goats were less than 8 years of age. Body weights were 63 to 87 kg on arrival, 64 to 78 kg at the start of acclimatisation and 61 to 73 kg at the end of the study. It is noted that the animals lost weight during the acclimatisation

period. Recovery occurred in three of the four animals. Average daily feed consumption during application was 1.848, 2.00, 1.545, and 1.566 kg/animal/day for goat 001F, 002F, 003F and 004F, respectively. Average daily milk production during application was 1.628, 2.199, 1.638, and 1.745 kg for goat 001F, 002F, 003F and 004F, respectively, and was not affected by the administration of isoxaflutole. The goats were sacrificed *ca* 23 hours after administration of the last dose. Selected tissues (skeletal muscle, renal and omental fat) and organs (liver and kidney) were removed. In addition the gastrointestinal tract and its contents were analysed in the case of animals 003F and 004F.

The total radioactive residue (TRR) was assessed by LSC or combustion/LSC. Results are shown in Table 2 and Table 3. The total recovered radioactivity amounted to 96.64% TAR in goat 001F, 88.00% TAR in goat 002F, 77.72% TAR in goat 003F and 72.64% TAR in goat 004F. The majority of the radioactivity was recovered from urine (27 to 54% TAR) and faeces (26 to 31% TAR). Levels of radioactivity in milk were not detectable in the low dose goat (001F) and low in the other three animals (0.57, 0.60 and 0.54% TAR in goat 002F, 003F and 004F, respectively). Moderate levels of radioactivity were found in the tissues (including skin), 11.3, 7.49, 9.66 and 8.83% TAR in goat 001F, 002F, 003F and 004F, respectively).

The total radioactive residues (TRR) in tissues and milk were 0.536 to 3.946 mg/kg eq in liver, 0.164–2.123 mg/kg eq in kidney, 0.011 to 0.235 mg/kg eq in omental fat, 0.037 to 0.927 mg/kg eq in muscle, and reaching a maximum of 0.060, 0.095 and 0.350 mg/kg eq in milk for the three highest dose levels (10, 10 and 50 mg ai/kg dry feed), respectively. A steady state was apparent 48 to 96 hours after the first dose for the two low dose levels (1 and 10 mg ai/kg dry feed) with steady state levels of 0.053 mg/kg eq and 0.076 mg/kg eq, respectively. For the high dose group, a steady state was observed by 120 hours after first dosing with a mean concentration of 0.338 mg/kg eq. No separation of the milk in skimmed milk and cream was performed.

Samples were stored at *ca* -20 °C and analysed within 6 months after sampling. Storage stability was established by a comparison of the nature of radiolabelled residues in urine collected from animal 002F in three HPLC systems over an 18 month period, demonstrating no notable qualitative or quantitative differences in the profiles.

Table 2 Distribution and recovery of administered radioactivity in lactating goats fed with isoxaflutole

Dose	1 mg ai/kg dry feed	10 mg ai/kg dry feed	10 mg ai/kg dry feed	50 mg ai/kg dry feed
	%TAR (mg/kg eq)	%TAR (mg/kg eq)	%TAR (mg/kg eq)	%TAR (mg/kg eq)
Urine	54.27	53.90	27.20	27.07
Faeces	31.04	26.04	28.29	29.35
GIT	n.a.	n.a.	1.642	2.496
Cage wash	nd	nd	11.77	5.836
Milk	nd	0.567	0.599	0.539
Edible tissues and organs (total)	11.34	7.49	7.1	5.3
Omental fat	0.232 (0.011)	0.104 (0.100)	0.187 (0.062)	0.198 (0.235)
Renal fat	0.069 (0.015)	0.042 (0.092)	0.082 (0.069)	0.043 (0.230)
Muscle	7.258 (0.037)	5.397 (0.276)	5.322 (0.263)	4.347 (0.927)
Liver	3.576 (0.536)	1.821 (2.260)	1.400 (2.100)	0.706 (3.946)
Kidney	0.208 (0.164)	0.125 (0.969)	0.085 (0.905)	0.052 (2.123)
Skin	n.a.	n.a.	0.939	0.990
Total	96.65	88.00	77.52	71.63

nd = not detected; n.a. = not applicable; GIT = gastro intestinal tract

Table 3 Mean total radioactive residue concentration in milk in mg/kg equivalents

Time (hr)	mg/kg eq			
	1 mg/kg feed	10 mg/kg feed	10 mg/kg feed	50 mg/kg feed
24	nd	0.032	0.045	0.159
48	nd	0.045	0.055	0.260
72	nd	0.048	0.063	0.286
96	nd	0.051	0.095	0.310
120	nd	0.054	0.093	0.350
144	nd	0.059	0.076	0.335
168	nd	0.060	0.074	0.329
174	nd	0.042	0.047	0.267

nd = not detected (≤ 0.002 mg eq/kg)

For further characterisation and identification the homogenates of the tissues of goat 003F and milk of goat 002F (10 mg ai/kg dry feed group) were subjected to further analysis.

Milk was mixed with chloroform and MeOH and partitioned. The aqueous MeOH fraction was removed and partitioned against chloroform. Chloroform fractions were pooled and reduced to low volume. The pellet from the initial extraction partition procedure was extracted with MeOH, which was pooled with the other MeOH fractions and then admixed with the concentrated chloroform extracts. This was subjected to SPE and eluted with MeOH. The aqueous residue was reconstituted with water prior to analysis by HPLC and HPLC-MS.

Kidney and liver homogenate was extracted sequentially with K_2HPO_4 buffer pH 7.5. Extracts were pooled and mixed with ACN and concentrated. The liver extract was reconstituted in mobile phase prior to HPLC and the kidney extract to HPLC. These initial analyses did not yield the requested results. Hence the extracts were further treated by mixing with ACN and particulate matter and precipitated salts were removed by centrifugation during concentration of the extract using nitrogen convection. The extracts were reconstituted in mobile phase prior to HPLC and HPLC-MS analysis.

Muscle homogenate was extracted sequentially with K_2HPO_4 pH 7.5 buffer and NH_4Ac pH 4.0 buffer. Extracts were pooled and mixed with ACN and concentrated. The extract was mixed with mobile phase and analysed by HPLC. A desalting procedure was undertaken as performed for kidney tissue, but the procedure had little effect on the HPLC chromatography. Fresh tissue sample was extracted in K_2HPO_4 pH 7.5 buffer. The extract was diluted 40 times with 2% aqueous formic acid and applied to a SPE column. Radioactivity was eluted from the column using 2% formic acid in acetone. Eluent was dried by nitrogen convection and reconstituted in HPLC mobile phase and analysed by HPLC. One minute fractions were collected and analysed by LSC.

A sample of the muscle extract was digested with protease in a similar manner as was done for the solid phase (see below). Further purification was performed by dilution with 2% aqueous formic acid and applying SPE as described above. The acetone eluent was reconstituted in HPLC mobile phase and analysed by HPLC. One minute fractions were collected and analysed by LSC.

Further processing of the solids was conducted by re-suspension in K_2HPO_4 buffer pH 7.5 with protease, incubation overnight (37 °C), freeze drying and mixing with mobile phase and ACN. The sample was concentrated and cleaned prior to reconstituting the extract with mobile phase and analysis by HPLC and HPLC-MS.

Renal fat was homogenised with hexane and mixed with K_2HPO_4 buffer pH 7.5. The mixture was centrifuged and organic and aqueous fractions removed. The procedure was repeated twice with the resultant pellet. The hexane fractions were combined, but not further characterized. The aqueous fractions were combined and the excess buffer removed by freeze drying. The resultant residue was mixed with ACN and excess particulate matter removed using centrifugation. The sample was concentrated and cleaned. The resultant residue was reconstituted in mobile phase prior to analysis by HPLC and HPLC-MS.

Omental fat was extracted in the same manner as renal fat. In addition, another extraction method was applied to a second sample, where omental fat was extracted sequentially with ACN (3×), MeOH, and acidified MeOH (2×). The resulting residue was mixed with hexane and partitioned sequentially against ACN, MeOH, acidified MeOH (3×), and water (2×). All extracts (excluding the hexane fraction) were combined, excess solvent removed and cleaned of particulate matter. The remaining aqueous sample was then analysed directly by HPLC.

The nature and identity of the residues in extracts (solvent and/or protease hydrolysates) of milk, kidney, muscle, omental fat and renal fat sampled from animals 002F and 003F were investigated using HPLC and HPLC-MS. Characterisation and/or identification in extracts were based on co-chromatography of reference standards IFT-DKN, IFT-BA, RPA 207048, and RPA 205834.

Results are shown in Table 4. Parent IFT was not found in any of the animal commodities. Three degradation products were identified in the different goat matrices. In milk, muscle, liver, kidney and fat, the metabolite IFT-DKN was the most abundant component of the residues (25–86% TRR or 0.015–1.80 mg/kg eq), followed by the metabolite RPA 207048 (12–26% TRR or 0.009–0.261 mg/kg eq) in all matrices and metabolite RPA 205834 (8.1–18.3% TRR or 0.005–0.011 mg/kg eq) in milk and omental fat only. Several unknown residues were characterized (2.66% TRR to 24.2% TRR or 0.007–0.050 mg/kg eq) in muscle, renal fat, omental fat and milk. Metabolite IFT-BA was not found in any fraction.

The solids remaining after initial extraction in kidney and muscle were treated with protease hydrolysis, resulting in a release of more IFT-DKN and RPA 207048 in muscle (respectively 0.061 mg/kg eq (23.2% TRR) and 0.009 mg/kg eq (3.8% TRR). Part of the radioactivity could not be attributed to any of the known metabolites (0.050 mg/kg eq (5.6% TRR) in kidney and 0.041 mg/kg eq (15.6% TRR) in muscle).

Table 4 Characterisation of residues in goat 002F (milk) and goat 003F (tissues) receiving 10 mg ai/kg dry feed

Tissue	TRR mg/kg eq	IFT-DKN mg/kg eq (%TRR)	RPA 207048 mg/kg eq (%TRR)	RPA 205834 mg/kg eq (%TRR)	Unk 1 mg/kg eq (%TRR)	Unk 2 mg/kg eq (%TRR)	Unk 3 mg/kg eq (%TRR)	PES mg/kg eq (%TRR)	Total %TRR
Milk	0.060	0.025 (41.7%)	0.009 (15.0%)	0.011 (18.3%)	0.012 (20.0%) ^a	—	—	—	95.0%
Liver	2.100	1.801 (85.8%)	0.261 (12.4%)	—	—	—	—	—	98.2%
Kidney	0.905	0.742 (82%)	0.105 (11.6%)	—	—	—	—	0.050 (5.57%)	99.2%
Muscle	0.263	0.048 (18.3%) 0.061 ^b (23.2%) ^b	0.024 (9.13%) 0.009 ^b (3.42%) ^b	—	0.007 (2.66%) ^b	0.010 (3.80%) ^b	0.041 (15.6%) ^{b, c}	—	76.0%
Omental fat	0.062	0.015 (24.2%)	0.016 (25.8%)	0.005 (8.07%)	0.010 (16.1%) ^d	0.015 (24.2%) ^e	—	—	98.4%
Renal fat	0.069	0.017 (26.6%)	0.013 (18.8%)	0.010 (14.5%)	0.011 (15.9%) ^f	0.013 (18.8%) ^e	—	—	92.8%

TRR: total recovered residue; Unknown 1 in aqueous fraction of omental fat and renal fat and in protease hydrolysate of muscle; Unknowns 2 in hexane fraction of omental fat and renal fat and in protease hydrolysate of muscle; Unknown 3 after protease hydrolysis of muscle solids

^a Composed of at least six radiolabelled metabolites (highest peak 0.009 mg/kg eq and < 10%TRR).

^b Released following protease hydrolysis of solids

^c Composed of at least two radiolabelled metabolites (highest peak 0.011 mg/kg eq, but < 10% TRR)

^d Composed of at least three radiolabelled metabolites in the aqueous fraction (highest peak 0.008 mg/kg eq, 12.1% TRR).

^e Partitioned into hexane, not further characterized. Taken into account the low residue levels and the common metabolism between plant and animals, this fraction is not expected to contain any toxicologically relevant residues.

^f Composed of at least three radiolabelled metabolites in the aqueous fraction (highest peak 0.011 mg/kg eq, 15.9% TRR)

Laying hens

Ten laying hens (*ISA Warren* strain) were orally dosed by gavage once daily with [U-¹⁴C-phenyl]-isoxaflutole at a nominal dose rate of 1 (group A) and 10 (group B) mg ai/kg dry feed (based on an assumed feed intake of 150 g dry matter) for 14 consecutive days [Lappin, 1995a, M-170844-01-1]. The nominal dose is equivalent to 0.15 mg ai/animal for group A and 1.5 mg ai/animal for group B. Average body weights were 1.78 and 1.82 kg at the start of the study for group A and B, respectively and 1.80 for both groups at necropsy (range 1.67–2.0 kg). The mean actual dose administered, based on the actual mean food consumption of 0.134 kg diet/day, was 1.135 and 11.35 mg ai/kg dry feed for dose group A and B, respectively. The eggs were collected twice daily and excreta in 24 hr intervals. Eggs were kept refrigerated and separated in egg yolks and egg whites prior to radio analysis. Approximately 23 hours after the last dose, the hens were sacrificed and the tissues (fat, muscle and skin) and organs (kidney and liver) were removed. Samples were stored at -20 °C.

The collected samples were analysed by combustion LSC. The total recovery of radioactivity was found to be 117.1% in dose group A. Radioactivity from the excreta and cage wash amounted to 112.4% of the total radioactivity administered. Negligible radioactivity was recovered in egg yolk (0.15% TAR) or tissues (1.7%). Levels of radioactivity were not detected in egg white. The total recovery of radioactivity in dose group B was found to be 92%. The majority of the radioactivity was recovered in the excreta (88.5%), negligible radioactivity was recovered in the egg yolk (0.10%), egg white (0.02%) or tissues (0.20%). Results are shown in Table 5.

Table 5 Distribution and recovery of total administered radioactivity (% TAR) in laying hens dosed with isoxaflutole

Matrix	1 mg ai/kg dry feed (n=5)	10 mg ai/kg dry feed (n=5)
Excreta	112.4	88.5
Cage wash	2.83	3.24
Egg white	nd	0.10
Egg yolk	0.15	0.02
Tissues (combined)	1.71	0.20
Muscle	< LOD	0.035 mg/kg eq
Fat	< LOD ^a	0.028 mg/kg eq
Liver	0.845 mg/kg eq	0.935 mg/kg eq
Kidney	0.055 mg/kg eq	0.155 mg/kg eq
Skin	0.008 mg/kg eq	0.068 mg/kg eq
Total	117.1	92.01

nd = not detected (limits of detection were calculated on the basis of the levels of the control samples and were between 0.002 and 0.007 mg/kg eq for all tissues)

^a except for one animal

In the low dose group (A) the concentrations of radioactivity in egg whites were below the limit of detection, < 0.002–0.003 mg/kg eq, at all-time points, and above the limit of detection in egg yolk (0.002–0.003 mg/kg eq) as from day 4, with maximum mean concentration of 0.028 mg/kg eq on day 10 and a steady state within 7 days after the first dose (*ca* 0.022 mg/kg eq). In the high dose group (B) the concentration of radioactivity in egg whites reached a maximum of 0.015 mg/kg eq after 10 days of exposure. A steady state (*ca* 0.010 mg/kg eq) in egg white was reached within 4 days of exposure. The levels of radioactivity in egg yolk were up to 16 times higher, with a maximum of 0.152 mg/kg eq after 12 days of exposure and a steady state concentration of *ca* 0.137 mg/kg eq within 7 days of exposure.

The highest radioactivity concentrations in edible tissues were found in the liver (0.845 and 0.935 mg/kg eq for dose group A and B, respectively) and kidney (0.055 and 0.155 mg/kg eq, respectively for A and B. Radioactivity concentrations in fat and muscle were only observed in the high (B) dose group, being 0.028 and 0.035 mg/kg eq, respectively. Some radioactivity was found in skin (0.008 and 0.068 mg/kg eq in dose groups A and B, respectively).

The nature of the radioactive residues was investigated in excreta and tissues of the animals of dose group B (10 mg/kg feed)

A variety of extraction and clean-up methods were employed to analyse residues in the edible tissues and eggs. Subsamples of eggs and homogenized subsamples of tissues and organs (combined samples of five animals from group B) were generally extracted with MeOH (3–4 times), sometimes followed by sequential extraction with acidified MeOH and water (kidney and skin). The aqueous residue was backwashed using hexane and the hexane wash was backwashed with MeOH. The MeOH wash was combined with the aqueous residue and reduced to low volume prior to analysis by HPLC and HPLC-MS. For kidney the aqueous extracts were freeze dried and reconstituted in MeOH and then pooled with the MeOH residue. Excess MeOH was removed and the residue reconstituted in water prior to analysis by HPLC-MS. Following analysis the remaining residue (kidney and liver) was mixed with MeOH and aqueous ACN, the excess solvent removed and reconstituted in water prior to analysis by HPLC.

Egg yolk was extracted subsequently with hexane, MeOH, ACN, acidified MeOH and water. Further extraction using ACN, EtOAc, acidified water and acidified EtOAc did not release any further radioactivity and were therefore not included. Other extracts were combined and excess solvent removed and cleaned up by hexane backwashes and centrifugation to remove participated particulate matter. The resultant residue was reconstituted in mobile phase prior to analysis by HPLC and HPLC-MS.

Egg white was extracted sequentially with ACN, MeOH, EtOAc, acidified MeOH, water and ACN. Quantitative recovery of radioactivity was not achieved following this exhaustive solvent extraction.

Remaining solids of kidney, skin, muscle and egg yolk and white were further subjected to protease digestion (48 hr, 37 °C) and subsequently to acid hydrolysis (6 M HCl at 95 °C for 7 days). The remaining pellets were analysed for residual radioactivity by combustion. For skin the only [¹⁴C] residue levels in the protease hydrolysate were greater than 0.010 mg/kg eq and for the muscle and egg yolk the levels in the acid hydrolysate were greater than 0.010 mg/kg eq. These fractions were further prepared for analysis by HPLC and HPLC-MS.

All fractions were analysed by LSC. The identification and quantification of metabolites in the various fractions was accomplished by HPLC and LC-MS. Characterisation and/or identification in extracts was based on co-chromatography of reference standards for IFT-DKN, IFT-BA, RPA 207048, and RPA 205834. Identification and characterisation of isoxaflutole related residues is shown in Table 6.

In egg yolk metabolites IFT-DKN (26.3% TRR, 0.036 mg/kg eq) and RPA 205834 (27.7%, 0.038 mg/kg eq) were identified. In the metabolic organs liver and kidney the majority of the radioactivity represented IFT-DKN (93.1% TRR and 73.6% TRR, respectively, equivalent with 0.887 mg/kg eq and 0.114 mg/kg eq). The same applies for the skin (61.8% TRR or 0.042 mg/kg eq, being the sum of the findings in the extractable residue and release after protease and acid hydrolysis). In muscle the main metabolite identified was RPA 207048, 48.5% TRR or 0.017 mg/kg eq (combined results of extractable residue and acid hydrolysate). In fat the main metabolites identified were IFT-DKN (28.6% TRR or 0.008 mg/kg eq) and RPA 207048 (21.4% TRR or 0.006 mg/kg eq).

Samples were stored at *ca* –20 °C and analysed within 6 months after sampling. Storage stability was established by a comparison of the nature of radiolabelled residues in excreta collected from animal 006F (group A) and 010F (group B) in three HPLC systems over an 18 month period, demonstrating no notable qualitative or quantitative differences in the profiles.

Note: More than 50% of the radioactivity in egg yolk could not be identified (12.4% TRR in solvent extract) and 46% TRR after acid hydrolysis.

Table 6 Identification and characterisation of isoxaflutole related residues in hens dosed with 10 mg ai/kg dry feed

Tissue	TRR mg/kg eq	IFT-DKN mg/kg eq (%TRR)	RPA 207048 mg/kg eq (%TRR)	RPA 205834 mg/kg eq (%TRR)	IFT-BA mg/kg eq (%TRR)	Unk mg/kg eq (%TRR)	Unk mg/kg eq (%TRR)	Unk mg/kg eq (%TRR)	PES mg/kg eq (%TRR)	Total (%TRR)
Liver	0.953	0.887 (93.1%)	— —	—	0.033 ^a (3.46%)	—	—	—	0.034 (3.57%)	100.1%
Kidney	0.155	0.114 (73.6%)	— —	—	0.001 ^b (0.65%)	—	0.025 ^{c,d} (16.1%)	0.003 ^e (1.94%)	—	92.3%
Muscle	0.035	0.002 ^e (5.71%)	0.011 (31.4%) 0.006 ^e (17.1%)	—	0.002 ^e (5.71%)	0.008 ^f (22.9%)	0.010 ^e (28.6%)	0.005 ^{e,g} (14.3%)	—	125.7%
Fat	0.028	0.008 (28.6%)	0.006 (21.4%)	—	—	0.012 ^h (42.9%)	—	—	—	92.9%
Skin	0.068	0.025 (36.8%) 0.017 ^j (25%)	—	—	—	0.011 ⁱ (16.2%)	0.002 ^{c,k} (2.94%) ^{c,k}	—	—	80.9%
Egg yolk	0.137	0.036 (26.3%) 0.023 ^e (16.8%)	—	0.038 ^l (27.7%)	—	0.017 ^m (12.4%)	—	0.040 ⁿ (29.2%)	—	112.42%
Egg white	0.010	—	—	—	—	0.005 (50%)	0.002 (20%) ^c	0.002 ^e (20%)	—	90%

^a Contains IFT-BA indicated by HPLC-MS.^b Resolved in only one HPLC system and tentatively identified as IFT-BA by HPLC-MS.^c Released after protease digestion^d Composed of at least three unknown radiolabelled metabolites, with the highest peak being 0.009 mg/kg eq.^e Released after acid hydrolysis^f Composed of at least three unknown radiolabelled metabolites in approximate ratio 4:3:1 (highest peak 0.004 mg/kg eq).^g Composed of at least two unknown radiolabelled metabolites in approximate ratio 3:2 (highest peak 0.003 mg/kg eq).^h Composed of at least two unknown radiolabelled metabolites in approximate ratio of 1:1 (highest peak 0.006 mg/kg eq)ⁱ Composed of at least three radiolabelled metabolites in the approximate ration of 5:4:2 (highest peak 0.005 mg/kg eq).^j 0.012 mg/kg eq (17.7% TRR) was released after protease digestion and 0.005 mg/kg eq (7.35%TRR) was released after acid hydrolysis.^k Composed of at least one metabolite.^l Identification based on similar chromatographic properties in a single HPLC system.^m Composed of at least two radiolabelled metabolites in the approximate ratio of 5:1 (highest peak 0.014 mg/kg eq)ⁿ Released following acid hydrolysis and composed of at least three radiolabelled metabolites (0.004–0.011–0.025 mg/kg eq). No radiolabelled metabolites were released following protease treatment.

Overview metabolic pathway in livestock

Isoxaflutole was transformed to a number of metabolites after administration to ruminants and poultry. The proposed metabolic pathway of isoxaflutole in livestock involves the opening of the oxazole ring and the formation of the diketo-nitrile derivative (IFT-DKN) or the diketo-amine derivative (RPA 205834). Further degradation occurs through deamination to form the diketo-hydroxy derivative (RPA 207048) or through further cleavage to form the benzoic acid derivative (IFT-BA). Further metabolism involves conjugation of IFT-DKN, RPA 207048 and/or IFT-BA with proteins or acid cleavable compounds. The pathway is shown schematically in Figure 2.

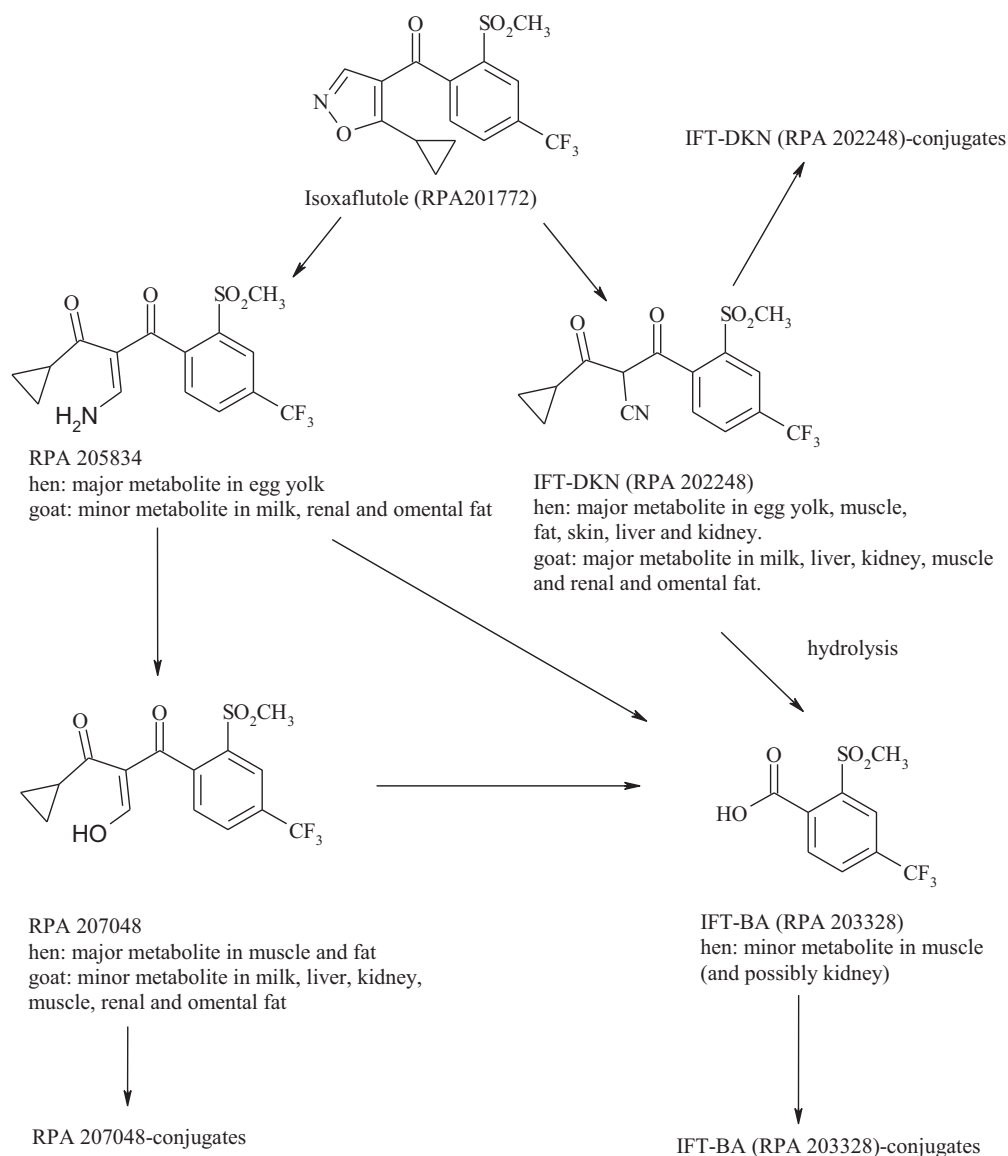


Figure 2 Proposed metabolic pathway of isoxaflutole in livestock

Plant metabolism

The Meeting received information on the uptake and metabolic fate of isoxaflutole in cereals (maize and wheat), pulses/oilseeds (soya beans, poppy seeds) and sugar cane. Further the Meeting received information on the effect of the addition of the safener cyprosulfamide on isoxaflutole related residues. The test item used in all studies was [U-¹⁴C-phenyl]-isoxaflutole (see Figure 1).

Study 1

The metabolic fate and distribution of isoxaflutole was studied outdoors in maize (*Zea mays L*) after either a pre-plant incorporated (PPI) or pre-emergence (PRE) application [Hampton and Pettaway, 1995, M-162883-01-1]. The total amount applied was 0.209 or 0.657 kg ai/ha for the PPI application and 0.227 or 1.075 kg/ha for the PRE application. The test item used was [U-¹⁴C-phenyl]-isoxaflutole. The soil characteristics were: sandy loam, pH 5.3, 1.43% om, 2.94 meq/100 g CEC. The active ingredient was applied on day 1 to the soil either before planting (PPI) or after planting (PRE) as dosing solution using pipettes and applying it in a criss-cross pattern to the soil. For the PPI treatment

the application was subsequently incorporated in the soil with a rake to the depth of approximately 2.5 cm, before planting. Plants were harvested at immature and mature stages (one plant of the container for the forage harvest and one for fodder and grain harvest). Forage was harvested at 41 DAP/DAT (BBCH growth stage not reported, plants were 51–61 cm tall) and comprised of the combined leaves and stems. The mature plants were harvested at 122 DAP/DAT (leaves and ears) and at 138 DAP/DAT (remaining stems). Fodder samples comprised the leaves, stems, husks, shanks, silks and cob. Grain samples consisted of the shelled grain only. The frozen samples were stored at -20 °C.

Homogenised samples were analysed by combustion LSC. Samples with TRRs greater than 0.01 mg/kg eq were extracted sequentially with hexane/EtOAc (9:1 v/v); ACN; H₂O (pH 5.5); and ACN/0.2M HCl (1:1 v/v). Remaining solids in forage and fodder were digested enzymatically by cellulase (6–72 hrs for forage and 24–120 hrs for fodder, 37 °C, pH 4.8). The digests were acidified (pH < 2) and partitioned against EtOAc. Extracts and remaining solids were quantified by LSC or combustion LSC. All aqueous extracts were acidified and partitioned against EtOAc. All organic extracts and EtOAc layers were concentrated. The concentrated extracts were analysed by HPLC and TLC using reference substances for IFT, IFT-DKN and IFT-BA. The identity of the parent and metabolites was confirmed by HPLC-MS-MS.

The total radioactive residues based on combustion of maize forage, grain and fodder are shown in Table 7. Exaggerated dose rates exhibited greater phytotoxicity. The exaggerated rate treatments were not further taken into account for determining extractability and identification of metabolites.

Table 7 Mean radioactive residues in maize forage, fodder, and grain after normal and exaggerated doses

Matrix	Treatment - harvest	Use rate kg ai/ha	TRR mg/kg eq
Forage	PPI-DAT 41	0	0.000
		0.209	0.198
		0.657	0.800
	PRE-DAT 41	0	0.000
		0.227	0.228
		1.075	0.491
Grain	PPI-DAT 122	0	0.000
		0.209	0.044
		0.657	0.152
	PRE-DAT 122	0	0.000
		0.227	0.039
		1.075	0.125
Fodder	PPI-DAT 122/138	0	0.000
		0.209	0.149
		0.657	0.661
	PRE-DAT 122/138	0	0.000
		0.227	0.120
		1.075	0.528

The calculated TRR values were used as 100% TRR for all further calculations. Extractability ranged from 81.3% in fodder to 102.1% TRR in forage. Enzymatic digests of forage and fodder contributed to another 4.0% and 6.5% TRR. Remaining solids in forage, fodder and grain were on average 1.5%, 10.7% and 6.5% TRR. The total accountability ranged from 90.9% to 103.3% TRR. The results are shown in Table 8 and Table 9. Approximately 70–80% of the TRR was identified as IFT-DKN and IFT-BA. Calculations showed an identification rate of 64–89% of the TRR comprising of metabolite IFT-BA, typically greater than 90% of the extracted radioactive residue, representing 64–89% of the TRR. Small amounts of IFT-DKN were found in enzyme treated fractions of forage (*ca.* 0.5% TRR) and in the ACN fraction of grain (7.5% TRR). The parent IFT was not detected in any maize RAC.

Storage stability of the stored treated maize forage, fodder and grain was tested at 0, 96 and 253 days. HPLC profiles were nearly identical to the spiking solution. Some breakdown of the parent compound to IFT-DKN occurred (up to 27%), but is considered not critically relevant for the study, as the parent was not found in the forage samples and IFT-DKN is relatively stable in storage.

Table 8 Extractability of radioactivity in maize treated pre-plant incorporated (PPI) or pre-emergence (PRE) soil applications at normal field use rate

RAC		TRR ^a	Readily extracted ^b		Enzyme released		Total extracted ^c		PES		Accountability
		mg/kg eq	mg/kg eq ^d	% TRR	mg/kg eq ^d	% TRR	mg/kg eq ^d	% TRR	mg/kg eq ^d	% TRR	% TRR
Forage	PPI	0.198	0.180	91.1	0.010	5.1	0.190	96.2	0.003	1.6	97.9
	PRE	0.228	0.226	99.1	0.007	3.0	0.233	102.1	0.003	1.3	103.3
Fodder	PPI	0.149	0.111	74.8	0.010	6.5	0.121	81.3	0.014	9.7	90.9
	PRE	0.120	0.095	78.9	0.008	6.5	0.102	85.4	0.014	11.8	97.2
Grain	PPI	0.044	0.038	87.4	n.a.	n.a.	0.038	87.4	0.003	7.5	94.9
	PRE	0.039	0.033	83.8	n.a.	n.a.	0.033	83.8	0.004	10.4	94.2

n.a.= not applicable; n.r. = not reported

^a TRR = based on initial TRR determined by combustion.

^b 4 extraction steps combined (HEX/EA, ACN, water and acid extraction);

^c Total extracted is the sum of the readily extracted and enzyme released radioactivity

^d calculated by the present reviewer based on %TRR and total TRR values for combustion

Table 9 Characterisation of isoxaflutole related residues from maize forage, fodder and grain

PPI/PRE	Extract	Total	IFT mg/kg eq (%TRR)	IFT-DKN mg/kg eq (%TRR)	IFT-BA mg/kg eq (%TRR)
Forage					
PPI 0.209 kg ai/ha DAT 41	TRR	0.190	nd	0.001 (0.53% TRR)	0.138 (72.6%TRR)
	HEX/EA	0.003 (1.4%TRR)	—	n.a.	—
	ACN	0.090 (45%TRR)	nd	trace	0.082 (43.2%TRR)
	water ^{a,b}	0.049 (27%TRR)	nd	trace	0.054 (28.4%TRR)
	ACID ^a	0.026 (14%TRR)	—	n.a.	—
	ENZ ^a	0.010 (5.1%TRR)	—	0.001 (0.53%TRR)	0.002 (1.1%TRR)
	Total extracted ^d	0.178 (94%TRR)		0.001 (conjugate) (0.53% TRR)	0.136 (free) (71.6% TRR) 0.002 (conjugate) (1.1% TRR)
	Total identified ^d		73.1% TRR		
PRE 0.227 kg ai/ha DAT 41	TRR	0.204	0.000	0.001 (0.49% TRR)	0.185 (89.2%TRR)
	HEX/EA	0.003 (1.4%TRR)			
	ACN	0.144 (69%TRR)	nd	trace	0.137 (67.2%TRR)
	water ^{a,b}	0.040 (19%TRR)	nd	trace	0.045 (22.1%TRR) ^{a, b}
	ACID ^{a,b}	0.012 (5.8%TRR)	—	—	—
	ENZ ^a	0.006	—	0.001	0.003

PPI/PRE	Extract	Total	IFT mg/kg eq (%TRR)	IFT-DKN mg/kg eq (%TRR)	IFT-BA mg/kg eq (%TRR)
		(3.0%TRR)		(0.49%TRR)	(1.5%TRR)
	Total extracted ^d	0.205 (100.5% TRR)	–	0.001 (conjugate) (0.49% TRR)	0.182 (free) (89.3% TRR) 0.003 (conjugate) (1.5% TRR)
	Total identified ^d		89.7%TRR		
Fodder					
PPI 0.209 kg ai/ha DAT 122/138	TRR	0.160	nd	trace	0.109 (68%TRR)
	HEX/EA	0.003 (1.71%TRR)	–	n.a.	–
	ACN	0.028 (18%TRR)	nd	trace	0.028 (17.5%TRR)
	water ^{a,b}	0.066 (41%TRR)	nd	nd	0.079 (49.4%TRR) ^{a, b}
	ACID ^{a,b}	0.021 (13%TRR)	–	–	– ^{a, b}
	ENZ ^a	0.010 (6.5%TTR)	nd	trace	0.002 (1.25% TRR)
	Total extracted ^d	0.119 (80%TRR)	–	–	0.107 (free) (66.9% TRR) 0.002 (conjugate) (1.25% TRR)
	Total identified ^d		68% TRR		
PRE 0.227 kg ai/ha DAT 122/138	TRR	0.113	nd	trace	0.072 (64%TRR)
	HEX/EA	0.002 (1.5%TRR)	–	n.a.	–
	ACN	0.023 (20%TRR)	nd	nd	0.023 (20.4%TRR)
	water ^{a,b}	0.045 (41%TRR)	nd	trace	0.046 (40.7%TRR) ^{a, b}
	ACID ^{a,b}	0.017 (14%TRR)	–	–	– ^{a, b}
	ENZ ^a	0.007 (6.5%TRR)	nd	trace	0.003 (2.7%TRR) conjugate
	Total extracted ^d	0.094 (83%TRR)	–	–	0.069 (free) (61.1%TRR) 0.003 (conjugate) (2.7% TRR)
	Total identified ^d		64%TRR		
Grain					
PPI 0.209 kg ai/ha DAT 122	TRR	0.053	nd	0.004 (7.5% TRR)	0.035 (66% TRR)
	HEX/EA	0.000	–	n.a.	–
	can ^c	0.032 (61%TRR)	nd	0.004 (7.5%TRR)	0.035 (66%TRR) ^c
	water ^c	0.010 (19%TRR)	–	–	– ^c
	ACID ^c	0.004 (6.9%TRR)	–	–	– ^c
	ENZ	n.a.			
	Total extracted ^d	0.046 (87%TRR)			0.035 (free) (66% TRR)
	Total		73.5%TRR		

PPI/PRE	Extract	Total	IFT mg/kg eq (%TRR)	IFT-DKN mg/kg eq (%TRR)	IFT-BA mg/kg eq (%TRR)
	identified ^d				
PRE 0.227 kg ai/ha DAT 122	TRR	0.043	nd	trace	0.029 (67%TRR)
	HEX/EA	0.000	—	—	—
	ACN ^c	0.025 (59%TRR)	nd	trace	0.029 (67%TRR)
	water	0.007 (18%TRR)	—	—	— ^c
	ACID ^c	0.003 (7%TRR)	—	—	— ^c
	ENZ ^a	n.a.	—	—	—
	Total extracted ^d	0.035 (82%TRR)	—	—	0.029 (free) (67% TRR)
	Total identified ^d		67%TRR		

n.a. = not analysed; nd = not detected (peaks of 200 DPM could still be detected)

^a Represents the results of the organic layer from partitioning with EtOAc, since the results from the aqueous layer were either not analysed or no radioactivity was observed.

^b The H₂O organic and acid organic extracts were combined prior to analysis due to insufficient radioactivity.

^c ACN, water- and ACID-organic extracts were combined prior to analyses due to low levels of radio activity.

^d Total extracted and total identified was calculated by the reviewer, based on reported values for individual extracts and individual compounds respectively. The % TRR for metabolites was calculated by the reviewer, based on mg/kg eq values.

Study 2

The metabolic fate and distribution of isoxaflutole was studied outdoors in maize (*N7070 BT*) after a post emergence application in combination with safener cyprosulfamide (equal weight fractions). Maize plants were treated with an SC formulation of [U-¹⁴C-phenyl]-isoxaflutole at an application rate of 0.211 kg ai/ha [Meyer and Ripperger, 2006, M-268739-01-2]. The soil characteristics were: sandy loam, pH 6.4, 1.7% om, 9.9 meq/100 g CEC. The active ingredient was applied 13 DAP at growth stage V2 (BBCH growth stage not reported) by hand-held pump sprayer. Plants were harvested for forage and sweet corn (kernels and cob with husks removed) on DAT 75 and for fodder and grain on DAT 106. For sweet corn and grain the ears of all the plants were combined. All samples were homogenized and stored frozen at –20 °C (for 4–10 days until extraction and for 4–33 days until analysis).

Aliquots of homogenised samples were combusted to determine the total radioactive residues (TRR) levels. Samples with TRRs greater than 0.01 ppm were extracted sequentially with ACN (3×), ACN/water (4:1) and ACN/water (1:1). Filtered extracts were combined. Extracts and solids were analysed by (combustion) LSC. After a clean-up through C18 SPE, the eluate was concentrated and adjusted to pH 2 with HCl and then partitioned with EtOAc. The EtOAc layer was concentrated and partitioned between hexane and MeOH/water (9:1). In case of forage and sweet corn, this layer was further fractionated by C18 solid-phase extraction. For forage and fodder, the aqueous fractions arising from the EtOAc partitioning were treated with 1 M NaOH (17 hours, 50 °C) and subsequently partitioned with DCM at both basic and acidic pH. The solids remaining after ACN/water extractions of fodder were subjected subsequently to ASE (Accelerated Solvent Extraction) with 0.5 N H₂SO₄/ACN (1:1) and aq NH₄OH/ACN (1:1). The extracts were sampled for LSC and the solids were sampled for drying and combustion. Identification and quantification in those extracts with sufficient radioactivity was performed by reverse-phase HPLC and confirmation by HPLC-MS-MS. Reference substances IFT, IFT-DKN, IFT-BA and RPA 205834 were used.

TRR (sum of extracts and solids) in forage accounted for 0.134 mg/kg eq, in sweet corn 0.010, fodder 0.10 and grain 0.015 mg/kg eq. TRR in the extracts ranged from 77.3 (grain)–96.3

(kernels + cobs with husks removed (K + CWHR)) % TRR (see Table 10). The TRR in the solids ranged from 3.7 (K + CWHR) to 22.7 (grain) %TRR, but were all < 0.01 mg/kg eq. Identification results are shown in Table 11. The residues in all the RACs were identified primarily as metabolite IFT-BA (61–67% TRR). A second metabolite, IFT-DKN, was found in the fractions of sweet corn, maize fodder and maize grain, accounting for the remaining identified radioactivity (< 10% TRR and ≤ 0.005 mg/kg eq). Parent IFT was not found.

Storage stability was not addressed as the samples were analysed within 33 days.

Table 10 Extractability of radioactivity in maize after treatment with 0.211 kg ai/ha

Matrix	DAT	TRR	ACN and water extracts		Solids	
		(mg/kg eq)	(% TRR)	(mg/kg eq)	(% TRR)	(mg/kg eq)
Forage	75 days	0.081	92.9	0.075	7.1	0.006
		0.156	nd	nd	nd	nd
		0.164	nd	nd	nd	nd
Mean		0.134				
Sweet corn (K+CWHR)	75 days	0.010	96.63	0.009	3.7	< 0.001
Fodder	106 days	0.120	87.9	0.106	12.1	0.015
		0.101	nd	nd	nd	nd
		0.078	nd	nd	nd	nd
Mean		0.100				
Grain	106 days	0.015	77.3	0.012	22.7	0.004

nd = not determined

Table 11 Characterisation and identification of radioactive residues in maize (0.211 kg ai/ha)

Compound	Forage (75 DAT)		Sweet corn (75 DAT)		Fodder (106 DAT)		Grain (106 DAT)	
	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq
TRR		0.081		0.010		0.100		0.015
IFT	–	–	–	–	–	–	–	–
IFT-BA	67.2	0.056	60.9	0.005	63.3	0.076	63.0	0.010
IFT-BA in EtOAc extract	–51.8	–0.043	60.9	0.005	–59.2	–0.071	–63.0	–0.010
IFT-BA organosoluble after base hydrolysis	–15.4	–0.013	–	–	–4.1	–0.005	–	–
IFT-DKN ^a	–	–	6.5	< 0.001	4.0	0.005	9.8	0.001
Total identified	67.2	0.056	67.4	0.006	67.3	0.081	72.8	0.011
Total characterized ^b	25.6	0.020	28.7	0.003	20.6	0.024	4.5	< 0.001
Other components ^a	–3.0	–0.002	–	–	– 11.8	– 0.014	–	–
Aqueous soluble after base hydrolysis	–15.1	–0.012	–25.6 ^c	–0.002 ^c	–7.7	–0.009	–4.0	–
Total extractable	92.9	0.075	96.3	0.009	87.9	0.106	77.3	0.012
PES ^d	7.1	0.006	3.7	< 0.001	12.1 ^e	0.015 ^e	22.7	0.004
Accountability ^f	86.1		114.5		114.8		113.2	

– = not detected (limit of detection was defined as the background radioactivity (25 DPM for LSC measurements). This was subtracted from each sample.

^a In EtOAc extract

^b Includes other components observed in HPLC, hexane, SPE fractions not analysed by HPLC, and water soluble (after base hydrolysis where applicable)

^c Water soluble 6.1% (< 0.001 mg/kg eq), Methanol soluble 14.3% (0.001 mg/kg eq), Other soluble 5.3% (< 0.001 mg/kg eq).

^d Residues remaining after exhaustive extractions.

^e Fibre further extracted with acid (4.3%), and base (1.5%). Remaining PES 6.3% (0.008 mg/kg eq)

^f Accountability = (TRR extracts + TRR solids)/(TRRs from combustion analysis) × 100.

Study 3

The metabolic fate and distribution of isoxaflutole was studied under field conditions in wheat (*Triticum aestivum*) [Unsworth and Clarke, 2000, M-211481-01-1]. [^{14}C -phenyl]-isoxaflutole was applied as a solution to immature plants (Zadoks growth stage 30, i.e. early stem elongation, pseudo stem erect - third node on the main stem) at a field rate of 0.055 kg ai/ha or at an exaggerated rate of 0.105 kg ai/ha. Only the results of the intended field rate were provided. The soil characteristics were: loam, pH 7.4, 3.3% om, 15.1 meq/100 g CEC. Plants were harvested at interim (hay) at growth stage Z58-Z73 (Zadoks) at DAT 41 or at final harvest at DAT 93 for grain and straw. All samples were homogenised and stored frozen at -20°C . Plant parts were weighed and homogenised. TRRs were determined by combustion.

The total radioactive residues (TRR) ranged from 0.058–0.172 mg/kg in hay, grain and straw (see Table 12). Samples were extracted by maceration with ACN and ACN/water. A total of 92.4% TRR, 96.5%TRR and 86.0% TRR were extracted from hay, grain and straw, respectively. For wheat straw, solids were soxhlet extracted with DCM/glacial acetic acid (4 hr) and an additional 3.0% TRR could be released. Following concentration, the combined extracts were subjected to quantitative and qualitative analyses by reverse-phase HPLC with radiodetection. Metabolite identification was confirmed by HPLC-MS-MS. Reference substances IFT, IFT-DKN, and IFT-BA were used.

The major metabolite in hay, grain and straw is IFT-BA, accounting for 65%TRR (0.112 mg/kg eq), 95.8%TTR (0.055 mg/kg eq) and 79.1% TRR (0.084 mg/kg eq), respectively. In hay and grain also metabolite IFT-DKN was found; representing 20.9%TRR (0.036 mg/kg eq) and 9.9%TRR (0.011 mg/kg eq), respectively. IFT was only found in hay (interim harvest), accounting for 6.5%TRR (0.011 mg/kg eq). Parent IFT was not found in grain and straw. A small fraction of the metabolites in straw might be attributed to conjugates, because 3% TRR was released through acid reflux. However, since the primary and refluxed extracts were mixed, this fraction cannot be indicated.

Storage stability was not addressed as the samples were analysed within 6 months (< 90 days) and the plant parts were stored frozen ($\leq -20^{\circ}\text{C}$) prior to extraction and refrigerated (4°C) between handling steps).

Table 12 Distribution of isoxaflutole related residues in wheat matrices following treatment with 0.055 kg ai/ha

	Hay—DAT 41		Grain—DAT 93		Straw—DAT 939	
TRR (mg/kg eq)	0.172		0.058		0.107	
	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq
IFT	6.5	0.011	—	—	—	—
IFT-BA	65.0	0.112	95.8	0.055	79.1	0.084
IFT-DKN	20.9	0.036	—	—	9.9	0.011
Unknowns	—	—	0.7	< 0.001	—	—
Solids	7.6	0.013	3.5	0.002	11.0	0.012

— = not detected (< 0.001 mg/kg)

Study 4

The metabolic fate and distribution of isoxaflutole were studied under greenhouse conditions in HPPD (p-hydroxyphenyl pyruvatedioxygenase) tolerant soya bean (FG72 Glytol soya bean) for pre-plant and foliar applications [Nguyen, 2010, M-368555-01-1]. [^{14}C -phenyl]-isoxaflutole was applied via hand-held sprayer as an SC formulation at an application rate of 0.330 kg ai/ha either directly to the soils prior to planting or applied uniformly to the soya bean plants at the full flowering stage (BBCH 65 or 57 DAP). The soil characteristics were: silty clay loam, pH 7.1, 1.7% om, 21.5 meq/100 g CEC. Plants were harvested for forage (BBCH 75), hay (BBCH 99) and seed (BBCH 99). All samples were homogenised and stored frozen at $\leq -20^{\circ}\text{C}$ prior to extraction.

Aliquots of homogenised samples were combusted to determine the total radioactive residues (TRR) levels. Samples were extracted several times with ACN/water (4:1) and filtered. The combined extracts were cleaned up with SPE. The remaining hay solids and soya bean seed solids were extracted with MeOH (reflux overnight) and subsequently treated with 1 M NaOH overnight at room temperature. Extracts and solids were analysed by (combustion) LSC. Identification and quantification of residues was accomplished by using reverse phase HPLC and confirmation by HPLC-MS-MS. Reference substances IFT, IFT-DKN, IFT-BA were used.

The total radioactive residues (TRR) in the RACs ranged from 0.149–0.268 mg/kg eq in pre plant RACs and from 0.259–13.128 mg/kg eq in post emergence application samples (Table 13 and Table 14).

The residues in the RACs of the pre-plant treated soya beans (Table 13) were identified primarily as metabolites IFT-amide (8–53%TRR), IFT-BA (27–66%TRR) and IFT-DKN (13–17%TRR). In hay an additional unidentified metabolite was detected (9%TRR (0.042 mg/kg eq)). Parent IFT was not found. A total of 91–93%TRR was identified.

Table 13 Distribution of metabolites in HPPD tolerant soya bean matrices following pre-plant treatment with 0.331 kg ai/ha

	Forage (74 DAT)		Hay (189 DAT)		Seed (189 DAT)	
TRR (mg/kg eq) ^a	0.268		0.492		0.149	
Metabolite/fraction	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq
ACN/water extract	93	0.270	91	0.448	92	0.144
IFT	–	–	–	–	–	–
IFT amide	53	0.154	13	0.062	8	0.013
IFT-BA	27	0.048	56	0.278	66	0.105
IFT-DKN	13	0.038	13	0.066	17	0.027
unknown (H3)	–	–	9	0.042	–	–
MeOH reflux fraction	n.a.	n.a.	5	0.024	2	0.003
1 M NaOH fraction	n.a.	n.a.	3	0.013	1	0.002
PES	7	0.021	2	0.008	5	0.008
Accountability ^b	100	0.291	101	0.493	100	0.157

n.a. = not applicable; n.r. = not reported

^a TRR determined by combustion

^b Determined by taking the sum of the extracted plus remaining solids as percentage of the TRR determined by combustion.

The residues in the forage samples of the post-emergence treated soya beans (Table 14) were identified primarily as IFT (72%TRR, 7.757 mg/kg eq), and metabolites IFT-DKN (18%TRR, 1.943 mg/kg eq), IFT-BA (6%TRR, 0.627 mg/kg eq) and an unidentified metabolite PE-F4 (3%TRR, 0.352 mg/kg eq). The residues in the hay samples of the post-emergence treated soya beans were identified primarily as metabolites IFT-BA (38%TRR, 0.608 mg/kg eq), IFT-DKN (21%TRR, 0.334 mg/kg eq), and IFT (25%TRR, 0.411 mg/kg eq) and IFT-amide (3%TRR, 0.055 mg/kg eq). In seed samples metabolites IFT-BA (62%TRR, 0.160 mg/kg eq), IFT-DKN (24%TRR, 0.061 mg/kg eq) and IFT-amide (8%TRR, 0.020 mg/kg eq) were identified. Parent IFT was not found.

Storage stability was not addressed as the samples were stored frozen immediately and analysed within 33 days.

Table 14 Distribution of metabolites in HPPD tolerant soya bean matrices following foliar treatment with 0.331 kg ai/ha

	Forage (17 DAT)		Hay (132 DAT)		Seed (132 DAT)	
TRR (mg/kg eq)	13.128		1.775		0.259	
Metabolite/fraction	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq
ACN/water extract	100	10.679	92	1.491	94	0.242
IFT	72	7.757	25	0.411	–	–
unknown (H1)	–	–	2	0.026	–	–

	Forage (17 DAT)		Hay (132 DAT)		Seed (132 DAT)	
TRR (mg/kg eq)	13.128		1.775		0.259	
Metabolite/fraction	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq
IFT amide	–	–	3	0.055	8	0.020
IFT-BA	6	0.627	38	0.608	62	0.160
IFT-DKN	18	1.943	21	0.334	24	0.061
unknown (F4)	3	0.352	–	–	–	–
unknown (H6)	–	–	3	0.056	–	–
MeOH reflux fraction	n.a.	n.a.	4	0.059	2	0.004
1 M NaOH fraction	n.a.	n.a.	2	0.030	1	0.003
PES	0.50	0.054	2	0.031	3	0.008
Accountability	82	10.73	91	1.61	99	0.257

n.a. = not applicable;

Study 5

The metabolic fate and distribution of isoxaflutole was studied under field conditions in poppies (*Papaver somniferum*, cultivar Mieszko) after a pre-emergence spray application, 3 DAS [Klempner, 2009, M-360799-01-1]. [^{14}C -phenyl]-isoxaflutole was applied as an SC formulation in combination with a non-radiolabelled safener cyprosulfamide via hand-held sprayer at an actual application rate of 0.108 kg ai/ha directly to bare soil. The soil characteristics were: sandy loam, pH 6.9, 2.12% om, 8.1 meq/100 g CEC. Poppy seeds, seed bolls with upper stem and poppy straw were harvested at maturity (BBCH stage 89–92) at DAT 110. All samples were homogenised and stored frozen at -18°C .

Aliquots of homogenised samples were combusted and radio assayed by LSC to estimate the total radioactive residues (TRR) levels. The total radioactive residues (TRR) in the RACs were 0.056, 0.779 and 0.725 mg/kg eq in seeds, seed bolls & upper stem, and straw, respectively (see Table 15).

Samples were extracted three times with ACN/water (8:2, v/v) and filtered. The solids were dried and analysed for radioactive residues by combustion and LSC. The extracts were radio assayed (LSC). The combined extracts were cleaned up with SPE. The eluate was collected and analysed by LSC. Less polar fractions were eluted with MeOH/tetrahydrofuran (1/1, v/v) and analysed by LSC.

The metabolic profiles of all extracts were analysed by radio-HPLC using reverse phase HPLC. Identification was mainly achieved by isolation of the metabolites from poppy extract by HPLC, followed by HPLC-MS and by HPLC and/or co-chromatography with reference substances IFT, IFT-DKN, IFT-BA and RPA 205834.

A total of 91.5–97.8% of the TRR was extracted. The residues in the RACs of the pre-plant treated soya beans were identified primarily as metabolite IFT-BA, being 6%TRR (0.037 mg eq/kg) in poppy seed, 94.3%TRR (0.734 mg/kg eq) in seed bolls & upper stem, and 88.7%TRR (0.643 mg eq/kg) in poppy straw). In seed bolls, upper stem and poppy straw minor amounts of AE 202248 were found (2.1%TRR and 3.6%TRR, respectively). This metabolite was not detected in poppy seed. In addition four minor, unidentified metabolites were detected in poppy seeds, two of them in seed bolls & upper stem, and one in poppy straw (range 1.0–5.4%TRR, 0.001–0.029 mg eq/kg). As they accounted for < 10% TRR, further analysis of these metabolites was not performed. Parent IFT was not found. A total of 66–96.4%TRR was identified.

Storage stability was not addressed as the samples were extracted and analysed within 14 days and 16 days (seed bolls with upper stem and poppy seeds, respectively) and 12 weeks (straw).

Table 15 Characterisation of residues of poppy matrices following pre-emergence treatment with 0.108 kg ai/ha

	Poppy seeds harvest DAT 110		Seed bolls & upper stem harvest DAT 110		Poppy straw harvest DAT 110	
TRR (mg/kg eq)	0.056		0.779		0.725	
	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq

	Poppy seeds harvest DAT 110		Seed bolls & upper stem harvest DAT 110		Poppy straw harvest DAT 110	
TRR (mg/kg eq)	0.056		0.779		0.725	
	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq
IFT	–	–	–	–	–	–
IFT-BA	66	0.037	94.3	0.734	88.7	0.643
IFT-DKN	–	–	2.1	0.016	3.6	0.026
Subtotal identified	66.0	0.037	96.4	0.751	92.3	0.670
Unknown 1	5.4	0.003	1.0	0.008	4.0	0.029
Unknown 2	2.5	0.001	–	–	–	–
Unknown 3	2.7	0.002	0.4	0.003	–	–
Unknown 4	7.1	0.004	–	–	–	–
Subtotal characterized	17.8	0.010	1.4	0.011	4.0	0.029
Extracts not analysed	7.8	0.004	–	–	0.5	0.003
Total extractable	91.5	0.051	97.8	0.762	96.8	0.702
PES	8.5	0.005	2.2	0.017	3.2	0.023
Accountability	100	0.056	100	0.779	100	0.725

– = not detected;

Study 6

The metabolic fate and distribution of isoxaflutole was studied under field conditions in sugar cane (variety *SP 79-1011*) [Unsworth, 1999, M-211498-01-1]. [^{14}C -phenyl]-isoxaflutole was applied as a solution either to soil just after sugar cane planting (pre-emergence) or on emerged sugar cane (foliar, 47 days after planting). The actual field rates were 0.210 kg ai/ha and 0.133 kg ai/ha, respectively, for pre-emergence and post-emergence treatments. The soil characteristics were: sandy clay, pH 6.2, 2.2% om, 8.1 meq/100 g CEC. Plants were harvested at DAT 81, 95 and 365 for pre-emergence application and at DAT 40, 95 and 365 for post emergence application. Whole plants were bagged and stored frozen until processing, except for the final harvest samples, where the leaves were separated from the cane. Plant parts were weighed and homogenized. All samples were stored frozen prior to homogenisation.

TRRs were determined by combustion and quantified by LSC. Results are shown in Table 16. Total radioactive residues in the DAT 365 samples were < 0.0001 mg/kg eq and in the DAT 95 samples after post emergence application 0.0065 mg/kg eq and therefore not further extracted. Only the DAT 40 (post-emergence), DAT 81 (pre-emergence) and DAT 95 (pre-emergence) samples were extracted. Extraction with ACN released 65.88%, 78.69% and 84% TRR, respectively in these samples. Remaining solids were sequentially soxhlet extracted with ACN (all samples) or ACN/water (80:20 vv, DAT 40 and DAT81). The solids remaining in the DAT 40 samples were extracted further with ACN/water (50:50, vv), 0.1 M HCl, 0.1 M ammonia, 0.1 M HCl at 60 °C, 0.1 M ammonia at 60 °C, reflux in 0.1 M HCl, reflux in 0.1 M ammonia. Extracts and solids were analysed by (combustion) LSC. A total of 90.4% TRR, 95.7%TRR and 93.5% TRR could be extracted in the DAT 40, DAT 81 and DAT 95 samples, respectively.

Following concentration, the combined extracts were subjected to quantitative and qualitative analyses by reverse-phase HPLC. Parent and metabolite identification was confirmed by HPLC-MS. Certified reference standards for IFT, IFT-DKN and IFT-BA were used.

The major metabolite in sugar cane is IFT-BA, accounting for 66.5%TRR (0.117 mg/kg eq) in DAT 40 plants treated with a post emergence application of isoxaflutole. It was also the major metabolite in DAT 81 and 95 sugarcane samples (pre-emergence application): 86–94%TRR, or 0.102 and 0.138 mg/kg eq at 81 DAT or 95 DAT harvested plants, respectively. IFT-DKN was only detected in the 40 DAT harvested sugar cane plants that had received a post emergence application (2.2%TRR or 0.004 mg/kg eq). Parent IFT was not found in any of the samples. Unknown compounds (9.8–10.8%TRR) were detected in the DAT 40/81 samples (pre- and post-emergence application), but were not detected in the DAT 95 or DAT 365 samples.

Storage stability was not addressed as the samples were analysed within 6 months after extraction and the plant parts were stored frozen ($\leq -20^{\circ}\text{C}$) prior to extraction and refrigerated (4°C) between handling steps). It is noted that it took 6 months between harvest and extraction and an additional month for HPLC extraction. Isoxaflutole degrades after 3 months to IFT-DKN (see section on storage stability). This could pose a problem. As the main metabolite in this case is IFT-BA, which is stable, it is not expected that the longer storage of the samples will have influenced the results of this study significantly.

Table 16 Characterisation of residues in sugar cane following a single pre- or post-emergence application of isoxaflutole

DAT	TRR (mg/kg eq)	IFT		IFT-BA		IFT-DKN		Unknowns (polar)		Total extracted	Solids
		%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR (mg/kg eq)	%TRR (mg/kg eq)
Pre-emergence application (field rate 0.210 kg ai/ha)											
81	0.1188	–	–	85.93	0.102	–	–	9.81	0.012	95.7 (0.1137)	4.3 (0.0051)
95	0.1473	–	–	93.50	0.138	–	–	–	–	93.5 (0.1377)	6.5 (0.096)
365	0.0008	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Post emergence application (field rate 0.133 kg ai/ha)											
40	0.1757	10.76	0.019	66.51	0.117	2.20	0.004	10.9	0.019	90.4 (0.1587)	9.6 (0.0170)
95	0.0065	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
365	0.0004	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. = not applicable; – = not detected;

Study 7

A study was conducted to demonstrate the effects of the safener cyprosulfamide (AE 0001789) on the metabolism of isoxaflutole in maize [Schulte, 2002, M-210791-01-1]. Three day old seedlings of Zea mays (maize variety: Lorenzo) plants were transferred with their primary roots into 3.5 ml vials. The roots were exposed to a nutrient solution containing $0.5\text{ }\mu\text{g ai/mL}$ as $[\text{U-}^{14}\text{C-phenyl}]\text{-isoxaflutole}$ alone or in combination with safener cyprosulfamide ($1\text{ }\mu\text{g/mL}$). Pure radio-labelled IFT was used without formulation. The safener cyprosulfamide was applied as WP20 formulation. The seedlings were incubated for 24 hr. During that time roots and shoots approximately duplicated their weight and an uptake of 1 ml to 2 ml of the application solution was observed. After 24 hr incubation the seedlings were transferred into beakers filled with nutrient solution (without IFT or safener). In these beakers plants grew for further 3 days in the plant chamber.

Plants treated with isoxaflutole alone had partially bleached leaves at DAT = 3, whereas the maize plants previously incubated with isoxaflutole in combination with the safener showed a clear reduction of leaf damage.

Plants were harvested at 3 DAT and material from 50 plants (shoots, seeds and roots) was used for preparation of one sample. The samples were homogenized and filtered subsequently with ACN/water (80/20, v/v), ACN/water (50/50), mixed with trifluoroacetic acid (TFA), and partitioned three times in EtOAc (shoot and root extracts only). The filtrates or acetyl extracts were subjected to radio-TLC. Metabolites were separated by their R_f values and their radioactivity was measured. The extracts were analysed to determine the levels of the two known IFT metabolites IFT-DKN and IFT-BA by combustion and LSC.

Distribution of radioactivity is shown in Table 17. After three days radioactive distribution over the plant is different for the isoxaflutole and isoxaflutole/safener combination. Planted seeds incorporated more radioactivity than shoots and roots.

Parent IFT was not found due to the rapid conversion to the IFT-DKN metabolite. Additionally plants treated with the isoxaflutole/safener combination show a lower ratio of the IFT-DKN/IFT-BA metabolites in the shoots compared to those plants treated with isoxaflutole alone (factor 2.3, see Figure 3). In seeds and roots no differences in the ratios between the IFT metabolites could be demonstrated and only small enzymatic degradation of IFT-DKN to the inactive IFT-BA metabolite was observed.

To check whether mono-oxygenase inhibitors 1-aminobenzotriazole (ABT) and piperonyl butoxide (PBO) antagonise safener activity of cyprosulfamide also treatment solutions containing ABT or PBO were tested. After treatment the seedlings of those inhibitor-treated plants were transferred to nutrient solution which also contained ABT or PBO. The addition of mono-oxygenase inhibitors did not reduce the safener effects, indicating that mono-oxygenases are not involved in the safener effects of cyprosulfamide.

The reduced uptake of radioactivity in the shoots of plants treated with the safener combination suggests that at least one of the protective effects of the safener might be due to a reduced translocation of IFT-DKN from the root system into the shoot.

Note: Compared to the roots relatively much radioactivity is observed in the planted seeds. According to the manufacturer the radioactivity is mainly located in the transition area between root and shoot and only a small distribution in the endosperm. The accumulation in the transition area between roots and shoots could be caused by the changes in the arrangement of the vascular bundles between roots and shoots [Bayer, 2013].

Table 17 Distribution of the radioactivity (sum of IFT, IFT-DKN and IFT-BA) between the different plant parts

	Isoxaflutole only treatment (% TAR)	Isoxaflutole + Safener treatment (% TAR)
Shoots	30.2	25.5
Seeds	42.1	48.3
Roots	27.8	26.2

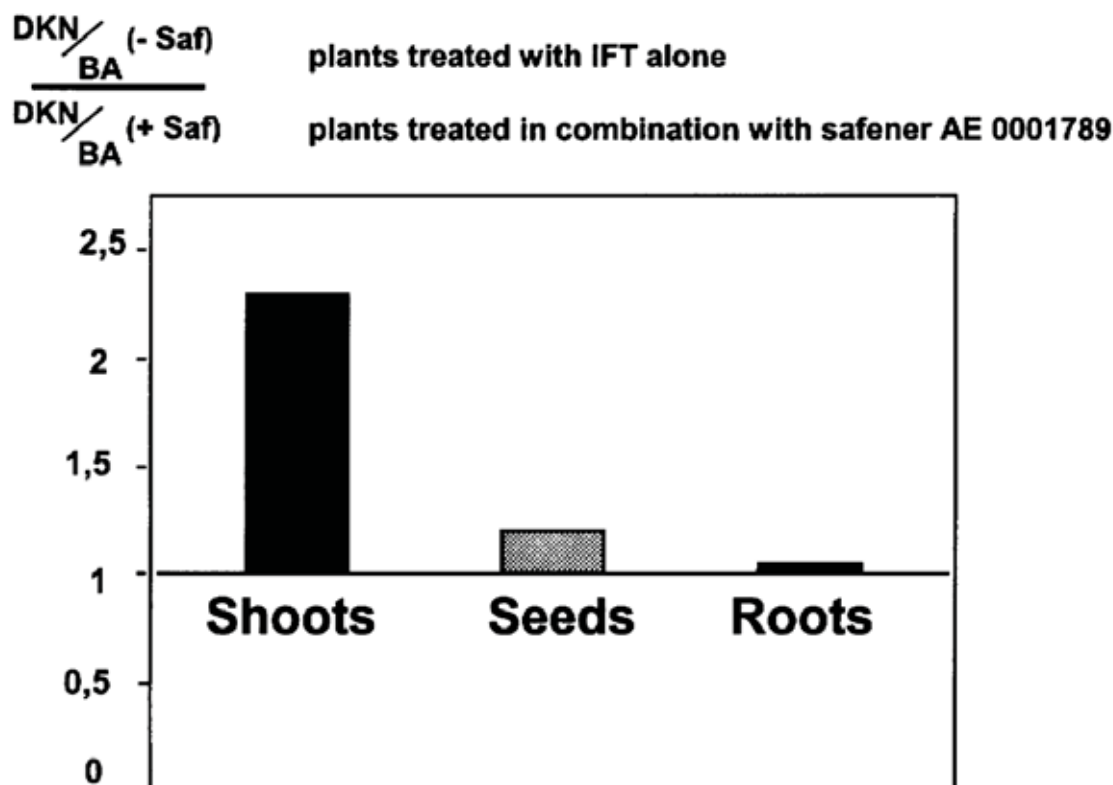


Figure 3 Ratio of IFT-DKN/IFT-BA for isoxaflutole and isoxaflutole/safener treatment

Overview metabolic pathway of isoxaflutole in plants

The same metabolic pathway of isoxaflutole was observed in the various metabolism studies on primary crops and rotational crops. The first hydrolytic step is the opening of the isoxazole ring to form IFT-DKN. Further hydrolytical cleavage of the carbonyl bridge and loss of the complete isoxazole moiety leads to the corresponding benzoic acid derivative (IFT-BA). The corresponding aminolysis to IFT amide could only be observed in the glyphosate/HPPD-tolerant soya beans. Application of a safener cyprosulfamide affects the breakdown of IFT-DKN to IFT-BA. The pathway is shown schematically in Figure 4.

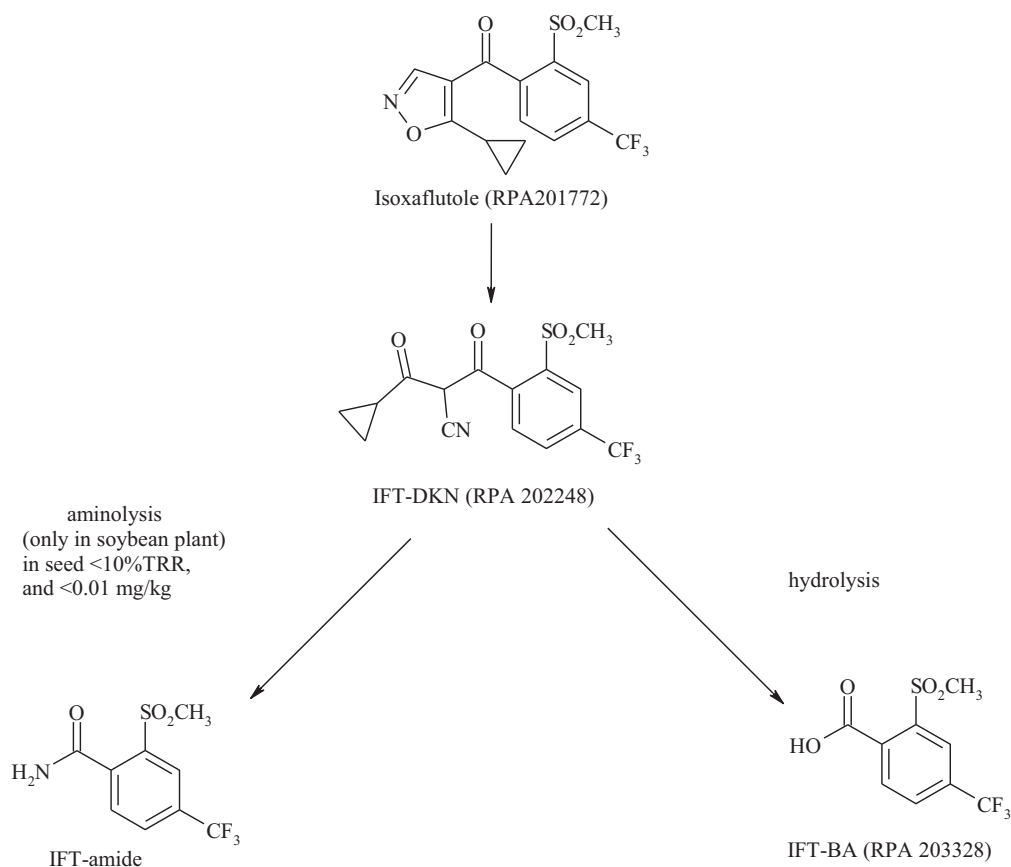


Figure 4 Proposed metabolic pathway of isoxaflutole in plant commodities

Environmental fate in soil

The Meeting received information on aerobic degradation in soil, photolysis on soil, and confined and field rotational crop studies. The fate and behaviour of isoxaflutole in the environment was investigated using [U-¹⁴C-phenyl]-isoxaflutole (see Figure 1).

Aerobic degradation in soil - laboratory studies

Study 1

The rate of aerobic degradation of isoxaflutole in a sandy loam soil at a temperature of 20 °C was investigated [Burr, 1996, M-240821-01-1]. Soil characteristics are reported in Table 18. Soils were stored aerobically at the test facility at 4 °C. The surface of a soil was then treated with [U-¹⁴C-phenyl]-isoxaflutole at a nominal rate of 0.2 mg ai/kg dry soil, corresponding with a field application rate of 0.20 kg ai/ha. Soil samples were incubated under aerobic conditions in the dark at 20 ± 2 °C and soil moisture of 45% of the maximum water holding capacity for up to 365 days.

Samples were taken at 0, 3 and 6 hours and at DAT = 1, 2, 3, 7, 14, 28, 59, 92, 120, 181, 273 and 365. All samples generated during the study were analysed as soon as possible, within a few days (maximum of 10 days) after generation.

The soil samples were extracted at ambient temperature using ACN/water followed by extraction with acidified (pH 3) ACN/water. Starting by day 59, samples were extracted with EtOAc in addition. Extracts were concentrated under reduced pressure by rotary evaporation at approximately

30 °C followed by reversed phase HPLC analysis and [^{14}C]-flow-through detection as primary and TLC as confirmatory analytical method.

Table 18 Soil characteristics

Soil texture (USDA) ^a	Sandy loam 95/04
Origin	Aldhams Farm, Manningtree Essex, UK
Sand (0.05–2 mm)	67.2
Silt (0.002–0.05 mm)	24.03
Clay (< 0.002 mm)	8.76
Organic Carbon (%)	2.2
Organic Matter ^b (%)	3.7
CEC (meq/100 g)	5.7
pH (water)	5.3
pH (CaCl ₂)	4.7
Moisture holding capacity @ 0.33 bar (%)	18.69
Moisture holding capacity @ 0.1 bar (%)	23.19
Maximum water holding capacity (MWHC, %)	60.28
Moisture content at incubation (%)	27.13
Bulk density (g/mL)	1.08
Microbial biomass (µg microbial carbon/g soil):	
—Initial	326
—After 4 months	215
—After 1 year	165

^a Classification according to United States Department of Agriculture

^b Organic matter calculated from organic carbon content $\times 1.7$

Isoxaflutole was degraded rapidly to form IFT-DKN and IFT-BA as major metabolites. Degradation was accompanied by the formation of minor metabolites including solids (9.13% TAR at study end, day 365) and volatile components and ^{14}C -CO₂ (1.76% TAR after 365 days of incubation). The distribution of radioactive residues is summarized in Table 19. Mass balances ranged between 94.3 and 103.8%.

Table 19 Distribution of radioactivity (% TAR) after aerobic incubation at 20 °C of soil treated with 0.2 mg ai/kg dry soil

Time	Isoxaflutole	IFT-DKN	IFT-BA	Total extracts ^a	Solids	^{14}C -CO ₂ ^b	Total
0 hours	92.74	1.42	nd	96.53	1.33	nd	97.8
3 hours	93.77	4.33	nd	100.35	1.62	0.01	102.0
6 hours	87.44	4.87	nd	94.47	1.66	0.01	96.1
1 day	74.55	20.01	0.38	97.24	3.23	0.01	100.5
2 days	56.02	37.82	1.42	98.62	4.19	0.01	102.8
3 days	37.74	51.97	3.52	96.26	5.61	0.02	101.9
7 days	13.49	62.13	16.54	92.70	1.50	0.07	94.3
14 days	6.73	46.19	43.30	96.71	5.19	0.23	102.1
28 days	0.37	20.02	66.98	92.31	2.85	0.61	95.8
59 days	nd	9.13	81.49	93.96	6.21	0.84	101.0
92 days	nd	11.18	75.31	91.02	6.15	0.95	98.1
120 days	nd	7.87	83.08	96.62	5.68	1.15	103.5
181 days	nd	5.90	77.16	88.23	8.15	1.23	97.6
273 days	nd	5.78	82.27	94.24	8.24	1.35	103.8
365 days	nd	4.44	77.27	90.95	9.13	1.76	101.8

^a Other minor components accounted for < 4.2% TAR each at any sampling interval

^b Values include other volatile radioactivity

nd = not detected

Best fit DT_{50} and DT_{90} values of isoxaflutole and its metabolite IFT-DKN were calculated using multi-compartment kinetic models while other approaches (i.e. linear regression analysis, Timme-Frehse) resulted in poor fits to experimental data. The data are summarized in Table 20.

Table 20 Best fit values of half-lives and DT_{90} of isoxaflutole and its metabolites in sandy loam soil 95/04

Compound	Multi compartment kinetic model		
	DT_{50} (days)	DT_{90} (days)	Fit ^a
Isoxaflutole	2.5	8.9	-0.999
IFT-DKN	19.5	218.6	-0.997
IFT-BA	— ^b	— ^b	— ^b

^a A value of ± 1.000 would represent a perfect fit to the experimental data

^b No calculation possible due to low extent of degradation observed under conditions of the test

Study 2

The rate of aerobic degradation of isoxaflutole in two soils at a temperature of 20 °C was investigated [Ferreira *et al.*, 1994, M-158435-01-1]. Soil characteristics are reported in Table 21. Soils were stored aerobically at the test facility at 4 °C. The surface of a soil was then treated with [U - ^{14}C -phenyl]-isoxaflutole at a nominal rate of 0.2 mg ai/kg dry soil, corresponding with a field application rate of 0.20 kg ai/ha. Soil samples were incubated under aerobic conditions in the dark at 21 ± 1 °C and soil moisture of 75% of the moisture holding capacity at 0.33 bar for up to 12 months. Samples were taken at 0, 2 and 6 hours and after 1, 2, 3, 7, 14 days and 1, 2, 3, 4, 6, 9 and 12 months of incubation after treatment (DAT). All samples generated during the study were analysed as soon as possible, within a few days (maximum of 10 days) after generation.

The soil samples were extracted at ambient temperature using ACN/water followed by extraction with acidified (pH 3) ACN/water. Starting by day 3 (clay soil) or after 1 month (sandy loam) samples were successively Soxhlet-extracted with EtOAc and hexane. Extracts were concentrated under reduced pressure by rotary evaporation at approximately 30 °C followed by reversed phase HPLC analysis and [^{14}C]-flow-through detection as primary and TLC as confirmatory analytical method.

Table 21 Soil characteristics

Texture (USDA) ^a	Sandy loam 93/7	Clay 93/6
Origin	American Agricultural Services Gourd Branch Road Lucama, NC, US	Coopers Shaw Road West Tilbury Marshes Essex, UK
Sand (0.05–2 mm)	69.95	11.58
Silt (0.05–0.002 mm)	23.79	38.78
Clay (< 0.002 mm)	6.26	49.64
Organic matter (%)	1.20	7.61
Organic carbon (%)	0.9	4.5
pH (water)	6.6	5.8
pH (1 M KCl)	5.7	4.6
CEC (mEq/100 g soil)	4.9	37.7
Bulk Density (g/mL)	1.54	0.88
Moisture Holding Capacity at 0.33 bar (%)	13.0	50.57
Fungi (organisms/g dry soil)	3.18×10^3	5.13×10^3
Bacteria (organisms/g dry soil)	2.9×10^6	2.18×10^6
Actinomycetes (organisms/g dry soil)	3.4×10^6	3.38×10^6
Biomass (μ g microbial carbon/g soil):		
—Beginning of Study	122.94	989.79
—End of Study	174	504
Soil Nomenclature (Series, Order, Sub-Order)	Norfolk, Ultisol, Typic Paleudults	Wallasea, Entisol, Typic Fluvaquent

^a Classification according to United States Department of Agriculture

Mass balances ranged between 90.7% and 108.0% of TAR for sandy loam soil 93/7 and 90.8% to 102.9% TAR for clay soil 93/6. Results for the extraction, distribution and identification of radioactivity are given in Table 22 and Table 23.

In both test soils the isoxaflutole degraded rapidly to form IFT-DKN and IFT-BA as major metabolites. Degradation was accompanied by the formation of minor metabolites including solids (15.44% TAR for sandy loam, 22.28% for clay after 12 months of incubation) and ¹⁴C-CO₂ (14.14% for sandy loam, 36.70% for clay loam after 12 months). Other volatile components were observed to a negligible extent. The distribution of radioactive residues is summarized in Tables 22 and 23.

Table 22 Isoxaflutole related residues in sandy loam soil 93/7 (% of TAR, mean values of two replicates)

Time	IFT	IFT-DKN	IFT-BA	Total extracts ^a	Solids	¹⁴ C-CO ₂ ^b	Total
0 hours	90.28	13.90	< 0.01	104.18	1.29	—	105.5
2 hours	96.30	9.87	< 0.01	106.17	1.83	0.01	108.0
6 hours	88.39	15.22	< 0.01	103.61	1.28	0.20	105.1
1 day	55.55	45.63	< 0.01	101.62	4.06	0.10	105.8
3 day	18.18	70.67	5.39	94.24	3.37	0.18	97.8
7 day	7.13	79.80	6.25	93.62	7.36	0.13	101.1
14 day	6.49	66.36	12.27	95.60	6.75	1.08	103.4
1 month	< 0.01	18.40	61.78	87.46	12.29	3.55	103.3
2 months	< 0.01	11.72	60.36	82.60	12.50	4.00	99.1
3 months	< 0.01	15.24	56.81	85.44	11.33	4.57	101.3
4 months	< 0.01	7.41	56.21	74.45	11.05	5.20	90.7
6 months	< 0.01	9.17	64.58	83.44	15.07	6.96	105.5
9 months	< 0.01	6.68	52.49	71.43	18.88	9.69	100.0
12 months	< 0.01	5.85	46.50	72.38	15.44	14.14	102.0

^a Other minor components each accounted for < 4.1% TAR at any sampling interval

^b Other volatile radioactivity accounted for < 0.2% TAR at any sampling interval

Table 23 Isoxaflutole related residues in clay soil 93/6 (% of TAR, mean values of two replicates)

Time	IFT	IFT-DKN	IFT-BA	Total extracts ^a	Solids	¹⁴ C-CO ₂ ^b	Total
0 hours	69.36	18.12	< 0.01	96.59	6.32	—	102.9
2 hours	50.91	27.77	< 0.01	93.29	5.35	0.01	98.7
6 hours	56.73	26.22	< 0.01	93.15	4.79	0.20	98.1
1 day	43.99	30.08	< 0.01	90.31	7.33	0.20	97.8
3 day	25.04	41.42	< 0.01	85.99	6.79	0.19	93.0
7 day	8.18	52.29	6.08	85.82	6.83	0.02	92.7
14 day	< 0.01	47.32	11.61	84.24	10.33	0.25	94.8
1 month	< 0.01	28.44	30.43	73.66	18.51	2.24	94.4
2 months	< 0.01	18.79	31.00	66.65	20.38	9.13	96.2
3 months	< 0.01	17.36	17.37	60.52	22.95	15.47	98.9
4 months	< 0.01	14.77	13.37	45.70	23.37	21.70	90.8
6 months	< 0.01	14.83	9.94	39.90	27.21	31.11	98.2
9 months	< 0.01	11.75	15.31	43.05	24.82	32.46	100.3
12 months	< 0.01	11.64	10.15	42.74	22.28	36.70	101.7

^a Other minor components each accounted for < 6.2% TAR at any sampling interval

^b Other volatile radioactivity accounted for < 0.1% TAR at any sampling interval

Half-lives of isoxaflutole and its metabolite IFT-DKN in the two soils were calculated using linear regression analysis. The results are summarized in Table 24.

Table 24 Half-lives of isoxaflutole and its metabolites IFT-DKN and IFT-BA in soils sandy loam 93/7 and clay 93/6

Compound	DT ₅₀ (days)			
	Sandy loam	r ²	Clay	r ²
Isoxaflutole	1.3	0.996	2.3	0.931
IFT-DKN	19.7	— ^a	37.2	— ^a
IFT-BA	977.4	— ^a	288.6	— ^a

^a Values not reported

Study 3

The rate of aerobic degradation of isoxaflutole in three soils at a temperature of 20 °C was investigated [Ferreira *et al.*, 1996, M-240822-01-1]. Soil characteristics are reported in Table 25. Soils were stored aerobically at the test facility at 4 °C. The surface of a soil was then treated with [U-¹⁴C-phenyl]-isoxaflutole at a nominal rate of 0.2 mg ai/kg dry soil, corresponding with a field application rate of 0.20 kg ai/ha. Soil samples were incubated under aerobic conditions in the dark at 20 ± 2 °C and soil moisture of 45% of the maximum moisture holding capacity. Samples of loam 95/02 soil were removed for analysis after 0, 1, 3, 5, 8, 16, 33, 64, 101 and 120 days of incubation while samples of loamy sand 95/06 were removed after 0, 0.25, 0.75, 1.67, 7, 15, 30, 63, 91 and 120 days. Finally, samples of clay loam 95/05 were removed after 0, 0.125, 0.25, 0.375, 3, 7, 17, 46, 82 and 120 days.

Soil samples of loam 95/02 and loamy sand 95/06 were extracted by using ACN/0.01 M aqueous calcium chloride followed by extraction with acidified (pH 3) ACN/water at ambient temperature. In case radioactive residues in extracted soil were > 10% TAR, samples were successively Soxhlet-extracted with acidified (pH 3) ACN/water and EtOAc. Samples of loamy sand 95/06 and incubated for 30 days were additionally extracted with aqueous 0.01 M diaminoethanetetraacetic acid (EDTA) solution at ambient temperature. Soil samples of clay loam 95/05 were extracted by using ACN/0.01 M aqueous calcium chloride at ambient temperature. In case radioactive residues remaining solids were > 10% TAR, samples were extracted with aqueous 0.01 M EDTA solution at ambient temperature followed by Soxhlet extraction with EtOAc. Extracts were concentrated under reduced pressure by rotary evaporation at approximately 30 °C followed by reversed phase HPLC analysis and [¹⁴C]-flow-through detection as primary and TLC as confirmatory analytical method. Selected soil extracts were investigated by HPLC-MS.

Table 25 Physico-chemical characteristics of the test soils

Texture (USDA) ^a	Loam 95/02	Loamy Sand 95/06	Clay Loam 95/05
Origin	Well Field Boarded Barns Farm Shelley, Ongar, Essex, UK	Flint Hill Farm Royston, Hertfordshire, UK	Roos Hall Beccles, Suffolk, UK
Particle size distribution (%)			
Sand (2–0.063 mm)	35.78	87.07	18.98
Silt (0.063–0.002 mm)	44.19	5.58	45.46
Clay (< 0.002 mm)	20.02	7.35	35.55
Organic carbon	1.9	1.1	2.5
Organic matter ^b	3.2	1.9	4.3
CEC (mEq/100 g)	1.9	1.1	2.5
pH in Water	4.8	7.4	8.2
pH (0.01 M CaCl ₂)	4.3	6.7	7.8
Moisture Holding Capacity at 0.33 bar ^c (%)	19.9	24.13	29.25
Moisture Holding Capacity at 0.1 bar ^d (%)	25.52	28.28	62.48
Maximum Holding Capacity (%)	59.91	38.82	77.79

Texture (USDA) ^a	Loam 95/02	Loamy Sand 95/06	Clay Loam 95/05
Origin	Well Field Boarded Barns Farm Shelley, Ongar, Essex, UK	Flint Hill Farm Roysten, Hertfordshire, UK	Roos Hall Beccles, Suffolk, UK
Moisture Content During Incubation (%)	26.96	17.47	35.01
Microbial Biomass (µg/g soil):			
—Beginning of Study	225	191	558
—End of Study	172	175	613

^a Classification according to United States Department of Agriculture

^b Calculated from organic carbon content x 1.7

^c Equivalent to pF = 2.5

^d Equivalent to pF = 0

The total recovery of radioactivity ranged 97.4–104.6% of TAR for soil loam 95/02, 91.6–102.5% for soil loamy sand 95/06 and 90.6–102.9% for soil clay loam 95/05 (mean values of two replicates).

In all test soils the isoxaflutole degraded rapidly to form IFT-DKN as a major metabolite. The further conversion proceeded via formation of IFT-BA as a major metabolite in soils loam 95/02 and loamy sand 95/06. In soil clay loam 95/05, IFT-BA was observed as a minor component (7.13% TAR by day 7 in maximum) along with the formation significant amounts of solids (31.22% by day 120) and ¹⁴C-CO₂ (34.62%, day 120).

Degradation was accompanied by the formation of minor metabolites including RPA 205834. In soils loam 95/02 and loamy sand 95/06, formation of solids (9.02% for loam 95/02, 4.09% for loamy sand 95/06 after 120 days of incubation) and ¹⁴C-CO₂ (1.26% for loam 95/02, 0.70% for loamy sand 95/06 after 120 days) was less pronounced indicating a slow transformation of isoxaflutole residues beyond IFT-BA under the conditions of the test. The distribution of radioactive residues is summarized in Table 26 to Table 28.

Table 26 Isoxaflutole related residues in loam soil 95/02 (% of TAR, mean values of two replicates)

Time [days]	IFT	IFT-DKN	IFT-BA	Total extracts ^a	Solids	¹⁴ C-CO ₂	Total
0	94.62	3.68	nd	98.30	1.95	n.m.	100.3
1	80.81	14.07	nd	94.88	2.80	n.m.	97.7
3	64.37	27.00	nd	91.37	5.92	0.05	97.4
5	35.76	51.92	4.37	93.09	7.94	0.05	101.1
8	24.57	63.78	6.78	97.07	1.84	0.02	98.9
16	11.20	71.22	16.81	101.55	2.84	0.21	104.6
33	5.62	55.75	30.85	94.33	3.99	0.29	98.6
64	1.82	38.21	49.98	91.98	5.94	0.72	98.7
101	0.64	31.45	60.01	93.56	6.14	0.97	100.7
120	nd	26.23	64.07	90.30	9.02	1.26	100.6

^a Other minor components including RPA 205834 each accounted for < 2.4% TAR at any sampling interval

n.m. = not measured

nd = not detected

Table 27 Isoxaflutole related residues in loamy sand soil 95/06 (% of TAR, mean values of two replicates)

Time [days]	IFT	IFT-DKN	IFT-BA	Total extracts ^a	Solids	¹⁴ C-CO ₂	Total
0	93.93	2.39	nd	96.32	0.23	n.m.	96.6
0.25	70.19	27.22	nd	97.41	0.47	n.m.	97.9
0.75	42.35	58.74	0.71	101.80	0.70	n.m.	102.5
1.67	8.28	85.84	2.25	96.36	1.37	n.m.	97.7
7	nd	94.60	1.84	96.44	1.79	0.18	98.4
15	nd	85.86	4.80	90.66	1.39	0.33	92.4
30	nd	41.75	41.84	84.08	4.76	2.61	91.6
63	nd	10.44	78.21	89.82	6.55	3.13	99.5
91	nd	5.21	89.83	95.25	3.93	0.59	99.8
120	nd	4.15	90.02	95.02	4.09	0.70	100.0

^a Other minor components including RPA 205834 each accounted for < 0.6% TAR at any sampling interval

n.m. = not measured

nd = not detected

Table 28 Isoxaflutole related residues in clay loam soil 95/05 (% of TAR, mean values of two replicates)

Time [days]	IFT	IFT-DKN	IFT-BA	Total extracts ^a	Solids	¹⁴ C-CO ₂	Total
0	92.13	4.31	nd	96.45	4.48	n.m.	100.9
0.125	74.64	23.03	nd	97.66	4.83	n.m.	102.5
0.25	52.92	40.83	nd	93.75	6.01	n.m.	99.8
0.375	41.31	51.00	nd	92.31	6.98	0.05	99.3
3	nd	96.39	3.66	100.05	2.73	0.14	102.9
7	1.36	83.89	7.13	92.38	3.81	0.45	96.6
17	1.33	72.18	6.80	79.19	9.46	4.43	94.8
46	nd	45.53	2.78	53.68	21.37	16.05	93.0
82	nd	28.80	1.64	33.11	27.96	26.22	90.6
120	nd	20.24	0.72	23.61	31.22	34.62	92.2

^a Other minor components including RPA 205834 each accounted for < 5.5% TAR at any sampling interval

n.m. = not measured

nd = not detected

Half-lives of isoxaflutole in the three soils were calculated using linear regression analysis assuming simple first order kinetics. For metabolites IFT-DKN and IFT-BA values for half-lives and DT₉₀ in aerobic soil were calculated, where possible, by using the software Kinetic Modelling (KIM). The results are summarized in Table 29.

Table 29 Half-lives and DT₉₀ of IFT and its metabolites IFT-DKN and IFT-BA in soils clay loam 95/02, loamy sand 95/06 and loam 95/05

Compound	IFT		
Soil	DT ₅₀	DT ₉₀	Correlation coefficient r ²
Loam 95/05	4 days	13.1 days	0.977
Loamy Sand 95/06	11.4 hours	37.8 hours	0.983
Clay Loam 95/02	7.6 hours	25.1 hours	0.992
Compound	IFT-DKN		
Soil	DT ₅₀	DT ₉₀	Fitting criterion
Loam 95/05	25 days	— ^a	−0.993
Loamy Sand 95/06	56 days	— ^a	−0.988
Clay Loam 95/02	41 days	— ^a	−0.998

Compound	IFT		
Soil	DT ₅₀	DT ₉₀	Correlation coefficient r ²
Compound	IFT-BA		
Loam 95/05	— ^c	— ^b	— ^b
Loamy Sand 95/06	— ^c	— ^b	— ^b
Clay Loam 95/02	— ^c	— ^b	— ^b

^a Not calculated

^b Not calculable, because study period was too short for this metabolite

Soil photolysis

The rate of photolysis was investigated on a 93/22/1 sandy loam soil [Ferreira, 1994, M-158351-01-1]. The soil was surface-treated with [U-¹⁴C-phenyl]-isoxaflutole at an exaggerated rate of 36.5 µg/sample, equivalent to 0.645 kg ai/ha. Soil samples were irradiated under aerobic conditions at 25 ± 1 °C and soil moisture of 75% of the moisture holding capacity at 0.33 bar. Another set of soil samples was incubated under aerobic conditions in the dark at 25 ± 1 °C and soil moisture of 75% of the moisture holding capacity at 0.33 bar to serve as dark controls. Samples of irradiated soil and dark controls were removed for analysis after 0, 0.125, 0.25, 0.67, 1, 2, 7, 14, 21 and 31 days of incubation. The characteristics of the test soils are given in Table 30.

Soil samples were extracted with aqueous ACN (day 0 samples) followed by extraction with acidified (pH 3) ACN/water at ambient temperature (samples of day 1, 2, 7, 14, 21 and 31). Dark controls of day 31 were Soxhlet-extracted using EtOAc, followed by hexane and 1 M HCl. Extracts were concentrated at approximately 31 °C followed by reversed phase HPLC analysis and ¹⁴C-flow-through detection as primary and TLC as confirmatory analytical method. Selected soil extracts were investigated by HPLC-MS.

Table 30 Physico-chemical characteristics of test soil

Soil texture (USDA) ^a	Sandy loam 93/22
Origin	Field Research Facility, American Agricultural Services, Lacama, NC, US
Sand (0.05–2 mm)	53.98
Silt (0.002–0.053 mm)	40.80
Clay (< 0.002 mm)	5.23
Organic Carbon (%)	1.3
Organic Matter ^b (%)	2.2
CEC (meq/100 g)	5.7
pH (water)	7.07
pH (0.01 M CaCl ₂)	5.54
Moisture holding capacity @ 0.33 bar (%)	11.00
Bulk density (g/mL)	1.59
Microbial activity (organisms per g of dry soil):	
—Fungi	4.53 × 10 ³
—Bacteria	2.63 × 10 ⁶
—Actinomycetes	1.365 × 10 ⁶

^a Classification according to United States Department of Agriculture

^b Organic matter calculated from organic carbon content × 1.7

The total recovery of radioactivity ranged from 88.5–101.4% of TAR for irradiated soil samples and from 91.6–101.5% for dark controls (mean values of two replicates). Isoxaflutole degraded rapidly to form IFT-DKN and IFT-BA as major metabolites in irradiated samples as well as in dark controls. Both metabolites have been observed as transformation products in aerobic soil degradation, IFT-DKN being the result of (abiotic and biotic) hydrolysis and IFT-BA to result from microbial degradation of IFT-DKN. In irradiated samples, solids were formed to a low extent (7.63% by day 31) accompanied by insignificant levels of ¹⁴C-CO₂ (0.13%, day 31). For dark controls

formation of solids and mineralisation to $^{14}\text{C-CO}_2$ was also low being at a similar level as observed for irradiated samples (NER: 4.02%, $^{14}\text{C-CO}_2$: 0.06%, both day 31).

Since the decline of parent compound and the extent of formation of metabolites observed in this experiment was virtually the same for both, i.e. irradiated samples and dark controls, there was no observation of components formed specifically from photo-transformation processes. This allows for the conclusion that the extent of photolytic degradation was insignificant. The distribution of radioactive residues is summarized in Table 31 for irradiated samples and in Table 32 for dark controls.

Table 31 Isoxaflutole related residues in irradiated samples of loam soil 93/22 (% of TAR, mean values of two replicates)

Time [days]	IFT	IFT-DKN	IFT-BA	Total extracts	Solids	$^{14}\text{C-CO}_2^a$	Total
0	95.40	4.04	< 0.01	99.43	0.20	n.m.	99.6
0.125	77.81	19.62	< 0.01	97.42	0.83	< 0.01	98.3
0.25	70.73	28.11	< 0.01	98.84	1.17	< 0.01	100.0
0.67	53.21	41.02	< 0.01	94.22	2.11	< 0.01	96.3
1	44.03	41.51	< 0.01	87.74	0.76	< 0.01	88.5
2	31.86	53.31	1.53	90.42	1.00	< 0.01	91.4
7	4.60	78.77	4.48	93.95	2.44	0.02	96.4
14	1.50	74.65	12.14	95.98	4.04	0.03	100.1
21	< 0.01	69.79	15.45	93.49	5.15	0.08	98.7
31 ^b	< 0.01	58.42	25.78	93.58	7.63	0.13	101.4

^a Other volatile components accounted for 0.01% or less at any sampling interval

^b Mean values of four replicates

n.m. = not measured

Table 32 Isoxaflutole related residues in dark controls of loam soil 93/22 (% of TAR, mean values of two replicates)

Time [days]	IFT	IFT-DKN	IFT-BA	Total extracts	Solids	$^{14}\text{C-CO}_2^a$	Total
0	95.40	4.04	< 0.01	99.43	0.20	n.m.	99.6
0.125	64.39	30.62	< 0.01	95.00	0.80	< 0.01	95.8
0.25	67.60	28.14	< 0.01	95.74	1.18	< 0.01	96.9
0.67	59.26	34.60	< 0.01	93.86	1.99	< 0.01	95.9
1	33.11	56.98	< 0.01	92.13	0.84	< 0.01	93.0
2	31.87	55.10	1.56	92.58	1.03	< 0.01	93.6
7	4.53	69.69	6.85	87.86	3.70	0.02	91.6
14	1.52	68.59	14.79	93.85	5.36	0.02	99.2
21	< 0.01	56.57	27.05	92.31	9.14	0.04	101.5
31 ^b	< 0.01	40.67	36.77	93.00	4.02	0.06	97.1

^a Other volatile components accounted for 0.01% or less at any sampling interval

^b Mean values of four replicates

n.m. = not measured

Half-lives of isoxaflutole derived from irradiated soil and after incubation in the dark were calculated using linear regression analysis assuming simple first order kinetics. The results are summarized in Table 33.

Table 33 Half-lives of isoxaflutole in irradiated and dark control samples in soil sandy loam 93/22

Compound	IFT		
	DT ₅₀	DT ₉₀	r ²
Irradiated	22.8 hours	— ^a	not reported
Dark controls	19.7 hours	— ^a	not reported

^a Not calculated

Proposed degradation pathway of isoxaflutole in/on soil

The first hydrolytic step in the aerobic degradation in soils is the opening of the isoxazole ring to form IFT-DKN. Further hydrolytical cleavage of the carbonyl bridge and loss of the complete isoxazole moiety leads to the corresponding benzoic acid derivative (IFT-BA). The proposed route of degradation is shown schematically in Figure 5. These same metabolites are also found in primary and rotational crops, as a result of uptake from the soil or metabolism within the plant.

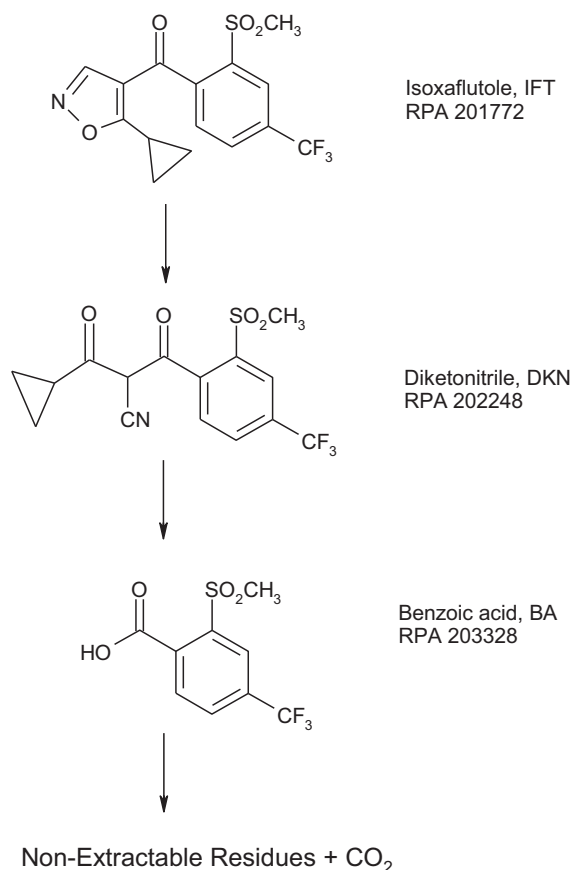


Figure 5 Proposed route of degradation of isoxaflutole in/on soil under aerobic conditions

Confined rotational crop studies

The metabolism of isoxaflutole was investigated in rotational crops that were sown in pre-treated soil [Hampton and Pettaway, 1995b, M 192308-01-1]. The treatment and cultivation of crops were conducted in an outdoor fenced facility in Lucama, NC, USA in 1993–1994. The application was done as soil surface pre-emergence or as pre-plant incorporated application, at actual application rates of 0.213 kg ai/ha as [U-¹⁴C-phenyl]-isoxaflutole. Each treatment (control, soil surface or incorporated application) was performed with an isoxaflutole solution in ACN/water (1/1, v/v) in a tank filled with a lower layer of gravel and a supernatant layer (35–45 cm) of sandy loam soil (1.8% om, pH 6.3, CEC 7.9 meq/100 g, 14.6% MWHC at 1/3 bar). Radish (var White Icicle), lettuce (var Butter crunch), grain sorghum (var Pioneer Hybrid 8222), mustard (var Southern Giant Curled) and winter wheat (var Pioneer 2548) were planted in the tanks. Radish, lettuce and grain sorghum were planted at PBI 34 days, radish, mustard and winter wheat at PBI 123 days and radish, lettuce and grain sorghum at PBI

365 days. Lettuce at the last rotational interval needed replanting at 375 days due to a seedling infectious disease which reduced the stand. Prior to each planting, the soil was tilled to depth of 5–10 cm. In each rotation, one sample was taken at immature (1 to 3 weeks before maturity) and mature stages of the plants. Mature wheat and sorghum was separated in grain and straw/fodder. Radish plants were shaken to remove adhering soil and subsequently separated in roots and tops. Sample sizes were: 0.048–0.23 kg immature lettuce, 0.19–0.68 kg immature radish leaf, 0.038–0.084 kg immature radish roots, 1.1–1.4 kg sorghum forage, 0.3–1.0 kg mature lettuce, 3.3–4.6 kg mature radish leaf, 2.2–4.0 kg mature radish root, 0.69–1.0 sorghum grain, 2.4–3.2 kg sorghum fodder. Soil sample cores of 0–15 and 15–30 cm depth were sampled at the time of application and at each planting. Soil and plant samples were stored at -3 °C or lower for 434–741 days.

Total radioactive residues (TRR) were determined in homogenised samples of crops and soil by combustion and LSC. Crop samples with TRRs greater than 0.01 mg/kg eq were subsequently extracted with hexane/EtOAc (9:1 v/v), ACN, water (pH 5.5) and ACN/0.2 M HCl (1:1 v/v). The pH for the water extraction was adjusted to pH 5.5, because at this pH hydrolysis of IFT or isoxaflutole related conjugates did not occur. Radioactive residues in extracts and remaining solids were quantified by (combustion) LSC. For samples with appropriate levels of radioactivity, the water and ACN/0.2 M HCl extracts were partitioned against EtOAc and both layers again analysed by LSC. Organic layers containing > 10% TRR or > 0.01 mg/kg eq were concentrated and subsequently analysed by HPLC with radioactive detection and co-chromatography of standards for IFT, IFT-DKN and IFT-BA. Parent and metabolites were confirmed by HPLC-MS-MS with APCI when feasible using standards for IFT, IFT-DKN, IFT-BA and RPA 205834.

Based on application rate, expected levels are 0.11 mg/kg eq in the top 0–15 cm soil. The TRR in the top 0–15 cm treated soil significantly decreased with time from 0.07–0.08 mg/kg eq at day 0 to a plateau of 0.02–0.03 mg/kg eq. The concentration at 15–30 cm was fairly stable at 0.01 mg/kg eq indicating very minor leaching of radioactivity. Radio-activity was not further characterized.

The results in rotational crops are shown in Table 34 (pre-plant incorporated) and Table 35 (pre-emergence). The highest total radioactive residue (TRR) of 0.24 mg/kg eq was found in sorghum forage of the first rotation after pre-plant incorporated soil application.

The metabolic profile was similar in all crops of the study. IFT was detected by HPLC-MS-MS in trace amounts (< 0.001 mg/kg eq) in radish leaves, sorghum grain and sorghum fodder of the first rotation (34 days) and wheat forage of the second rotation (123 days). IFT-BA represented the major compound and was present in the RACs of the first (34 days), second (123 days) and third rotation (365 days) at levels between < 0.001–0.11 mg/kg eq. IFT-DKN was only found in radish leaves and sorghum grain at levels up 0.005 mg/kg eq in the first rotation (34 days). RPA 205834 was detected by HPLC-MS-MS in trace amounts (< 0.001 mg/kg eq) in mature lettuce of the first rotation (34 days). A fourth metabolite (U1) was found in the RACs of the first (34 days), second (123 days) and third rotation (365 days) at levels between < 0.001–0.022 mg/kg eq. This metabolite was analysed by HPLC-MS-MS after extensive purification and a relative molecular weight of 192 was determined. The polarity of this metabolite, as evidenced by its relative retention time, suggests it is a carboxylic acid degradation product of IFT-BA with the structural formula $\text{CF}_3\text{-C}_6\text{H}_4\text{-COOH}$ (4-trifluoromethyl benzoic acid).

Based on storage stability study 6, it was concluded that after 23 months of storage at -20 °C, IFT partially converts to IFT-DKN and RPA 203328 in sorghum forage, sorghum fodder, sorghum grain, lettuce, radish leaves and radish roots. Total residues (sum of IFT, IFT-DKN and IFT-BA) remained stable for at least 23 months in each matrix tested. Results from the aerobic soil degradation studies showed that isoxaflutole had a short half-life (30 hrs) in sandy loam soil and that IFT-BA was the predominant residue in soil after 1 month. These findings suggest that the likelihood that isoxaflutole was present in the soil in the PBI 34 day is low and that IFT-BA is the main metabolite present for plant uptake.

Table 34 TRR and nature of residues in rotational crops after pre-plant-soil incorporated application

PBI days (rotation number)	Matrix	DAP	DAT	TRR mg/kg eq	IFT %TRR	IFT-DKN % TRR (mg/kg eq)	IFT-BA %TRR (mg/kg eq)	U1 %TRR (mg/kg eq)	Solids %TRR	Total %TRR
34 (1 st)	Immature radish leaf	21	55	0.014	0 (< 0.001)	7.1 (0.001)	78.6 (0.011)	0 (< 0.001)	9.2	94.9
	Mature radish leaf	41	75	0.019	0 (< 0.001)	26.3 (0.005)	36.8 (0.007)	0 (< 0.001)	5.5	68.6
	Immature radish root	21	55	0.008 _{NE}	—	—	—	—	—	—
	Mature radish root	41	75	0.003 _{NE}	—	—	—	—	—	—
34 (1 st)	Immature lettuce leaf	41	75	0.042	0 (< 0.001)	0 (< 0.001)	74.4 (0.029)	23.8 (0.010)	3.3	101.5
	Mature lettuce leaf	49	83	0.022	0 (< 0.001)	0 (< 0.001)	59.1 (0.013)	31.8 (0.007)	6.3	97.2
34 (1 st)	Sorghum forage	41	75	0.24	0 (< 0.001)	0 (< 0.001)	100 (0.24)	0 (< 0.001)	1.9	101.9
	Mature sorghum fodder	134	168	0.13	0 (< 0.001)	0 (< 0.001)	74.6 (0.097)	0 (< 0.001)	7.1	81.7
	Mature sorghum grain	134	168	0.12	0 (< 0.001)	0.8 (0.001)	67.2 (0.080)	10.1 (0.012)	11.4	89.5
123 (2 nd)	Immature radish leaf	45	168	0.002 _{NE}	—	—	—	—	—	—
	Mature radish leaf	58	181	0.002 _{NE}	—	—	—	—	—	—
	Immature radish root	45	168	0.001 _{NE}	—	—	—	—	—	—
	Mature radish root	58	181	0.001 _{NE}	—	—	—	—	—	—
123 (2 nd)	Immature mustard leaf	45	168	0.004 _{NE}	—	—	—	—	—	—
	Mature mustard leaf	58	181	0.002 _{NE}	—	—	—	—	—	—
123 (2 nd)	Immature wheat forage	133	256	0.013	0 (< 0.001)	0 (< 0.001)	100 (0.013)	0 (< 0.001)	5.3	105.3
	Mature wheat straw	239	362	0.030	0 (< 0.001)	0 (< 0.001)	70.0 (0.021)	0 (< 0.001)	25.7	95.7
	Mature wheat grain	239	362	0.018 ^a	0 (< 0.001)	0 (< 0.001)	100 ^a (0.018)	0 (< 0.001)	6.4 ^a (0.0012)	106.4 ^a
365 (3 rd)	Immature radish leaf	28	393	0.008 _{NE}	—	—	—	—	—	—
	Mature radish leaf	38	403	0.011 ^a	0 (< 0.001)	0 (< 0.001)	18.2 ^a (0.002)	81.8 ^a (0.009)	3.9 (< 0.001)	103.9 ^a
	Immature radish root	28	393	0.002 _{NE}	—	—	—	—	—	—
	Mature radish root	38	403	0.001 _{NE}	—	—	—	—	—	—
375 (3 rd)	Immature lettuce leaf	51	426	0.006 _{NE}	—	—	—	—	—	—
	Mature lettuce leaf	71	446	0.005 _{NE}	—	—	—	—	—	—
365 (3 rd)	Sorghum forage	38	403	0.051	0 (< 0.001)	0 (< 0.001)	31.4 (0.016)	33.3 (0.017)	3.4	68.1
	Mature sorghum	110	475	0.041 ^a	0 (< 0.001)	0 (< 0.001)	46.3 ^a (0.019)	46.3 ^a (0.019)	7.3 ^a (0.003)	99.9 ^a

PBI days (rotation number)	Matrix	DAP	DAT	TRR mg/kg eq	IFT %TRR	IFT-DKN % TRR (mg/kg eq)	IFT-BA %TRR (mg/kg eq)	U1 %TRR (mg/kg eq)	Solids %TRR	Total %TRR
	fodder									
	Mature sorghum grain	110	475	0.007 _{NE}	—	—	—	—	—	—

NE = not extracted due to matrix TRR being at or below 0.01 mg/kg eq

^a Adapted by the reviewer, based on individual values for metabolites. Original TRR values measured by combustion were 0.017 mg/kg eq for mature wheat grain PBI 123 days, 0.010 mg/kg eq for mature radish leaves PBI 365 days and 0.029 mg/kg eq for mature sorghum fodder PBI 365 days.

Table 35 TRR and nature of residues in rotational crops after pre-emergence soil surface application

PBI days (rotation number)	Matrix	DAP	DAT	TRR mg/kg eq	RPA 201722 %TRR (mg/kg eq)	IFT-DKN %TRR (mg/kg eq)	IFT-BA %TRR (mg/kg eq)	U1 %TRR (mg/kg eq)	Solids %TRR	Total %TRR
34 (1 st)	Immature radish leaf	21	55	0.015	0 (< 0.001)	0 (< 0.001)	86.7 (0.013)	0 (< 0.001)	12.4	99.1
	Mature radish leaf	41	75	0.011	0 (< 0.001)	27.3 (0.003)	81.8 (0.009)	0 (< 0.001)	5.4	114.5
	Immature radish root	21	55	0.010 _{NE}	—	—	—	—	—	—
	Mature radish root	41	75	0.003 _{NE}	—	—	—	—	—	—
34 (1 st)	Immature lettuce leaf	41	75	0.056 ^a	0 (< 0.001)	0 (< 0.001)	94.6 ^a (0.053)	0 (< 0.001)	5.9 ^a (0.003)	100.5
	Mature lettuce leaf	49	83	0.030	0 (< 0.001)	0 (< 0.001)	63.3 (0.019)	26.7 (0.008)	5.3	90.0
34 (1 st)	Sorghum forage	41	75	0.126	0 (< 0.001)	0 (< 0.001)	86.5 (0.11)	0 (< 0.001)	2.3	88.8
	Mature sorghum fodder	134	168	0.037	0 (< 0.001)	0 (< 0.001)	24.3 (0.009)	47.1 (0.016)	7.1	78.5
	Mature sorghum grain	134	168	0.038	0 (< 0.001)	5.3 (0.002)	63.2 (0.024)	15.8 (0.006)	12.6	91.6
123 (2 nd)	Immature radish leaf	45	168	0.002 _{NE}	—	—	—	—	—	—
	Mature radish leaf	58	181	0.002 _{NE}	—	—	—	—	—	—
	Immature radish root	45	168	0.001 _{NE}	—	—	—	—	—	—
	Mature radish root	58	181	< 0.001 _{NE}	—	—	—	—	—	—
123 (2 nd)	Immature mustard leaf	45	168	0.004 _{NE}	—	—	—	—	—	—
	Mature mustard leaf	58	181	0.002 _{NE}	—	—	—	—	—	—
123 (2 nd)	Wheat forage	133	256	0.009	0 (< 0.001)	0 (< 0.001)	55.6 (0.005)	33.3 (0.003)	4.6	93.5
	Mature wheat straw	239	362	0.042	0 (< 0.001)	0 (< 0.001)	73.8 (0.031)	0 (< 0.001)	21.9	95.7
	Mature wheat grain	239	362	0.015	0 (< 0.001)	0 (< 0.001)	100 (0.015)	0 (< 0.001)	7.9	107.9
365 (3 rd)	Immature radish leaf	28	393	0.010 _{NE}	—	—	—	—	—	—
	Mature radish leaf	38	403	0.010	0 (< 0.001)	0 (< 0.001)	0 (< 0.001)	100 (0.010)	4.8	104.8
	Immature radish root	28	393	0.002 _{NE}	—	—	—	—	—	—
	Mature radish root	38	403	0.001 _{NE}	—	—	—	—	—	—

PBI days (rotation number)	Matrix	DAP	DAT	TRR mg/kg eq	RPA 201722 %TRR (mg/kg eq)	IFT-DKN %TRR (mg/kg eq)	IFT-BA %TRR (mg/kg eq)	U1 %TRR (mg/kg eq)	Solids %TRR	Total %TRR
375 (3 rd)	Immature lettuce leaf	51	426	0.008 ^{NE}	—	—	—	—	—	—
	Mature lettuce leaf	71	446	0.010 ^{NE}	—	—	—	—	—	—
365 (3 rd)	Sorghum forage	38	403	0.030	0 (< 0.001)	0 (< 0.001)	13.3 (0.004)	46.7 (0.014)	2.8	62.8
	Mature sorghum fodder	110	475	0.029	0 (< 0.001)	0 (< 0.001)	6.9 (0.002)	75.9 (0.022)	3.6	86.4
	Mature sorghum grain	110	475	0.004 ^{NE}	—	—	—	—	—	—

NE = not extracted due to matrix TRR being at or below 0.01 mg/kg eq

^a Adapted by the reviewer, based on individual values for metabolites. Original TRR values measured by combustion were 0.037 mg/kg eq for mature lettuce leaves PBI 23 days, 0.010 mg/kg eq for mature radish leaves PBI 365 days, and 0.029 mg/kg eq for mature sorghum fodder PBI 365 days.

Field rotational crop studies

A study was conducted in the USA during the 1997–1999 growing seasons to determine the isoxaflutole related residues in rotational crops [Mickelson, 2000, M-240710-01-1]. One trial was established in Illinois and one in Ohio. In each trial isoxaflutole was applied once at a rate of 0.154–0.161 kg ai/ha in a minimum spray volume of 93.5 L/ha to bare ground as pre-plant or pre-emergence application of the primary crop (maize). Maize plants were harvested and/or removed from the plots prior to the planting of the rotational crops [Bayer, 2013]. The study was designed to investigate three representative rotational crop groups (leafy vegetables (mustard and soya bean), root crops (sugar beet, turnip, and radish) and small grains (winter wheat and sorghum)) at four plant-back intervals (30 days, 100–120 days, 150–180 days and 365 days). Each test site selected the variety best suited for the growing area within each crop group. Replicate field samples of the following commodities were sampled for residue analysis: mustard (leaves), sugar beet (top and root), turnip (top and root), radish (top and root), wheat (forage, hay, straw and grain), soya bean (forage, hay, wheat and grain) and sorghum (forage, hay, wheat and grain). Sample sizes were at least 0.5 kg for hay, straw and fodder and at least 1 kg for grains, seeds and cereal forage (except 0.45–0.68 kg for wheat grain). Sample sizes were 1.1–3.0 kg for mustard leaves, 1.4–3.6 kg for turnip roots + tops, 0.45–2.5 kg for radish roots + tops, 2.5–18 kg for sugar beets + tops, but the number of items was not indicated. All samples were stored at –5 °C or lower for a maximum period of 721 days (24 months).

IFT, IFT-DKN and IFT-BA were determined according to modification A and B of HPLC-MS-MS method CAL#019-03. Average concurrent recovery data for modification A (n=1/level, at 0.01–0.05–0.5 mg/kg) were within 70–120% for all analytes in wheat hay, wheat grains, wheat straw, soya bean seeds, soya bean hay, sorghum grains, sorghum fodder. Recoveries are not satisfactory for IFT-BA in wheat hay (62%, n=1, 0.01 mg/kg), wheat straw (68%, n=1, 0.01 mg/kg) and soya bean seeds (64%, n=1, 0.01 mg/kg). No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control samples. Average concurrent recovery data for modification B were within (at n=1/level, 0.01–0.05–0.5 mg/kg) were within 70–120% for all analytes in mustard leaves, turnip roots, turnip tops, wheat forage, soya bean forage, radish roots, radish tops and sorghum forage. Recoveries are not satisfactory for IFT-BA in turnip tops (69%, n=1, 0.01 mg/kg) and wheat forage (69%, n=1, 0.01 mg/kg). No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control samples.

The average sample results are summarized in Table 36. None of the analysed samples showed IFT or its metabolite IFT-DKN greater than the LOQ of 0.01 mg/kg. The same applies to metabolite IFT-BA, except that it was found in samples of soya bean hay (0.010 mg/kg) and soya bean forage (0.038 mg/kg) in one trial in Ohio.

Table 36 Results of field rotational crop trials conducted with isoxaflutole in the USA

Location Year	Rotational Crop Variety	PBI (days)	Portion analysed	GS at sampling	DAT (days)	Residues (mg/kg)		
						IFT	IFT-DKN	IFT-BA
Pre-emergence application for primary crop: Maize (planted 2 June 1997) Formulation: 75 WG, 1 application (3 June 1997); rate: 0.159 kg ai/ha and 0.170 kg ai/hL Soil: silt loam, 2.6% om, pH 6.7, CEC 7.8 meq/100 g; 31% moisture at 1/3 bar								
Clinton IL, USA 1997/1998	Soya bean V397RR	29	forage	6–7 node	79	n.a.	n.a.	n.a.
			hay	Mid bloom	94	< 0.01	< 0.01	< 0.01
			seed	Maturity	135	n.a.	n.a.	n.a.
	Sugar beets variety not stated		tops	Maturity	148	n.a.	n.a.	n.a.
			roots	Maturity	148	n.a.	n.a.	n.a.
	Sorghum Dekalb DK28E		forage	Soft dough	111	n.a.	n.a.	n.a.
			grain	Maturity	148	n.a.	n.a.	n.a.
		stover	Maturity	148	n.a.	n.a.	n.a.	
	Mustard Florida Broadleaf	104	leaves	10–12 leaf	167	< 0.01	< 0.01	< 0.01
	Turnips Purple Top White Globe		tops	Early bulb	167	< 0.01	< 0.01	< 0.01
			roots	Early bulb	167	< 0.01	< 0.01	< 0.01
	Winter Wheat Pioneer 2571	120	forage	BBCH 36	324	< 0.01	< 0.01	< 0.01
			hay	Full bloom	344	< 0.01	< 0.01	< 0.01
			grain	Maturity	381	< 0.01	< 0.01	< 0.01
			straw	Maturity	381	< 0.01	< 0.01	< 0.01
	Soya bean Pioneer 9363	365	forage	6–7 node	413	< 0.01	< 0.01	< 0.01
			hay	R3–R4	449	< 0.01	< 0.01	< 0.01
			Seed/ grain	Maturity	493	< 0.01	< 0.01	< 0.01
	Radish Cherry Bell		tops	Normal harvest	426	< 0.01	< 0.01	< 0.01
			roots	Normal harvest	426	< 0.01	< 0.01	< 0.01
	Sorghum Northrup King K5310		forage	Soft dough	456	< 0.01	< 0.01	< 0.01
			grain	Maturity	493	< 0.01	< 0.01	< 0.01
			stover	Maturity	493	< 0.01	< 0.01	< 0.01
Pre-plant application for primary crop: Maize (planted 13 April and 12 May 1998) Formulation: 75 WG 1 application (2 April 1998); use rate: 0.161 kg ai/ha; 0.172 kg ai/hL Soil: silt loam, 2.6% om, pH 6.7, CEC 7.8 meq/100 g; 31% moisture at 1/3 bar								
Clinton IL, USA 1997/1998	Mustard Florida Broadleaf	151	leaves	Vegetative	190	< 0.01	< 0.01	< 0.01
	Radish Cherry Bell		tops	Maturity	190	< 0.01	< 0.01	< 0.01
			roots	Maturity	190	< 0.01	< 0.01	< 0.01
	Winter Wheat Clark	180	forage	Starting to join	376	< 0.01	< 0.01	< 0.01
			hay	Dough	414	< 0.01	< 0.01	< 0.01
			grain	Normal harvest	442	< 0.01	< 0.01	< 0.01
			straw	Normal harvest	442	< 0.01	< 0.01	< 0.01
Pre-plant application for primary crop: Maize (planted 22 May 1997) Formulation: 75 WG 1 application (22 May 1997) Use rate: 0.158 kg ai/ha; 0.169 kg ai/hL Soil: clay loam, 2.2% om, pH 7.2, CEC 10.9 meq/100 g; 26% moisture at 1/3 bar								
Fayette OH, USA 1997/1998	Soya bean Asgrow 3701	30	forage	V3	60	< 0.01	< 0.01	0.010
			hay	R3 begin. pod	88	< 0.01	< 0.01	0.038
			grain	Maturity	144	n.a.	n.a.	n.a.
	Sugar Beets		tops	Maturity	144	n.a.	n.a.	n.a.

Location Year	Rotational Crop Variety	PBI (days)	Portion analysed	GS at sampling	DAT (days)	Residues (mg/kg)		
						IFT	IFT-DKN	IFT-BA
	variety not stated		roots	Maturity	144	n.a.	n.a.	n.a.
	Sorghum RS200E		forage	Soft/hard dough	116	n.a.	n.a.	n.a.
			grain	Maturity	181	n.a.	n.a.	n.a.
			stover	Maturity	181	n.a.	n.a.	n.a.
	Mustard Florida Broadleaf	119	leaves	Maturity	180	< 0.01	< 0.01	< 0.01
	Turnips Purple Top White Globe		tops	Root development	180	< 0.01	< 0.01	< 0.01
			roots		180	< 0.01	< 0.01	< 0.01
	Winter Wheat		forage	6–8 in./& flag leaf	342	< 0.01	< 0.01	< 0.01
			hay	Dough	392	< 0.01	< 0.01	< 0.01
			grain	Maturity	413	< 0.01	< 0.01	< 0.01
			straw	Maturity	413	< 0.01	< 0.01	< 0.01
	Soya bean CX368		forage	R2–full bloom	421	< 0.01	< 0.01	< 0.01
		hay	Maturity	436	< 0.01	< 0.01	< 0.01	
		Seed/ grain	Maturity	498	< 0.01	< 0.01	< 0.01	
	Radish Crimson Globe		tops	Maturity	419	< 0.01	< 0.01	< 0.01
			roots	Maturity	419	< 0.01	< 0.01	< 0.01
	Sorghum RS200E		forage	Dough	466	< 0.01	< 0.01	< 0.01
			grain	Maturity	515	< 0.01	< 0.01	< 0.01
			stover	Maturity	515	< 0.01	< 0.01	< 0.01
Pre-plant application for primary crop: maize (planted 14 May 1998) Formulation: 75 WG, 1 application (2 April 1998) Use rate: 0.154 kg ai/ha; 0.165 kg ai/hL Soil: clay loam, 2.2% om, pH 7.2, CEC 10.9 meq/100 g; 26% moisture at 1/3 bar								
Fayette OH, USA 1997/1998	Mustard Florida Broadleaf	166	leaves	Maturity	231	< 0.01	< 0.01	< 0.01
	Radish China Rose	180	tops	Maturity	244	< 0.01	< 0.01	< 0.01
			roots	Maturity	244	< 0.01	< 0.01	< 0.01
	Winter Wheat		forage	Feeks 6	385	< 0.01	< 0.01	< 0.01
			hay	Feeks 11.1– 11.2	432	< 0.01	< 0.01	< 0.01
			grain	Maturity	449	< 0.01	< 0.01	< 0.01
straw			Maturity	449	< 0.01	< 0.01	< 0.01	

GS = growth stage; n.a: not analysed.

Environmental fate in water/sediment systems

No data submitted. Not relevant for the present intended use.

RESIDUE ANALYSIS

The Meeting received information on enforcement/monitoring methods for the determination of isoxaflutole and its metabolites in plant and animal commodities. In addition the Meeting received information on analytical methods for the determination of isoxaflutole and its metabolites as used in the various study reports (supervised residue trials, storage stability studies, processing studies, feeding studies). The analytical residue methods have been evaluated according to the guidance provided by OECD (Series on Pesticides number 39) as indicated on page 25 of the FAO manual 2009.

Validation results are required for every commodity submitted for MRL-setting: at least one full validation for a commodity within the five defined crop groups (high acid content, high water content, high oil content, high protein content, high starch content) and a reduced validation for every other commodity within a certain crop group. Where validation results do not meet the criteria given below, this is indicated.

When the analytical method is validated according to a full validation scheme, it means that:

- at least five recovery experiments per level were conducted on at least two levels (LOQ and $10\times$ LOQ) and average recovery per level was shown to be between 70–120% and the relative standard deviation (RSD_r or CV) per level was shown to be $< 20\%$
- at least two control samples were analysed and were shown to be below $0.3\times$ LOQ
- the calibration was conducted with at least five single points or at least three duplicate points and was shown to be linear (either standards in solvent or matrix matched standards).

When the analytical method is validated according to a reduced validation scheme, it means that:

- a full validation is available for a crop in the same crop group (high acid content, high water content, high oil content, high protein content, high starch content)
- at least three recovery experiments per level were conducted on at least two levels (LOQ and $10\times$ LOQ) and the average recovery per level was shown to be between 70–120% and the relative standard deviation (RSD_r or CV) per level was $< 20\%$
- at least two control samples were analysed and shown to be below $0.3\times$ LOQ
- the calibration was conducted with at least five single points or at least three duplicate points and was shown to be linear (only relevant for matrix matched standards; standards in solvent are already covered by full validation).

Analytical methods for enforcement in plant commodities

HPLC-MS-MS method 01021

HPLC-MS-MS method 01021 is intended as enforcement method for the determination of parent isoxaflutole and its diketone nitrile metabolite IFT-DKN in/on plant material [Schoening, 2007, M-282394-02-1]. Plant material was extracted with MeOH/1% formic acid solution (9/1, v/v) using a blender. After filtration of the extract the solution was made up to volume, diluted and subjected to HPLC-MS-MS. Isoxaflutole and IFT-DKN were quantified against external matrix-matched mixed standards. Two MRM transitions were monitored for each analyte and each matrix tested (m/z 360 $\rightarrow$ 251 for quantification and m/z 360 $\rightarrow$ 220 for confirmation of IFT and m/z 358 $\rightarrow$ 79 for quantification and m/z 358 $\rightarrow$ 64 for confirmation of IFT-DKN). Analyte levels were expressed as IFT equivalents.

HPLC-MS-MS Method 01021 was validated according to the full validation scheme for commodities with high acid content (orange fruit), high water content (tomato fruit), high starch content (wheat grains) and high oil content (rape seeds) [Schoening, 2007, M-282394-02-1]. The validation was performed for the quantification transition ions as well as for the confirmation transition ions. Mixed analyte solutions were used for fortification of samples. Average recoveries at 0.01 mg/kg and 0.1 mg/kg were within 70–120% limits and RSDs were within 20%. Linearity was observed in a range from 0.125–5.00 $\mu\text{g/L}$ on all mass transitions (equivalent concentration in the samples not stated). The correlation coefficients for a $1/\times$ weighted regression were $r > 0.99$ using five triplicate matrix matched standards. No interfering peaks $> 0.3\text{LOQ}$ (i.e. 0.003 mg/kg) were detected in any of the control extracts. The valid LOQ was 0.01 mg/kg for each commodity.

HPLC-MS-MS Method 01021 was validated according to the full validation scheme by an independent laboratory (ILV) for tomato fruit and wheat grain [Class, 2007, M-286476-01-1]. Slight modifications were introduced: 0.1% formic acid was used instead of 1% formic acid. The validation was performed for the quantification transition ions as well as for the confirmation transition ions.

Mixed analyte solutions were used for fortification of samples. Average recoveries at 0.01 mg/kg and 0.1 mg/kg were within 70–120% limits and RSDs were within 20%. Linearity (coefficient of correlation $r > 0.99$) was observed in the range of 0.050–5.0 ng/mL for each analyte using six single matrix matched standards. The equivalent concentration in the samples was not stated. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control samples. The valid LOQ was 0.01 mg/kg for each commodity.

Conclusion: The method is considered valid for use as enforcement method in plant material with an LOQ of 0.01 mg/kg for isoxaflutole and IFT-DKN.

Analytical methods for enforcement in animal commodities

QuEChERS multi-residue method

The official multi-residue method QuEChERS was validated for the individual determination of isoxaflutole and its metabolite IFT-DKN in animal commodities. No multiresidue methods were available for determination of isoxaflutole related residues in plant commodities.

In the QuEChERS method (also named BCS method 01300/M009) animal commodities were extracted with acetonitrile and water (1:1, v/v) [Winter and Amann, 2013, M454397-01-1]. Samples with low water content ($< 80\%$) require the addition of water before the initial extraction to get a total of approximately 10 g of water. After addition of magnesium sulphate, sodium chloride and buffering citrate salts, the mixture was shaken intensively and centrifuged for phase separation. An aliquot of the extract was taken, diluted and subjected to HPLC-MS-MS. Two MRM transitions were monitored for isoxaflutole: 358.0 to 277.9 for quantification and 358.0–78.9 for confirmation. Two MRM transitions were monitored for IFT-DKN: 358.0 to 277.9 for quantification and 358.0–78.9 for confirmation.

The validation was conducted on milk, eggs, bovine meat, bovine fat, bovine liver and bovine kidney [Winter and Amann, 2013, M454397-01-1]. To avoid the degradation of the isoxaflutole parent compound, hydrochloric acid was added to the bovine meat matrix before spiking and extraction of the samples. Matrix effects of $\geq 20\%$ were measured for isoxaflutole and IFT-DKN in kidney and for isoxaflutole in liver. For milk, eggs, meat, fat and liver (IFT-DKN only) minor matrix effects ($< 20\%$) were detected. Therefore, for all tested matrices, quantification was performed with matrix-matched standards. Average recoveries at 0.01 and 0.10 mg/kg (five replicates per level) were within 70–120% limits and RSDs were within 20% for each analyte and for both MRM transitions. Linearity was observed in the range of 0.25–60 ng/mL for IFT and IFT-DKN matrix matched standards. The equivalent concentration in the samples was not stated. The coefficient of determination was $R^2 > 0.99$ using six single matrix matched standards. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control extracts. The valid LOQ was 0.01 mg/kg in milk, eggs, meat, fat, liver and kidney. Two MRM transitions were validated for all matrices and therefore an additional confirmatory method is not necessary.

Conclusion: The method is considered valid for use as enforcement method in animal commodities with an LOQ of 0.01 mg/kg for isoxaflutole and IFT-DKN.

HPLC-UV method AR 109-95

HPLC-UV method AR 109-95 is intended as enforcement method for the determination of isoxaflutole, its diketonitrile metabolite IFT-DKN and its benzoic acid metabolite IFT-BA in animal commodities (fat, kidney, milk and eggs) [Guillet, *et al.*, 1995, M-213160-01-1; Le Gren, 1995a/b/c, M-213162-01-1, M-262409-01-1, M-213164-01-1].

Milk residues were extracted by macerating with a mixture of 0.1% trifluoroacetic acid acidified water/ACN. The extract was purified using an Octyl cartridge, IFT and IFT-DKN being eluted in the same fraction.

Fat residues were extracted by macerating with a mixture of 0.1% trifluoroacetic acid acidified water/ACN. The extract was purified using an Octyl cartridge followed by a Diol cartridge.

IFT-BA was eluted directly on the Octyl cartridge and IFT and IFT-DKN were eluted consecutively on the Diol cartridge.

Kidney residues were extracted by macerating with ACN. The extract was purified using an Octyl cartridge for IFT-DKN and additionally using a Diol cartridge for IFT. For determination of IFT-BA, the extract was purified using a Diol cartridge first followed by the purification using an Rdx cartridge.

Egg residues were extracted by macerating with ACN. The extract containing IFT-DKN was purified using an Octyl cartridge followed by a Diol cartridge for IFT-DKN. Attempts to analyse IFT in eggs were not successful, even with acidified extraction solvent, because IFT rapidly degrades onto IFT-DKN in presence of a basic matrix like eggs (pH around 9).

Quantification was carried out by HPLC-UV on a C18 column at 270 or 300 nm. Quantification of residues was done by external calibration using standards in solvent. Analyte levels were expressed as the corresponding analyte.

HPLC-UV Method AR 109-95 was validated according to a reduced validation scheme for bovine fat, bovine kidney, cow milk and hen eggs [Guillet, *et al.*, 1995, M-213160-01-1; Le Gren, 1995a/b/c, M-213162-01-1, M-262409-01-1, M-213164-01-1]. Mixed analyte solutions were used for fortification of samples. Average recoveries at 0.01 mg/kg (milk), 0.02 mg/kg (eggs, tissues) and 0.1 mg/kg were within 70–120% limits and RSDs were within 20% for each analyte. Linearity was observed in the range of 10–1000 ug/L for IFT and IFT-DKN and in the range 25–1000 ug/L for IFT-BA. The equivalent concentration in the samples was not stated. The coefficient of correlation was $r > 0.99$ using 4–7 duplicate solvent standards. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg in milk, 0.006 mg/kg in eggs, fat and kidney) were detected in any of the control extracts. The valid LOQ was 0.01 mg/kg in milk (IFT, IFT-DKN), 0.02 mg/kg in eggs (IFT-DKN) and 0.02 mg/kg in fat and kidney (IFT, IFT-DKN and IFT-BA).

Conclusion: HPLC-UV method AR 109-95 is considered insufficiently validated for use as enforcement method, since a reduced validation scheme is used ($n=3/\text{level}$), a confirmation method is not available and no validation is available for muscle/meat and liver.

HPLC-UV method RPAC #45532

HPLC-UV method RPAC #45532, version 2.0, 4 March 1998, is intended as enforcement method for the determination of IFT, IFT-DKN and RPA 205834 in animal commodities (milk, eggs and tissues) [Lopes *et al.*, 1998, M-166734-01-2].

Milk (50 g) was extracted by macerating with a mixture of 0.1% aqueous trifluoroacetic acid and ACN (5:18 v/v). The extract was purified using a C-8 cartridge column. The cartridge is eluted subsequently with water/ACN (90:10, v/v) and water/ACN (50:50, v/v). The first fraction contains IFT-BA and this fraction is discarded. Isoxaflutole, IFT-DKN and RPA 205834 were eluted and collected together in the second fraction.

Eggs were extracted with ACN. The extract was purified using a C-8 cartridge column, IFT-DKN being collected in the second fraction.

Tissues were analysed by a common moiety technique. Kidney, liver and muscle (10 g) were extracted using 0.1% aqueous trifluoroacetic acid. For beef fat or chicken skin with adhering fat (10 g) the extraction solvent was a 2:1 mixture of hexane and water. The fat hexane extracts were partitioned against an 18:5 mixture of ACN and water. The ACN-water phase was added to the aqueous extract and evaporated to remove all ACN. Isoxaflutole was converted to IFT-DKN by treatment of the extract with 10% NaOH. Trace enrichment/purification was obtained using a C-18 cartridge. IFT-DKN was eluted from the C-18 cartridge and collected in the second fraction.

All residue analyses were accomplished by HPLC-UV on a C-8 column at 270 or 300 nm. Quantification of residues was done by external calibration using standards in solvent. Analyte levels in milk and eggs were expressed as the corresponding analyte. For the animal tissue analysis the isoxaflutole related residues were determined as IFT-DKN but were reported as isoxaflutole. The

molecular weight of isoxaflutole and IFT-DKN are the same, therefore, a correction factor for differences in molecular weight is not necessary.

HPLC-UV method RPAC #44882 is identical to HPLC-UV method RPAC #45532 for milk, except that fraction 1, containing IFT-BA, was analysed as well. HPLC-UV method RPAC #44882 was validated according to a full validation scheme for cow milk for IFT, IFT-DKN, RPA 205834 and IFT-BA [Shaffer, 1995, M-192304-01-2]. Two trials were required to optimize the method. Trial 1 was not successful due to low and highly variable recoveries of IFT-DKN. The retention times shifted significantly when the pH of the final solution was changed from 2.13 to 2.07. A second milk trial, incorporating the developer's suggestions and taking care to mix the sample extract well, was successful. Mixed analyte solutions were used for the fortification of milk. Average recoveries at 0.02 and 2.0 mg/kg were within 70–120% limits and RSDs were within 20% for each analyte and matrix tested. Linearity (coefficient of correlation $r > 0.9999$) was observed in the range of 20–100 ng/mL using five single or duplicate standards in solvent. Equivalent concentrations in the samples were not stated. No interfering peaks > 0.3 LOQ (i.e. 0.006 mg/kg) were detected in any of the control samples. The valid LOQ was 0.02 mg/kg for IFT, IFT-DKN, RPA 205834 and IFT-BA.

HPLC-UV method RPAC #44933 (identical to HPLC-UV method RPAC #45532 for eggs) was validated according to a full validation scheme for IFT-DKN in hen eggs [Tew, 1995b, M-192317-01-1, Lowder, 1996, M-192281-01-2-01]. Average recoveries at 0.05 mg/kg ($n=8$) and 0.25 mg/kg ($n=6$) were within 70–120% limits and RSDs were within 20% for IFT-DKN in eggs. Linearity (coefficient of determination $R^2 > 0.999$) was observed in the range of 20–200 ng/mL using six single standards in solvent. Equivalent concentrations in the samples were not stated. No interfering peaks $>$ LOQ (i.e. 0.05 mg/kg) were detected in any of the control extracts ($n > 2$). The valid LOQ was 0.05 mg/kg in eggs for IFT-DKN.

HPLC-UV method RPAC #45532 was validated by an independent laboratory according to a full validation scheme for milk, eggs, meat and kidney [Kaune, 2002, M-213302-01-1]. Validation was conducted for IFT, IFT-DKN and RPA 205834 in milk, IFT-DKN in eggs and IFT, IFT-DKN in meat and kidney. Animal origin for the tissues is not indicated for these samples. Separate solutions for each individual analyte were used for fortification of eggs and tissues. Mixed analyte solutions were used for fortification of milk. Average recoveries at 0.01–0.1 mg/kg for milk and eggs or 0.2–2.0 mg/kg for tissues were within 70–120% limits and RSDs were within 20% for each analyte and matrix tested. The calibration curve was not linear: a curve of the type $y = a + bx + cx^2$ was applicable over the tested range of 5 to 50 ng (0.05 to 0.5 mg/L) using 4–5 single or duplicate standards in solvent. Equivalent concentration in the samples was not stated. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control extracts. The valid LOQ was 0.01 mg/kg in milk (IFT, IFT-DKN and RPA 205834), 0.01 mg/kg in eggs (IFT-DKN), 0.2 mg/kg in meat and kidney (IFT, IFT-DKN).

Conclusion: HPLC-UV method RPAC #45532 is considered insufficiently validated for use as enforcement method, since a confirmation method is not available, the method for tissues is a common moiety method and no validation is available for fat and liver.

HPLC-UV method RPAC #45532 is considered valid for use as pre-registration analytical method in the range 0.02–2.0 mg/kg IFT, IFT-DKN, RPA 205834 and IFT-BA in milk and at 0.05–0.25 mg/kg IFT-DKN in eggs when using a linear calibration curve. The LOQ may be lowered to 0.01 mg/kg in milk and eggs when using a second order calibration curve.

HPLC-UV method RPAC #45532 is considered not suitable for use as pre-registration analytical method since the residues are analysed as a common moiety.

Analytical methods used in study reports in plant commodities

GC-MS method 00473 and its modifications

GC-MS method 00473, version January 1995, code HWI 6224-215, is a common moiety method for the determination of isoxaflutole related residues (sum of IFT, IFT-DKN and IFT-BA) in plant

commodities [Nandihalli, 1995, M-020184-01-1]. Homogenised samples (25 g) were extracted by maceration with MeOH (3× 125 mL). Combined extracts were filtered. After addition of 2% NaOH solution isoxaflutole was hydrolysed to IFT-DKN in 1 hr at room temperature. The MeOH was evaporated off and 10 mL saturated NaCl was added to the low volume aqueous phase. The aqueous phase was washed subsequently with DCM and petroleum ether. Acidification (12 M HCl, pH 1.0) of the aqueous phase then allowed liquid-liquid partition of both IFT-DKN and IFT-BA into DCM (3×). The DCM phase was drained through anhydrous Na₂SO₄ and evaporated to dryness. The residue was re-dissolved in 1 M methanolic NaOH solution and heated for 1 hr at 100 °C, whereby residues of IFT-DKN were hydrolysed to IFT-BA. Acidification (12 M HCl, pH 1.0) of the aqueous phase then allowed liquid-liquid partition of IFT-BA into DCM (3×). The DCM phase was drained through anhydrous Na₂SO₄ and evaporated to dryness. The residue was redissolved in DCM and IFT-BA was methylated to RPA 204497 using diazomethane (1 hr 30 °C). Excess diazomethane was destroyed by addition of HAc. Residues of the ester derivative RPA 204497 are detected by GC-MS at m/z 251 (quantification) and m/z 267 (confirmation). Residues are quantified as RPA 204497, but are expressed as isoxaflutole equivalents in the trials.

GC-MS method 00473 was used in maize storage stability studies [Nandihalli, 1996, M-089371-01-1]. GC-MS method 00473 was validated according to a full validation scheme for maize forage, maize silage, maize grain and maize fodder [Nandihalli, 1995, M-020184-01-1]. Samples were fortified separately with IFT, IFT-DKN or IFT-BA. Average recoveries at 0.01 and 0.05 mg/kg (n=6 each) were within 70–120% limits, except IFT-BA in maize grain (0.01/0.05 mg/kg, average 67%/64%, n=6 each). Individual recoveries and RSDs were not reported. Additional recovery data from the storage stability study indicated that average recoveries at 0.2 mg/kg in maize silage and maize fodder and at 0.1 mg/kg in maize grain were within 70–120% limits (n=12, each analyte, each matrix) and RSD at this level was within 20%. Linearity (coefficient of correlation $r > 0.9999$) was observed in the range of 0.01–0.5 mg/L using six single solvent standards. The equivalent concentration in the samples was not stated. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control extracts. The valid LOQ is 0.01 mg/kg for isoxaflutole related residues, expressed as isoxaflutole.

GC-MS-MS modification A of method 00473 was used in the Australian sugarcane supervised residue trials & storage stability studies (dated April 1999) [Davis and Keats, 1999a/b/c/d/e/f, M-284383-01-1, M-284347-01-1, M-284356-01-1, M-284369-01-1, M-284408-01-1 M-284324-01-1]. Modifications involved changes in sample types, extraction volumes, conditions for hydrolysis, diazomethane methylation and MS conditions. Homogenised samples of sugarcane billets (25 g) or sugarcane forage (25 g) were extracted with 2× 80 mL MeOH. Further sample preparation was identical to the original method except that an aliquot equivalent to 5 g sample matrix was taken for further analysis. The hydrolysis of IFT-DKN to IFT-BA was conducted at a lower temperature of 60 °C. Diazomethane was directly added to the last DCM phase and IFT-BA was methylated to RPA 204497 (30 min, room temperature). Excess diazomethane was destroyed by addition of HAc and toluene was added to the extract. The extract was then reduced to the toluene phase. The toluene phase was filtered using a 0.45 µm PTFE filter and clean-up on a Florisil cartridge. The analytes were eluted with a toluene/acetone mixture (90:10, v/v). Residues of the ester derivative of RPA 204497 are detected by GC-MS-MS at m/z 251 and m/z 252 (parent ions as well as quantification ions).

GC-MS-MS modification A of method 00473 was partially validated for sugarcane billets and sugarcane forage [Davis and Keats, 1999a/b/c/d/e/f, M-284383-01-1, M-284347-01-1, M-284356-01-1, M-284369-01-1, M-284408-01-1 M-284324-01-1]. Samples were fortified separately with IFT, IFT-DKN or IFT-BA. Average recoveries at 0.01 mg/kg (n=5) for each compound were within 70–120% limits. Additional recovery data from the storage stability study indicated that average recoveries at 0.1 mg/kg in maize silage and maize fodder and at 0.1 mg/kg in maize grain were within 70–120% limits (n=12, each analyte, each matrix) and RSD at this level was within 20%. Recoveries at 10× LOQ were not verified. However, since residue levels in the trials were $< \text{LOQ}$, this is considered acceptable. Linearity (coefficient of correlation $r > 0.9999$) was observed in the range of 0.01–0.1 mg/L using three duplicate solvent standards. The equivalent concentration in the samples

was not stated. No interfering peaks > LOQ were detected in any of the control extracts ($n > 2$, each matrix). The valid LOQ is 0.01 mg/kg for isoxaflutole related residues, expressed as isoxaflutole.

GC-MS-MS modification B of method 00473 was used in the 1999 chickpea supervised residue trials & storage stability studies (dated December–February 2000) [Lynch and Keats, 1999a/b, M-432364-01-1, M-432374-01-1, Lynch and Keats, 2000a/b/c, M-432434-01-1, M-432441-01-1, M-432444-01-1]. Modifications involved changes in sample types, extraction volumes, conditions for hydrolysis, diazomethane methylation and MS conditions. Homogenised chickpea seeds (25 g), chickpea forage (25 g) or chickpea straw (10 g) were extracted with 2×100 mL MeOH. Further sample preparation was identical to the original method except that an aliquot equivalent to 5 g sample matrix was taken for further analysis and aqueous phases were washed with diethyl ether instead of petroleum ether. The hydrolysis of IFT-DKN to IFT-BA was conducted at a lower temperature of 60 °C. The last DCM phase was drained through anhydrous Na_2SO_4 . After addition of diazomethane IFT-BA was methylated to RPA 204497 (30 min, room temperature). Excess diazomethane was removed by nitrogen at 30–35 °C and ACN was added to the extract. The extract was then reduced to 1 mL of ACN, made up to 5 mL with ACN and filtered using a 0.45 μm PTFE filter cartridge. Residues of the ester derivative of RPA 204497 are detected by GC-MS-MS at m/z 251 (parent ion) and m/z 189 and m/z 221 (quantification ions).

GC-MS-MS modification B of method 00473 was validated for chickpea seeds, chickpea forage and chickpea straw [Lynch and Keats, 1999a/b, M-432364-01-1, M-432374-01-1, Lynch and Keats, 2000a/b/c, M-432434-01-1, M-432441-01-1, M-432444-01-1]. Samples were fortified separately with IFT, IFT-DKN or IFT-BA. Average recoveries at 0.01 and 0.1 mg/kg ($n=3$ or 6) for each compound were within 70–120% limits. Individual recoveries and RSDs were not reported. Linearity was not observed: a second order calibration curve (correlation coefficient $r > 0.99$) was fitted to the data in the range 0.005–0.5 mg/L using six triplicate solvent standards. The equivalent concentration in the samples was not stated. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control extracts ($n > 2$, each matrix). The valid LOQ is 0.01 mg/kg for isoxaflutole related residues, expressed as isoxaflutole.

GC-MS modification C of method 00473 was used in the Brazilian sugarcane supervised residue trials (dated March 2000) [Tornisielo, 2000a/b, M-287038-01-1, M-287041-01-1]. Modifications involved changes in sample types, extraction volumes and diazomethane methylation. Homogenised sugarcane billets (20 g) were extracted by maceration with 2×95 mL MeOH. Further sample preparation was identical to the original method. The last DCM phase was reduced to 5 mL. After addition of diazomethane, IFT-BA was methylated to RPA 204497 (time and temperature not stated) and the sample was evaporated to dryness. The residue was redissolved in hexane.

GC-MS modification C of method 00473 was validated for sugarcane billets [Tornisielo, 2000a/b, M-287038-01-1, M-287041-01-1]. Samples were fortified with IFT only. Average recoveries at 0.01 and 0.02 mg/kg ($n=3$, each) were within 70–120% limit and RSD was within 20% at these levels. Recoveries at $10 \times$ LOQ were not verified. However, since residue levels in the trials were < LOQ, this is considered acceptable. Linearity (coefficient of determination $R^2 > 0.999$) was observed in the range of 0.02–0.15 ng/mL using five single solvent standards. The equivalent concentration in the samples was not stated. No interfering peaks > LOQ were detected in any of the control extracts ($n=2$). The valid LOQ is 0.01 mg/kg for isoxaflutole related residues, expressed as isoxaflutole.

GC-MS modification D of method 00473 was used in the Mexican sugarcane supervised residue trials (dated November 2000) [Gough, 2000, M-238729-01-1]. Modifications involved changes in sample types and diazomethane methylation. Homogenised samples of sugarcane billets (12.5 g) were extracted with 3×125 mL MeOH (3×125 mL). The last DCM phase was drained through anhydrous Na_2SO_4 . After addition of diazomethane, IFT-BA was methylated to RPA 204497 (30 min, room temperature) and the sample was evaporated to dryness. The residue was redissolved in DCM and cleaned-up on a Florisil cartridge. The analytes were eluted with an EtOAc/DCM (1:1, v/v). The eluent was evaporated to dryness and redissolved in DCM.

GC-MS modification D of method 00473 was validated for sugarcane billets [Gough, 2000, M-238729-01-1]. Samples were fortified separately with IFT, IFT-DKN or IFT-BA. Only limited

validation results are available. Average recoveries at 0.01, 0.02, 0.05, 0.1 mg/kg analyte were within 70–120% limits (n=1–4 each), except for IFT at 0.01 mg/kg (128%, n=2) and IFT-DKN at 0.01 mg/kg (122%, n=2). The RSD was within 20% at 0.02 mg/kg IFT and at 0.01 mg/kg IFT-DKN or IFT-BA; the RSD was not verified at other levels. This is considered acceptable, since the residue levels in the trials are at LOQ. Linearity was not verified, since this is covered by the original method. No interfering peaks > LOQ (i.e. 0.01 mg/kg) were detected in any of the control extracts (n > 2). The valid LOQ is 0.01 mg/kg for isoxaflutole related residues, expressed as isoxaflutole.

Overall, GC-MS method 00473 and its modifications are considered fit for purpose:

- The original method is considered valid at 0.01–0.2 mg/kg total residues in maize forage, maize grain and maize fodder.
- Modification A is considered valid at 0.01 mg/kg total residues in sugarcane billets and sugarcane forage.
- Modification B is considered valid at 0.01–0.1 mg/kg total residues in dry chickpea seeds, chickpea forage and chickpea straw. However, since residue values for chickpea forage in the supervised trials ranged from < 0.01–0.19 mg/kg, validation at higher levels is desirable.
- Modification C is considered valid at 0.01–0.02 mg/kg total residues in sugarcane billets.
- Modification D is considered valid at 0.01–0.02 mg/kg total residues in sugarcane billets.

HPLC-MS-MS method CAL#19-03 and its modifications

HPLC-MS-MS method CAL#019-03, revision 1, issued 29 December 1998, allows the individual determination of IFT and its metabolites IFT-DKN and IFT-BA in plant commodities [Wickremesinhe, 1998a, M-286215-01-1]. Revision 1 differs from the original version (issued on August 18, 1998) in that it includes the results from the validation study [Wickremesinhe, 1998b, M-240820-01-1]. Homogenised samples (10 g) were mixed with 10 mL 1% formic acid and left for 5–10 min (to hydrate dry matrices and to stabilize isoxaflutole). The sample mixture was extracted with 90 mL MeOH and homogenised. The filtered extract was acidified (1 M HCl) and 10% NaCl was added. The extract was purified by liquid-liquid partitioning into methylene chloride. After acidification with 1% formic acid, the methylene chloride phase was evaporated to the aqueous remainder. The residue was diluted with 1% formic acid and further purified by solid-phase extraction (RP 102 column) using 40–70% ACN in water. Two fractions were collected: fraction 1 contained IFT-DKN and IFT-BA and fraction 2 contained IFT. Fractions were adjusted to 100 mL with ACN and water to contain 40% ACN in water. Quantification was performed by HPLC-MS-MS analysis. A turbo-ion interface (atmospheric pressure ionization) was used for the analysis of fraction 1 (with IFT-DKN and IFT-BA), whereas a heated nebulizer interface was used for the analysis of fraction 2 (with IFT, to avoid matrix suppression). The mass transitions monitored were m/z 358 → 79 for IFT-DKN and m/z 267 → 159 for IFT-BA (fraction 1) and m/z 358 → 79 for IFT (fraction 2). For all analytes quantification was done using external calibration with standards in solvent.

HPLC-MS-MS method CAL#019-03, revision 1, was used in the 1998 supervised residue trials on maize in the US [Mickelson, 1999a, M-240663-01-1]. HPLC-MS-MS method CAL#019-03, was validated according to the full validation scheme for maize grains, maize flour, wheat straw and mustard leaves [Wickremesinhe, 1998b, M-240820-01-1]. Samples were fortified with a mixture of IFT, IFT-DKN or IFT-BA. Average recoveries at 0.01 and 0.10 mg/kg (n=5 each) were within 70–120% limits and RSDs were within 20% for each analyte and matrix. An exception is wheat straw at 0.10 mg/kg IFT-BA with an average recovery of 65% (n=5, range 62–72%). Additional limited validation data are available in the supervised residue trials [Mickelson, 1999a, M-240663-01-1]. Average recoveries at 0.01, 0.1 and 10 mg/kg (n=2 each) in maize forage and maize fodder were within 70–120% limits for each analyte. Linearity (correlation coefficient $r > 0.99$) was observed in the range of 0.5–5 ng/mL using four duplicate standards in solvent. A 0.5–5 ng/mL standard is equivalent to 0.005–0.05 mg/kg in the sample. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control samples. The valid LOQ is 0.01 mg/kg for each analyte. After validation, the validation results were included in the method description and the method became revision 1.

Modification A of HPLC-MS-MS method CAL#019-03 was used in the field rotational crop study for matrices with low moisture content (fodder, hay, straw and grains) [Mickelson, 2000, M-240710-01-1]. Modifications involved changes in extraction. Low moisture samples (5 g) were extracted with 20 mL 1% formic acid and 100 mL MeOH (20:100, v/v). The extract was cleaned up as described in revision 1 of the method. Final fractions were adjusted to 50 mL instead of 100 mL. Only limited concurrent recovery data (n=1/level, at 0.01–0.05–0.5 mg/kg, within 70–120%, all analytes) are available for wheat hay, wheat grains, wheat straw, soya bean seeds, soya bean hay, sorghum grains and sorghum fodder. Recoveries are not satisfactory for IFT-BA in wheat hay (62%, n=1, 0.01 mg/kg), wheat straw (68%, n=1, 0.01 mg/kg) and soya bean seeds (64%, n=1, 0.01 mg/kg). No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control samples.

Modification B of HPLC-MS-MS method CAL#019-03 was used in the field rotational crop study on fresh commodities [Mickelson, 2000, M-240710-01-1]. Modifications involved only minor changes in the RP102 clean-up part of the method. Only limited concurrent recovery data are available for mustard leaves, turnip roots, turnip tops, wheat forage, soya bean forage, radish roots, radish tops, sorghum forage (at n=1/level, 0.01–0.05–0.5 mg/kg, within 70–120%, all analytes). Recoveries are not satisfactory for IFT-BA in turnip tops (69%, n=1, 0.01 mg/kg) and wheat forage (69%, n=1, 0.01 mg/kg). Linearity (coefficient of correlation $r > 0.99$) was observed in the range of 0.5–5 ng/mL using four single standards in solvent. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control samples.

Modification C of HPLC-MS-MS method CAL#019-03 was used in the 2005 and 2006 Canadian and US supervised field trials on maize [Fischer and Helfrich, 2007, M-285889-01-1; Vaughn and Cosgrove, 2007, M-286216-02-1]. Modifications involved changes in extraction, addition of internal standards and omission of the RP 102 clean-up step and a different MS system. Homogenised samples (5 g) were extracted with 10 mL 1% formic acid and 90 mL MeOH. Mixed internal standards ($^{13}\text{C}_6$ -IFT, $^{13}\text{C}_6$ -IFT-DKN, $^{13}\text{C}_6$ -IFT-BA, and 0.025 mg/L each) were added together with the HCl solution. After liquid-liquid partition, the DCM phase was acidified with 1% formic acid and evaporated to 1 mL. The sample was diluted with 1% aqueous formic acid solution and ACN (50:50 or 60:40, v/v, 100 mL). A 0.1 mL aliquot was used for injection. HPLC-MS-MS with electrospray ionization was used for the analysis of IFT, IFT-DKN and IFT-BA. The mass transitions monitored were m/z 358 $\rightarrow$ 79 for IFT, m/z 358 $\rightarrow$ 79 for IFT-DKN and m/z 267 $\rightarrow$ 159 for IFT-BA as well as the mass transitions for their ^{13}C isotopes.

Modification C of HPLC-MS-MS method CAL#019-03 was validated according to a reduced scheme for maize forage, maize grains and maize fodder [Fischer and Helfrich, 2007, M-285889-01-1]. Samples were fortified separately with IFT, IFT-DKN or IFT-BA. Average recoveries at 0.01 mg/kg (n=14–22) and 0.20 mg/kg (n=3, IFT) or 0.27 mg/kg (n=3, IFT-DKN, IFT-BA) were within 70–120% limits for each analyte. The RSD was within 20%, except for IFT-DKN and IFT-BA at 0.01 mg/kg in maize forage (24%, 21%) and for IFT-BA at 0.01 mg/kg in maize fodder (27%). Linearity (1/ $\times$ weighted, correlation coefficient $r > 0.99$) was observed in the range of 0.002–2.0 mg/kg using seven duplicate standards in solvent with internal standards. No interfering peaks > LOD (i.e. 0.003 mg/kg IFT, 0.005–0.007 mg/kg IFT-DKN, 0.006–0.01 mg/kg IFT-BA) were detected in any of the control extracts (n> 2), except 0.007 mg/kg IFT-BA in maize grain. Based on these results, the valid LOQ is 0.01 mg/kg for IFT, 0.02 mg/kg for IFT-DKN and 0.03 mg/kg for IFT-BA.

Conclusion: HPLC-MS-MS method CAL#19-03 is generally insufficiently validated. Modification C needs adaption of LOQs to 0.02 mg/kg for IFT-DKN and 0.03 mg/kg for IFT-BA. Additional validation data are needed for commodities analysed in the field rotational crop study:

- Revision 1 is considered valid at 0.01–0.10 mg/kg IFT, IFT-DKN and IFT-BA in maize grains, maize flour, mustard leaves, maize forage and maize fodder. The method is not valid in wheat straw. Since IFT-BA levels in the supervised trials on maize forage were in the range < 0.01–0.15 mg/kg, validation at higher levels is desirable.
- Modification A is considered insufficiently validated. Additional validation data for the commodities analysed in the field rotational crop study are needed.

- Modification B is considered insufficiently validated. Additional validation data for the commodities analysed in the field rotational crop study are needed.
- Modification C is considered valid at 0.01–0.2 mg/kg IFT, 0.02–0.3 mg/kg IFT-DKN and 0.03–0.3 mg/kg IFT-BA in maize forage, maize grains and maize fodder. Results below 0.02 mg/kg IFT-DKN and below 0.03 mg/kg IFT-BA in the supervised field trials need to be reported as < 0.02 mg/kg IFT-DKN and < 0.03 mg/kg IFT-BA.

HPLC-MS-MS method 00985/M001

HPLC-MS-MS method 00985/M001, version 13 November 2006, was developed to determine individual residues of IFT and its metabolites IFT-DKN and IFT-BA in plant materials [Schoening and Wolters, 2006, M-280607-01-1]. Samples (10 g) were extracted with MeOH/1% formic acid (90:10, v/v). After filtering, the corresponding $^{13}\text{C}_6$ labelled analytes were added. The solution was made up to volume with water (pH 3, using formic acid) and MeOH. An aliquot of the extract was 5× diluted with water/ACN (90/10, v/v, pH 3 using formic acid), filtered and subjected to HPLC-MS-MS analysis with electrospray ionisation. For quantification external calibration with standard solutions was used quoting the peak area ratio of the analytes and the corresponding isotopically labelled internal standards. Quantification was carried out by monitoring the ion transitions m/z 360/366 → 251/257 (IFT), m/z 358/364 → 79/79 (IFT-DKN) and m/z 267/273 → 159/165 (IFT-BA).

HPLC-MS-MS method 00985/M001 was used in the EU maize and poppy seed trials [Zimmer and Wieland, 2007, M-282674-01-1; Wolters and Erler, 2007a/b, M-284416-01-1, M-284423-01-1; Wolters, 2007a/b, M-285005-01-1, M-285014-01-1; Zimmer, 2006, M-281611-01-1; Billian and Reinecke, 2010, M-360144-02-1; Billian and Krusell, 2010a/b, M-364166-01-1, M-360114-02-1; Noss and Reinecke, 2010, M-366025-01-1]. HPLC-MS-MS method 00985/M001 was validated according to the full validation scheme for maize grains, maize forage and sweet corn (cobs without husks) [Schoening and Wolters, 2006, M-280607-01-1] and poppy seeds [Billian and Reinecke, 2010, M-360144-02-1]. Grinding of poppy seeds led to residues about a factor 2 higher compared to non-grinded seeds. Therefore, poppy seeds need to be grinded prior to extraction (e.g. 30 sec using an IKA A11 basic mixer or pestling by hand). Samples were fortified with a mixture of IFT, IFT-DKN or IFT-BA. Average recoveries at 0.01 mg/kg and 0.10 mg/kg were within 70–120% limits and RSDs were within 20% for each analyte and matrix. Linearity (coefficient of correlation $r > 0.99$ for $1/\times$ weighted) was observed in the range of 0.01–50 ng/mL standards using nine single solvent standards and internal standards at 1 ng/mL. Equivalent concentrations in the samples were not stated. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control extracts. The valid LOQ is 0.01 mg/kg for each analyte in all matrices tested.

Conclusion: HPLC-MS-MS method 00985/M001 is considered valid at 0.01–0.10 mg/kg IFT, IFT-DKN and IFT-BA in maize grains, maize forage, sweet corn (cobs without husks) and poppy seeds (which need to be grinded prior to extraction). Additional validation data are needed for maize fodder. Since IFT and IFT-DKN levels in the supervised residue trials on maize forage ranged from < 0.01 –13 mg/kg and < 0.01 –2.6 mg/kg, respectively, validation at higher levels is desirable.

HPLC-MS-MS method IS-004-P10 and its modifications

HPLC-MS-MS method IS-004-P10-01, issued 18 February 2010, was developed for the analysis of IFT and IFT-DKN in plant matrices [Stoughton, 2010a, M368825-01-1]. Homogenized samples (5 g) were extracted by blending with a 1% aqueous formic acid/MeOH (5:20, v/v) solution. The extraction was repeated with MeOH. The extract was filtered using a Bond Elute cartridge. An isotopic internal standard mixture ($^{13}\text{C}_6$ -IFT, $^{13}\text{C}_6$ -IFT-DKN, 1 mg/L each) was added to the extract. An aliquot of the sample was then diluted 1:1 with 0.1% formic acid in water. The sample was analysed by HPLC-MS-MS for IFT and IFT-DKN. Quantification was based on the use of internal standards and comparisons of peak areas with those of known standards. The detection by MS-MS was performed with a turbo ion spray interface operated in positive ion mode and multiple reaction monitoring (MRM): m/z 360 to 251 for IFT and m/z 358 to 79 for IFT-DKN.

HPLC-MS-MS method IS-004-P10-01 was used in soya bean residue trials [Dallstream and Fisher, 2010, M-368661-01-1; Beedle and Dallstream, 2010, M-368669-01-1]. HPLC-MS-MS method IS-004-P10-01 was validated according to the full validation scheme for soya bean seed [Stoughton, 2010c, M-368828-01-1]. Samples were fortified with a mixture of IFT and IFT-DKN. Average recoveries at 0.01 mg/kg and 0.10 mg/kg were within 70–120% limits and RSDs were within 20% for each analyte in soya bean seeds. Linearity (coefficient of determination $R^2 > 0.99$) was observed in the range of 0.12–9.0 ng/mL using seven duplicate solvent standards. Equivalent concentrations in the samples were 0.0024–0.180 mg/kg. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control extracts. The valid LOQ is 0.01 mg/kg for each analyte. On completion of the validation study, method IS-004-P10-01 was updated to include the confirmatory MRM transitions m/z 358 to 64 for IFT and m/z 358 to 64 for IFT-DKN. The updated method was issued and assigned a method number of IS-004-P10-02 (dated 12 May 2010) [Stoughton 2010b, M368826-01-1].

Modification A of HPLC-MS-MS method IS-004-P10-01 was used in soya bean processing studies [Fischer, 2010, M-368662-01-1]. The modification involved changes in sample type and sample weight. Samples of 5 g soya bean seed, soya bean meal, soya bean hulls, soya bean oil, soymilk or 1.0 g for soya bean aspirated grain fractions were homogenised before extraction.

Modification A of HPLC-MS-MS method IS-004-P10-01 was validated according to a reduced validation scheme for soya bean seed, soya bean meal, soya bean hulls, soya bean oil, soymilk and soya bean aspirated grain fractions [Fischer, 2010, M-368662-01-1]. Samples were fortified with a mixture of IFT and IFT-DKN. Average recoveries at 0.01 mg/kg ($n=3$) and 0.10 mg/kg ($n=3$) or 0.5 mg/kg ($n=2$, aspirated grain fractions) were within 70–120% limits and RSDs were within 20% for each analyte and matrix. Linearity (correlation coefficient $r > 0.99$) was observed in the range of 0.0–9.0 ng/mL using seven duplicate solvent standards. Equivalent concentrations in the samples were 0.0–0.180 mg/kg. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control extracts. The valid LOQ is 0.01 mg/kg for each analyte and matrix.

Modification B of HPLC-MS-MS method IS-004-P10-01 was used in storage stability studies [Klasmeier, 2012, M-442915-01-1]. The modification involved changes in extraction and addition of filtration steps. Homogenized samples (5 g) were extracted by blending once with a 1% aqueous formic acid/MeOH (10:40, v/v) solution. The extract was filtered on glass wool. Just prior to analysis the sample was filtered with 0.45 μ m Nylon filter. The detection by MS-MS was performed with a turbo ion spray interface operated in positive ion mode at m/z 360.1 to 250.9 and 219.8 for isoxaflutole and in negative ion mode at m/z 358.0 to 79.0 and 64.0 for IFT-DKN for quantification and confirmation.

Modification B of HPLC-MS-MS IS-004-P10-01 was partially validated for oranges, soya bean seeds, dry pinto beans and sugarcane billets [Klasmeier, 2012, M-442915-01-1]. Samples were fortified separately with isoxaflutole or IFT-DKN. Average recoveries at 0.1 mg/kg ($n=3$) were within 70–120% limits for each analyte. The RSD was within 20%. Recoveries at the LOQ were not verified, but this is considered acceptable for the storage stability studies at 0.1 mg/kg. Linearity ($1/\times$ weighted, correlation coefficient $r > 0.99$) was observed in the range of 0.12–9.0 ng/mL using five single standards in solvent with internal standards. No interfering peaks $> LOD$ (i.e. 0.003 mg/kg) were detected in any of the control extracts ($n > 2$).

Conclusion: HPLC-MS-MS method IS-004-P10 and its modifications are considered fit for purpose:

- The original method is considered valid at 0.01–0.1 mg/kg in dry soya bean seed.
- Modification A is considered valid at 0.01–0.1 mg/kg in dry soya bean seed, soya bean meal, soya bean hulls, soya bean oil, soymilk and 0.01–0.5 mg/kg in soya bean aspirated grain fractions.
- Modification B is considered valid at 0.1 mg/kg in oranges, dry soya bean seeds, dry pinto beans, and sugarcane billets.

HPLC-MS-MS method ATM-0054.01

HPLC-MS-MS method ATM-0054.01, version August 2011, was developed to determine individual residues of IFT, IFT-DKN and IFT-BA in plant materials [Ellis, 2012, M-425905-02-1]. Homogenised samples (10 g) were extracted with 20:80 water:ACN. An aliquot of the extract was reduced to dryness and reconstituted in water acidified with 0.22% formic acid. The reconstituted sample was then filtered and subjected to analysis by HPLC-MS-MS. Quantitation was achieved using matrix matched analytical standards and $^{13}\text{C}_6$ -labelled internal standards for isoxaflutole, diketonitrile metabolite and the benzoic acid metabolite. The monitored ion transitions were m/z 360 $\rightarrow$ 251 for IFT, m/z 358 $\rightarrow$ 79 for IFT-DKN and m/z 267 $\rightarrow$ 159 for IFT-BA. The metabolites are not expressed as isoxaflutole equivalents.

HPLC-MS-MS method ATM-0054.01 was validated according to the full validation scheme for oat grain, lupin seed, and mung bean forage [Ellis, 2012, M-425905-02-1]. Samples were fortified with a mixture of IFT, IFT-DKN and IFT-BA. Average recoveries at 0.01 mg/kg and 1.0 mg/kg were within 70–120% limits and RSDs were within 20% for each analyte and matrix. Linearity (coefficient of correlation $r > 0.999$ for $1/\times$ weighted) was observed in the range of 0.5–150 $\mu\text{g/L}$ using five single matrix matched standards. Equivalent concentrations in the samples were not stated. No interfering peaks > 0.3 LOQ (i.e. 0.003 mg/kg) were detected in any of the control samples. The valid LOQ is 0.01 mg/kg for each analyte and matrix tested.

Modification A HPLC-MS-MS method ATM-0054.01 was used in the Australian chickpea trials [Ellis, 2012, M-425905-02-1]. The method modification involved using less sample material (5 g), increased extraction volumes and modified aliquots for further analysis.

Modification A was validated according to a full validation scheme for chickpea seeds and chickpea straw and a reduced validation scheme for chickpea forage [Ellis, 2012, M-425905-02-1]. Samples were fortified with a mixture of IFT, IFT-DKN or IFT-BA. Average recoveries at 0.01 mg/kg and 1.0 mg/kg were within 70–120% limits and RSDs were within 20% for each analyte and matrix. Linearity (coefficient of correlation $r > 0.999$ for $1/\times$ weighted) was observed in the range of 0.5–150 $\mu\text{g/L}$ using six single matrix matched standards. Equivalent concentrations in the samples were not stated. No interfering peaks were detected in any of the control samples (< 0.01 mg/kg for each analyte). The valid LOQ is 0.01 mg/kg for each analyte and matrix tested and 0.03 mg/kg for total residues.

Conclusion: HPLC-MS-MS method ATM-0054.01 and its modifications are considered fit for purpose:

- The original method is considered valid at 0.01–0.1 mg/kg in oat grain, lupin seed, and mung bean forage.
- Modification A is considered valid at 0.01–0.1 mg/kg in dry chickpea seeds, chickpea forage and chickpea straw. Since IFT-BA levels in the supervised trials on chickpea forage ranged from < 0.01 –0.55 mg/kg and in chickpea straw ranged from < 0.01 –0.12 mg/kg, validation at higher levels is desirable.

*Analytical methods used in study reports in animal commodities**HPLC-UV method RPAC #44882*

HPLC-UV method RPAC #44882, version 2.0, 27 October 1995, was developed to determine individual residues of IFT and its metabolites IFT-DKN, RPA 205834, and IFT-BA in milk [Tew, 1995a, M-192311-01-1]. The method was used in dairy cow feeding studies [Tew, 1995a, M-192311-01-1] and storage stability studies in milk [Lowder, 1996, M-192281-01-2-01]. The method is identical to HPLC-UV method RPAC #45532 for milk except that fraction 1, containing IFT-BA, is kept. Validation results for IFT, IFT-DKN, RPA 205834 and IFT-BA are available in the section describing method RPAC #45532.

HPLC-UV method RPAC #44933

HPLC-UV method RPAC #44933, version 2.0, 17 November 1995 was developed to determine metabolite IFT-DKN in eggs [Tew, 1995b, M-192317-01-1]. The method is identical to HPLC-UV method RPAC #45532 for eggs and was used in laying hen feeding studies [Tew, 1995b, M-192317-01-1] and storage stability studies in eggs [Lowder, 1996, M-192281-01-2-01]. Validation results for IFT-DKN are available in the section describing method RPAC #45532.

HPLC-MS-MS method RPAC #44996 and its modifications

HPLC-MS-MS method RPAC #44996, version 1.0, 4 December 1995, was developed to determine RPA 207048 in animal tissues [Tew, 1995a/b, M-192311-01-1, M-192317-01-1, Lowder, 1996, M-192281-01-2-01]. Samples (25 g) were extracted twice with 0.1% aqueous trifluoroacetic acid and ACN (25:90, v/v). The combined filtered extracts were washed with hexane. A portion of the extract was reduced by evaporation and then diluted with NaCl solution. Residues are then partitioned into DCM and drained through anhydrous Na₂SO₄. The DCM phase was evaporated and the remaining residue was dissolved in water/ACN (80:20) prior to quantification by HPLC-MS-MS. Matrix matched standards were used to compensate for any matrix effects that may enhance or depress the analyte signal. The ion transitions monitored were 361/79 (RPA 207048).

HPLC-MS-MS method RPAC #44996, version 1.0 also provided good results for the parent compound and metabolites IFT-DKN and RPA 205834. Therefore the method was rewritten as HPLC-MS-MS method RPAC 44996, version 2.0, 29 January 1996, to incorporate these metabolites as well [Hudson *et al.*, 1996, M-262714-01-1]. The ion transitions monitored were 358/79 (IFT), 361/79 (RPA 207048), 358/79 (IFT-DKN), and 360/79 (RPA 205834). During sample extraction and clean-up, parent IFT is partially degraded to IFT-DKN. Parent IFT is only stable at pH 2; metabolite RPA 207048 is unstable at pH 2. Since the method measures IFT and IFT-DKN, any degradation of IFT is measured as increased IFT-DKN, so that the entire amount of residue in the original sample is measured even though the character of the residue may have changed. For this reason, separate samples need to be prepared for verification of recovery for IFT, since residues will appear as IFT and its metabolite IFT-DKN.

HPLC-MS-MS method #44996 was used during the conduct of the dairy cow feeding studies, the laying hen feeding studies and storage stability studies in animal tissues [Tew, 1995a/b, M-192311-01-1, M-192317-01-1, Lowder, 1996, M-192281-01-2-01]. The method was validated by either fortifying IFT alone, or a mixture of IFT-DKN, RPA 207048, and RPA 205834. The recoveries for IFT were measured by summing up residues of IFT and IFT-DKN. Concurrent recovery results from the cow and hen feeding studies are summarized in the validation report [Hudson *et al.*, 1996, M-262714-01-1]. Only limited recovery data (n=1–2/level, within 70–120%) are available for IFT, IFT-DKN, RPA 205834 and RPA 207048 in bovine liver (0.05, 0.25 and 2.0 mg/kg), bovine kidney (0.05, 0.45 and 0.60 mg/kg), bovine muscle (0.05 mg/kg only), bovine fat (0.05 mg/kg only), chicken liver (0.05, 0.45, 0.60 and 1.0 mg/kg), chicken muscle (0.05 mg/kg only) and chicken skin plus fat (0.05 and 0.45 mg/kg). An RSD within 20% was found for IFT in bovine liver at 0.05 mg/kg (n=3) and for IFT-DKN in chicken liver at 0.05 mg/kg (n=3). Additional recovery and precision data are available from the storage stability study. Average recoveries at 0.25 mg/kg for each analyte were within 70–120% limits and RSDs were within 20% for each analyte and matrix. Linearity (coefficient of correlation $r > 0.99$) was observed in the range of 0–150 ng/mL or 0–75 ng/mL using 6–7 single matrix matched standards. Equivalent concentrations in the samples were not stated. No interfering peaks were detected in any of the control samples (< 0.05 mg/kg for each analyte). The reported LOQ is 0.05 mg/kg for each analyte and matrix tested, but precision data at this level are not available (except in chicken and bovine liver).

Conclusion: HPLC-MS-MS method #44996 is considered suitable for determination of IFT, IFT-DKN, RPA 205834 and RPA 207048 in animal tissues. However, the method is considered insufficiently validated. Validation is sufficient at 0.25 mg/kg for each analyte and each tissue. Additional validation data are needed for muscle, kidney, and fat in order to establish precision at the

reported LOQ of 0.05 mg/kg, since only 1–2 recoveries were available. Isoxaflutole is partly degraded because of extraction conditions, but is measured as an increased amount of IFT-DKN.

Since residue levels in the feeding studies ranged from < 0.05–0.503 mg/kg for IFT-DKN in bovine kidney, < 0.05–1.84 mg/kg for IFT-DKN in bovine liver, 0.123–0.645 mg/kg for IFT-DKN in hen liver, < 0.05–0.810 mg/kg for RPA 205834 mg/kg in bovine liver, additional validation at higher levels is desirable for kidney and liver.

Because the extraction solvent resembles the extraction solvent used in HPLC-UV method RPAC #45532 for milk and eggs, the method is possibly also suitable for milk and eggs; validation data on these commodities are desirable.

Stability of pesticide residues in stored analytical samples

The Meeting received information on storage stability of parent and its metabolites IFT-DKN and IFT-BA in plant commodities. In addition the Meeting received information on storage stability of parent and its metabolites IFT-DKN, RPA 205834 and RPA 207048 in animal commodities.

Study 1

Storage stability was investigated in maize commodities [Nandihalli, 1996, M-089371-01-1]. Homogenized untreated sample materials (25 g each) were independently spiked with IFT, IFT-DKN and IFT-BA. Fortification levels were 0.210 mg/kg for maize forage and maize fodder, 0.105 mg/kg for maize grain. The samples were stored at –10 °C or lower for 15 months. Samples were analysed in duplicate at various intervals using GC-MS method 00473 (common moiety method), where IFT, IFT-DKN and IFT-BA are converted into RPA 204497 (and expressed as spiked analyte). Average concurrent recoveries at 0.21 mg/kg for maize silage and maize fodder and at 0.105 mg/kg for maize grain were within 70–120%. Levels in control samples were < 0.003 mg/kg (0.3 LOQ).

During the storage period the temperature increased to –5.5 to –3.9 °C on two consecutive days, –0.4 to +2.0 °C on two consecutive days and –8.2 to –2.2 °C on four consecutive days. Since the samples remained frozen, this deviation did not significantly affect the results of the study. Storage stability results and concurrent recoveries are shown in Table 37. The presented results for the stored samples are not corrected by the concurrent (freshly spiked) recoveries.

Conclusion: The storage stability results indicate that there were no significant losses of total isoxaflutole residues (sum of IFT, IFT-DKN and IFT-BA) in maize grains, maize forage and maize fodder stored at –10 °C for at least 15 months. Any degradation from IFT to IFT-BA or from IFT-DKN to IFT-BA remains undetected, because of the common moiety method used.

Table 37 Storage stability of 0.1–0.2 mg/kg IFT, IFT-DKN or IFT-BA in frozen maize commodities at –10 °C

Commodity	Storage time (months)	IFT % remaining mean, n=2	IFT concurrent recovery mean, n=2	IFT-DKN % remaining mean, n=2	IFT-DKN concurrent recovery, mean, n=2	IFT-BA % remaining mean, n=2	IFT-BA concurrent recovery, mean, n=2
Maize forage	0	–	78	–	102	–	86
	1	96	89	81	90	85	99
	2	77	85	68	79	79	87
	3	85	74	63	85	83	79
	6	77	88	72	84	81	90
	12	74	87	71	92	81	87
	15	88	95	82	92	89	90
Maize fodder	0	–	97	–	78	–	92
	1	84	73	64	82	83	95
	2	78	86	60	70	79	85
	3	77	83	61	74	73	78
	6	71	81	63	75	77	86
	12	75	88	66	72	71	78
	15	87	91	74	90	83	90
Maize	0	–	79	–	77	–	79

Commodity	Storage time (months)	IFT % remaining mean, n=2	IFT concurrent recovery mean, n=2	IFT-DKN % remaining mean, n=2	IFT-DKN concurrent recovery, mean, n=2	IFT-BA % remaining mean, n=2	IFT-BA concurrent recovery, mean, n=2
grain	1	90	100	70	71	77	85
	2	74	82	67	76	61	74
	3	83	85	74	78	68	67
	6	62	85	64	72	62	80
	12	78	92	75	84	59	69
	15	77	89	77	86	62	75

Study 2

Storage stability was investigated in chickpea commodities [Lynch and Keats, 1999b, M-432374-01-1, Lynch and Keats, 2000a, M-432434-01-1]. Homogenized untreated sample materials of chickpea forage, chickpea seeds and chickpea straw were independently spiked with IFT, IFT-DKN and IFT-BA at a fortification level of 0.10 mg/kg. The samples were stored at -20°C for 11 months. Samples were analysed in triplicate at various intervals using GC-MS-MS modification B of method 00473 (common moiety method), where IFT, IFT-DKN and IFT-BA are converted into RPA 204497 (and expressed as spiked analyte). Average concurrent recoveries at 0.01 mg/kg were within 70–120% for each analyte and matrix. Levels in control samples were < 0.003 mg/kg (0.3 LOQ).

Storage stability results and concurrent recoveries are shown in Table 38. Presented results for the stored samples are not corrected by the concurrent (freshly spiked) recoveries.

Conclusion: The storage stability results indicate that there were no significant losses of total isoxaflutole residues (sum of IFT, IFT-DKN and IFT-BA) in chickpea forage, chickpea seeds or chickpea straw stored at -20°C for at least 11 months. Any degradation from IFT to IFT-BA or from IFT-DKN to IFT-BA remains undetected, because of the common moiety method used.

Table 38 Storage stability of 0.1 mg/kg IFT, IFT-DKN or IFT-BA in chickpea commodities at -20°C

Commodity	Storage time	IFT % remaining mean, n=3	IFT concurrent recovery mean, n=3	IFT-DKN %remaining, mean, n=3	IFT-DKN concurrent recovery mean, n=3	IFT-BA % remaining mean, n=3	IFT-BA concurrent recovery, mean, n=3
Chickpea forage	3 days	78	79	78	75	78	81
	11 months	73	95	73	72	73	99
Chickpea grain	3 days	76	78	76	76	76	82
	11 months	78	80	78	75	78	87
Chickpea straw	3 days	73	79	73	77	73	76
	11 months	74	80	74	82	74	87

Study 3

Storage stability was investigated in sugarcane commodities [Davis and Keats, 1999e/f, M-284408-01-1, M-284324-01-1] Homogenised untreated samples of sugarcane billets and sugarcane forage were independently spiked with IFT, IFT-DKN and IFT-BA at a fortification level of 0.10 mg/kg eq. The samples were stored at -20°C for a period of 20 months. Samples were analysed in duplicate at various intervals using GC-MS modification A of method 00473 (common moiety method), where IFT, IFT-DKN and IFT-BA are converted into RPA 204497 and residues were expressed as isoxaflutole equivalents. Average concurrent recoveries at 0.01 mg/kg eq were within 70–120% for each analyte and matrix. Levels in control samples were < 0.01 mg/kg (LOQ).

Storage stability results and concurrent recoveries are shown in Table 39. The presented results for the stored samples are not corrected by the concurrent (freshly spiked) recoveries.

Conclusion: The storage stability results indicate that there were no significant losses of total isoxaflutole residues (sum of IFT, RPA 202238 and IFT-BA) in sugarcane billets or sugarcane forage stored at -20°C for at least 20 months. Any degradation from IFT to IFT-BA or from IFT-DKN to IFT-BA remains undetected, because of the common moiety method used.

Table 39 Storage stability of IFT, IFT-DKN and IFT-BA in sugarcane commodities

Commodity	Storage time months	IFT % remaining mean, n=2-4 ^a	IFT concurrent recovery mean, n=5	IFT-DKN % remaining mean, n=2-4 ^a	IFT-DKN concurrent recovery, mean, n=5	IFT-BA % remaining mean, n=2-4 ^a	IFT-BA concurrent recovery, mean, n=5
Sugarcane billets	20	84	88	88	86	88	88
Sugarcane forage	20	79	93	85	95	82	93

^a mean of two replicates for sugarcane, mean of four replicates for forage

Study 4

Storage stability was investigated in oranges, soya bean seeds, dry pinto beans, and sugarcane billets [Klasmeier, 2012, M-442915-01-1]. Homogenized untreated sample materials were individually spiked with IFT and IFT-DKN at a fortification level of 0.1 mg/kg. The samples were stored at -10°C or lower for a period of 6 months. Samples were analysed in duplicate at various intervals using modification B of HPLC-MS-MS method IS-004-P10-01. Average concurrent recoveries for mixtures of IFT and IFT-DKN each at 0.1 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ).

Storage stability results and concurrent recoveries are shown in Table 40. The presented results for the stored samples are not corrected for the concurrent (freshly spiked) recoveries.

Additional results for this storage stability are available covering a storage period of 374-377 days (see Table 40) but there is no corresponding report available yet [Bayer, 2013].

Conclusion: After 3 months of storage at -10°C , IFT partially converts to IFT-DKN in dry pinto beans while this conversion was observed at 6 months for oranges, soya bean seeds and sugarcane billets. Total residues (sum of IFT and IFT-DKN) and IFT-DKN alone remained stable for at least 1 year in each matrix tested. Storage stability of IFT-BA alone or further degradation of IFT or IFT-DKN to IFT-BA was not verified, but this is considered desirable.

No storage stability studies have been conducted on chickpea seeds, chickpea forage, chickpea straw, sweetcorn, maize forage, maize grains and maize fodder. Most of these commodities can be extrapolated from the present data: dry chickpea seeds vs dry pinto beans, chickpea forage vs sugarcane billets, sweetcorn vs sugarcane billets and maize forage vs sugarcane billets. Storage stability data on chickpea straw, maize grains and maize fodder cannot be extrapolated; these are desirable. Since maize forage, maize grains, maize fodder in the supervised residue trials have been stored for 593, 544 and 546 days, respectively, storage stability data for longer periods are desirable.

Table 40 Storage stability of IFT and IFT-DKN in various commodities

Commodity	Storage time days	IFT % remaining mean, n=2	IFT concurrent recovery mean, n=2-3	IFT-DKN % remaining mean, n=2	IFT-DKN concurrent recovery, mean, n=2-3
Oranges	0	-	88	-	73
	31	91	92	71	79
	96	88	93	75	93
	188	74 (IFT) + 21 (IFT-DKN) = 95 ^a	88	70	87
	377 ^b	74 (IFT) + 19 (IFT-DKN) = 93 ^a	89	79	87
Pinto beans	0	-	95	-	81
	36	71	97	80	92
	94	58 (IFT) + 31 (IFT-DKN) = 90 ^a	88	75	90
	184	49 (IFT) + 36 (IFT-DKN) = 85 ^a	71	77	73
	374 ^b	48 (IFT) + 41 (IFT-DKN) = 89 ^a	70	75	74

Commodity	Storage time days	IFT % remaining mean, n=2	IFT concurrent recovery mean, n=2-3	IFT-DKN % remaining mean, n=2	IFT-DKN concurrent recovery, mean, n=2-3
Soya bean seeds	0	—	81	—	74
	35	76	94	66	79
	94	72	84	75	84
	183	58 (IFT) + 24 (IFT-DKN) = 82 ^a	86	78	86
	374 ^b	51 (IFT) + 31 (IFT-DKN) = 82 ^a	72	70	70
Sugarcane billets	0	—	93	—	75
	29	82	80	72	75
	95	94	92	77	92
	185	76 (IFT) + 9.0 (IFT-DKN) = 86 ^a	89	78	88
	375 ^b	78 (IFT) + 12 (IFT-DKN) = 90 ^a	88	81	91

^a Due to apparent partial conversion of IFT to IFT-DKN during storage, the recovery value reflects the sum of IFT and IFT-DKN (in isoxaflutole equivalents)

^b Additional results are available but there is no corresponding report available yet [Bayer, 2013].

Study 5

Storage stability was investigated for incurred residues in poppy seeds and poppy straw [Klempner, 2010, M-366215-01-1-01]. Poppy seeds and straw originated from the poppy metabolism study [Klempner, 2009, M1731775-1] where 100 g [phenyl-UL-14C]-Isoxaflutole per hectare was applied onto the bare soil (pre-emergence application). Samples from this study were stored at -18°C or lower. Samples were extracted and analysed after 16.1 months of storage by HPLC-UV with radiodetection. The method used in the storage stability study was the same method used in the metabolism study.

Aliquots of 20 g of the homogenised samples were extracted three times with a mixture of ACN/water (8/2, v/v). Extracts were combined and filtered by suction. The TRR values of the poppy matrices were determined by summing up the radioactivity determined in the combined extracts and the radioactivity in the remaining solids after extraction. The extracts were subjected to a clean-up step using an SPE RP 18 cartridge (Varian Mega Bond Elut C18). The flow-through fraction (percolate) was collected and mixed with emulsifier and/or defoamer and evaporated to the aqueous remainder (= final extract). The final extracts were analysed by HPLC-UV with radiodetection. Storage stability was assessed IFT-DKN and IFT-BA, because parent IFT was not detected in poppy matrices.

Comparison of the metabolic profiles of the poppy seeds and poppy straw from the metabolism study (extraction after 16 days of storage for seeds and 12 weeks of storage for straw) and at 16.1 months showed that the distribution of components did not significantly change during this storage period. No significant transformation of compounds was found in this storage period. Residue results from both studies are shown in Table 41.

Conclusion: The reference time point for this storage stability study is the first analysis day in the metabolism study: 16 days for poppy seeds and 12 weeks for poppy straw. Since the reference point for poppy seeds is shortly after harvest, levels of IFT-DKN and IFT-BA in poppy seeds can be considered stable for a period of at least 16 months. No conclusion can be drawn for the storage stability in poppy straw, since residues have not been measured shortly after harvest. Consequently it is not clear, whether the analytes had already been degraded to a plateau level at the start of the analysis (i.e. 12 weeks after harvest). No storage stability information is available for IFT, but this is considered desirable.

Table 41 Storage stability of incurred residues of IFT-DKN and IFT-BA in poppy seeds at -18 °C

Matrix	Storage period (days)	Origin	TRR mg/kg eq	IFT-DKN (mg/kg eq)	IFT-DKN % remaining ^a	IFT-BA (mg/kg eq)	IFT-BA % remaining ^a
Poppy seeds	16	metabolism study	0.056	–	–	0.037	–
	482	storage stab study	0.056	–	–	0.039	105
Poppy straw	84	metabolism study	0.725	0.026	–	0.643	–
	482	storage stab study	0.721	0.027	104	0.630	98

^a The concentrations found for isoxaflutole equivalent residue in the metabolism study were set to 100%.

Study 6

Homogenised samples of sorghum forage, sorghum fodder, sorghum grain, lettuce, radish leaves and radish roots were fortified with a mixture of 14C IFT, 14C-IFT-DKN and 14C-RPA203328 as total 2 mg/kg eq per sample [Hampton, 1996; M-192325-01-1]. Samples were stored at –20 °C for 700 days. Duplicate samples were subsequently extracted with hexane/EtOAc (9:1 v/v), ACN, water (pH 5.5) and ACN/0.2 M HCl (1:1 v/v). The pH for the water extraction was adjusted to pH 5.5, because at this pH hydrolysis of parent compound or conjugates did not occur. Radioactive residues in extracts were quantified by HPLC with radiodetection and co-chromatography of standards for IFT, IFT-DKN and IFT-BA.

Results are shown in Table 42. Extraction of day 0 spiked samples demonstrated a TRR of 99.3% present on average as 49% IFT, 33% IFT-DKN and 18% IFT-BA. After 700 days of storage the mean recovered TRR was 93.7% compared to 99.3% at day 0. The composition of the TRR changed. IFT was not sufficiently stable in storage, a decrease from 42.8–54.7% TRR (day 0) to 0.0–29.3% TRR after 700 days of storage was reported depending on matrix. Recovery for the intermediate metabolite IFT-DKN increased from 25.2–40.5% TRR (day 0) to 41.9–57.6% TRR (day 700) for most matrices, while a decrease of 34.2–40.5% TRR (day 0) to 26.4–31.4% TRR (day 700) was found in sorghum forage and sorghum grain. Also amounts of IFT-BA increased from 15.4–23.0% TRR at day 0 to 40.0–59.9% TRR after 700 days suggesting that degradation of Isoxaflutole to RPA202248 and subsequently from IFT-DKN to IFT-BA had occurred.

Conclusion: After 23 months of storage at –20 °C, isoxaflutole partially or completely converts to IFT-DKN and IFT-BA in sorghum forage, sorghum fodder, sorghum grain, lettuce, radish leaves and radish roots. Total residues (sum of IFT, IFT-DKN and IFT-BA) remained stable for at least 23 months. Storage stability of IFT-DKN alone or IFT-BA alone is masked by the isoxaflutole degradation. However, since the amount of IFT-BA increases with time, it indicates that IFT-DKN degrades further to IFT-BA. Storage stability studies with individual fortifications of IFT, IFT-DKN and IFT-BA are desirable.

Table 42 Storage stability of IFT, IFT-DKN and IFT-BA in various commodities

Commodity	Storage time days	TRR	IFT %TRR mean, n=2	IFT %remaining	IFT-DKN %TRR mean, n=2	IFT-BA %TRR mean, n=2	Sum ^a %TRR
Sorghum forage	0	98.9	49.7	–	34.2	16.1	100.0
	700	93.4	29.3	59	26.4	43.5	99.2
Lettuce	0	98.6	51.8	–	25.2	23.0	100.0
	700	96.2	4.9	9.5	57.6	40.0	102.5
Radish leaf	0	99.1	54.7	–	26.4	19.0	100.1
	700	94.1	0.0	0.0	48.7	51.0	99.7
Radish root	0	99.0	43.8	–	39.2	17.1	100.1
	700	91.4	5.1	12	41.9	53.0	100.0
Sorghum grain	0	100.3	42.8	–	40.5	16.8	100.1
	700	92.0	8.2	19	31.4	59.9	99.5
Sorghum fodder	0	99.9	50.0	–	34.7	15.4	100.1
	700	95.0	12.9	26	46.1	40.9	99.9

^a Sum of IFT, IFT-DKN and IFT-BA

Study 7

Storage stability was investigated in animal commodities purchased from a local food vender [Lowder, 1996, M-192281-01-2]. Milk samples were fortified with IFT, IFT-DKN, RPA 205834 and IFT-BA at 0.1 mg/kg each. Egg samples were fortified with IFT-DKN at 0.25 mg/kg. Bovine liver, kidney, muscle and fat samples were fortified with IFT, IFT-DKN, RPA 205834 and RPA 207048 at 0.25 mg/kg each. The storage samples were spiked individually with each analyte. The samples were stored frozen at -20 °C for up to 4 months. Samples were analysed at various intervals using HPLC-UV method RPAC #44882 for milk, HPLC-UV method RPAC #44933 for eggs and HPLC-MS-MS method RPAC #44996, version 2.0 for tissues. The analyses included a control sample, a freshly fortified control sample and duplicates of the storage samples.

For milk, the freshly fortified (i.e. concurrent recovery) samples were spiked with a mixture of IFT, IFT-DKN, RPA 205834, and IFT-BA at a level of 0.1 mg/kg for each analyte. For egg, the freshly fortified (i.e. concurrent recovery) samples were spiked with IFT-DKN at a level of 0.25 mg/kg. For liver, kidney, muscle, and fat tissues, two freshly fortified (i.e. concurrent recovery) samples were prepared: one with IFT alone, and one with a mixture of IFT-DKN, RPA 205834, and RPA 207048, each at 0.25 mg/kg. The tissue fortification procedure was necessary, because isoxaflutole is partially degraded to IFT-DKN during the tissue extraction procedure of HPLC-UV method RPAC #44996 and recovery of isoxaflutole in tissues can only be calculated as the sum of IFT and IFT-DKN. Levels in control samples were < 0.02 mg/kg (LOQ) in milk and < 0.05 mg/kg (LOQ) in eggs and tissues.

Storage stability results and concurrent recoveries are shown in Table 43 and Table 44. In these tables, the presented results for the stored samples are shown as not corrected and corrected (cr) by the concurrent (freshly spiked) recoveries. The power was off to the freezer for about 40 hours during the storage period. During this outage, temperatures rose to +5 °C. The outage would affect the "4 month" liver and muscle analyses.

Conclusion: The results for milk indicate that IFT-DKN, RPA 205834 and IFT-BA are stable for at least 127–128 days. Parent IFT is stable for a maximum period of 85 days, but degrades significantly thereafter (43% remaining at 127–128 days). The degradation of isoxaflutole on to IFT-DKN has not been verified. Storage stability of RPA 207048 has not been verified.

The results for eggs indicate that IFT-DKN is stable in the egg matrix for at least 129 days. Since parent IFT is immediately converted to IFT-DKN in the egg matrix, no fresh recovery of IFT is possible. Storage stability of metabolites RPA 205834 and RPA 207048 has not been verified.

The results for the tissues indicate that parent IFT and IFT-DKN are stable for at least 130 days in liver, 115 days in kidney, 113 days in fat, 131 days for IFT-DKN in muscle and a maximum period of 85 days for isoxaflutole in muscle. Metabolite RPA 205834 is stable for a period of 113–131 days in kidney, muscle, fat. Metabolite RPA 205834 is stable for a maximum storage period of 94 days in liver and degrades significantly thereafter (36% remaining after 130 days). Metabolite RPA 207048 is not stable in any animal commodity. RPA 207048 degrades instantaneously in kidney to a level of about 45% which is maintained from 13–115 days. RPA 207048 is stable for a maximum storage period of 28 days in muscle (70% remaining), a maximum period of 40 days in liver (74% remaining), and a maximum period of 84 days in fat (100% remaining) and thereafter remains stable at a level of about 50% of the original residue level for a period up to 85–113 days.

Table 43 Storage stability in milk and eggs

Matrix	Storage time days	IFT % remaining mean, n=2	IFT concurrent recovery mean, n=2-3	IFT-DKN % remaining mean, n=2	IFT-DKN concurrent recovery, mean, n=2-3	IFT-BA % remaining mean, n=2	IFT-BA concurrent recovery, mean, n=2-3	RPA 205834 % remaining mean, n=2	RPA 205834 concurrent recovery, mean, n=2-3
Milk	0	—	^a	—	^a	—	74	—	87
	15	66 (97 ^{cr})	68	69	72	86	72	99	100
	29	70 (81 ^{cr})	86	83	81	93	97	93	95
	56	71 (78 ^{cr})	91	82	82	81	87	92	96
	85	62 (81 ^{cr})	77	78	74	100	84	92	90
	127/128	43 (43 ^{cr})	99	100	88	94	92	94	94
Eggs	0	—	—	—	95	—	—	—	—
	15	—	—	98	99	—	—	—	—
	29	—	—	96	99	—	—	—	—
	56	—	—	85	95	—	—	—	—
	88	—	—	91	101	—	—	—	—
	129	—	—	92	95	—	—	—	—

^a Data not reported in the study report: the recoveries were too low to provide meaningful corrected results in the aged samples

cr = corrected for concurrent recovery

Table 44 Storage stability for animal tissues

Matrix	Storage time days	IFT % remaining mean, RSD _r , n=2	IFT concurrent recovery mean, n=2-3	IFT-DKN % remaining mean, RSD _r , n=2	IFT-DKN concurrent recovery, mean, n=2-3	RPA 207048 % remaining mean, RSD _r , n=2	RPA 207048 concurrent recovery, mean, n=2-3	RPA 205834 % remaining mean, RSD _r , n=2	RPA 205834 concurrent recovery, mean, n=2-3
bovine liver	0	—	^a	—	91	—	^a	—	^a
	10	72	69	72	69	57 (90 ^{cr})	63	86	84
	40	76	89	82	104	68 (74 ^{cr})	92	79	108
	60	68	75	84	89	53 (61 ^{cr})	87	74	96
	94	84	89	70	97	44 (57 ^{cr})	77	81	101
	130 t	72	94	77	100	24 (29 ^{cr})	83	36	101
bovine kidney	0	—	72	—	94	—	88	—	^a
	13	^a	^a	82	102	46 (48 ^{cr})	95	96	96
	27	^b	^b	86	97	45 (58 ^{cr})	77	82	93
	62	88	83	86	93	44 (48 ^{cr})	91	78	95
	84	86	80	82	122	42 (40 ^{cr})	104	102	116
	115	88	100	116	122	42 (40 ^{cr})	104	102	116
bovine muscle	0	—	^a	—	92	—	71	—	82
	14	^a	^a	128	101	79 (98 ^{cr})	81	^a	^a
	28	^a	^a	114	87	55 (70 ^{cr})	78	86	90
	63	85	94	94	100	54 (62 ^{cr})	87	90	100
	85	86	83	94	79	46 (62 ^{cr})	74	74	97
	131 t	^a	^a	120	113	43 (45 ^{cr})	95	86	99
bovine fat	0	—	^a	—	70	—	69	—	73
	13	82	97	66	120	85 (90 ^{cr})	94	88	89
	28	81	79	100	89	74 (90 ^{cr})	82	88	89
	62	84	80	88	82	56 (70 ^{cr})	80	94	92
	84	82	85	94	95	79 (101 ^{cr})	78	87	90
	113	88	84	98	120	51 (54 ^{cr})	94	94	110

^a Data not reported in the study report: the recoveries were too low to provide meaningful corrected results in the aged samples

^b Data not reported in the study report: poor calibration curve for all analytes ($r^2 < 0.99$) due to shift in detector response during the run

cr = corrected for concurrent method recovery

t = The power was off to the freezer for about 40 hours during the storage period. During this outage, temperatures rose to +5 °C

USE PATTERN

The herbicide isoxaflutole belongs to the chemical class of isoxazoles and acts as a pigment photosynthesis inhibitor of 4-hydroxyphenyl-pyruvate-dioxygenase (4-HPPD). Isoxaflutole controls a wide spectrum of grasses and broadleaf weeds by bleaching emerging or emerged weeds following herbicide uptake via the root system.

Isoxaflutole is a registered herbicide in several countries and the original registered labels in the original language as well as their English translation were submitted for Australia, Canada, France, Hungary, Italy, Spain and the USA. Use patterns were submitted for sweetcorn, chickpeas, maize, sugarcane and poppy seed. An overview is presented in Table 45.

The Australian, Canadian and USA labels warn against crop damage:

- Soils with low organic carbon (OC) and low CEC have a reduced capacity to adsorb the herbicide in the soil, which may result in the herbicide leaching past the weed root zone into the crop root zone. Crop root uptake of isoxaflutole may result in phytotoxicity, which is evident as bleaching of leaves. To minimise the risk of sugarcane root uptake, isoxaflutole is not recommended for use on soil with a CEC below 4.5 meq/100 g, or an OC of 1.0% or less. Chickpeas planted in sandy or gravelly soils or soils low in clay or organic matter may result in crop damage. Maize or IFT-soya beans grown on loamy sands, sandy loams or sands and/or soils with less than 1.5–2.0% om or pH > 7.5 may result in crop damage. US labels have soil specific application rates: lowest dose rate for sand, loamy sand or sandy loam; medium dose rate for loam, silt loam, silt or sandy clay loam; highest dose rate for silty clay loam, clay loam, sandy clay, silty clay, or clay.
- Failure to thoroughly close and firm the seed furrow for chickpeas and maize may allow herbicide to directly contact the seed which may cause crop injury. Maize seeds need to be planted at least 4 cm deep.
- Isoxaflutole is activated by rainfall or irrigation, which is required to carry the herbicide into the root zone of the germinating weeds. Heavy rains after the application of isoxaflutole to chickpeas may cause crop damage, particularly in sandy or gravelly soils.

Table 45 Registered pre-harvest uses of isoxaflutole

Crop	Country	Form g ai/kg g ai/L	Application				PHI, days
			Method & Timing	Rate kg ai/ha	Spray conc, kg ai/hL	No	
chickpea	Australia	WG 750	ground based equipment only - just after planting (after furrow closure) to prior to emergence of the crop	0.075	< 0.15	1	seeds: NA ^a forage/fodder: at least 6 weeks after application
Maize: Field corn	Canada	SC 240	ground based equipment only - pre-plant: up to 14 days prior to planting (soil surface treatment) - just after planting to prior to emergence of the crop - early post-emergence up to 3-leaf stage	0.079–0.106	< 0.070	1	grains: at least 110 days after any application forage/fodder: at least 60 days after application
	Canada	SC 480	ground based equipment only - pre-plant: 14–0 days prior to planting (soil surface treatment) - just after planting to	0.079–0.106	< 0.070	1	grains: at least 136 days after any application forage/fodder: at least 60 days after application

Crop	Country	Form g ai/kg g ai/L	Application				PHI, days
			Method & Timing	Rate kg ai/ha	Spray conc, kg ai/hL	No	
			prior to emergence of the crop				
Maize	France	SC 44 ^a	post-sowing pre-emergence of crop - early post-emergence of crop at BBCH 00–13	0.099	0.033–0.050	1	NA
Maize	Hungary	SC 240 ^a	10–0 days before planting of the crop - after planting, pre-emergence of the crop - early post-emergence: up to 3 leaf stage of the crop	0.077–0.106	0.026–0.042	1	NA
Maize	Italy	SC 50 ^{a, b}	pre-emergence of crop - early post-emergence up to 3 leaf stage of the crop	0.075–0.100	0.019–0.050	1	NA
Maize	Spain	WG 750	normal spray - pre-emergence of crop	0.052–0.10	0.010–0.051	1	NA
Maize: Field corn	USA	WG 750 ^e	ground based equipment for broadcast or banded applications - pre-plant: 30–0 days before planting maize (surface applied or incorporated in the soil at < 5 cm deep) - pre-emergence: during planting (after furrow closure) or before crop emerges	0.053–0.16	< 0.17	1 or 2 ^f	NA
	USA	SL 479 (40.5% w/w) ^e	ground based equipment for broadcast or banded applications - pre-plant: 30–0 days before planting (surface applied or incorporated in the soil at < 5 cm deep) - pre-emergence: during planting (after furrow closure) or before crop emerges	0.053–0.105	< 0.11	1 or 2 ^f	NA
	USA	SC 225 (19.0% w/w) ^{a, b, c}	ground based equipment for broadcast or banded applications - pre-plant: 30–0 days before planting (surface applied or incorporated in the soil at < 5 cm deep) - pre-emergence: during planting (after furrow closure) or before crop emerges - early post-emergence up to 2 leaf-collar growth stage of maize (V2,	0.055–0.092	< 0.099	1	grains: NA forage: at least 45 days after early post-emergence treatment

Crop	Country	Form g ai/kg g ai/L	Application				PHI, days
			Method & Timing	Rate kg ai/ha	Spray conc, kg ai/hL	No	
			where the first leaf has a rounded tip)				
	USA	SC 240 (20.0% w/w ^{a, c})	ground based equipment for broadcast or banded applications - pre-plant: 30–0 days before planting (surface applied or incorporated in the soil at < 5 cm deep) - pre-emergence: during planting (after furrow closure) or before crop emerges - early post-emergence up to 2 leaf-collar growth stage of maize (V2, where the first leaf has a rounded tip)	0.053–0.105	< 0.11	1 or 2 ^f	grains: NA forage: at least 45 days after early post-emergence treatment
sweetcorn	France	SC 44 ^a	post sowing pre-emergence of crop at BBCH 00–08	0.099	0.033–0.050	1	NA
poppy seed	Hungary	SC 240 ^a	pre-emergence: within 2–3 days after planting of the crop	0.077–0.106	0.026–0.042	1	NA
	Spain	WG 750	normal spray - pre-emergence of crop	0.045–0.060	0.009–0.030	1	NA
sugar cane	Australia	WG 750 ^c	ground based equipment only ^d -Pre- to early post-emergence of plant cane (up to 3–4 leaf crop stage) applied as broadcast or band spray over the top of the plant cane-After harvest of ratoon cane (up to 2 leaf crop stage) applied as broadcast or band spray - Prior to the “out-of-hand” stage of plant and ratoon cane applied as directed inter-row spray to the soil surface (sugarcane > 0.75 m height)	0.150	< 0.060	1	canes: at least 19 weeks after application forage: do not graze animals on treated crops

SC (suspension concentrate), WG (water dispersible granule), SL (soluble concentrate)

NA: PHI not applicable, because of the restriction in timing of the application

^a This product also contains the safener cyprosulfamide

^b This product also contains the herbicide thiencazuron-methyl.

^c Do not apply with wetting agents, crop oils or adjuvants

^d Do not apply to soils with CEC below 4.5 meq/100 g or < 1.0% organic carbon.

^e Crop oil concentrate or methylated seed oil is recommended when weeds are present at the time of treatment.

^f Either one application with 100% of the recommended rate can be made at the timing period indicated or two split applications can be made with 60% of the recommended broadcast rate applied 15 to 30 days prior to planting (pre-plant surface applied) and the remaining 40% applied at planting.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised residue trials of isoxaflutole for the following crops:

Group	Table	Commodity
Fruiting vegetables other than cucurbits	46	Sweet corn
Pulses	47	Chickpea seeds
	48	Glyphosate/HPPD tolerant soya beans seeds
Cereals	49	Maize grains
Grasses for sugar or syrup production	50	Sugarcane billets
Oilseeds	51	Poppy seeds
Legume animal feeds	52	Chickpea forage
	53	Chickpea straw
Straw, fodder and forage of cereal grains and grasses	54	Maize forage
	55	Maize fodder
Miscellaneous forage and fodder crops	56	sugarcane forage

Application rates and spray concentrations have been rounded to three figures; residues have been rounded to two figures. Residue data are recorded unadjusted for percentage recoveries or for residue values in control samples unless otherwise stated. Unquantifiable residues are shown as below the reported LOQ (e.g. < 0.01 mg/kg). Where multiple samples were taken from a single plot or where multiple analyses were conducted on a single sample, the average value is reported. Where results from separate plots with distinguishing characteristics such as different formulations, crop varieties or treatment schedules were reported, results are listed separately for each plot. Residues from the trials conducted according to critical GAP have been used for the estimation of maximum residue levels, STMR and HR values. Those results are underlined.

The residues presented in the tables are given as individual compound (and expressed as such) or as total residue. The total residue represents the sum of parent + IFT-DKN, expressed as isoxaflutole, unless stated otherwise. Since the relative molecular weight of IFT-DKN is the same as the relative molecular weight of isoxaflutole, no conversion for molecular weight is necessary. Where residues of were < 0.01 mg/kg, these were calculated as being at 0.01 mg/kg (expressed as metabolite).

Sweet corn

Supervised trials on maize were conducted in Spain, Italy, Greece, Portugal, Germany, France, Netherlands and the United Kingdom in 2005 and 2006 [Zimmer and Wieland, 2007, M-282674-01-1, report RA-2587/05; Wolters and Erler, 2007b, M-284423-01-1, report RA-2510/06; Wolters, 2007b, M-285014-01-1, report RA-2615/06; Zimmer, 2006, M-281611-01-1, report RA-2588/05; Wolters and Erler, 2007a, M-284416-01-1, report RA-2511/06; Wolters, 2007a, M-285005-01-1, report RA-2616/06]. Small plots of maize (50–1700 m²) were treated as indicated in Table 46 using knapsack, tractor/ATV mounted or wheelbarrow sprayers with spray volumes ranging from 90–300 L/ha

Four treatment scenarios were tested in the plots:

- a single application of isoxaflutole in combination with the safener cyprosulfamide at BBCH 12–14,
- a single application of isoxaflutole in combination with thienencarbazone-methyl and the safener cyprosulfamide at BBCH 13–14.

- a single bare ground application of isoxaflutole in combination with the safener cyprosulfamide (pre-emergence of the crop) followed by a second application with thiencarbazone-methyl in combination with the safener cyprosulfamide at BBCH 18.

Single field samples of ears without husks were taken as “baby corn” (BBCH 61), as “sweet corn” (milk ripeness, BBCH 79) or as “silage stage corn” (BBCH 85). All sample sizes were at least 2 kg and at least 12 items (in accordance with FAO manual 2009), except for some baby corn samples (0.6–1.2 kg) as indicated in Table 46. All samples were stored frozen with a maximum storage period of 244 days (8 months) at -18 °C.

Isoxaflutole and its metabolites IFT-DKN and IFT-BA were determined using HPLC-MS-MS method 00985/M001. This method is considered valid in the range 0.01–1.0 mg/kg for sweet corn. Average concurrent recoveries at 0.01–1.0 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.01 mg/kg (LOQ) for each analyte. Average concentrations for single field samples are shown in Table 46.

Note: Storage stability studies on commodities with high water content showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 20 months. Storage stability studies on commodities with high water content showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage and IFT-DKN is stable for at least 12 months but converts to IFT-BA within 23 months of storage. Since sweet corn has been stored for less than 12 months residues are considered reliable.

Note: All trials listed in Table 46 on sweet corn have been conducted with the safener cyprosulfamide. The manufacturer submitted summaries of six European trials (three from southern Europe and three from northern Europe) for sweet corn for the use of isoxaflutole in pre-emergence at 0.10 or 0.30 kg ai/ha without the safener cyprosulfamide, where it is shown that the presence of the safener cyprosulfamide does not affect the residue levels of IFT-DKN and IFT-BA. In these additional trials, the residue data were measured using a common-moiety method (sum of isoxaflutole, IFT-DKN and IFT-BA, expressed as isoxaflutole). In all trials, residue levels in the ear/cob harvested at DAT 76–158 were found to be < 0.013 mg/kg eq [Bayer, 2013]. These trials were not further investigated, since they have been conducted with a common moiety method and they confirm the residues found in the studies in Table 46.

Table 46 Isoxaflutole related residues after post-emergent treatment in sweet corn (ears without husks)

SWEET CORN Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS ¹	GS ²	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	total residues mg/kg eq	Study Trial
Germany Monheim (Nordrhein- Westfalen) 2005, (Romario) Soil: SaL	SC _a	1	0.10	0.034	13	79 85	78 111	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2587/05; R 2005 0623/6
Germany Monheim (Nordrhein- Westfalen) 2006, (Romario), Soil: SaSi	SC _b	1	0.099	0.033	13	61 79	55 ^d 77	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2510/06 R 2006 0795/4
Germany Euskirchen - Kessenich (Nordrhein-Westfalen), 2005 (Egrin FAO 220), Soil: SiC	SC _a	1	0.10	0.034	13	79 85	90 112	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2587/05 R 2005 0961/8
Germany Leverkusen (Nordrhein- Westfalen),	SC _c	1 ^c	0.10	0.034	05	61 79	71 ^d 91	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2615/06 R 2006

SWEET CORN Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS ¹	GS ²	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	total residues mg/kg eq	Study Trial
2006 (Bunguy); Soil: SaL												0801/2
Germany Werl (Nordrhein-Westfalen), 2006, (Delitop); Soil: SiL	SC _c	1 ^c	0.10	0.034	06	61 79	80 ^d 116	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2615/06 R 2006 0802/0
United Kingdom Cambridge (Cambridgeshire), 2005, (RK210), Soil: SaL	SC _a	1	0.10	0.034	13	79 85	103 124	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2587/05 R 2005 0959/6
United Kingdom Cambridge (Cambridgeshire) 2006, (Nexxos); Soil: SaL	SC _b	1	0.099	0.033	14	61 79	51 ^d 93	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2510/06 R 2006 0796/2
United Kingdom, EYE (Suffolk) 2006, (Algans); Soil: SiL	SC _c	1 ^c	0.10	0.034	07	61 79	84 ^d 101	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2615/06 R 2006 0800/4
Netherlands Zwaagdijk-Oost (Noord- Holland) 2005, (Rosalie), Soil: C	SC _a	1	0.10	0.034	13	79 85	116 128	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2587/05 R 2005 0962/6
N-France Saint Symphorien d'Ancelles (Bourgogne) 2005, (Surtep), Soil: S	SC _a	1	0.10	0.034	14	79 85	71 83	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2587/05 R 2005 0958/8
N-France Chaussy (Ile-de-France) 2006, (Moncada), Soil: CSa	SC _b	1	0.099	0.033	13	61 79	62 96	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2510/06 R 2006 0073/9
-	SC _c	1 ^c	0.10	0.034	01	61 79	86 120	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2615/06 R 2006 0627/3
N-France Chambourg sur indre (Centre) 2006, (Anasta); Soil: CSi	SC _c	1 ^c	0.10	0.034	00	61 79	89 ^d 112	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2615/06 R 2006 0799/7
S-France Savenes (Midi- Pyrenees), 2005, (PR33A46); Soil: CL	SC _a	1	0.10	0.034	13	79 85	83 106	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2588/05 R 2005 0624/4
S-France Vouille (Poitou- Charentes)	SC _b	1	0.099	0.033	13	61 79	74 ^d 98	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2511/06 R 2006

SWEET CORN Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS ¹	GS ²	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	total residues mg/kg eq	Study Trial
2006, (dkc 4845) Soil: SiC												0074/7
S-France Beauzelle (Midi- Pyrenees) 2006, (Ferry) Soil: SaSi	SC _c	1 ^c	0.10	0.034	06	61 79	79 ^d 105	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0628/1
S-France Laudun (Languedoc- Roussillon) 2006, (Cecilia) Soil: CL	SC _c	1 ^c	0.10	0.034	01	61 79	64 ^d 91	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0803/9
Spain Vila-sacra (Cataluña) 2005, (DKc6575); Soil: SaL	SC _a	1	0.10	0.034	13	79 85	84 98	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2588/05 R 2005 0963/4
Spain Vila-sacra (Cataluña), 2006, (PR33P67) Soil: SaL	SC _b	1	0.099	0.033	14	61 79	56 ^d 67	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2511/06 R 2006 0798/9
	SC _c	1 ^c	0.10	0.034	07	61 79	78 ^d 89	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0804/7
Spain Alginet (Comunidad Valenciana) 2006, (Constanza) Soil: SiC	SC _c	1 ^c	0.10	0.034	00	61 79	65 78	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0806/3
Italy San Carlo (FE), Emilia- Romagna 2005, (DK 440); Soil: SaC	SC _a	1	0.10	0.034	13	79 85	79 93	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2588/05 R 2005 0964/2
Italy San Carlo (FE), Emilia- Romagna 2006, (PR34N43) Soil: SaC	SC _b	1	0.099	0.033	13	61 79	53 ^d 75	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2511/06 R 2006 0797/0
	SC _c	1 ^c	0.10	0.034	01	61 79	78 ^d 100	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0805/5
Greece Chalastra (Macedonia) 2005, (Decalp 743); Soil: L	SC _a	1	0.10	0.034	13	79 85	77 105	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2588/05 R 2005 0965/0
Portugal Golegã (Ribatejo e Oeste) 2005, (PRN 43); Soil: SiL	SC _a	1	0.10	0.034	13	79 85	80 100	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2588/05 R 2005 0966/9

GS: BBCH grows stage: GS¹ - at application; GS² - at harvest

Soil: C = Clay, L = loam, Si = silt; Sa = sand; CL = clay loam; CSa = clay sand, CSi = clay silt; LSa = loamy sand; SiC = silty clay; SaCL = sandy clay loam; SiCL = silty clay loam, SiL = silty loam; SaC = sandy clay; SaL = sandy loam, SaSi = sandy silt;

Total = sum of IFT and IFT-DKN, expressed as isoxaflutole equivalents. Since the molecular weight of IFT-DKN is identical to the molecular weight of the parent compound (MW 359.3), no correction for molecular weight is necessary.

^a SC formulation contained 20.4% w/w isoxaflutole and 20.3% w/w cyprosulfamide (safener); or 240 g/L each

^b SC formulation contained 225 g/L isoxaflutole, 150 g/L cyprosulfamide (safener) and 90 g/L thien carbazole-methyl

^c A first spray application was performed with an SC formulation (containing 240 g/L isoxaflutole and 240 g/L cyprosulfamide (safener)) at the pre-emergence stage followed by a second application with an SC formulation (containing 225 g/L thien carbazole-methyl and 225 g/L cyprosulfamide (safener)) at growth stage BBCH 18. Days after last treatment (DAT) are related to the isoxaflutole treatment (i.e. days after the first treatment).

^d Sample sizes were less than the required minimum of 2 kg (in accordance with FAO manual 2009): 0.6–1.1 kg at BBCH 61 (baby corn) in reports RA-2510/06, RA-2615/06, RA-2511/06. Samples are considered not representative and trials cannot be selected for MRL derivation, if according to cGAP.

Pulses

Supervised trials were conducted on chickpeas and glyphosate/HPPD tolerant soya beans.

Chickpea seeds (dry harvested)

Supervised trials on chickpeas were conducted in Australia during the 1999 and 2011 season [Lynch and Keats, 1999a, M-432364-01-1, report AK99054; Lynch and Keats, 1999b, M-432374-01-1, report AK99056; Lynch and Keats, 2000a, M-432434-01-1, report AQ00001; Lynch and Keats, 2000b, M-432441-01-1, report AQ00002; Lynch and Keats, 2000c, M-432444-01-1, report AQ00003; Ellis, 2012, M-425905-02-1, report BCS-0370]. Small plots of chickpeas (20–135 m²) were treated as indicated in Table 47 using a hand held boom sprayer or a small plot sprayer with spray volumes ranging from 50–230 L/ha.

In 1999, different application scenarios were tested on parallel plots. Plots were treated once at different application rates and/or growth stages (before emergence of the crop or at 3 nodes stage).

In 2011, four application scenarios were tested on parallel plots. Isoxaflutole was applied at rates of 0.075 kg ai/ha and 0.150 kg ai/ha to bare soil either as a single fallow application approximately four month before sowing the chickpea crops, or in conjunction with a second application at planting.

Replicate field samples of dry pea seeds were taken at maturity (marketable specimens). In report AK99054, chickpea plots were mechanically harvested and seeds were randomly selected from a harvester bin. In report AK99056, BCS-370 and AQ reports dry pea seeds were sampled by hand, cutting random samples of chickpea pods from at least 10 separate plants from all over the plot. Sample sizes were at least 1 kg in report AQ00003 and AK99054. Sample sizes from all other reports were below the required minimum of 1 kg (in accordance with FAO manual 2009): 0.1 kg in report AK99056, 0.25 kg in AQ00001 and AQ00002, 0.5 kg in BCS-370. Samples were stored frozen with a maximum storage period of 2–21 days at –20 °C (AK99054 and AQ reports), 11 months at –20 °C (AK99056) or 21 days at –8 °C (BCS-370).

In the trials from 1999, samples were analysed for total residues using GC-MS-MS modification B of method 00473 (common moiety method), where IFT, IFT-DKN and IFT-BA are converted into RPA 204497 and total residues are expressed as isoxaflutole equivalents. This method is considered valid in the range 0.01–0.1 mg/kg for dry chickpea seeds. Average concurrent recoveries at 0.01 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3LOQ). Average concentrations for duplicate field samples are shown in Table 47.

In the trials from 2011, samples were analysed for IFT, IFT-DKN and IFT-BA using modification A of HPLC-MS-MS method ATM-0054.01. This method is considered valid in the range 0.01–0.1 mg/kg in dry chickpea seeds. Average concurrent recoveries at 0.01–1.0 mg/kg were

within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ). Average concentrations for duplicate field samples are shown in Table 47.

Note: In the AK and AQ reports, some data (application rate and date of application) were found to be inconsistent between the summary and appendices. The data coming from the field presented in the “residue sample submission form” were considered as being the valid ones.

Note: Storage stability studies on commodities with high protein content showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 11 months. Storage stability studies on commodities with high protein content showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage and IFT-DKN is stable for at least 12 months but converts to IFT-BA within 23 months of storage. Since chickpeas have been stored for a maximum of 11 months in the trials where a common moiety method was used and chickpeas have been stored for less than 3 months in trials where individual compounds have been measured, all results are considered reliable.

Table 47 Isoxaflutole related residues after pre- or post-emergent treatment of chickpeas (dry harvested seeds)

CHICK PEA Location, year, (variety)	Form	No & interval d	kg ai/ha	kg ai/hL	timing	DAT	IFT, mg/kg	IFT-DKN, mg/kg	IFT-BA, mg/kg	Total, mg/kg eq	report, trial
Australia Pittsworth QLD, 1999 (Norwin) Soil: black earth	WG	1	0.075	0.075	Post planting, pre- emergent	185	NA	NA	NA	< 0.01 ^a	AK99054 99NST26 -A
	WG	1	0.15	0.150	Post planting, pre- emergent	185	NA	NA	NA	< 0.01 ^a	AK99054 99NST26 -B
Australia Biniguy NSW, 1999, (Amethyst) Soil: brown clay loam	WG	1	0.075	0.100	3 days post sowing	155	NA	NA	NA	< 0.01 ^a	AK99056 99NST01 -A ^c
	WG	1	0.15	0.25	3 days post sowing	155	NA	NA	NA	< 0.01 ^a	AK99056 99NST01 -B ^c
Australia Horsham VIC, 1999, (Sona) Soil: Wimmera gray clay	WG	1	0.075	0.100	Post sow/ Pre- emergent	184	NA	NA	NA	< 0.01 ^a	AQ00001 99h011-A ^c
	WG	1	0.15	0.20	Post sow/ Pre- emergent	184	NA	NA	NA	< 0.01 ^a	AQ00001 99h011-B ^c
	WG _d	1	0.056	0.075	Early Post- emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a	AQ00002 99h015-A ^c
	WG _d	1	0.075	0.100	Early Post- emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a	AQ00002 99h015-B ^c
	WG _d	1	0.094	0.13	Early Post- emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a	AQ00002 99h015-C ^c

CHICK PEA Location, year, (variety)	Form	No & interval ^d	kg ai/ha	kg ai/hL	timing	DAT	IFT, mg/kg	IFT-DKN, mg/kg	IFT-BA, mg/kg	Total, mg/kg eq	report, trial
	WG ^c	1	0.056	0.075	Early Post-emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a	AQ00002 99h015-D ^c
	WG ^c	1	0.075	0.100	Early Post-emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a	AQ00002 99h015-E ^c
	WG ^c	1	0.094	0.13	Early Post-emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a	AQ00002 99h015-F ^c
Australia Bruce Rock WA, 1999, (Tyson) Soil: brown loam	WG ^d	1	0.075	0.15	Post sow/Pre-emergent	188	NA	NA	NA	< 0.01 ^a	AQ00003 99h010-
	WG ^d	1	0.15	0.30	Post sow/Pre-emergent	188	NA	NA	NA	< 0.01 ^a	AQ00003 99h010-B
	WG ^d	1	0.20	0.40	Post sow/Pre-emergent	188	NA	NA	NA	< 0.01 ^a	AQ00003 99h010-C
	WG ^c	1	0.075	0.15	Post sow/Pre-emergent	188	NA	NA	NA	< 0.01 ^a	AQ00003 99h010-D
	WG ^c	1	0.15	0.30	Post sow/Pre-emergent	188	NA	NA	NA	< 0.01 ^a	AQ00003 99h010-E
	WG ^c	1	0.20	0.40	Post sow/Pre-emergent	188	NA	NA	NA	< 0.01 ^a	AQ00003 99h010-F
Australia Northam WA, 2011, (Desi) Soil: sandy loam	WG	1	0.075	0.033	bare soil 121 days before sowing	295	< 0.01	< 0.01	< 0.01	< 0.02 ^b	BCS- 0370, C601 ^c
	WG	1	0.15	0.066	bare soil 121 days before sowing	295	< 0.01	< 0.01	< 0.01	< 0.02 ^b	^c
	WG	2 (121 days)	0.075 0.075	0.0330.0 75	1 st bare soil, 2 nd at sowing	174	< 0.01	< 0.01	< 0.01	< 0.02 ^b	^c
	WG	2 (121 days)	0.15 0.15	0.0660.1 50	1 st bare soil, 2 nd at sowing	174	< 0.01	< 0.01	< 0.01	< 0.02 ^b	^c
Australia Warwick QLD, 2011, (Hatrick) Soil: black clay loam	WG	1	0.075	0.057	bare soil 127 days before sowing	284	< 0.01	< 0.01	< 0.01	< 0.02 ^b	BCS- 0370, C602 ^c
	WG	1	0.15	0.11	bare soil 127 days before sowing	284	< 0.01	< 0.01	< 0.01	< 0.02 ^b	^c
	WG	2 (127	0.075 0.075	0.0550.0 57	1 st bare soil, 2 nd at	157	< 0.01	< 0.01	< 0.01	< 0.02 ^b	^c

CHICK PEA Location, year, (variety)	Form	No & interval ^d	kg ai/ha	kg ai/hL	timing	DAT	IFT, mg/kg	IFT-DKN, mg/kg	IFT-BA, mg/kg	Total, mg/kg eq	report, trial
		days)			sowing						
	WG	2 (127 days)	0.15 0.15	0.11- 0.11	1 st bare soil, 2 nd at sowing	157	< 0.01	< 0.01	< 0.01	< 0.02 ^b	^c
Australia Shepparton East, VIC, 2011, (Kabul) Soil: clay loam	WG	1	0.075	0.075	bare soil 107 days before sowing	324	< 0.01	< 0.01	< 0.01	< 0.02 ^b	BCS- 0370, C603 ^c
	WG	1	0.15	0.150	bare soil 107 days before sowing	324	< 0.01	< 0.01	< 0.01	< 0.02 ^c	^c
	WG	2 (107 days)	0.0750. 072	0.0750.0 75	1 st bare soil, 2 nd at sowing	217	< 0.01	< 0.01	< 0.01	< 0.02 ^b	^c
	WG	2 (107 days)	0.15 0.15	0.150	1 st bare soil, 2 nd at sowing	217	< 0.01	< 0.01	< 0.01	< 0.02 ^b	^c

^a Total residue obtained by common moiety method, whereby residues are converted into RPA 204497 and expressed as isoxaflutole equivalent (residue includes IFT, IFT-DKN and IFT-BA)

^b Total residue calculated by summing up residues of IFT and IFT-DKN and expressed as isoxaflutole equivalents. Since the molecular weight of IFT-DKN is identical to the molecular weight of the parent compound (MW 359.3), no correction for molecular weight is necessary.

^c Sample sizes were below the required minimum of 1 kg (in accordance with FAO manual 2009): 0.1 kg in report AK99056, 0.25 kg in AQ00001 and AQ00002, 0.5 kg in BCS-370. However, two samples were taken from each trial plot (each from at least 10 plants in the AK and AQ reports) and the results are the mean of both samples. Therefore results can be considered representative and trials can be selected for MRL derivation, if according to cGAP.

^d Added adjuvant: 0.25% X-77

^e Added adjuvant: Uptake oil

Glyphosate/HPPD tolerant soya beans

Supervised trials on glyphosate/HPPD tolerant soya beans were conducted in the USA and Canada during the 2009 season [Dallstream and Fisher, 2010, M-368661-01-1, study RAISP006; Beedle and Dallstream, 2010, M-368669-01-1, study RAISP010]. Small plots of soya beans (500–1800 ft² or 46–167 m²) were treated as indicated in Table 48 using backpack or tractor mounted sprayers with spray volumes ranging from 9–26 GPA or 84–243 L/ha.

In report RAISP006 three different application scenarios were tested in parallel plots: a) single pre-plant or pre-emergence soil application, b) single foliar application from BBCH 13 (trifoliate leaf on the 3rd node unfolded) to BBCH 15 (trifoliate leaf on the 5th node unfolded) or c) single foliar application from BBCH 51 (first flower buds visible) to BBCH 66 (about 60% of flowers open). The pre-emergent applications occurred within 3 days following planting.

In report RAISP010 two different application scenarios were tested on parallel plots:

- In the first plot a single pre-emergent application of glyphosate-isoxaflutole spray mix was made, followed by two additional foliar applications of glyphosate.
- For the second plot, a single pre-emergent application of glyphosate was made, followed by a single foliar application of glyphosate-isoxaflutole spray mix between growth stages BBCH 51 (first flower buds visible) and BBCH 62 (about 20% of flowers open), and an additional foliar application of glyphosate 8–11 days later.

The pre-emergent applications occurred within 3 days following planting.

Replicate field samples of soya bean seed were collected at earliest commercial harvest (BBCH 89). Seed samples were a composite from at least 12 areas of the plot, avoiding the edges and ends of the plot. Samples sizes were 1 kg (in accordance with FAO manual 2009), except for trial IS007-09DA (0.20–0.44 kg). All samples were stored frozen with a maximum storage period of 188 days at 0 °C (or lower in report RAISP006) or 218 days at –20 °C (or lower in report RAISP010).

Samples were analysed for IFT and IFT-DKN using HPCL-MS-MS method IS-004-P10-01. The method is considered valid in the range 0.01–0.1 mg/kg in dry soya bean seed. Average concurrent recoveries at 0.01 and 0.1 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ) for each analyte. Average concentrations for duplicate field samples are shown in Table 48.

Note: Storage stability studies on various commodities showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 11–20 months. Storage stability studies on commodities with high oil content showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage and IFT-DKN is stable for at least 16 months but converts to IFT-BA within 23 months of storage. Since dry soya beans have been stored for longer than 6 months, part of the IFT may have degraded to IFT-DKN. Since dry soya beans have been stored for less than 16 months, levels of IFT-DKN are not further degraded to IFT-BA and can be considered reliable. As the residue definition includes both IFT and IFT-DKN, residues can be taken for MRL derivation, if according to cGAP.

Note: Isoxaflutole inhibits the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD) while glyphosate inhibits the enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS). The glyphosate/HPPD tolerant soya bean line (FG72) was produced by direct gene transfer of the transgenic insert to conventional soya bean cells. FG72 soya bean expresses the *hppdPFW336* gene from *Pseudomonas fluorescens* and the *2mepsps* gene derived from maize. These genes confer tolerance to the herbicide isoxaflutole and glyphosate-containing herbicides, respectively [COGEM advice CGM/120104-02].

Note: Crops can be made tolerant against herbicides in two different ways:

- Some tolerant crops are able to detoxify the herbicide via a specific chemical modification of the pesticide which makes it unable to react with its molecular target. The detoxification is usually mediated by an enzyme which is very specific for the herbicide under consideration. Interaction with other pesticides cannot be completely excluded but normally will not occur at high level. Thus a significant impact on the metabolism and residue behaviour of other pesticides is quite unlikely.
- Other crops are made tolerant to herbicides via a modification of the target enzyme which makes the modified enzyme insensitive against the herbicide. The FG72 soya bean variety contains a gene coding for the modified enzyme HPPDW336 which differs only by a single amino acid from the natural HPPD enzyme. While HPPDW336 has the same biological activity as HPPD it is not deactivated by isoxaflutole. The FG72 soya bean variety also contains a gene for the modified enzyme 2mEPSPS which has a biological activity comparable to that of the natural EPSPS but is not deactivated by glyphosate.

Metabolism studies and field trials all have been conducted with the glyphosate/HPPD tolerant soya bean line (FG72). No trials have been conducted with a soya bean variety where only the HPPD tolerant gene is present. Since in the FG72 soya bean variety the tolerance against glyphosate and isoxaflutole is not based on detoxification, the tolerance to glyphosate is not expected to modify the nature and levels of isoxaflutole-derived residues in treated soya beans. Similarly the tolerance to isoxaflutole is not expected to modify the nature and levels of glyphosate residues.

Table 48 Isoxaflutole related residues after pre-emergent or foliar treatment on soya beans (dry harvested seeds)

SOYA BEAN Location, year, (variety), soil type	Form	No	kg ai/ha	kg ai/hL	GS appl	DAT	IFT, mg/kg	IFT-DKN, mg/kg	IFT-BA, mg/kg	Total, mg/kg eq	% DM	Report, trial, (remarks)
Canada Rockwood ON, 2009, (FG 72) Soil: L	SC ^b	1	0.103	0.0786	00	151	< 0.01	< 0.01	NA	< 0.02	80	RAISP006 IS008-09HA
		1	0.130	0.0663	15	120	< 0.01	0.011	NA	0.021	81	
		1	0.106	0.0675	51	99	< 0.01	< 0.01	NA	< 0.02	79	
	SC ^{a, b}	1	0.106	0.0791	00	90	< 0.01	< 0.01	NA	< 0.02	80	RAISP010 IS035-09HA
		1	0.106	0.0803	51	90	< 0.01	< 0.01	NA	< 0.02	83	
USA, Chula, GA, 2009 (FG 72), soil LSa	SC ^b	1	0.103	0.0551	00	144	< 0.01	< 0.01	NA	< 0.02	91	RAISP006, IS002-09HA
		1	0.105	0.0461	15	120	< 0.01	< 0.01	NA	< 0.02	89	
		1	0.104	0.0477	66	98	< 0.01	0.021	NA	0.031	89	
USA, Shorter, AL, 2009, (FG 72) soil LSa	SC ^b	1	0.103	0.0673	01	120	< 0.01	< 0.01	NA	< 0.02	85	RAISP006, IS003-09HA
		1	0.103	0.0682	15	94	< 0.01	< 0.01	NA	< 0.02	85	
		1	0.103	0.0673	62	82	< 0.01	0.016	NA	0.026	81	
USA Shorter AL, 2009, (FG 72) Soil SaL	SC ^{a, b}	1	0.103	0.0673	01	72	< 0.01	< 0.01	NA	< 0.02	85	RAISP010 IS032-09HA
		1	0.103	0.0673	62	72	< 0.01	0.027	NA	0.037	85	
USA, Cheneyville, LA, 2009, (FG 72) soil SiL	SC ^b	1	0.107	0.0787	00	128	< 0.01	< 0.01	NA	< 0.02	77	RAISP006 IS004-09DA
		1	0.105	0.0673	13	106	< 0.01	< 0.01	NA	< 0.02	79	
		1	0.106	0.0711	59	87 89 91 93 95	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	NA NA NA NA NA	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	88 73 78 85 88	
USA, Greenville, MS, 2009, (FG 72) soil CL	SC ^b	1	0.104	0.0754	00	132	< 0.01	< 0.01	NA	< 0.02	89	RAISP006 IS005-09HA
		1	0.105	0.0789	15	110	< 0.01	< 0.01	NA	< 0.02	88	
		1	0.105	0.0820	61	126	< 0.01	< 0.01	NA	< 0.02	89	
USA Proctor, AR, 2009, (FG 72) Soil CL	SC ^b	1	0.104	0.0717	00	111	< 0.01	< 0.01	NA	< 0.02	85	RAISP006 IS006-09HA

SOYA BEAN Location, year, (variety), soil type	Form	No	kg ai/ha	kg ai/hL	GS appl	DAT	IFT, mg/kg	IFT-DKN, mg/kg	IFT- BA, mg/kg	Total, mg/kg eq	% DM	Report, trial, (remarks)
		1	0.104	0.0717	15	87	< 0.01	< 0.01	NA	< 0.02	70	
		1	0.104	0.0717	60	72	< 0.01	< 0.01	NA	< 0.02	87	
	SC ^{a, b}	1	0.104	0.0717	00	62	< 0.01	< 0.01	NA	< 0.02	89	RAISP01 0 IS033- 09HA
		1	0.104	0.0722	60	62	< 0.01	< 0.01	NA	< 0.02	87	
USA, Jefferson, IA, 2009, (FG 72) Soil SaL	SC ^b	1	0.107	0.13	00	130	< 0.01	< 0.01	NA	< 0.02	82	RAISP00 6 IS007- 09DA c
		1	0.104	0.0765	13	94	< 0.01	< 0.01	NA	< 0.02	89	c
		1	0.105	0.0621	51	77 79 81 83 85	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 0.014 0.010 0.011	NA NA NA NA NA	< 0.02 < 0.02 0.024 0.020 0.021	84 82 82 87 85	c
USA Richland IA, 2009, (FG 72) Soil SiCL	SC ^b	1	0.105	0.0714	00	138	< 0.01	< 0.01	NA	< 0.02	81	RAISP00 6 IS015- 09HA
		1	0.098	0.054	13	115	< 0.01	< 0.01	NA	< 0.02	80	
		1	0.103	0.0589	60	95	< 0.01	< 0.01	NA	< 0.02	78	
USA Farlin IA, 2009, (FG 72) Soil CL	SC ^{a, b}	1	0.106	0.13	00	77	< 0.01	< 0.01	NA	< 0.02	89	RAISP01 0 IS034- 09HA
		1	0.104	0.13	60	77	< 0.01	0.015	NA	0.025	89	
USA Marysville OH, 2009, (FG 72) Soil CL	SC ^b	1	0.103	0.0610	00	139	< 0.01	< 0.01	NA	< 0.02	91	RAISP00 6 IS009- 09HA
		1	0.103	0.0632	15	107	< 0.01	< 0.01	NA	< 0.02	91	
		1	0.103	0.0624	60	93	< 0.01	< 0.01	NA	< 0.02	91	
	SC ^{a, b}	1	0.103	0.0609	00	78	< 0.01	< 0.01	NA	< 0.02	92	RAISP01 0 IS036- 09HA
		1	0.105	0.0644	60	78	< 0.01	0.017	NA	0.027	91	
USA Dudley MO, 2009, (FG 72) Soil SiL	SC ^b	1	0.106	0.0564	05	123	< 0.01	< 0.01	NA	< 0.02	85	RAISP00 6 IS010- 09HA
		1	0.106	0.0567	15	98	< 0.01	< 0.01	NA	< 0.02	86	
		1	0.105	0.0565	60	88	< 0.01	0.012	NA	0.022	84	
USA Clarence MO, 2009, (FG 72) Soil SiCL	SC ^b	1	0.106	0.0573	00	129	< 0.01	< 0.01	NA	< 0.02	87	RAISP00 6 IS011- 09HA
		1	0.110	0.0570	14	99	< 0.01	< 0.01	NA	< 0.02	86	
		1	0.104	0.0594	60	90	< 0.01	< 0.01	NA	< 0.02	88	
	SC ^{a, b}	1	0.105	0.0571	00	80	< 0.01	< 0.01	NA	< 0.02	89	RAISP01

SOYA BEAN Location, year, (variety), soil type	Form	No	kg ai/ha	kg ai/hL	GS appl	DAT	IFT, mg/kg	IFT-DKN, mg/kg	IFT- BA, mg/kg	Total, mg/kg eq	% DM	Report, trial, (remarks)
												0 IS038- 09HA
		1	0.107	0.0549	60	80	< 0.01	< 0.01	NA	< 0.02	90	
USA Campbell MN, 2009, (FG 72) Soil SaCL	SC ^b	1	0.105	0.0561	00	130	< 0.01	< 0.01	NA	< 0.02	82	RAISP00 6 IS012- 09HA
		1	0.104	0.0556	15	95	< 0.01	< 0.01	NA	< 0.02	82	
		1	0.105	0.0561	60	88	< 0.01	< 0.01	NA	< 0.02	82	
	SC ^{a,b}	1	0.105	0.0561	00	79	< 0.01	< 0.01	NA	< 0.02	82	RAISP01 0 IS039- 09HA
		1	0.105	0.0561	60	79	< 0.01	< 0.01	NA	< 0.02	86	
USA Geneva MN, 2009, (FG 72) Soil SaCL	SC ^b	1	0.106	0.0688	00	151	< 0.01	< 0.01	NA	< 0.02	78	RAISP00 6 IS019- 09HA
		1	0.105	0.0618	15	116	< 0.01	< 0.01	NA	< 0.02	73	
		1	0.105	0.0636	60	92	< 0.01	< 0.01	NA	< 0.02	82	
USA York NE, 2009, (FG 72) Soil SiL	SC ^b	1	0.107	0.0569	00	139	< 0.01	< 0.01	NA	< 0.02	90	RAISP00 6 IS013- 09HA
		1	0.104	0.0556	15	107	< 0.01	< 0.01	NA	< 0.02	90	
		1	0.106	0.0555	60	97	< 0.01	< 0.01	NA	< 0.02	89	
	SC ^{a,b}	1	0.108	0.0568	00	89	< 0.01	< 0.01	NA	< 0.02	90	RAISP01 0 IS040- 09HA
		1	0.105	0.0555	60	89	< 0.01	< 0.01	NA	< 0.02	89	
USA Springfield NE, 2009, (FG 72) Soil SiL	SC ^b	1	0.107	0.0829	00	140	< 0.01	< 0.01	NA	< 0.02	89	RAISP00 6 IS020- 09HA
		1	0.103	0.0798	15	112	< 0.01	< 0.01	NA	< 0.02	91	
		1	0.107	0.0829	60	87	< 0.01	0.013	NA	0.023	87	
USA Gardner KS, 2009, (FG 72) Soil SiL	SC ^b	1	0.104	0.0727	01	140	< 0.01	< 0.01	NA	< 0.02	89	RAISP00 6 IS014- 09HA d
		1	0.106	0.0746	13	114	< 0.01	< 0.01	NA	< 0.02	90	d
		1	0.105	0.0755	60	91	< 0.01	< 0.01	NA	< 0.02	89	d
	SC ^{a,b}	1	0.104	0.0754	01	81	< 0.01	< 0.01	NA	< 0.02	92	RAISP01 0 IS041- 09HA
		1	0.104	0.0732	60	8181	< 0.01	< 0.01	NA	< 0.02	92	
USA Carlyle IL, 2009,	SC ^b	1	0.105	0.0528	00	130	< 0.01	< 0.01	NA	< 0.02	87	RAISP00 6 IS016-

SOYA BEAN Location, year, (variety), soil type	Form	No	kg ai/ha	kg ai/hL	GS appl	DAT	IFT, mg/kg	IFT-DKN, mg/kg	IFT- BA, mg/kg	Total, mg/kg eq	% DM	Report, trial, (remarks)
(FG 72) Soil SiL												09HA
		1	0.104	0.0433	14	104	< 0.01	0.013	NA	0.023	88	
		1	0.104	0.0743	51	97	< 0.01	0.027	NA	0.037	87	
USA Arkansas WI, 2009, (FG 72) Soil SaL	SC ^b	1	0.106	0.0564	00	144	< 0.01	< 0.01	NA	< 0.02	84	RAISP00 6 IS017- 09HA
		1	0.105	0.0559	15	110	< 0.01	< 0.01	NA	< 0.02	80	
		1	0.106	0.0558	60	82	< 0.01	0.011	NA	0.021	85	
USA Northwood ND, 2009, (FG 72) Soil SiL	SC ^b	1	0.104	0.0553	NS	147	< 0.01	< 0.01	NA	< 0.02	80	RAISP00 6 IS018- 09HA
		1	0.105	0.0561	15	110	< 0.01	< 0.01	NA	< 0.02	80	
		1	0.107	0.0566	60	97	< 0.01	< 0.01	NA	< 0.02	84	
USA Sheridan IN, 2009, (FG 72) Soil SiL	SC ^b	1	0.102	0.0554	00	133	< 0.01	< 0.01	NA	< 0.02	85	RAISP00 6 IS021- 09HA
		1	0.106	0.0599	15	104	< 0.01	< 0.01	NA	< 0.02	85	
		1	0.103	0.0595	60	94	< 0.01	< 0.01	NA	< 0.02	85	
USA Dudley MO, 2009, (FG 72) Soil SiL	SC ^{a, b}	1	0.106	0.0564	05	80	< 0.01	< 0.01	NA	< 0.02	87	RAISP01 0 IS037- 09HA
		1	0.106	0.0567	60	80	< 0.01	0.019	NA	0.029	86	

Soil LSa=loamy sand, SiL = silty loam, CL=clay loam, SaL=sandy loam, L=loam, SiCL=silty clay loam, SaCL=sandy clay loam

GS growth stage, according to BBCH,

NS not stated, NA = not analysed

Total = sum of IFT and IFT-DKN, expressed as isoxaflutole equivalents. Since the molecular weight of IFT-DKN is identical to the molecular weight of the parent compound (MW 359.3), no correction for molecular weight is necessary.

^a spray mix prepared from SC 480 g/L isoxaflutole and SC 480 g/L of the isopropylammonium salt of glyphosate (see introductory text)

^b Additionally, adjuvants were used, which included AMS at 2% w/w, a non-ionic surfactant ranging from 0.5% to 1% v/v, a drift control agent, and if necessary anti-foam.

^c Sample sizes were below the required minimum of 1 kg (in accordance with FAO manual 2009): (200–440 g). Samples are considered not representative and trials cannot be selected for MRL derivation, if according to cGAP.

^d Seeds were planted in an area that received isoxaflutole in the previous growing season. However, this did not affect the results, since no isoxaflutole residues were found in the control samples (< LOQ).

Maize (grains)

Supervised trials on maize were conducted in Spain, Italy, Greece, Portugal, Germany, France, Netherlands and the United Kingdom in 2005 and 2006 and in USA and Canada in 1998, 2005 and 2006 [Zimmer and Wieland, 2007, M-282674-01-1, report RA-2587/05; Wolters and Erler, 2007b, M-284423-01-1, report RA-2510/06; Wolters, 2007b, M-285014-01-1, report RA-2615/06; Zimmer, 2006, M-281611-01-1, report RA-2588/05; Wolters and Erler, 2007a, M-284416-01-1, report RA-2511/06; Wolters, 2007a, M-285005-01-1, report RA-2616/06; Mickelson, 1999a, M-240663-01-1, report AA98714495; Fischer and Helfrich, 2007, M-285889-01-1, report RAUBP008; Vaughn and

Cosgrove, 2007, M-286216-02-1, report RAUBP011]. Small plots of maize (50–1700 m²) were treated as indicated in Table 49 using knapsack, tractor/ATV mounted or wheelbarrow sprayers with spray volumes ranging from 90–300 L/ha

Four treatment scenarios were tested in the plots:

- a single bare ground application of isoxaflutole (pre-emergence of the crop)
- a single application of isoxaflutole in combination with the safener cyprosulfamide at BBCH 12–14,
- a single application of isoxaflutole in combination with thien carbazon-methyl and the safener cyprosulfamide at BBCH 13–14.
- a single bare ground application of isoxaflutole in combination with the safener cyprosulfamide (pre-emergence of the crop) followed by a second application with thien carbazon-methyl in combination with the safener cyprosulfamide at BBCH 18.

Field samples of maize grains were taken as: “immature kernel” (milk ripeness, BBCH 79, sweetcorn kernel) or “field corn” (earliest commercial harvest, mature, BBCH 89). Single field samples were taken in the EU trials, duplicate field samples were taken in the USA trials. All sample sizes were at least 1 kg (in accordance with FAO manual 2009). All samples were stored frozen with a maximum storage period of 244 days at -18 °C (EU trials), 185 days at -10 °C (AA987144495) or 544 days at -15 °C (RAUBP008), 139 days at -20 °C (Canadian trials).

In the EU trials, isoxaflutole and its metabolites IFT-DKN and IFT-BA were determined using HPLC-MS-MS method 00985/M001. This method is considered valid in the range 0.01–0.1 mg/kg in maize grains. Average concurrent recoveries at 0.01–5.0 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.01 mg/kg (LOQ) for each analyte. Average concentrations for single field samples are shown in Table 49.

In the 1998 US trials, isoxaflutole and its metabolites IFT-DKN and IFT-BA were determined using HPLC-MS-MS method CAL#019-03 revision 1. This method is considered valid in the range 0.01–0.10 mg/kg in maize grains. Individual concurrent recoveries at 0.01, 0.1 and 10 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ). Average concentrations for duplicate field samples are shown in Table 49.

In the 2005 and 2006 Canadian and US trials, isoxaflutole and its metabolite IFT-DKN and IFT-BA were determined using modification C of HPLC-MS-MS method CAL#019-03. Modification C is considered valid in the range 0.01–0.2 mg/kg for IFT, 0.02–0.3 mg/kg for IFT-DKN and 0.03–0.3 mg/kg for IFT-BA in maize grains. Average concurrent recoveries at 0.01, 0.05 and 0.2 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.01 mg/kg (reported LOQ). Average concentrations for duplicate field samples are shown in Table 49. Because of validation results, the LOQs were increased to 0.02 mg/kg for IFT-DKN and 0.03 mg/kg for IFT-BA (indicated by note f).

Note: Storage stability studies on commodities with high starch content showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 15 months. Storage stability studies on various commodities showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage and IFT-DKN is stable for at least 12 months but converts to IFT-BA within 23 months of storage. Since maize grains have been stored for longer than 3 months, part of the IFT may have degraded to IFT-DKN. Except for trials in report RAUBP008, maize grains have been stored for less than 12 months and these results are considered reliable. Samples from report RAUBP008 have been stored for longer than 12 months and part of the IFT-DKN may have degraded to IFT-BA. However, IFT, IFT-DKN and IFT-BA are all below LOQ and degradation remains unnoticed. Therefore, these results are considered reliable as well.

Table 49 Isoxaflutole related residues after pre- or post-emergent treatment in maize grains

MAIZE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial
Germany Monheim (Nordrhein- Westfalen) 2005, (Romario) Soil: SaL	SC ^a	1	0.10	0.034	13	79 ^g 89	78 127	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2587/05 ; R 2005 0623/6
Germany Monheim (Nordrhein- Westfalen) 2006, (Romario), Soil: SaSi	SC ^b	1	0.099	0.033	13	79 ^g 89	77 135	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2510/06 R 2006 0795/4
Germany Euskirchen - Kessenich (Nordrhein- Westfalen) (Egrin FAO 220), Soil: SiC	SC ^a	1	0.10	0.034	13	79 ^g 89	90 128	< 0.01 < 0.01	< 0.01 < 0.01	0.01 0.01	< 0.02 <u>< 0.02</u>	RA- 2587/05 R 2005 0961/8
Germany Leverkusen (Nordrhein- Westfalen), 2006 (Bunguy); Soil: SaL	SC ^c	1 ^c	0.10	0.034	05	79 ^g 89	91 140	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2615/06 R 2006 0801/2
Germany Werl (NordrheinW estfalen), 2006, (Delitop); Soil: SiL	SC ^c	1 ^c	0.10	0.034	06	79 ^g 89	116 167	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2615/06 R 2006 0802/0
United Kingdom Cambridge (Cambridges hire), 2005, (RK210), Soil: SaL	SC ^a	1	0.10	0.034	13	79 ^g 89	103 148	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2587/05 R 2005 0959/6
United Kingdom Cambridge (Cambridges hire) 2006, (Nexxos); Soil: SaL	SC ^b	1	0.099	0.033	14	79 ^g 89	93 123	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2510/06 R 2006 0796/2
United Kingdom, EYE (Suffolk) 2006, (Algans); Soil: SiL	SC ^c	1 ^c	0.10	0.034	07	79 ^g 85	101 124	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2615/06 R 2006 0800/4
Netherlands	SC ^a	1	0.10	0.034	13	79 ^g	116	< 0.01	< 0.01	< 0.01	< 0.02	RA-

MAIZE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial
Zwaagdijk- Oost (Noord- Holland) 2005, (Rosalie), Soil: C						89	143	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	2587/05 R 2005 0962/6
N-France Saint Symphorien d'Annelles (Bourgogne) 2005, (Surtep), Soil: S	SC ^a	1	0.10	0.034	14	79 ^g 89	71 127	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2587/05 R 2005 0958/8
N-France Chaussy (Ile- de-France) 2006, (Moncada), Soil: CSa	SC ^b	1	0.099	0.033	13	79 ^g 89	96 139	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2510/06 R 2006 0073/9
	SC ^c	1 ^c	0.10	0.034	01	79 ^g 89	120 163	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2615/06 R 2006 0627/3
N-France Chambourg sur indre (Centre) 2006, (Anasta); Soil: CSi	SC ^c	1 ^c	0.10	0.034	00	79 ^g 89	112 179	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2615/06 R 2006 0799/7
S-France Savenes (Midi- Pyrenees), 2005, (PR33A46); Soil: CL	SC ^a	1	0.10	0.034	13	79 ^g 89	83 148	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2588/05 R 2005 0624/4
S-France Vouille (Poitou- Charentes) 2006, (dkc 4845) Soil: SiC	SC ^b	1	0.099	0.033	13	79 ^g 89	98 153	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2511/06 R 2006 0074/7
S-France Beauzelle (Midi- Pyrenees) 2006, (Ferry) Soil: SaSi	SC ^c	1 ^c	0.10	0.034	06	79 ^g 89	105 170	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0628/1
S-France Laudun (Languedoc- Roussillon) 2006, (Cecilia) Soil: CL	SC ^c	1 ^c	0.10	0.034	01	79 ^g 89	91 128	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0803/9
Spain Vila-sacra (Cataluña)	SC ^a	1	0.10	0.034	13	79 ^g 89	84 141	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2588/05 R 2005

MAIZE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial
2005, (DKc6575); Soil: SaL												0963/4
Spain Vila-sacra (Cataluña), 2006, (PR33P67) Soil: SaL	SC ^b	1	0.099	0.033	14	79 ^g 89	67 132	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2511/06 R 2006 0798/9
	SC ^c	1 ^c	0.10	0.034	07	79 ^g 89	89 154	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0804/7
Spain Alginet (Comuni dad Valen ciana) 2006, (Constan za) Soil: SiC	SC ^c	1 ^c	0.10	0.034	00	79 ^g 89	78 128	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0806/3
Italy San Carlo (FE) Emilia- Romagna 2005, (DK 440); Soil: SaC	SC ^a	1	0.10	0.034	13	79 ^g 89	79 128	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2588/05 R 2005 0964/2
Italy San Carlo (FE) Emilia- Romagna, 2006, (PR34N43) Soil: SaC	SC ^b	1	0.099	0.033	13	79 ^g 89	75 124	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2511/06 R 2006 0797/0
	SC ^c	1 ^c	0.10	0.034	01	79 ^g 89	100 149	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0805/5
Greece Chalastra (Macedonia) 2005, (Decalp 743); Soil: L	SC ^a	1	0.10	0.034	13	79 ^g 89	77 137	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 0.02	< 0.02 <u>< 0.02</u>	RA- 2588/05 R 2005 0965/0
Portugal Golegã (Ribatejo e Oeste) 2005, (PRN 43); Soil: SiL	SC ^a	1	0.10	0.034	13	79 ^g 89	80 133	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 <u>< 0.02</u>	RA- 2588/05 R 2005 0966/9
USA Lehigh PA, 1998 (Mycogen 2598) Soil: SiL	WG	1	0.16	0.089	bare soil	Mat	143	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 01
USA Wilson NC, 1998, (Pioneer	WG	1	0.16	0.084	bare soil	Mat	133	< 0.01	< 0.01	0.041	<u>< 0.02</u>	AA9871 4495 14495-

MAIZE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial
3163) Soil: SaL												02
USA Greene IA, 1998, (Dekalb DK 561SR) Soil: L	WG	1	0.16	0.089	bare soil	Mat	139	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 04
USA Percival IA, 2005, (Sucrossco 2009) Soil: SiL	SC ^a	1	0.13	0.10	12	ECH	125	< 0.01	< 0.02 ^f	< 0.03 ^f	<u>< 0.03^f</u>	RAUBP 008, UB086- 05H
USA Jefferson IA, 2005 (DKC63-81) Soil: L	SC ^a	1	0.13	0.10	12	ECH	120	< 0.01	< 0.02 ^f	< 0.03 ^f	<u>< 0.03^f</u>	RAUBP 008, UB091- 05H
USA Shelby MO, 1998, (Novartis NK 6800) Soil: L	WG	1	0.16	0.091	bare soil	Mat	132	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 05
Soil: SiL	WG	1	0.16	0.090	bare soil	Mat	140	< 0.01	< 0.01	< 0.01	< 0.02	AA9871 4495 14495- 21
USA Stoddard MO, 1998, (Pioneer 3394) Soil: SiL	WG	1	0.16	0.096	bare soil	Mat	115	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 10
USA Butler MO, 2005, (Garst 8287 RR) Soil: SiCL	SC ^a	1	0.13	0.098	12	ECH	133	< 0.01	< 0.02 ^f	< 0.03 ^f	<u>< 0.03^f</u>	RAUBP 008, UB081- 05H
USA Clarence MO, 2005, (Pioneer 35P12) Soil: CL	SC ^a	1	0.13	0.094	12	ECH	102	< 0.01	< 0.02 ^f	< 0.03 ^f	<u>< 0.03^f</u>	RAUBP 008, UB088- 05H
USA Fayette OH, 1998, (SC 1096) Soil: SiCL	WG	1	0.15	0.092	bare soil	Mat	153	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 06
(SC 1068) Soil: SiL	WG	1	0.16	0.094	bare soil	22% Dent 19% 19% 19% moist ure	124 131 138 145 152	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	AA9871 4495 14495- 19
USA Marysville	SC ^a	1	0.13	0.079	12	ECH	108	< 0.01	< 0.02 ^f	< 0.03 ^f	<u>< 0.03^f</u>	RAUBP 008,

MAIZE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial
OH, 2005, (Shur Grow SG-751) Soil: CL												UB089- 05H
USA New Holland OH, 2005 (Crows 7R321) Soil: L	SC ^a	1	0.13	0.092	12	ECH	147	< 0.01	< 0.02 ^f	< 0.03 ^f	<u>< 0.03^f</u>	RAUBP 008, UB092- 05H
USA Clay SD, 1998, (Dekalb DK 493RR) Soil: L	WG	1	0.16	0.092	bare soil	Mat	143	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 07
USA Yankton SD, 1998 (Dekalb, DK 493RR) Soil: SiCL	WG	1	0.17	0.094	bare soil	Mat	144	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 08
USA Grand Forks ND, 1998, (Mycogen 2110 R3) Soil: SiL	WG	1	0.16	0.11	bare soil	Mat	146	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 09
USA Steele ND, 1998, (Mycogen 2110 R3) Soil: SiL	WG	1	0.16	0.11	bare soil	Mat	138	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 16
USA Northwood ND, 2005, (39D81) Soil: L	SC ^a	1	0.13	0.094	12	ECH	132	< 0.01	< 0.02 ^f	< 0.03 ^f	<u>< 0.03^f</u>	RAUBP 008, UB093- 05H
USA Stark IL, 1998 (Pioneer 3394) Soil: SiL	WG	1	0.16	0.10	bare soil	Mat	142	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 11
USA Bond IL, 1998, (Pioneer 3394) Soil: SiL	WG	1	0.16	0.12	bare soil	Mat	111	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 12
USA Clinton IL, 1998, (Pioneer 33V08) Soil: SiL	WG	1	0.16	0.16	bare soil	R6	134	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA9871 4495 14495- 20
USA Seymour IL, 2005 (Garst 8550) Soil: SiL	SC ^a	1	0.13	0.10	12	ECH	129	< 0.01	< 0.02 ^f	< 0.03 ^f	<u>< 0.03^f</u>	RAUBP 008, UB082- 05D

MAIZE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial
USA Monticello IL, 2005 (Pioneer 37H26) Soil: SiL	SC ^a	1	0.13	0.087	12	ECH	102	< 0.01	< 0.02 ^f	0.030	≤ 0.03 ^f	RAUBP 008, UB083- 05H
USA Carlyle IL, 2005 (FS 6455 RR/YGCB) Soil: SiL	SC ^a	1	0.13	0.080	12	ECH	126	< 0.01	< 0.02 ^f	< 0.03 ^f	≤ 0.03 ^f	RAUBP 008, UB094- 05H
USA York NE, 1998, (Northrup King N3030BT) Soil: SiL	WG	1	0.16	0.11	bare soil	Mat	106	< 0.01	< 0.01	< 0.01	≤ 0.02	AA9871 4495
	WG	1	0.16	0.11	bare soil	32% 25% 17% 15% 15% moist ure	103 109 116 123 130	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	AA9871 4495 14495- 18
USA Polk NE, 1998, (Northrup King N3030BT) Soil: LSa	WG	1	0.16	0.11	bare soil	Mat	109	< 0.01	< 0.01	0.013	≤ 0.02	AA9871 4495
												14495- 14
USA Springfield NE, 2005 (NK70T9) Soil: SiL	SC ^a	1	0.13	0.10	12	ECH	123	< 0.01	< 0.02 ^f	< 0.03 ^f	≤ 0.03 ^f	RAUBP 008, UB085- 05H
USA Stafford KS, 1998, (Pioneer 3737) Soil: LSa	WG	1	0.15	0.14	bare soil	Mat	103	< 0.01	< 0.01	0.012	≤ 0.02	AA9871 4495
												14495- 15
USA Stilwell KS, 2006, (Garst 8478 LL/CB/GT) Soil: SiL	SC ^a	1	0.14	0.10	12	ECH	119	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 008, UB080- 05DA
												^d
USA Clay TX, 1998, (Northrup King 512RR) Soil: Sa	WG	1	0.16	0.12	bare soil	Mat	104	< 0.01	< 0.01	< 0.01	≤ 0.02	AA9871 4495
												14495- 17
USA East Bernard TX, 2005 (DKC69-71) Soil: SaL	SC ^a	1	0.13	0.094	12	ECH	91	< 0.01	< 0.02 ^f	< 0.03 ^f	≤ 0.03 ^f	RAUBP 008, UB097- 05H
USA	SC ^a	1	0.13	0.098	12	ECH	103	< 0.01	< 0.02 ^f	< 0.03 ^f	≤ 0.03 ^f	RAUBP

MAIZE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial
Bumpass VA, 2005, (Dekalb) Soil: SaCL												008, UB078- 05H
USA Tifton GA, 2005 (Pioneer 31N26) Soil: SaL	SC ^a	1	0.13	0.078	12	ECH	157	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 008, UB079- 05H
USA Gosport IN, 2005, (Pioneer 34D71) Soil: SiL	SC ^a	1	0.13	0.10	12	ECH	136	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 008, UB084- 05H
USA Sheridan IN, 2005, (Golden Harvest RR) Soil: SiL	SC ^a	1	0.13	0.076	12	ECH	127	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 008, UB095- 05H
USA Sabin MN, 2005, (Pioneer 39H85) Soil: Si	SC ^a	1	0.14	0.15	12	ECH	133	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 008, UB087- 05H
USA Campbell MN, 2005, (Croplan 212RR2) Soil: CL	SC ^a	1	0.13	0.094	13	ECH	114	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 008, UB090- 05H
USA Arkansaw WI, 2005, (Dekalb DKC 46-28 RR) Soil: SaL	SC ^a	1	0.13	0.075	12	ECH	135	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 008, UB096- 05H
Canada Clarksburg, ON, 2006, (Pioneer 39F27) Soil: L	SC ^a	1	0.21	0.11	13	—	114	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 01-06H
Canada Metz, ON, 2006 (Pioneer 39H86) Soil: L	SC ^a	1	0.21	0.11	12-13	—	112	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 02-06H
Canada Rockwood, ON, 2006 (Pioneer 38K35) Soil: L	SC ^a	1	0.21	0.11	13	—	96 103 110 117	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 ^f < 0.02 ^f < 0.02 ^f < 0.02 ^f	< 0.03 ^f < 0.03 ^f < 0.03 ^f < 0.03 ^f	< 0.03 ^f < 0.03 ^f < 0.03 ^f < 0.03 ^f	RAUBP 011, 03-06D
Canada Breslau, ON, 2006,	SC ^a	1	0.21	0.11	13	—	110	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 04-06H

MAIZE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial
(Pioneer 39F28) Soil: SaL												
Canada Greenfield, ON, 2006, (Pioneer 39F28) Soil: SaL	SC ^a	1	0.21	0.11	13	–	110	< 0.01	< 0.02 ^f	0.036	< 0.03 ^f	RAUBP 011, 05-06H
Canada Woodstock, ON, 2006, (NK N29G7) Soil: L	SC ^a	1	0.22	0.11	13	–	110	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 06-06H
Canada Port Burwell, ON, 2006, (Pioneer 38A24) Soil: SaL	SC ^a	1	0.21	0.11	13	–	113	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 07-06H
Canada Paris, ON, 2006 (Dekalb 4057) Soil: SaL	SC ^a	1	0.21	0.11	12–13	–	108	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 10-06H
Canada Springford, ON, 2006 (DKC42-70) Soil: SaL	SC ^a	1	0.22	0.11	12–13	–	110	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 11-06H
Canada Branchton, ON, 2006 (Hybrid Corn 38-B84) Soil: SiL	SC ^a	1	0.22	0.11	12–13	–	96 103 110 117	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 ^f < 0.02 ^f < 0.02 ^f < 0.02 ^f	< 0.03 ^f < 0.03 ^f < 0.03 ^f < 0.03 ^f	< 0.03 ^f < 0.03 ^f < 0.03 ^f < 0.03 ^f	RAUBP 011, 12-06D
Canada Pike River, QC, 2006, (ZP172) Soil: L	SC ^a	1	0.23	0.11	13	–	111	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 08-06H
Canada St-Pie-de- Bagot, QC, 2006, (ZP172) Soil: LSa	SC ^a	1	0.21	0.10	13	–	111	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 09-06H
Canada St-Marc-sur- Richelieu, QC, 2006, (Pioneer RR38P09) Soil: CL	SC ^a	1	0.21	0.12	13	–	111	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 13-06H
Canada Acton Vale, QC, 2006, (NK N16- N7) Soil: Sa	SC ^a	1	0.22	0.13	13	–	110	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP 011, 14-06H
Canada	SC ^a	1	0.21	0.12	13	–	111	< 0.01	< 0.02 ^f	< 0.03 ^f	< 0.03 ^f	RAUBP

MAIZE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial
Ste- Madeleine, QC, 2006, (Mycogen 2P172) Soil: SaL												011, 15-06H

Soil: C = Clay, L = loam, Si = silt; Sa = sand; CL = clay loam; CSa = clay sand, CSi = clay silt; LSa = loamy sand; SiC = silty clay; SaCL = sandy clay loam; SiCL = silty clay loam, SiL = silty loam; SaC = sandy clay; SaL = sandy loam, SaSi = sandy silt;

GS Mat = mature, R6 = reproductive stage 6, equivalent to BBCH 89, ECH = earliest commercial harvest

Total = sum of IFT and IFT-DKN, expressed as isoxaflutole equivalents. Since the molecular weight of IFT-DKN is identical to the molecular weight of the parent compound (MW 359.3), no correction for molecular weight is necessary.

^a SC formulation contained 20.4% w/w isoxaflutole and 20.3% w/w cyprosulfamide (safener); or 240 g/L each

^b SC formulation contained 225 g/L isoxaflutole, 150 g/L cyprosulfamide (safener) and 90 g/L thien carbazole-methyl

^c A first spray application was performed with an SC formulation (containing 240 g/L isoxaflutole and 240 g/L cyprosulfamide (safener)) at the pre-emergence stage followed by a second application with an SC formulation (containing 225 g/L thien carbazole-methyl and 225 g/L cyprosulfamide (safener)) at growth stage BBCH 18. Days after last treatment (DAT) are related to the isoxaflutole treatment (i.e. days after the first treatment).

^d Trial UB080-05D was repeated in 2006 as UB080-05DA due to improper application timing in the original trial.

^e Individual results for IFT and IFT-DKN not considered reliable, because samples have been stored for longer than 12 months.

^f LOQ for IFT-DKN needs to be increased to 0.02 mg/kg and LOQ for IFT-BA needs to be increased to 0.03 mg/kg. This increase has been taken into account in total residue calculation.

^g kernel immature (milk ripe)

Sugar cane (billets)

Supervised trials on sugarcane were conducted in Australia during the 1996–1998 growing seasons [Davis and Keats, 1999a, M-284383-01-1, Report AK99009; Davis and Keats, 1999b, M-284347-01-1, Report AK99010; Davis and Keats, 1999c, M-284356-01-1, Report AK99011; Davis and Keats, 1999d, M-284369-01-1, Report AK99012; Davis and Keats, 1999e, M-284408-01-1, Report AK99017], in Mexico during the 1999 growing season [Gough, 2000, M-238729-01-1, Report 99717930] and in Brazil during the 1998-1999 growing season [Tornisielo, 2000b, M-287041-01-1 Report USP BRA98R27-1; Tornisielo, 2000a, M-287038-01-1 Report USP BRA98R27-2].

In Australia, small plots of sugar cane (15–40 m²) were treated as indicated in Table 50 using plot boom sprayers or spray bars with spray volumes ranging from 238–265 L/ha. In two parallel plots sugarcane in the 5–8 leaf stage received a single soil application of isoxaflutole at two different application rates.

In Mexico, small plots of sugar cane (210–216 m²) were treated as indicated in Table 50 using commercial ground equipment for broadcast application with spray volumes ranging from 252–411 L/ha. The application was made at the regrowth stage, up to 4 months after harvest of the previous crop, and about 8–10 months before expected crop maturity.

In Brazil, small plots of sugar cane (72–78 m²) were treated as indicated in Table 50 using backpack sprayers with spray volumes of 200 L/ha. Sugarcane was treated twice with isoxaflutole. The first application was performed at pre-emergence and the second one after emergence. In parallel plots, different application rates were tested.

Field samples of whole canes were collected at a harvestable maturity: single field samples in Australia: replicate field samples in Mexico. Samples from each plot were taken from at least 15 whole canes randomly from the entire plot (in accordance with the FAO 2009 manual). The top 30 cm of the whole canes were then cut off using secateurs to provide forage (tops) and cane. The remaining cane was cut into billets of 20–25 cm in length. Equal portions of tops, middle and bottom were

sampled from at least 12 stalks to provide at least 1 kg of whole cane billets. All samples were stored frozen for a maximum storage period of 33 days at -10 °C (Mexican trials), 5 months at -20 °C (AK 99009, AK 99010) or 10 months at -20 °C (AK 99011, AK 99012) or 20 months at -20 °C (AK 99017), 24 months at -10 °C (Brazilian trials).

In the Australian trials, samples were analysed using GC-MS-MS modification A of method 00473 (common moiety method), where IFT, IFT-DKN and IFT-BA are converted into RPA 204497 and total residues are expressed as isoxaflutole equivalents. This method is considered valid at 0.01 mg/kg in sugar cane billets. Average concurrent recoveries at 0.01 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.01 mg/kg (LOQ). Average results of the replicate field samples are reported in Table 50.

In the Mexican trials, samples were analysed using GC-MS modification D of method 00473 (common moiety method), where IFT, IFT-DKN and IFT-BA are converted into RPA 204497 and total residues are expressed as isoxaflutole equivalents. This method is considered valid in the range 0.01–0.02 mg/kg in sugar cane billets. Average concurrent recoveries at 0.01, 0.02, 0.1 mg/kg analyte were within 70–120% limits (n=1–2 each), except for IFT at 0.01 mg/kg (128%, n=2) and IFT-DKN at 0.01 mg/kg (122%, n=2). Levels in control samples were < 0.01 mg/kg (LOQ). Average results of the replicate field samples are reported in Table 50.

In the Brazilian trials, samples were analysed using GC-MS-MS modification C of method 00473 (common moiety method), where IFT, IFT-DKN and IFT-BA are converted into RPA 204497 and total residues are expressed as isoxaflutole equivalents. This method is considered valid in the range 0.01–0.02 mg/kg in sugar cane billets. Average concurrent recoveries at 0.01 and 0.02 mg/kg were within 70–120% for IFT. Recoveries for other metabolites were not verified. Levels in control samples were < 0.01 mg/kg (LOQ). Average results of the replicate field samples are reported in Table 50.

Note: Storage stability studies on commodities with high water content showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 20 months. Since sugarcanes have been stored for 20 months or shorter, all results are considered reliable.

Table 50 Isoxaflutole related residues after pre-harvest soil directed treatment in sugarcane (billets i.e. raw canes)

SUGAR CANE Location, year, (variety)	FL	No (in ter val)	kg ai/ha	kg ai/hL	GS last appl	GS harv	DAT	IFT mg/kg	RPA 202 248 mg/kg	RPA 203 328 mg/kg	Total mg/kg eq	Study, Trial
Australia Tolga Mareeba, QLD, 1998, (Q 120) Soil: SaCL	WG	1	0.150	0.057	120 cm	CH	166	NA	NA	NA	< 0.01	AK99009
	WG	1	0.225	0.085	120 cm	CH	166	NA	NA	NA	< 0.01	
Australia Atherton, QLD, 1998, (Q 124) Soil: CL	WG	1	0.150	0.057	120 cm	CH	133	NA	NA	NA	< 0.01	AK99010
	WG	1	0.225	0.087	120 cm	CH	133	NA	NA	NA	< 0.01	
Australia Murwillumbah QLD, 1997/98, (Q 170) Soil: peat	WG	1	0.150	0.058	110 cm (30 cm TVD)	CH	167	NA	NA	NA	< 0.01	AK99011
	WG	1	0.225	0.086	110 cm (30 cm	CH	167	NA	NA	NA	< 0.01	

SUGAR CANE Location, year, (variety)	FL	No (in ter val)	kg ai/ha	kg ai/hL	GS last appl	GS harv	DAT	IFT mg/kg	RPA 202 248 mg/kg	RPA 203 328 mg/kg	Total mg/kg eq	Study, Trial
					TVD)							
Australia Rocky Point, QLD, 1997/98 (Q 154) Soil: peat	WG	1	0.150	0.058	100 cm (30 cm TVD)	CH	193	NA	NA	NA	< 0.01	AK99012
	WG	1	0.225	0.086	100 cm (30 cm TVD)	CH	193	NA	NA	NA	< 0.01	
Australia Jardine QLD, 1996 (Q 96) Soil: baratter cracking C	WG ^c	1	0.150	0.063	5–7 leaves (25– 30 cm TVD)	CH	206	NA	NA	NA	< 0.01	AK99017
	WG ^c	1	0.300	0.126	5–7 leaves (25– 30 cm TVD)	CH	206	NA	NA	NA	< 0.01	
Mexico Cordoba, Veracruz, 1999-2000 (Mex 69-290) Soil: SaL	WG	1	0.123	0.030	38 cm re- growth ^a	CH	258	NA	NA	NA	< 0.01	99717930, 17930-01
Mexico Ahualulco de Mercado, Jalisco, 1999-2000 (Mex 57-473) Soil: SaL	WG	1	0.121	0.048	100 cm re-growth ^a	CH	255	NA	NA	NA	< 0.01	99717930, 17930-02
Mexico Tres Valles, Veracruz, 1999-2000 (Mex 69-290) Soil: SaL	WG	1	0.120	0.030	20 cm re- growth ^a	CH	257	NA	NA	NA	< 0.01	99717930, 17930-03
Brazil Cosmopolis Sao Paulo, 1999-2000 (RB-72-454) Soil: C	WG	2 (92)	0.075 0.075	0.038 0.038	^b	–	95	NA	NA	NA	< 0.01	USP BRA98R27 -1 trial A
	WG	2 (92)	0.150 0.150	0.075 0.075	^b	–	95	NA	NA	NA	< 0.01	USP BRA98R27 -1 trial B
Brazil Assis, Sao Paulo, 1998 (RB-79- 1011) Soil: medium C	WG	2 (61)	0.075 0.075	0.038 0.038	^b	–	92	NA	NA	NA	< 0.01	USP BRA98R27 -2 trial A
	WG	2 (61)	0.15 0.15	0.075 0.075	^b	–	92	NA	NA	NA	< 0.01	USP BRA98R27 -2 trial B

Soil: C = clay, CL = clay loam, SaCL = sandy clay loam, SaL = sandy loam

Total = Total residues of IFT = measured sum of IFT, RPA 20248 and IFT-BA residues, expressed as isoxaflutole equivalents. The total residue is determined via a common moiety method which converts isoxaflutole, IFT-DKN and IFT-BA onto the derivative RPA 204497

TVD = top visible dewlap

CH = commercial harvest (normal crop maturity, marketable specimens)

^a regrowth stage: up to 4 months after harvest of the previous crop

^b first application in pre-emergence followed by a second application post-emergence

^c X-77 wetting agent (250 ml/hL) was added

Poppy seed

Supervised trials on poppy were conducted in France, Spain, Germany, Netherlands and Hungary in 2008 and 2009 [Billian and Reinecke, 2010, M-360144-02-1, Report 08-2095; Billian and Krusell, 2010b, M-360114-02-1, Report 08-2094; Billian and Krusell, 2010a, M-364166-01-1, Report 09-2085; Noss and Reinecke, 2010, M-366025-01-1, report 09-2022]. Small plots of poppy (45–910 m²) were treated as indicated in Table 51 using knapsack or tractor mounted boom sprayers with spray volumes ranging from 300–400 L/ha. Poppy plants were treated with a single application of isoxaflutole in combination with the safener cyprosulfamide at pre-emergence stage of the crop.

In some trials phytotoxicity signs were seen a few weeks after treatment: dead plants, plants with burning damage or symptoms of discoloration, plants with reduced growth, reduced emergence of plants (trial 08-2094-02&03&04, trial 08-2095/02&04). These phytotoxicity problems affected the yield of the poppy seeds.

Single field samples of seed were taken at harvest (BBCH 89). All sample sizes were at least 1 kg (in accordance with FAO manual 2009), except in trials 09-2022/01&02 and 08-2095/02&04 (0.1–0.7 kg) as indicated in Table 51. All samples were stored frozen at –18 °C with a maximum storage period of 111 days (report 0902085), 134 days (report 09-2022) or 447 days (report 08-2094 and 08-2095).

Isoxaflutole and its metabolites IFT-DKN and IFT-BA were determined using HPLC-MS-MS method 00985/M001. This method is considered valid in the range 0.01–0.10 mg/kg in poppy seeds. Average concurrent recoveries at 0.01–0.1 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.01 mg/kg (LOQ) for each analyte. Average concentrations for single field samples are shown in Table 51.

Note: Seeds need to be grinded prior to analyses, since residue levels may increase upon grinding. At first instance seeds were not grinded prior to extraction. In those cases, where residues of IFT-BA were seen, the analysis was repeated by grinding the seeds prior to extraction. All results are therefore considered reliable.

Note: Storage stability studies on various commodities showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 11–20 months. Storage stability studies on commodities with high oil content showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage and IFT-DKN is stable for at least 16 months but converts to IFT-BA within 23 months of storage. Since poppy seeds have been stored for longer than 3 months, part of the IFT may have degraded to IFT-DKN. Since poppy seeds have been stored for less than 16 months, levels of IFT-DKN are not further degraded to IFT-BA and can be considered reliable. If the residue definition includes both IFT and IFT-DKN, residues can be taken for MRL derivation, if according to cGAP.

Table 51 Isoxaflutole related residues after pre-emergent treatment in poppy seeds

POPPY Location, year, (variety)	FL	No	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	Total mg/kg eq	Study, Trial
Netherlands Beenster 2008, (Pulchinella) Soil: C	SC ^a	1	0.10	0.034	00	89	100	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	08-2094- trial 02 ^b
Germany Burscheid, 2008 (Mieszko) Soil: CSi	SC ^a	1	0.10	0.034	00	89	130	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	08-2094- trial 03 ^b
Hungary Soponya Fejér 2009, (Korona) Soil: SaL	SC ^a	1	0.10	0.034	00 pre- em	89	129	< 0.01	< 0.01	< 0.01	< 0.02	09-2022- trial 01 ^{c d}
Hungary Arpadhalom Csongrád 2009, (Korona) Soil: SaL	SC ^a	1	0.10	0.034	00	89	119	< 0.01	< 0.01	< 0.01	< 0.02	09-2022- trial 02 ^{c d}
N-France Chilly, 2008, (Mieszko) Soil: SiL	SC ^a	1	0.10	0.034	00	89	126	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	08-2094- trial 04 ^b
S-France Boe 2008, (Mieszko) Soil: CSi	SC ^a	1	0.079	0.020	00	89	110	< 0.01	< 0.01	< 0.01	< 0.02	08-2095- trial 02 ^{b d}
S-France Chazay 2008, (Mieszko) Soil: L	SC ^a	1	0.079	0.026	00	89	110	< 0.01	< 0.01	0.02	< 0.02	08-2095- trial 04 ^{c d}
Spain Minaya 2008, (Luisiana) Soil: C	SC ^a	1	0.079	0.026	03	89	119	< 0.01	< 0.01	< 0.01	< 0.02	08-2095- trial 01 ^b
Spain Minaya 2009 (Luisiana) Soil: C	SC ^a	1	0.079	0.026	00	89	140	< 0.01	< 0.01	< 0.01	< 0.02	09-2085- trial 02 ^{b, d}
Spain Albacete 2008, (Luisiana) Soil: C	SC ^a	1	0.079	0.026	03	89	128	< 0.01	< 0.01	< 0.01	< 0.02	08-2095- trial 03 ^b

POPPY Location, year, (variety)	FL	No	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	Total mg/kg eq	Study, Trial
Spain La Herrera 2009, (Luisiana) Soil: SaL	SC ^a	1	0.079	0.026	00	89	133	< 0.01	< 0.01	< 0.01	< 0.02	09-2085- trial 01 ^c
Spain Pozohondo 2009 (Luisiana) Soil: SaL	SC ^a	1	0.079	0.026	00	89	132	< 0.01	< 0.01	< 0.01	< 0.02	09-2085- trial 03 ^{b, d}
Spain Tinarejos 2009, (Luisiana) Soil: SaL	SC ^a	1	0.079	0.026	00	89	125	< 0.01	< 0.01	< 0.01	< 0.02	09-2085- trial 04 ^b

Soil: C = Clay, L = loam, Si = silt; Sa = sand; CL = clay loam; CSa = clay sand, CSi = clay silt; LSa = loamy sand; SiC = silty clay; SaCL = sandy clay loam; SiCL = silty clay loam, SiL = silty loam; SaC = sandy clay; SaL = sandy loam, SaSi = sandy silt;

total = sum of IFT and IFT-DKN, expressed as isoxaflutole equivalents. Since the molecular weight of IFT-DKN is identical to the molecular weight of the parent compound (MW 359.3), no correction for molecular weight is necessary.

^a SC formulation contained 20.4% w/w isoxaflutole and 20.3% w/w cyprosulfamide (safener); or 240 g/L each

^b Before analysis, the seeds were not grinded.

^c Before analyses, the seeds were grinded/homogenised for 30 sec using a basic mixer. Grinding the seeds leads to residues of IFT-BA about a factor 2 higher compared to non-grinded seeds.

^d Sample sizes were less than the required minimum of 1 kg (in accordance with FAO manual 2009): 0.1–0.9 kg. In plot 082095-02&04, the reduced sample size is due to phytotoxicity effects: bad growing and bad conditions of plants. Samples are considered not representative and trials cannot be selected for MRL derivation, if according to cGAP.

Legume animal feeds

Supervised residue trials were conducted on chickpea forage and chickpea straw.

Chickpea forage

Supervised trials on chickpeas were conducted in Australia during the 1999 and 2011 season [Lynch and Keats, 1999a, M-432364-01-1, report AK99054; Lynch and Keats, 1999b, M-432374-01-1, report AK99056; Lynch and Keats, 2000a, M-432434-01-1, report AQ00001; Lynch and Keats, 2000b, M-432441-01-1, report AQ00002; Lynch and Keats, 2000c, M-432444-01-1, report AQ00003; Ellis, 2012, M-425905-02-1, report BCS-0370]. Small plots of chickpeas (20–135 m²) were treated as indicated in Table 52 using a hand held boom sprayer or a small plot sprayer with spray volumes ranging from 50–230 L/ha.

In 1999, different application scenarios were tested on parallel plots. Plots were treated once at different application rates and/or growth stages (before emergence of the crop or at 3 nodes stage). In 2011, four application scenarios were tested on parallel plots. Isoxaflutole was applied at rates of 0.075 kg ai/ha and 0.150 kg ai/ha to bare soil either as a single fallow application approximately four month before sowing the chickpea crops, or in conjunction with a second application at planting.

Replicate field samples of forage (or green material) were taken at pre-flowering (AK99056) or at 3–4 node stage (AQ reports) or 42–49 DAS (BCS-0370). Forage was sampled by hand with secateurs, cutting random samples of a chickpea plant down to 5 cm above ground level, from at least 10 separate plants from all over the plot. All sample sizes were less than the required minimum of 1 kg (in accordance with FAO manual 2009): 0.10 kg in report AK99056, 0.20 kg in BCS-0370,

0.25 kg in AQ00001 and AQ00003, 0.5 kg in AQ00002. Samples were stored frozen with a maximum storage period of 3–21 days at –20 °C (AQ reports), 11 months at –20 °C (AK99056) or 135 days at –9 °C (BCS-0370).

In the trials from 1999, samples were analysed for total residues using GC-MS-MS modification B of method 00473 (common moiety method), where IFT, IFT-DKN and IFT-BA are converted into RPA 204497 and total residues are expressed as isoxaflutole equivalents. This method is considered valid in the range 0.01–0.1 mg/kg in chickpea forage. Since total residue levels in the supervised trials ranged from 0.01–0.19 mg/kg, validation at higher levels is desirable. Average concurrent recoveries at 0.01 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ). Average concentrations for duplicate field samples are shown in Table 52.

In the trials from 2011, samples were analysed for IFT, IFT-DKN and IFT-BA using modification A of HPLC-MS-MS method ATM-0054.01. This method is considered valid in the range 0.01–0.1 mg/kg in chickpea forage. Since IFT-BA levels in the supervised trials ranged from 0.01–0.55 mg/kg, validation at higher levels is desirable. Average concurrent recoveries at 0.01–1.0 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ). Average concentrations for duplicate field samples are shown in Table 52.

Note: In the AK and AQ reports, some data (application rate and date of application) were found to be inconsistent between the summary and appendices. The data coming from the field presented in the “residue sample submission form” were considered as being the valid ones.

Note: Storage stability studies on commodities with high water content showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 20 months. Storage stability studies on commodities with high water content showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage and IFT-DKN is stable for at least 12 months but converts to IFT-BA within 23 months of storage. Since chickpea forages have been stored for a maximum of 11 months in the trials where a common moiety method was used and chickpea forages have been stored for less than 3 months in trials where individual compounds have been measured, all results are considered reliable.

Table 52 Isoxaflutole related residues after pre-or post-emergent treatment of chickpeas (forage or green material)

CHICK PEA FORAGE Location, year, (variety)	FL	No & interval	kg ai/ha	kg ai/hL	timing	DAT	IFT mg/kg	IFT-DKN, mg/kg	IFT-BA, mg/kg	Total, mg/kg	report, trial
Australia Biniguy NSW, 2009, (Amethyst) Soil: brown Clay Loam	WG	1	0.075	0.100	3 days post sowing	70	NA	NA	NA	< 0.01 ^a	AK99056 99NST01-A ^c
	WG	1	0.15	0.25	3 days post sowing	70	NA	NA	NA	0.034 ^a	AK99056 99NST01-B ^c
Australia Horsham VIC, 2009, (Sona) Soil: Wimmera gray clay	WG	1	0.075	0.100	Post sow/ Pre-emergent	30	NA	NA	NA	0.028 ^a	AQ00001 99h011-A ^c
	WG	1	0.15	0.20	Post sow/ Pre-emergent	30	NA	NA	NA	0.16 ^a	AQ00001 99h011-B ^c
	WG ^d	1	0.056	0.075	Early Post-emergent	46	NA	NA	NA	0.040 ^a	AQ00002 99h015-A ^c

CHICK PEA FORAGE Location, year, (variety)	FL	No & interval	kg ai/ha	kg ai/hL	timing	DAT	IFT mg/kg	IFT- DKN, mg/kg	IFT- BA, mg/kg	Total, mg/kg	report, trial
					(3 nodes)						
	WG _d	1	0.075	0.100	Early Post-emergent (3 nodes)	46	NA	NA	NA	0.12 _a	AQ00002 99h015-B ^c
	WG _d	1	0.094	0.13	Early Post-emergent (3 nodes)	46	NA	NA	NA	0.16 _a	AQ00002 99h015-C ^c
	WG _e	1	0.056	0.075	Early Post-emergent (3 nodes)	46	NA	NA	NA	0.085 _a	AQ00002 99h015-D ^c
	WG _e	1	0.075	0.100	Early Post-emergent (3 nodes)	46	NA	NA	NA	0.11 _a	AQ00002 99h015-E ^c
	WG _e	1	0.094	0.13	Early Post-emergent (3 nodes)	46	NA	NA	NA	0.11 _a	AQ00002 99h015-F ^c
Australia Bruce Rock WA, 2009, (Tyson) Soil: brown loam	WG _d	1	0.075	0.15	Post sow/Pre-emergent	28	NA	NA	NA	0.095 _a	AQ00003 99h010-A ^c
	WG _d	1	0.15	0.30	Post sow/Pre-emergent	28	NA	NA	NA	0.15 _a	AQ00003 99h010-B ^c
	WG _d	1	0.20	0.40	Post sow/Pre-emergent	28	NA	NA	NA	0.19 _a	AQ00003 99h010-C ^c
	WG _e	1	0.075	0.15	Post sow/Pre-emergent	28	NA	NA	NA	0.11 _a	AQ00003 99h010-D ^c
	WG _e	1	0.15	0.30	Post sow/Pre-emergent	28	NA	NA	NA	0.15 _a	AQ00003 99h010-E ^c
	WG _e	1	0.20	0.40	Post sow/Pre-emergent	28	NA	NA	NA	0.15 _a	AQ00003 99h010-F ^c
Australia Northam WA, 2011, (Desi) Soil: sandy loam	WG	1	0.075	0.033	bare soil 121 days before sowing	163 169 177	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.20 0.16 0.12	< 0.02 < 0.02 < 0.02 ^b	BCS-0370, C601 ^c
	WG	1	0.15	0.066	bare soil 121 days before sowing	163 169 177	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.32 0.28 0.22	< 0.02 < 0.02 < 0.02 ^b	^c
	WG	2 (121 days)	0.075 0.075	0.033 0.075	1 st bare soil, 2 nd at sowing	42 48 56	< 0.01 < 0.01 < 0.01	0.060 0.045 0.030	0.34 0.29 0.24	0.070 0.055 0.040 ^b	^c
	WG	2 (121 days)	0.15 0.15	0.066 0.150	1 st bare soil, 2 nd at sowing	42 48 56	< 0.01 < 0.01 < 0.01	0.075 0.050 0.065	0.55 0.47 0.44	0.085 0.060 0.075 ^b	^c
Australia Warwick QLD, 2011, (Hattrick) Soil: black clay loam	WG	1	0.075	0.057	bare soil 127 days before sowing	168 175 182	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 ^b	BCS-0370, C602 ^c
	WG	1	0.15	0.11	bare soil	168	< 0.01	< 0.01	< 0.01	< 0.02	^c

CHICK PEA FORAGE Location, year, (variety)	FL	No & interval	kg ai/ha	kg ai/hL	timing	DAT	IFT mg/kg	IFT-DKN, mg/kg	IFT-BA, mg/kg	Total, mg/kg	report, trial
					127 days before sowing	175 182	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02 ^b	
	WG	2 (127 days)	0.075 0.075	0.055 0.057	1 st bare soil, 2 nd at sowing	41 48 55	< 0.01 < 0.01 < 0.01	0.025 0.015 < 0.01	0.28 0.28 0.15	0.035 0.025 < 0.02 ^b	^c
	WG	2 (127 days)	0.15 0.15	0.11- 0.11	1 st bare soil, 2 nd at sowing	41 48 55	< 0.01 < 0.01 < 0.01	0.025 0.020 < 0.01	0.40 0.28 0.22	0.035 0.030 < 0.02 ^b	^c
Australia Shepparton East VIC, 2011, (Kabul) Soil: clay loam	WG	1	0.075	0.075	bare soil 107 days before sowing	156 164 171	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 ^b	BCS-0370, C603 ^c
	WG	1	0.15	0.150	bare soil 107 days before sowing	156 164 171	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.020 0.030 0.030	< 0.02 < 0.02 < 0.02 ^b	^c
	WG	2 (107 days)	0.075 0.072	0.075 0.075	1 st bare soil, 2 nd at sowing	49 57 64	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.10 0.12 0.11	< 0.02 < 0.02 < 0.02 ^b	^c
	WG	2 (107 days)	0.15 0.15	0.150	1 st bare soil, 2 nd at sowing	49 57 64	< 0.01 < 0.01 < 0.01	0.020 0.020 0.020	0.24 0.22 0.20	0.03 0.03 0.03 ^b	^c

^a Total residue obtained by common moiety method, whereby residues are converted into RPA204497 and expressed as isoxaflutole equivalent (residue includes IFT, IFT-DKN and IFT-BA)

^b Total residue calculated by summing up residues of IFT and IFT-DKN and expressed as isoxaflutole equivalents. Since the molecular weight of IFT-DKN is identical to the molecular weight of the parent compound (MW 359.3), no correction for molecular weight is necessary.

^c All sample sizes were less than the required minimum of 1 kg (in accordance with FAO manual 2009): 0.10 kg in report AK99056, 0.20 kg in BCS-0370, 0.25 kg in AQ00001 and AQ00003, 0.5 kg in AQ00002. However, two samples were taken from each trial plot (each from at least 10 plants in the AK and AQ reports) and the results are the mean of both samples. Therefore results can be considered representative and trials can be selected for MRL derivation, if according to cGAP.

^d added adjuvant: 0.25% X-77

^e added adjuvant: Uptake oil

Chickpea fodder

Supervised trials on chickpeas were conducted in Australia during the 1999 and 2011 season [Lynch and Keats, 1999a, M-432364-01-1, report AK99054; Lynch and Keats, 1999b, M-432374-01-1, report AK99056; Lynch and Keats, 2000a, M-432434-01-1, report AQ00001; Lynch and Keats, 2000b, M-432441-01-1, report AQ00002; Lynch and Keats, 2000c, M-432444-01-1, report AQ00003; Ellis, 2012, M-425905-02-1, report BCS-0370]. Small plots of chickpeas (20–135 m²) were treated as indicated in Table 53 using a hand held boom sprayer or a small plot sprayer with spray volumes ranging from 50–230 L/ha.

In 1999, different application scenarios were tested on parallel plots. Plots were treated once at different application rates and/or growth stages (before emergence of the crop or at 3 nodes stage).

In 2011, four application scenarios were tested on parallel plots. Isoxaflutole was applied at rates of 0.075 kg ai/ha and 0.150 kg ai/ha to bare soil either as a single fallow application

approximately four month before sowing the chickpea crops, or in conjunction with a second application at planting.

Replicate field samples of chickpea fodder were taken at maturity. In report AK99054, chickpea plots were mechanically harvested and fodder was randomly selected from the trash coming out of the back of the harvester. In report AK99056, BCS-370 and AQ reports fodder was sampled by hand with secateurs, cutting random samples of a dry chickpea plant down to 5 cm above ground level, from at least 10 separate plants from all over the plot. Sample sizes were at least 0.5 kg in report BCS-0370, AQ00003 and AK99054. Sample sizes from all other reports were below the required minimum of 0.5 kg (in accordance with FAO manual 2009): 0.1 kg in report AK99056, 0.25 kg in AQ00001 and AQ00002. Samples were stored frozen with a maximum storage period of 2–21 days at -20 °C (AK99054 and AQ reports), or 11 months at -20 °C (AK99056) or 25 days at -8 °C (BCS-0370).

In the trials from 1999, samples were analysed for total residues using GC-MS-MS modification B of method 00473 (common moiety method), where IFT, IFT-DKN and IFT-BA are converted into RPA 204497 and total residues are expressed as isoxaflutole equivalents. This method is considered valid in the range 0.01–0.1 mg/kg in chickpea straw. Average concurrent recoveries at 0.01 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ). Average concentrations for duplicate field samples are shown in Table 53.

In the trials from 2011, samples were analysed for isoxaflutole, IFT-DKN and IFT-BA using modification A of HPLC-MS-MS method ATM-0054.01. This method is considered valid in the range 0.01–0.1 mg/kg in chickpea straw. Since IFT-BA levels in chickpea straw ranged from < 0.01–0.12 mg/kg validation at higher levels is desirable. Average concurrent recoveries at 0.01–1.0 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ). Average concentrations for duplicate field samples are shown in Table 53.

Note: In the AK and AQ reports, some data (application rate and date of application) were found to be inconsistent between the summary and appendices. The data coming from the field presented in the “residue sample submission form” were considered as being the valid ones.

Note: Storage stability studies on straw showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 15 months. Storage stability studies on various commodities showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage and IFT-DKN is stable for at least 12 months but converts to IFT-BA within 23 months of storage. Since chickpea straw has been stored for a maximum of 11 months in the trials where a common moiety method was used and chickpea straw has been stored for less than 3 months in trials where individual compounds have been measured, all results are considered reliable.

Table 53 Isoxaflutole related residues after pre- or post-emergent treatment of chickpeas (straw)

CHICK PEA STRAW Location, year, (variety)	FL	No & interval	kg ai/ha	kg ai/hL	timing	DAT	IFT mg/kg	IFT- DKN, mg/kg	IFT- BA, mg/kg	Total, mg/kg	% dm	Report, trial
Australia Pittsworth QLD, 2009 (Norwin) Soil: black earth	WG	1	0.075	0.075	Post planting, pre- emergent	185	NA	NA	NA	< 0.01 ^a		AK99054 99NST26- A
	WG	1	0.15	0.150	Post planting, pre- emergent	185	NA	NA	NA	< 0.01 ^a		AK99054 99NST26- B
Australia Biniguy NSW, 2009,	WG	1	0.075	0.100	3 days post sowing	155	NA	NA	NA	< 0.01 ^a		AK99056 99NST01- A ^c

CHICK PEA STRAW Location, year, (variety)	FL	No & interval	kg ai/ha	kg ai/hL	timing	DAT	IFT mg/kg	IFT- DKN, mg/kg	IFT- BA, mg/kg	Total, mg/kg	% dm	Report, trial
(Amethyst) Soil: brown CL												
	WG	1	0.15	0.25	3 days post sowing	155	NA	NA	NA	< 0.01 ^a		AK99056 99NST01- B ^c
Australia Horsham VIC, 2009, (Sona) Soil: Wimmera gray clay	WG	1	0.075	0.100	Post sow/ Pre- emergent	184	NA	NA	NA	< 0.01 ^a		AQ00001 99h011-A ^c
	WG	1	0.15	0.20	Post sow/ Pre- emergent	184	NA	NA	NA	< 0.01 ^a		AQ00001 99h011-B ^c
	WG ^d	1	0.056	0.075	Early Post- emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a		AQ00002 99h015-A ^c
	WG ^d	1	0.075	0.100	Early Post- emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a		AQ00002 99h015-B ^c
	WG ^d	1	0.094	0.13	Early Post- emergent (3 nodes)	147	NA	NA	NA	0.012 ^a		AQ00002 99h015-C ^c
	WG ^e	1	0.056	0.075	Early Post- emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a		AQ00002 99h015-D ^c
	WG ^e	1	0.075	0.100	Early Post- emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a		AQ00002 99h015-E ^c
	WG ^e	1	0.094	0.13	Early Post- emergent (3 nodes)	147	NA	NA	NA	< 0.01 ^a		AQ00002 99h015-F ^c
Australia Bruce Rock WA, 2009, (Tyson) Soil: brown loam	WG ^d	1	0.075	0.15	Post sow/Pre- emergent	188	NA	NA	NA	< 0.01 ^a		AQ00003 99h010-A
	WG ^d	1	0.15	0.30	Post sow/Pre- emergent	188	NA	NA	NA	< 0.01 ^a		AQ00003 99h010-B
	WG ^d	1	0.20	0.40	Post sow/Pre- emergent	188	NA	NA	NA	0.018 ^a		AQ00003 99h010-C
	WG ^e	1	0.075	0.15	Post sow/Pre- emergent	188	NA	NA	NA	< 0.01 ^a		AQ00003 99h010-D
	WG ^e	1	0.15	0.30	Post sow/Pre- emergent	188	NA	NA	NA	< 0.01 ^a		AQ00003 99h010-E
	WG ^e	1	0.20	0.40	Post sow/Pre- emergent	188	NA	NA	NA	< 0.01 ^a		AQ00003 99h010-F
Australia Northam WA, 2011, (Desi)	WG	1	0.075	0.033	bare soil 121 days before sowing	295	< 0.01	< 0.01	0.030	< 0.02 ^b	59	BCS-0370, C601

CHICK PEA STRAW Location, year, (variety)	FL	No & interval	kg ai/ha	kg ai/hL	timing	DAT	IFT mg/kg	IFT- DKN, mg/kg	IFT- BA, mg/kg	Total, mg/kg	% dm	Report, trial
Soil: sandy loam												
	WG	1	0.15	0.066	bare soil 121 days before sowing	295	< 0.01	< 0.01	0.055	< 0.02 ^b	59	
	WG	2 (121 days)	0.075 0.075	0.033 0.075	1 st bare soil, 2 nd at sowing	174	< 0.01	< 0.01	0.075	< 0.02 ^b	59	
	WG	2 (121 days)	0.15 0.15	0.066 0.150	1 st bare soil, 2 nd at sowing	174	< 0.01	< 0.01	0.12	< 0.02 ^b	59	
Australia Warwick QLD, 2011, (Hattrick) Soil: black clay loam	WG	1	0.075	0.057	bare soil 127 days before sowing	284	< 0.01	< 0.01	< 0.01	< 0.02 ^b	42	BCS-0370, C602
	WG	1	0.15	0.11	bare soil 127 days before sowing	284	< 0.01	< 0.01	< 0.01	< 0.02 ^b	42	
	WG	2 (127 days)	0.075 0.075	0.055 0.057	1 st bare soil, 2 nd at sowing	157	< 0.01	< 0.01	0.065	< 0.02 ^b	42	
	WG	2 (127 days)	0.15 0.15	0.11- 0.11	1 st bare soil, 2 nd at sowing	157	< 0.01	< 0.01	0.030	< 0.02 ^b	42	
Australia Shepparton East VIC, 2011, (Kabul) Soil: clay loam	WG	1	0.075	0.075	bare soil 107 days before sowing	324	< 0.01	< 0.01	< 0.01	< 0.02 ^b	27	BCS-0370, C603
	WG	1	0.15	0.150	bare soil 107 days before sowing	324	< 0.01	< 0.01	< 0.01	< 0.02 ^b	27	
	WG	2 (107 days)	0.075 0.072	0.075 0.075	1 st bare soil, 2 nd at sowing	217	< 0.01	< 0.01	0.015	< 0.02 ^b	27	
	WG	2 (107 days)	0.15 0.15	0.150	1 st bare soil, 2 nd at sowing	217	< 0.01	< 0.01	0.060	< 0.02 ^b	27	

^a Total residue obtained by common moiety method, whereby residues are converted into RPA204497 and expressed as isoxaflutole equivalent (residue includes IFT, IFT-DKN and IFT-BA)

^b Total residue calculated by summing up residues of IFT and IFT-DKN and expressed as isoxaflutole equivalents. Since the molecular weight of IFT-DKN is identical to the molecular weight of the parent compound (MW 359.3), no correction for molecular weight is necessary.

^c Sample sizes were below the required minimum of 0.5 kg (in accordance with FAO manual 2009): 0.1 kg in report AK99056, 0.25 kg in AQ00001 and AQ00002. However, two samples were taken from each trial plot (each from at least 10 plants in the AK and AQ reports) and the results are the mean of both samples. Therefore results can be considered representative and trials can be selected for MRL derivation, if according to cGAP.

^d added adjuvant: 0.25% X-77

^e added adjuvant: Uptake oil

Forage and fodder of cereal grains and grasses

Supervised residue trials were available for maize forage and maize fodder.

Maize forage

Supervised trials on maize were conducted in Spain, Italy, Greece, Portugal, Germany, France, Netherlands and the United Kingdom in 2005 and 2006 and in USA and Canada in 1998, 2005 and 2006 [Zimmer and Wieland, 2007, M-282674-01-1, report RA-2587/05; Wolters and Erler, 2007b, M-284423-01-1, report RA-2510/06; Wolters, 2007b, M-285014-01-1, report RA-2615/06; Zimmer, 2006, M-281611-01-1, report RA-2588/05; Wolters and Erler, 2007a, M-284416-01-1, report RA-2511/06; Wolters, 2007a, M-285005-01-1, report RA-2616/06; Mickelson, 1999a, M-240663-01-1, report AA98714495; Fischer and Helfrich, 2007, M-285889-01-1, report RAUBP008; Vaughn and Cosgrove, 2007, M-286216-02-1, report RAUBP011]. Small plots of maize (50–1700 m²) were treated as indicated in Table 54 using knapsack, tractor/ATV mounted or wheelbarrow sprayers with spray volumes ranging from 90–300 L/ha

Four treatment scenarios were tested in the plots:

- a single bare ground application of isoxaflutole (pre-emergence of the crop)
- a single application of isoxaflutole in combination with the safener cyprosulfamide at BBCH 12–14,
- a single application of isoxaflutole in combination with thienencarbazone-methyl and the safener cyprosulfamide at BBCH 13–14.
- a single bare ground application of isoxaflutole in combination with the safener cyprosulfamide (pre-emergence of the crop) followed by a second application with thienencarbazone-methyl in combination with the safener cyprosulfamide at BBCH 18.

Field samples of forage (whole plants) were taken at various growth stages: BBCH 13–85 in the EU trials, late milk—dent stage (BBCH 85–87) in the US trials and BBCH 75–85 in the Canadian trials. Forage harvested at growth stage BBCH 85 or later still contains the cobs/kernels, but the material itself will be very dry and is not green anymore. Single field samples were taken in the EU trials, duplicate field samples were taken in the US and Canadian trials. Sample sizes were at least 1 kg (in accordance with FAO manual 2009), except for some DAT = 0 samples (0.1–0.8 kg) as indicated in Table 54. Samples were stored frozen at -18 °C with a maximum storage period of 327 days (EU trials), 185 days at -10 °C (AA987144495) or 593 days at -15 °C (RAUBP008), 189 days at -20 °C (Canadian trials).

In the EU trials, isoxaflutole and its metabolite IFT-DKN and IFT-BA were determined using HPLC-MS-MS method 00985/M001. This method is considered valid in the range 0.01–0.10 mg/kg for maize forage. Since IFT and IFT-DKN levels in the supervised residue trials on maize forage ranged from < 0.01–13 mg/kg and < 0.01–2.6 mg/kg, respectively, validation at higher levels is desirable. Average concurrent recoveries at 0.01–5.0 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.01 mg/kg (LOQ) for each analyte. Average concentrations for single field samples are shown in Table 54.

In the 1998 US trials, isoxaflutole and its metabolite IFT-DKN and IFT-BA were determined using HPLC-MS-MS method CAL#019-03 revision 1. The method is considered valid in the range 0.01–0.10 mg/kg for maize forage. Since IFT-BA levels in the supervised trials on maize forage were in the range < 0.01–0.15 mg/kg, validation at higher levels is desirable. Individual concurrent recoveries at 0.01, 0.1 and 10 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ). Average concentrations for duplicate field samples are shown in Table 54.

In the 2005 and 2006 Canadian and US trials, isoxaflutole and its metabolites IFT-DKN and IFT-BA were determined using modification C of HPLC-MS-MS method CAL#019-03. This method is considered valid in the range 0.01–0.2 mg/kg IFT, 0.02–0.3 mg/kg IFT-DKN and 0.03–0.3 mg/kg IFT-BA in maize forage. Average concurrent recoveries at 0.01, 0.05 and 0.2 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.01 mg/kg (reported LOQ). Average

concentrations for duplicate field samples are shown in Table 54. Because of validation results, the LOQs were increased to 0.02 mg/kg for IFT-DKN and 0.03 mg/kg for IFT-BA (indicated by note ^g).

Note: Storage stability studies on commodities with high water content showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 20 months. Storage stability studies on commodities with high water content showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage and IFT-DKN is stable for at least 12 months but converts to IFT-BA within 23 months of storage. Since maize forage has been stored for longer than 3 months, part of the IFT may have degraded to IFT-DKN. Except for trials in report RAUBP008, maize forage has been stored for less than 12 months and these results are considered reliable. Samples from report RAUBP008 have been stored for longer than 12 months and part of the IFT-DKN may have degraded to IFT-BA. However, in those trials where IFT, IFT-DKN and IFT-BA are all below LOQ, any degradation remains unnoticed and these results are considered reliable. In a few trials where IFT-BA was found to be above LOQ and where the storage period exceeded 12 months, individual results for IFT and IFT-DKN are not considered reliable. These are indicated by note ^f.

Table 54 Isoxaflutole related residues after pre- or post-emergent treatment in maize forage (whole plant including cobs)

MAIZE FORAGE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial (Remarks)
Germany Monheim (Nordrhein-Westfalen) 2005, (Romario) Soil: SaL	SC ^a	1	0.10	0.034	13	13 19	0 ^c 41	2.2 < 0.01	0.71 < 0.01	< 0.01 0.03	2.9 < 0.02	RA-2587/05; R 2005 0623/6
Germany Monheim (Nordrhein-Westfalen) 2006, (Romario), Soil: SaSi	SC ^b	1	0.099	0.033	13	13 33 85	0 ^c 40 98	6.2 0.28 < 0.01	1.5 0.06 < 0.01	< 0.01 0.02 0.03	7.7 0.34 < 0.02	RA-2510/06 R 2006 0795/4
Germany Euskirchen - Kessenich (Nordrhein-Westfalen) (Egrin FAO 220), Soil: SiC	SC ^a	1	0.10	0.034	13	13 35	0 ^c 41	2.9 < 0.01	1.0 < 0.01	< 0.01 0.01	3.9 < 0.02	RA-2587/05 R 2005 0961/8
Germany Leverkusen (Nordrhein-Westfalen), 2006 (Bunguy); Soil: SaL	SC ^c	1 ^c	0.10	0.034	05	18 71 85	41 81 111	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02	RA-2615/06 R 2006 0801/2
Germany Werl (Nordrhein-Westfalen), 2006, (Delitop); Soil: SiL	SC ^c	1 ^c	0.10	0.034	06	18 65 85	45 85 139	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.02 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02	RA-2615/06 R 2006 0802/0
United Kingdom Cambridge (Cambridges)	SC ^a	1	0.10	0.034	13	13 34	0 ^c 40	3.2 < 0.01	0.53 < 0.01	< 0.01 0.02	3.7 < 0.02	RA-2587/05 R 2005 0959/6

MAIZE FORAGE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial (Remarks)
hire), 2005, (RK210), Soil: SaL												
United Kingdom Cambridge (Cambridges hire) 2006, (Nexxos); Soil: SaL	SC ^b	1	0.099	0.033	14	14 37 85	0 ° 39 106	4.5 0.01 < 0.01	0.42 < 0.01 < 0.01	0.01 0.01 0.03	4.9 0.02 < 0.02	RA- 2510/06 R 2006 0796/2
United Kingdom, EYE (Suffolk) 2006, (Algans); Soil: SiL	SC ^c	1 ^c	0.10	0.034	07	18 71	46 87	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2615/06 R 2006 0800/4
Netherlands Zwaagdijk- Oost (Noord- Holland) 2005, (Rosalie), Soil: C	SC ^a	1	0.10	0.034	13	13 19	0 ° 40	1.1 < 0.01	0.20 < 0.01	< 0.01 < 0.01	1.3 <u>< 0.02</u>	RA- 2587/05 R 2005 0962/6
N-France Saint Symphorien d'Ancelles (Bourgogne) 2005, (Surtep), Soil: S	SC ^a	1	0.10	0.034	14	14 39	0 ° 40	2.7 < 0.01	0.64 < 0.01	< 0.01 0.03	3.3 < 0.02	RA- 2587/05 R 2005 0958/8
N-France Chaussy (Ile- de-France) 2006, (Moncada), Soil: CSa	SC ^b	1	0.099	0.033	13	13 19 85	0 ° 40 110	7.1 < 0.01 < 0.01	1.2 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	8.3 <u>< 0.02</u> < 0.02	RA- 2510/06 R 2006 0073/9
	SC ^c	1 ^c	0.10	0.034	01	18 69 85	55 94 134	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02	RA- 2615/06 R 2006 0627/3
N-France Chambourg sur indre (Centre) 2006, (Anasta); Soil: CSi	SC ^c	1 ^c	0.10	0.034	00	18 63 85	52 91 126	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.03 < 0.01 0.02	< 0.02 < 0.02 < 0.02	RA- 2615/06 R 2006 0799/7
S-France Savenes (Midi- Pyrenees), 2005, (PR33A46); Soil: CL	SC ^a	1	0.10	0.034	13	13 34	0 ° 40	1.9 < 0.01	0.46 < 0.01	< 0.01 0.01	2.4 <u>< 0.02</u>	RA- 2588/05 R 2005 0624/4
S-France Vouille (Poitou-	SC ^b	1	0.099	0.033	13	13 19 85	0 ° 40 116	13 < 0.01 < 0.01	2.6 < 0.01 < 0.01	0.01 < 0.01 < 0.01	16 <u>< 0.02</u> < 0.02	RA- 2511/06 R 2006

MAIZE FORAGE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial (Remarks)
Charentes) 2006, (dkc 4845) Soil: SiC												0074/7
S-France Beauzelle (Midi- Pyrenees) 2006, (Ferry) Soil: SaSi	SC ^c	1 ^c	0.10	0.034	06	18 69 85	49 90 115	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.03 0.03 0.03	< 0.02 < 0.02 < 0.02	RA- 2616/06 R 2006 0628/1
S-France Laudun (Languedoc- Roussillon) 2006, (Cecilia) Soil: CL	SC ^c	1 ^c	0.10	0.034	01	18 67 85	30 70 109	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02	RA- 2616/06 R 2006 0803/9
Spain Vila-sacra (Cataluña) 2005, (DKc6575); Soil: SaL	SC ^a	1	0.10	0.034	13	13 19	0 ^c 40	4.9 < 0.01	0.71 < 0.01	0.02 < 0.01	5.6 < 0.02	RA- 2588/05 R 2005 0963/4
Spain Vila-sacra (Cataluña), 2006, (PR33P67) Soil: SaL	SC ^b	1	0.099	0.033	14	14 36 85	0 ^c 41 77	7.2 < 0.01 < 0.01	1.2 < 0.01 < 0.01	0.01 < 0.01 < 0.01	8.4 < 0.02 < 0.02	RA- 2511/06 R 2006 0798/9
	SC ^c	1 ^c	0.10	0.034	07	18 85	48 99	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA- 2616/06 R 2006 0804/7
Spain Alginet (Comunidad Valenciana) 2006, (Constanza) Soil: SiC	SC ^c	1 ^c	0.10	0.034	00	18 73 85	32 72 86	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02	RA- 2616/06 R 2006 0806/3
Italy San Carlo (FE) Emilia- Romagna 2005, (DK 440); Soil: SaC	SC ^a	1	0.10	0.034	13	13 35	0 40	3.7 < 0.01	0.95 < 0.01	< 0.01 < 0.01	4.6 < 0.02	RA- 2588/05 R 2005 0964/2
Italy San Carlo (FE) Emilia- Romagna, 2006, (PR34N43) Soil: SaC	SC ^b	1	0.099	0.033	13	13 35 85	0 ^c 40 88	5.4 < 0.01 < 0.01	0.32 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	5.7 < 0.02 < 0.02	RA- 2511/06 R 2006 0797/0
	SC ^c	1 ^c	0.10	0.034	01	18 63 85	43 84 113	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02	RA- 2616/06 R 2006 0805/5
Greece Chalastra	SC ^a	1	0.10	0.034	13	13 31	0 ^c 39	4.5 < 0.01	0.34 < 0.01	< 0.01 0.01	4.8 < 0.02	RA- 2588/05

MAIZE FORAGE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial (Remarks)
(Macedonia) 2005, (Decalp 743); Soil: L												R 2005 0965/0
Portugal Golegã (Ribatejo e Oeste) 2005, (PRN 43); Soil: SiL	SC ^a	1	0.10	0.034	13	13 35	0 ^c 41	3.0 < 0.01	0.61 < 0.01	< 0.01 < 0.01	3.6 ≤ 0.02	RA- 2588/05 R 2005 0966/9
USA Lehigh PA, 1998 (Mycogen 2598) Soil: SiL	WG	1	0.16	0.089	bare soil	De	107	< 0.01	< 0.01	< 0.01	< 0.02	AA987144 95 14495-01
USA Wilson NC, 1998, (Pioneer 3163) Soil: SaL	WG	1	0.16	0.084	bare soil	De	73	< 0.01	< 0.01	0.15	< 0.02	AA987144 95 14495-02
USA Greene IA, 1998, (Dekalb DK 561SR) Soil: L	WG	1	0.16	0.089	bare soil	EaDe	109	< 0.01	< 0.01	< 0.01	< 0.02	AA987144 95 14495-04
USA Percival IA, 2005, (Sucrossco 2009) Soil: SiL	SC ^a	1	0.13	0.10	12	EaFo ECH	45 76	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	< 0.03 ^g < 0.03 ^g	RAUBP00 8, UB086- 05H
USA Jefferson IA, 2005 (DKC63-81) Soil: L	SC ^a	1	0.13	0.10	12	ECH	87	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP00 8, UB091- 05H
USA Bagley IA, 2006 (FA6508) Soil: CL	SC ^a	1	0.13	0.11	12	EaFo	45	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP00 8, UB091- 05HA d
USA Shelby MO, 1998, (Novartis NK 6800) Soil: L	WG	1	0.16	0.091	bare soil	EaDe	88	< 0.01	< 0.01	< 0.01	< 0.02	AA987144 95 14495-05
USA Shelby MO, 1998, (Novartis NK 6800) Soil: SiL	WG	1	0.16	0.090	bare soil	EaDe	88	< 0.01	< 0.01	< 0.01	< 0.02	AA987144 95 14495-21
USA Stoddard	WG	1	0.16	0.096	bare soil	LaDo	80	< 0.01	< 0.01	0.014	< 0.02	AA987144 95

MAIZE FORAGE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial (Remarks)
MO, 1998, (Pioneer 3394) Soil: SiL												14495-10
USA Butler MO, 2005, (Garst 8287 RR) Soil: SiCL	SC ^a	1	0.13	0.098	12	EaFo Fo	43 104	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g 0.034	< 0.03 ^g < 0.03 ^{fg}	RAUBP00 8, UB081- 05H
USA Clarence MO, 2005, (Pioneer 35P12) Soil: CL	SC ^a	1	0.13	0.094	12	ECH	79	< 0.01	< 0.02 ^g	0.031	< 0.03 ^{fg}	RAUBP00 8, UB088- 05H
USA Clarence MO, 2006, (-) Soil: SiL	SC ^a	1	0.13	0.070	12	EaFo	45	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP00 8, UB088- 05HA ^d
USA Fayette OH, 1998, (SC 1096) Soil: SiCL	WG	1	0.15	0.092	bare soil	EaDe	105	< 0.01	< 0.01	0.019	< 0.02	AA987144 95 14495-06
USA Fayette OH, 1998, (SC 1068) Soil: SiL	WG	1	0.16	0.094	bare soil	EaDo Do EaDe De De	46 103 110 117 124	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	AA987144 95 14495-19
USA Marysville OH, 2005, (Shur Grow SG-751) Soil: CL	SC ^a	1	0.13	0.079	12	EaFo ECH	45 86	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	< 0.03 ^g < 0.03 ^g	RAUBP00 8, UB089- 05H
USA New Holland OH, 2005 (Crows 7R321) Soil: L	SC ^a	1	0.13	0.092	12	EaFo ECH	45 93	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	< 0.03 ^g < 0.03 ^g	RAUBP00 8, UB092- 05H
USA Clay SD, 1998, (Dekalb DK 493RR) Soil: L	WG	1	0.16	0.092	bare soil	EaDe	95	< 0.01	< 0.01	< 0.01	< 0.02	AA987144 95 14495-07
USA Yankton SD, 1998 (Dekalb, DK 493RR) Soil: SiCL	WG	1	0.17	0.094	bare soil	EaDe	93	< 0.01	< 0.01	0.015	< 0.02	AA987144 95 14495-08
USA Grand Forks ND, 1998, (Mycogen 2110 R3)	WG	1	0.16	0.11	bare soil	EaDe	114	< 0.01	< 0.01	0.014	< 0.02	AA987144 95 14495-09

MAIZE FORAGE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial (Remarks)
Soil: SiL												
USA Steele ND, 1998, (Mycogen 2110 R3) Soil: SiL	WG	1	0.16	0.11	bare soil	EaDe	108	< 0.01	< 0.01	0.017	< 0.02	AA987144 95 14495-16
USA Northwood ND, 2005, (39D81) Soil: L	SC ^a	1	0.13	0.094	12	EaFo ECH	43 90	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	< 0.03 ^g < 0.03 ^g	RAUBP00 8, UB093-05H
USA Stark IL, 1998 (Pioneer 3394) Soil: SiL	WG	1	0.16	0.10	bare soil	EaDe	91	< 0.01	< 0.01	< 0.01	< 0.02	AA987144 95 14495-11
USA Bond IL, 1998, (Pioneer 3394) Soil: SiL	WG	1	0.16	0.12	bare soil	LaDo	86	< 0.01	< 0.01	0.012	< 0.02	AA987144 95 14495-12
USA Clinton IL, 1998, (Pioneer 33V08) Soil: SiL	WG	1	0.16	0.16	bare soil	EaDe	91	< 0.01	< 0.01	< 0.01	< 0.02	AA987144 95 14495-20
USA Seymour IL, 2005 (Garst 8550) Soil: SiL	SC ^a	1	0.13	0.10	12	EaFo EaFo EaFo EaFo EaFo Fo	30 37 44 51 58 106	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.02 ^g < 0.02 ^g < 0.02 ^g < 0.02 ^g < 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g < 0.03 ^g < 0.03 ^g < 0.03 ^g < 0.03 ^g	< 0.03 ^g < 0.03 ^g < 0.03 ^g < 0.03 ^g < 0.03 ^g < 0.03 ^g	RAUBP00 8, UB082-05D
USA Monticello IL, 2005 (Pioneer 37H26) Soil: SiL	SC ^a	1	0.13	0.087	12	EaFo Fo	45 88	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	0.034 0.064	< 0.03 ^g < 0.03 ^g	RAUBP00 8, UB083-05H
USA Carlyle IL, 2005 (FS 6455 RR/YGCB) Soil: SiL	SC ^a	1	0.13	0.080	12	EaFo ECH	45 95	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	< 0.03 ^g < 0.03 ^g	RAUBP00 8, UB094-05H
USA York NE, 1998, (Northrup King N3030BT) Soil: SiL	WG	1	0.16	0.11	bare soil	EaDe	89	< 0.01	< 0.01	0.023	< 0.02	AA987144 95 14495-13
	WG	1	0.16	0.11	bare soil	LaMi Do EaDe LaDo De	74 81 88 95 102	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	AA987144 95 14495-18
USA	WG	1	0.16	0.11	bare	EaDe	93	< 0.01	< 0.01	0.036	< 0.02	AA987144

MAIZE FORAGE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial (Remarks)
Polk NE, 1998, (Northrup King N3030BT) Soil: LSa					soil							95 14495-14
USA Springfield NE, 2005 (NK70T9) Soil: SiL	SC ^a	1	0.13	0.10	12	EaFo ECH	45 76	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	<u>< 0.03^g</u> < 0.03 ^g	RAUBP00 8, UB085- 05H
USA Stafford KS, 1998, (Pioneer 3737) Soil: LSa	WG	1	0.15	0.14	bare soil	EaDe	83	< 0.01	< 0.01	0.11	< 0.02	AA987144 95 14495-15
USA Stilwell KS, 2006, (Garst 8478 LL/CB/GT) Soil: SiL	SC ^a	1	0.14	0.10	12	EaFo EaFo EaFo EaFo EaFo	31 38 45 51 59 94	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.02 ^g < 0.02 ^g < 0.02 ^g < 0.02 ^g < 0.02 ^g < 0.02 ^g	0.030 0.043 0.054 0.046 0.052 0.055	< 0.03 ^{f,g} < 0.03 ^{f,g} < 0.03 ^{f,g} < 0.03 ^{f,g} < 0.03 ^{f,g} < 0.03 ^{f,g}	RAUBP00 8, UB080- 05DA ^d
USA Clay TX, 1998, (Northrup King 512RR) Soil: Sa	WG	1	0.16	0.12	bare soil	EaDe	79	< 0.01	< 0.01	0.012	< 0.02	AA987144 95 14495-17
USA East Bernard TX, 2005 (DKC69-71) Soil: SaL	SC ^a	1	0.13	0.094	12	EaFo ECH	45 67	< 0.01 0.015	< 0.02 ^g < 0.02 ^g	0.065 0.069	< 0.03 ^{f,g} < 0.03 ^{f,g}	RAUBP00 8, UB097- 05H
USA Bumpass VA, 2005, (Dekalb) Soil: SaCL	SC ^a	1	0.13	0.098	12	EaFo Fo	45 77	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	<u>< 0.03^g</u> < 0.03 ^g	RAUBP00 8, UB078- 05H
USA Tifton GA, 2005 (Pioneer 31N26) Soil: SaL	SC ^a	1	0.13	0.078	12	EaFo Fo	45 81	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	0.034 < 0.03 ^g	< 0.03 ^{f,g} < 0.03 ^g	RAUBP00 8, UB079- 05H
USA Gosport IN, 2005, (Pioneer 34D71) Soil: SiL	SC ^a	1	0.13	0.10	12	EaFo ECH	45 100	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	<u>< 0.03^g</u> < 0.03 ^g	RAUBP00 8, UB084- 05H
USA Sheridan IN, 2005, (Golden Harvest RR) Soil: SiL	SC ^a	1	0.13	0.076	12	EaFo ECH	43 90	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	<u>< 0.03^g</u> < 0.03 ^g	RAUBP00 8, UB095- 05H
USA Sabin MN, 2005, (Pioneer	SC ^a	1	0.14	0.15	12	EaFo ECH	45 118	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	< 0.03 ^{f,g} < 0.03 ^g	RAUBP00 8, UB087- 05H

MAIZE FORAGE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial (Remarks)
39H85) Soil: Si												
USA Campbell MN, 2005, (Croplan 212RR2) Soil: CL	SC ^a	1	0.13	0.094	13	EaFo ECH	45 97	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g	< 0.03 ^g < 0.03 ^g	RAUBP00 8, UB090- 05H
USA Arkansas WI, 2005, (Dekalb DKC 46-28 RR) Soil: SaL	SC ^a	1	0.13	0.075	12	EaFo ECH	43 96	< 0.01 < 0.01	< 0.02 ^g < 0.02 ^g	0.065 0.035	< 0.03 ^{f,g} < 0.03 ^{f,g}	RAUBP00 8, UB096- 05H
Canada Clarksburg, ON, 2006, (Pioneer 39F27) Soil: L	SC ^a	1	0.21	0.11	13	75-85	60	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP01 1, 01-06H
Canada Metz, ON, 2006 (Pioneer 39H86) Soil: L	SC ^a	1	0.21	0.11	12-13	75-85	61	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP01 1, 02-06H
Canada Rockwood, ON, 2006 (Pioneer 38K35) Soil: L	SC ^a	1	0.21	0.11	13	75-85 75-85 75-85 75-85	48 54 61 67	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 ^g < 0.02 ^g < 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g < 0.03 ^g < 0.03 ^g	< 0.03 ^g < 0.03 ^g < 0.03 ^g < 0.03 ^g	RAUBP01 1, 03-06D
Canada Breslau, ON, 2006, (Pioneer 39F28) Soil: SaL	SC ^a	1	0.21	0.11	13	75-85	61	< 0.01	< 0.02 ^g	0.036	< 0.03 ^g	RAUBP01 1, 04-06H
Canada Greenfield, ON, 2006, (Pioneer 39F28) Soil: SaL	SC ^a	1	0.21	0.11	13	75-85	61	< 0.01	< 0.02 ^g	0.042	< 0.03 ^g	RAUBP01 1, 05-06H
Canada Woodstock, ON, 2006, (NK N29G7) Soil: L	SC ^a	1	0.22	0.11	13	75-85	60	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP01 1, 06-06H
Canada Port Burwell, ON, 2006, (Pioneer 38A24) Soil: SaL	SC ^a	1	0.21	0.11	13	75-85	61	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP01 1, 07-06H
Canada Paris, ON, 2006 (Dekalb 4057)	SC ^a	1	0.21	0.11	12-13	75-85	62	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP01 1, 10-06H

MAIZE FORAGE Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	total mg/kg eq	Study Trial (Remarks)
Soil: SaL												
Canada Springford, ON, 2006 (DKC42-70) Soil: SaL	SC ^a	1	0.22	0.11	12-13	75-85	61	< 0.01	< 0.02 ^g	0.061	< 0.03 ^g	RAUBP01 1, 11-06H
Canada Branchton, ON, 2006 (Hybrid Corn 38-B84) Soil: SiL	SC ^a	1	0.22	0.11	12-13	75-85 75-85 75-85 75-85	48 53 60 67	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 ^g < 0.02 ^g < 0.02 ^g < 0.02 ^g	< 0.03 ^g < 0.03 ^g 0.035 0.034	< 0.03 ^g < 0.03 ^g < 0.03 ^g < 0.03 ^g	RAUBP01 1, 12-06D
Canada Pike River, QC, 2006, (ZP172) Soil: L	SC ^a	1	0.23	0.11	13	75-85	61	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP01 1, 08-06H
Canada St-Pie-de-Bagot, QC, 2006, (ZP172) Soil: LSa	SC ^a	1	0.21	0.10	13	75-85	60	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP01 1, 09-06H
Canada St-Marc-sur-Richelieu, QC, 2006, (Pioneer RR38P09) Soil: CL	SC ^a	1	0.21	0.12	13	75-85	64	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP01 1, 13-06H
Canada Acton Vale, QC, 2006, (NK N16-N7) Soil: Sa	SC ^a	1	0.22	0.13	13	75-85	63	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP01 1, 14-06H
Canada Ste-Madeleine, QC, 2006, (Mycogen 2P172) Soil: SaL	SC ^a	1	0.21	0.12	13	75-85	61	< 0.01	< 0.02 ^g	< 0.03 ^g	< 0.03 ^g	RAUBP01 1, 15-06H

Soil: C = Clay, L= loam, Si = silt; Sa= sand; CL = clay loam; CSa = clay sand, CSi= clay silt; LSa = loamy sand; SiC = silty clay; SaCL=sandy clay loam; SiCL = silty clay loam, SiL = silty loam; SaC = sandy clay; SaL = sandy loam, SaSi = sandy silt;

GS: EaFo = early forage, Fo = forage, LaMi = late milk; EaDo = early dough, Do = dough; LaDo= late dough; EaDe= early dent; De = dent;; ECH = earliest commercial harvest, 75-85 = kernels in the middle of the cob are yellowish white to dough state.

total = sum of IFT and IFT-DKN, expressed as isoxaflutole equivalents. Since the molecular weight of IFT-DKN is identical to the molecular weight of the parent compound (MW 359.3), no correction for molecular weight is necessary.

^a SC formulation contained 20.4% w/w isoxaflutole and 20.3% w/w cyprosulfamide (safener); or 240 g/L each

^b SC formulation contained 225 g/L isoxaflutole, 150 g/L cyprosulfamide (safener) and 90 g/L thienicarbazone-methyl

^c A first spray application was performed with an SC formulation (containing 240 g/L isoxaflutole and 240 g/L cyprosulfamide (safener)) at the pre-emergence stage followed by a second application with an SC formulation (containing 225 g/L thienicarbazone-methyl and 225 g/L cyprosulfamide (safener)) at growth stage BBCH 18. Days after last treatment (DAT) are related to the isoxaflutole treatment (i.e. days after the first treatment).

^d Trials UB088-05HA and UB091-05HA were repeated in 2006 in order to collect early forage samples at DAT = 45.

Trial UB080-05DA was repeated in 2006 due to improper application timing in the original trial.

^e Sample sizes were less than the required minimum of 1 kg (in accordance with FAO manual 2009): 0.1–0.8 kg at DAT = 0 in report RA-2587/05, RA-2510/06 and RA-2588/05. Samples are considered not representative and trials cannot be selected for STMR or HR derivation, if according to cGAP.

^f Individual results for IFT and IFT-DKN not considered reliable, since samples were stored for longer than 12 months.

Maize fodder

Supervised trials on maize were conducted in Spain, Italy, Greece, Portugal, Germany, France, Netherlands and the United Kingdom in 2005 and 2006 and in USA and Canada in 1998, 2005 and 2006 [Zimmer and Wieland, 2007, M-282674-01-1, report RA-2587/05; Wolters and Erler, 2007b, M-284423-01-1, report RA-2510/06; Wolters, 2007b, M-285014-01-1, report RA-2615/06; Zimmer, 2006, M-281611-01-1, report RA-2588/05; Wolters and Erler, 2007a, M-284416-01-1, report RA-2511/06; Wolters, 2007a, M-285005-01-1, report RA-2616/06; Mickelson, 1999a, M-240663-01-1, report AA98714495; Fischer and Helfrich, 2007, M-285889-01-1, report RAUBP008; Vaughn and Cosgrove, 2007, M-286216-02-1, report RAUBP011]. Small plots of maize (50–1700 m²) were treated as indicated in table 55 using knapsack, tractor/ATV mounted or wheelbarrow sprayers with spray volumes ranging from 90–300 L/ha

Four treatment scenarios were tested in the plots:

- a single bare ground application of isoxaflutole (pre-emergence of the crop)
- a single application of isoxaflutole in combination with the safener cyprosulfamide at BBCH 12–14,
- a single application of isoxaflutole in combination with thien carbazon-methyl and the safener cyprosulfamide at BBCH 13–14.
- a single bare ground application of isoxaflutole in combination with the safener cyprosulfamide (pre-emergence of the crop) followed by a second application with thien carbazon-methyl in combination with the safener cyprosulfamide at BBCH 18.

Field samples of maize fodder (plants after removal cobs/kernels) were taken as sweet corn fodder (BBCH 79) or as field corn fodder (mature, BBCH 85–89). Single field samples were taken in the EU trials, duplicate field samples were taken in the USA trials. All sample sizes were at least 1 kg and at least 12 plants (in accordance with FAO manual 2009), except some Canadian trials (0.8–0.9 kg) as indicated in Table 55. All samples were stored frozen with a maximum storage period of 244 days at -18 °C (EU trials), 185 days at -10 °C (AA987144495) or 546 days at -15 °C (RAUBP008), 147 days at -20 °C (Canadian trials).

In the EU trials, isoxaflutole and its metabolite IFT-DKN and IFT-BA were determined using HPLC-MS-MS method 00985/M001. This method is considered valid in the range 0.01–0.01 mg/kg in maize grains and maize forage, but maize fodder has not been validated. Additional validation results for maize fodder are desirable. Concurrent recoveries in maize fodder were not verified, although recoveries for maize grains, sweet corn and maize forage were within 70–120%. Levels in control samples were < 0.01 mg/kg (LOQ) for each analyte. Average concentrations for duplicate field samples are shown in Table 55.

In the 1998 US trials, isoxaflutole and its metabolite IFT-DKN and IFT-BA were determined using HPLC-MS-MS method CAL#019-03 revision 1. This method is considered valid in the range 0.01–0.10 mg/kg for maize fodder. Individual concurrent recoveries at 0.01, 0.1 and 10 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ). Average concentrations for duplicate field samples are shown in Table 55.

In the 2005 and 2006 Canadian and US trials, isoxaflutole and its metabolites IFT-DKN and IFT-BA were determined using modification C of HPLC-MS-MS method CAL#019-03. This modification is considered valid in the range 0.01–0.2 mg/kg for IFT, 0.02–0.3 mg/kg for IFT-DKN and 0.03–0.3 mg/kg for IFT-BA in maize fodder. Average concurrent recoveries at 0.01, 0.05 and 0.2 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.01 mg/kg (reported LOQ). Average concentrations for duplicate field samples are shown in Table 55. Because

of validation results, the LOQs were increased to 0.02 mg/kg for IFT-DKN and 0.03 mg/kg for IFT-BA (indicated by note ^h).

Note: Storage stability studies on straw showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 15 months. Storage stability studies on various commodities showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage and IFT-DKN is stable for at least 12 months but converts to IFT-BA within 23 months of storage. Since maize fodder has been stored for longer than 3 months, part of the IFT may have degraded to IFT-DKN. Except for trials in report RAUBP008, maize fodder has been stored for less than 12 months and these results are considered reliable. Samples from report RAUBP008 have been stored for longer than 12 months and part of the IFT-DKN may have degraded to IFT-BA. However, in those trials where IFT, IFT-DKN and IFT-BA are all below LOQ, any degradation remains unnoticed and these results are considered reliable. In a few trials where IFT-BA was found to be above LOQ and where the storage period exceeded 12 months, individual results for IFT and IFT-DKN are not considered reliable. These are indicated by note ^g.

Table 55 Isoxaflutole related residues after pre- or post-emergent treatment in maize fodder (plant without cobs, or cobs)

MAIZE FODDER Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT- BA mg/kg	total mg/kg eq	Study Trial
Germany Monheim (Nordrhein- Westfalen) 2005, (Romario) Soil: SaL	SC ^a	1	0.10	0.034	13	<u>79</u> 85 89 cob 89	78 111 127 cob 127	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.03 0.03 0.03 0.03 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	RA-2587/05; R 2005 0623/6
Germany Monheim (Nordrhein- Westfalen) 2006, (Romario), Soil: SaSi	SC ^b	1	0.099	0.033	13	<u>79</u>	77	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.02 0.02 0.02 0.02 0.02	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	RA-2510/06 R 2006 0795/4
Germany Euskirchen - Kessenich (Nordrhein- Westfalen) (Egrin FAO 220), Soil: SiC	SC ^a	1	0.10	0.034	13	<u>79</u> 85 89 cob 89	90 112 128 cob 128	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.04 0.03 0.02 0.02 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	RA-2587/05 R 2005 0961/8
Germany Leverkusen (Nordrhein- Westfalen), 2006 (Bunguy); Soil: SaL	SC ^c	1 ^c	0.10	0.034	05	79	91	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	RA-2615/06 R 2006 0801/2
Germany Werl (NordrheinWestfalen), 2006, (Delitop); Soil: SiL	SC ^c	1 ^c	0.10	0.034	06	79	116	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.01 0.01 0.01 0.01 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	RA-2615/06 R 2006 0802/0
United Kingdom Cambridge (Cambridgeshire), 2005, (RK210), Soil: SaL	SC ^a	1	0.10	0.034	13	<u>79</u> 85 89 cob 89	103 124 148 cob 148	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.02 0.02 0.02 0.02 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	RA-2587/05 R 2005 0959/6
United Kingdom Cambridge (Cambridgeshire)	SC ^b	1	0.099	0.033	14	79	93	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.04 0.04 0.04 0.04 0.04	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	RA-2510/06 R 2006 0796/2

MAIZE FODDER Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT- BA mg/kg	total mg/kg eq	Study Trial
2006, (Nexxos); Soil: SaL												
United Kingdom, EYE (Suffolk) 2006, (Algans); Soil: SiL	SC ^c	1 ^c	0.10	0.034	07	79 85	101 124	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	RA-2615/06 R 2006 0800/4
Netherlands Zwaagdijk-Oost (Noord-Holland) 2005, (Rosalie), Soil: C	SC ^a	1	0.10	0.034	13	79 85 89 cob 89	116 128 143 cob 143	< 0.01 < 0.01 < 0.01 cob < 0.01	< 0.01 < 0.01 < 0.01 cob < 0.01	< 0.01 < 0.01 < 0.01 cob < 0.01	<u>< 0.02</u> < 0.02 < 0.02 cob < 0.02	RA-2587/05 R 2005 0962/6
N-France Saint Symphorien d'Anelles (Bourgogne) 2005, (Surtep), Soil: S	SC ^a	1	0.10	0.034	14	79 85 89 cob 89	71 83 127 cob 127	< 0.01 < 0.01 < 0.01 cob < 0.01	< 0.01 < 0.01 < 0.01 cob < 0.01	0.04 0.04 0.04 cob < 0.01	< 0.02 < 0.02 < 0.02 cob < 0.02	RA-2587/05 R 2005 0958/8
N-France Chaussy (Ile-de- France) 2006, (Moncada), Soil: CSa	SC ^b	1	0.099	0.033	13	79	96	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	RA-2510/06 R 2006 0073/9
	SC ^c	1 ^c	0.10	0.034	01	79	120	< 0.01	< 0.01	< 0.01	< 0.02	RA-2615/06 R 2006 0627/3
N-France Chambourg sur indre (Centre) 2006, (Anasta); Soil: CSi	SC ^c	1 ^c	0.10	0.034	00	79	112	< 0.01	< 0.01	< 0.01	< 0.02	RA-2615/06 R 2006 0799/7
S-France Savenes (Midi- Pyrenees), 2005, (PR33A46); Soil: CL	SC ^a	1	0.10	0.034	13	79 85 89 cob 89	83 106 148 cob 148	< 0.01 < 0.01 < 0.01 cob < 0.01	< 0.01 < 0.01 < 0.01 cob < 0.01	0.03 0.03 0.02 cob < 0.01	<u>< 0.02</u> < 0.02 < 0.02 cob < 0.02	RA-2588/05 R 2005 0624/4
S-France Vouille (Poitou- Charentes) 2006, (dkc 4845) Soil: SiC	SC ^b	1	0.099	0.033	13	79	98	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	RA-2511/06 R 2006 0074/7
S-France Beauzelle (Midi- Pyrenees) 2006, (Ferry) Soil: SaSi	SC ^c	1 ^c	0.10	0.034	06	79	105	< 0.01	< 0.01	0.04	< 0.02	RA-2616/06 R 2006 0628/1
S-France Laudun (Languedoc- Roussillon) 2006, (Cecilia) Soil: CL	SC ^c	1 ^c	0.10	0.034	01	79	91	< 0.01	< 0.01	< 0.01	< 0.02	RA-2616/06 R 2006 0803/9
Spain Vila-sacra (Cataluña)	SC ^a	1	0.10	0.034	13	79 85	84 98	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	<u>< 0.02</u> < 0.02	RA-2588/05 R 2005

MAIZE FODDER Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT- BA mg/kg	total mg/kg eq	Study Trial
2005, (DKc6575); Soil: SaL						89 cob 89	141 cob 141	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	< 0.02 < 0.02	0963/4
Spain Vila-sacra (Cataluña), 2006, (PR33P67) Soil: SaL	SC ^b	1	0.099	0.033	14	79	67	< 0.01	< 0.01	< 0.01	< 0.02	RA-2511/06 R 2006 0798/9
	SC ^c	1 ^c	0.10	0.034	07	79	89	< 0.01	< 0.01	< 0.01	< 0.02	RA-2616/06 R 2006 0804/7
Spain Alginet (Comunidad Valenciana) 2006, (Constanza) Soil: SiC	SC ^c	1 ^c	0.10	0.034	00	79	78	< 0.01	< 0.01	< 0.01	< 0.02	RA-2616/06 R 2006 0806/3
Italy San Carlo (FE) Emilia-Romagna 2005, (DK 440); Soil: SaC	SC ^a	1	0.10	0.034	13	<u>79</u> 85 89 cob89	79 93 128 cob 128	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	<u>< 0.02</u> < 0.02 < 0.02 < 0.02	RA-2588/05 R 2005 0964/2
Italy San Carlo (FE), Emilia-Romagna 2006, (PR34N43) Soil: SaC	SC ^b	1	0.099	0.033	13	<u>79</u>	75	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	RA-2511/06 R 2006 0797/0
	SC ^c	1 ^c	0.10	0.034	01	79	100	< 0.01	< 0.01	< 0.01	< 0.02	RA-2616/06 R 2006 0805/5
Greece Chalastra (Macedonia) 2005, (Decalp 743); Soil: L	SC ^a	1	0.10	0.034	13	<u>79</u> 85 89 cob 89	77 105 137 cob 137	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 0.01 < 0.01	<u>< 0.02</u> < 0.02 < 0.02 < 0.02	RA-2588/05 R 2005 0965/0
Portugal Golegã (Ribatejo e Oeste) 2005, (PRN 43); Soil: SiL	SC ^a	1	0.10	0.034	13	<u>79</u> 85 89 cob 89	80 100 133 cob 133	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	0.01 0.02 0.03 < 0.01	<u>< 0.02</u> < 0.02 < 0.02 < 0.02	RA-2588/05 R 2005 0966/9
USA Lehigh PA, 1998 (Mycogen 2598) Soil: SiL	WG	1	0.16	0.089	bare soil	Mat	143	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA98714495 14495-01
USA Wilson NC, 1998, (Pioneer 3163) Soil: SaL	WG	1	0.16	0.084	bare soil	Mat	133	< 0.01	< 0.01	0.023	<u>< 0.02</u>	AA98714495 14495-02
USA Greene IA, 1998, (Dekalb DK 561SR) Soil: L	WG	1	0.16	0.089	bare soil	Mat	139	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA98714495 14495-04
USA Percival IA, 2005,	SC ^a	1	0.13	0.10	12	ECH	125	< 0.01	< 0.02 ^h	< 0.03 ^h	<u>< 0.03^h</u>	RAUBP008, UB086-05H

MAIZE FODDER Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT- BA mg/kg	total mg/kg eq	Study Trial
(Sucrossco 2009) Soil: SiL												
USA Jefferson IA, 2005 (DKC63-81) Soil: L	SC ^a	1	0.13	0.10	12	ECH	120	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP008, UB091-05H
USA Shelby MO, 1998, (Novartis NK 6800) Soil: L	WG	1	0.16	0.091	bare soil	Mat	132	< 0.01	< 0.01	< 0.01	< 0.02	AA98714495 14495-05
Soil: SiL	WG	1	0.16	0.090	bare soil	Mat	140	< 0.01	< 0.01	< 0.01	< 0.02	AA98714495 14495-21
USA Stoddard MO, 1998, (Pioneer 3394) Soil: SiL	WG	1	0.16	0.096	bare soil	Mat	115	< 0.01	< 0.01	0.013	< 0.02	AA98714495 14495-10
USA Butler MO, 2005, (Garst 8287 RR) Soil: SiCL	SC ^a	1	0.13	0.098	12	ECH	133	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP008, UB081-05H
USA Clarence MO, 2005, (Pioneer 35P12) Soil: CL	SC ^a	1	0.13	0.094	12	ECH	102	< 0.01	< 0.02 ^h	0.035	< 0.03 ^{g,h}	RAUBP008, UB088-05H
USA Fayette OH, 1998, (SC 1096) Soil: SiCL	WG	1	0.15	0.092	bare soil	Mat	153	< 0.01	< 0.01	< 0.01	< 0.02	AA98714495 14495-06
(SC 1068) Soil: SiL	WG	1	0.16	0.094	bare soil	Dent Dent Mat Mat	124 131 138 145 152	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.013 < 0.01 < 0.01 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	AA98714495 14495-19
USA Marysville OH, 2005, (Shur Grow SG-751) Soil: CL	SC ^a	1	0.13	0.079	12	ECH	108	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP008, UB089-05H
USA New Holland OH, 2005 (Crows 7R321) Soil: L	SC ^a	1	0.13	0.092	12	ECH	147	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP008, UB092-05H
USA Clay SD, 1998, (Dekalb DK 493RR) Soil: L	WG	1	0.16	0.092	bare soil	Mat	143	< 0.01	< 0.01	< 0.01	< 0.02	AA98714495 14495-07
USA Yankton SD, 1998 (Dekalb, DK 493RR) Soil: SiCL	WG	1	0.17	0.094	bare soil	Mat	144	< 0.01	< 0.01	< 0.01	< 0.02	AA98714495 14495-08
USA Grand Forks	WG	1	0.16	0.11	bare soil	Mat	146	< 0.01	< 0.01	< 0.01	< 0.02	AA98714495

MAIZE FODDER Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT- BA mg/kg	total mg/kg eq	Study Trial
ND, 1998, (Mycogen 2110 R3) Soil: SiL												14495-09
USA Steele ND, 1998, (Mycogen 2110 R3) Soil: SiL	WG	1	0.16	0.11	bare soil	Mat	138	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA98714495 14495-16
USA Northwood ND, 2005, (39D81) Soil: L	SC ^a	1	0.13	0.094	12	ECH	132	< 0.01	< 0.02 ^h	< 0.03 ^h	<u>< 0.03^h</u>	RAUBP008, UB093-05H
USA Stark IL, 1998 (Pioneer 3394) Soil: SiL	WG	1	0.16	0.10	bare soil	Mat	142	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA98714495 14495-11
USA Bond IL, 1998, (Pioneer 3394) Soil: SiL	WG	1	0.16	0.12	bare soil	Mat	111	< 0.01	< 0.01	0.022	<u>< 0.02</u>	AA98714495 14495-12
USA Clinton IL, 1998, (Pioneer 33V08) Soil: SiL	WG	1	0.16	0.16	bare soil	R6	134	< 0.01	< 0.01	< 0.01	<u>< 0.02</u>	AA98714495 14495-20
USA Seymour IL, 2005 (Garst 8550) Soil: SiL	SC ^a	1	0.13	0.10	12	ECH	129	< 0.01	< 0.02 ^h	< 0.03 ^h	<u>< 0.03^h</u>	RAUBP008, UB082-05D
USA Monticello IL, 2005 (Pioneer 37H26) Soil: SiL	SC ^a	1	0.13	0.087	12	ECH	102	< 0.01	< 0.02 ^h	0.13	< 0.03 ^{g,h}	RAUBP008, UB083-05H
USA Carlyle IL, 2005 (FS 6455 RR/YGCB) Soil: SiL	SC ^a	1	0.13	0.080	12	ECH	126	< 0.01	< 0.02 ^h	< 0.03 ^h	<u>< 0.03^h</u>	RAUBP008, UB094-05H
USA York NE, 1998, (Northrup King N3030BT) Soil: SiL	WG	1	0.16	0.11	bare soil	Mat	106	< 0.01	< 0.01	0.047	< 0.02	AA98714495 14495-13
	WG	1	0.16	0.11	bare soil	Dent MatMat Mat Mat	103 109 116 123 130	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	<u>< 0.02</u> <u>< 0.02</u> <u>< 0.02</u> <u>< 0.02</u> <u>< 0.02</u>	AA98714495 14495-18
USA Polk NE, 1998, (Northrup King N3030BT) Soil: LSa	WG	1	0.16	0.11	bare soil	Mat	109	< 0.01	< 0.01	0.071	<u>< 0.02</u>	AA98714495 14495-14
USA Springfield	SC ^a	1	0.13	0.10	12	ECH	123	< 0.01	< 0.02 ^h	< 0.03 ^h	<u>< 0.03^h</u>	RAUBP008, UB085-05H

MAIZE FODDER Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT- BA mg/kg	total mg/kg eq	Study Trial
NE, 2005 (NK70T9) Soil: SiL												
USA Stafford KS, 1998, (Pioneer 3737) Soil: LSa	WG	1	0.15	0.14	bare soil	Mat	103	< 0.01	< 0.01	0.089	<u>< 0.02</u>	AA98714495 14495-15
USA Stilwell KS, 2006, (Garst 8478 LL/CB/GT) Soil: SiL	SC ^a	1	0.14	0.10	12	ECH	119	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP008, UB080- 05DA d
USA Clay TX, 1998, (Northrup King 512RR) Soil: Sa	WG	1	0.16	0.12	bare soil	Mat	104	< 0.01	< 0.01	0.022	<u>< 0.02</u>	AA98714495 14495-17
USA East Bernard TX, 2005 (DKC69-71) Soil: SaL	SC ^a	1	0.13	0.094	12	ECH	91	< 0.01	< 0.02 ^h	0.084	< 0.03 ^{g,h}	RAUBP008, UB097-05H
USA Bumpass VA, 2005, (Dekalb) Soil: SaCL	SC ^a	1	0.13	0.098	12	ECH	103	< 0.01	< 0.02 ^h	< 0.03 ^h	<u>< 0.03^h</u>	RAUBP008, UB078-05H
USA Tifton GA, 2005 (Pioneer 31N26) Soil: SaL	SC ^a	1	0.13	0.078	12	ECH	157	< 0.01	< 0.02 ^h	< 0.03 ^h	<u>< 0.03^h</u>	RAUBP008, UB079-05H
USA Gosport IN, 2005, (Pioneer 34D71) Soil: SiL	SC ^a	1	0.13	0.10	12	ECH	136	< 0.01	< 0.02 ^h	< 0.03 ^h	<u>< 0.03^h</u>	RAUBP008, UB084-05H
USA Sheridan IN, 2005, (Golden Harvest RR) Soil: SiL	SC ^a	1	0.13	0.076	12	ECH	127	< 0.01	< 0.02 ^h	< 0.03 ^h	<u>< 0.03^h</u>	RAUBP008, UB095-05H
USA Sabin MN, 2005, (Pioneer 39H85) Soil: Si	SC ^a	1	0.14	0.15	12	ECH	134 e	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP008, UB087-05H
USA Campbell MN, 2005, (Croplan 212RR2) Soil: CL	SC ^a	1	0.13	0.094	13	ECH	114	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP008, UB090-05H
USA Arkansaw WI, 2005, (Dekalb DKC 46-28 RR) Soil: SaL	SC ^a	1	0.13	0.075	12	ECH	135	< 0.01	< 0.02 ^h	< 0.03 ^h	<u>< 0.03^h</u>	RAUBP008, UB096-05H
Canada	SC ^a	1	0.21	0.11	13	—	114	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP011,

MAIZE FODDER Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT- BA mg/kg	total mg/kg eq	Study Trial
Clarksburg, ON, 2006, (Pioneer 39F27) Soil: L												01-06H
Canada Metz, ON, 2006 (Pioneer 39H86) Soil: L	SC ^a	1	0.21	0.11	12-13	—	112	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP011, 02-06H
Canada Rockwood, ON, 2006 (Pioneer 38K35) Soil: L	SC ^a	1	0.21	0.11	13	—	96 103 110 117	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 ^h < 0.02 ^h < 0.02 ^h < 0.02 ^h	< 0.03 ^h < 0.03 ^h < 0.03 ^h < 0.03 ^h	< 0.03 ^h < 0.03 ^h < 0.03 ^h < 0.03 ^h	RAUBP011, 03-06D
Canada Breslau, ON, 2006, (Pioneer 39F28) Soil: SaL	SC ^a	1	0.21	0.11	13	—	110	< 0.01	< 0.02 ^h	0.032	< 0.03 ^h	RAUBP011, 04-06H
Canada Greenfield, ON, 2006, (Pioneer 39F28) Soil: SaL	SC ^a	1	0.21	0.11	13	—	110	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP011, 05-06H f
Canada Woodstock, ON, 2006, (NK N29G7) Soil: L	SC ^a	1	0.22	0.11	13		110	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP011, 06-06H
Canada Port Burwell, ON, 2006, (Pioneer 38A24) Soil: SaL	SC ^a	1	0.21	0.11	13	—	113	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP011, 07-06H
Canada Paris, ON, 2006 (Dekalb 4057) Soil: SaL	SC ^a	1	0.21	0.11	12-13	—	108	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP011, 10-06H
Canada Springford, ON, 2006 (DKC42-70) Soil: SaL	SC ^a	1	0.22	0.11	12-13	—	110	< 0.01	< 0.02 ^h	0.13	< 0.03 ^h	RAUBP011, 11-06H
Canada Branchton, ON, 2006 (Hybrid Corn 38-B84) Soil: SiL	SC ^a	1	0.22	0.11	12-13	—	96 103 110 117	< 0.01 < 0.01 < 0.01 < 0.01	< 0.02 ^h < 0.02 ^h < 0.02 ^h < 0.02 ^h	0.16 0.087 0.070 0.050	< 0.03 ^h < 0.03 ^h < 0.03 ^h < 0.03 ^h	RAUBP011, 12-06D
Canada Pike River, QC, 2006, (ZP172) Soil: L	SC ^a	1	0.23	0.11	13	—	111	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP011, 08-06H
Canada St-Pie-de-Bagot, QC, 2006, (ZP172) Soil: LSa	SC ^a	1	0.21	0.10	13	—	111	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP011, 09-06H f
Canada St-Marc-sur- Richelieu, QC, 2006, (Pioneer RR38P09) Soil: CL	SC ^a	1	0.21	0.12	13	—	111	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP011, 13-06H
Canada	SC ^a	1	0.22	0.13	13	—	110	< 0.01	< 0.02 ^h	< 0.03 ^h	< 0.03 ^h	RAUBP011,

MAIZE FODDER Location, year, (variety)	FL	no	kg ai/ha	kg ai/hL	GS appl	GS harv	DAT	IFT mg/kg	IFT- DKN mg/kg	IFT- BA mg/kg	total mg/kg eq	Study Trial
Acton Vale, QC, 2006, (NK N16-N7) Soil: Sa												14-06H
Canada Ste-Madeleine, QC, 2006, (Mycogen 2P172) Soil: SaL	SC ^a	1	0.21	0.12	13	—	111	< 0.01	< 0.02 ^h	0.080	< 0.03 ^h	RAUBP011, 15-06H

Soil: C = Clay, L= loam, Si = silt; Sa= sand; CL = clay loam; CSa = clay sand, CSi= clay silt; LSa = loamy sand; SiC = silty clay; SaCL=sandy clay loam; SiCL = silty clay loam, SiL = silty loam; SaC = sandy clay; SaL = sandy loam, SaSi = sandy silt;

GS mat = mature; R6 = reproductive stage 6, equivalent to BBCH 89, ECH = earliest commercial harvest

total = sum of IFT and IFT-DKN, expressed as isoxaflutole equivalents. Since the molecular weight of IFT-DKN is identical to the molecular weight of the parent compound (MW 359.3), no correction for molecular weight is necessary.

^a SC formulation contained 20.4% w/w isoxaflutole and 20.3% w/w cyprosulfamide (safener); or 240 g/L each

^b SC formulation contained 225 g/L isoxaflutole, 150 g/L cyprosulfamide (safener) and 90 g/L thiencarbazone-methyl

^c A first spray application was performed with an SC formulation (containing 240 g/L isoxaflutole and 240 g/L cyprosulfamide (safener)) at the pre-emergence stage followed by a second application with an SC formulation (containing 225 g/L thiencarbazone-methyl and 225 g/L cyprosulfamide (safener)) at growth stage BBCH 18. Days after last treatment (DAT) are related to the isoxaflutole treatment (i.e. days after the first treatment).

^d Trial UB080-05D was repeated in 2006 as UB080-05DA due to improper application timing in the original trial.

^e Trial UB087-05H was harvested at DAT = 133 for grain and DAT = 134 for straw. Since grain and straw are derived from the same commodity it is assumed that the straw has been left to dry for 1 day in the field before sampling.

^f Sample sizes were less than the required minimum of 1 kg (in accordance with FAO manual 2009): 0.8 kg. Samples are considered not representative and trials cannot be selected for MRL derivation, if according to cGAP.

^g Individual results for IFT and IFT-DKN are not considered reliable because samples were stored for longer than 12 months.

^h Results reported below 0.02 mg/kg IFT-DKN and below 0.03 mg/kg IFT-BA, were reported as < 0.02 mg/kg IFT-DKN and < 0.03 mg/kg IFT-BA because of validation results.

Miscellaneous forage and fodder crops

Supervised trials were available for sugarcane forage.

Sugar cane forage

Supervised trials on sugarcane were conducted in Australia during the 1996–1998 growing seasons [Davis and Keats, 1999a, M-284383-01-1, Report AK99009; Davis and Keats, 1999b, M-284347-01-1, Report AK99010; Davis and Keats, 1999c, M-284356-01-1, Report AK99011; Davis and Keats, 1999d, M-284369-01-1, Report AK99012; Davis and Keats, 1999f, M-284324-01-1, Report AK99013; Davis and Keats, 1999e, M-284408-01-1, Report AK99017], in Mexico during the 1999 growing season [Gough, 2000, M-238729-01-1, Study 99717930] and in Brazil during the 1998–1999 growing season [Tornisielo, 2000b, M-287041-01-1, report USP BRA98R27-1; Tornisielo, 2000a, M-287038-01-1, report USP BRA98R27-2].

In Australia, small plots of sugar cane (15–40 m²) were treated as indicated in Table 56 using plot boom sprayers or spray bars with spray volumes ranging from 238–265 L/ha. In two parallel plots sugarcanes in the 5–8 leaf stage received a single soil application of isoxaflutole at two different application rates.

Single field samples of whole canes were collected at a harvestable maturity at DAT = 133–209. Samples from each plot were taken from at least 12 separate plants. The top 30 cm of the whole canes were then cut off using secateurs to provide forage (tops). At least 1 kg of sample was supplied from each plot (in accordance with the FAO 2009 manual). All samples were stored frozen for a

maximum storage period of 5 months at -20 °C (AK 99009, AK 99010), 10 months at -20 °C (AK 99011, AK 99012) or 19–20 months at -20 °C (AK 99013, AK 99017).

Samples were analysed using GC-MS-MS modification A of method 00473 (common moiety method), where IFT, IFT-DKN and IFT-BA are converted into RPA 204497 and total residues are expressed as isoxaflutole equivalents. This method is considered valid at 0.01 mg/kg in sugarcane forage. Average concurrent recoveries at 0.01 mg/kg were within 70–120% for each analyte. Levels in control samples were < 0.01 mg/kg (LOQ). Average results of the replicate field samples are reported in Table 56.

Note: Storage stability studies on commodities with high water content showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 20 months. Since sugarcane forage has been stored for 20 months or shorter, all results are considered reliable.

Table 56 Isoxaflutole related residues after pre-harvest soil directed treatment in sugarcane (forage/tops)

SUGAR CANE FORAGE Location, year, (variety)	FL	No	kg ai/ha	kg ai/hL	GS appl	GS harv	DA T	IFT mg/ kg	RPA 202 248 mg/kg	IFT- BA mg/kg	Total mg/kg eq	Study, Trial
Australia Tolga Mareeba, QLD, 1998, (Q 120) Soil: SaCL	WG	1	0.150	0.057	120 cm	CH	166	NA	NA	NA	< 0.01	AK99009
	WG	1	0.225	0.085	120 cm	CH	166	NA	NA	NA	< 0.01	
Australia Atherton, QLD, 1998, (Q 124) Soil: CL	WG	1	0.150	0.057	120 cm	CH	133	NA	NA	NA	< 0.01	AK99010
	WG	1	0.225	0.0856	120 cm	CH	133	NA	NA	NA	< 0.01	
Australia Murwillum bah QLD, 1997/98, (Q 170) Soil: peat	WG	1	0.150	0.058	110 cm, (30 cm TVD)	CH	167	NA	NA	NA	< 0.01	AK99011
	WG	1	0.225	0.086	110 cm, (30 cm TVD)	CH	167	NA	NA	NA	< 0.01	
Australia Rocky Point, QLD, 1997/98 (Q 154) Soil: peat	WG	1	0.150	0.058	100 cm (30 cm TVD)	CH	193	NA	NA	NA	< 0.01	AK99012
	WG	1	0.225	0.086	100 cm (30 cm TVD)	CH	193	NA	NA	NA	< 0.01	
Australia Bundaberg, QLD, 1997 (Q 124) Soil: podzolic	WG	1	0.150	0.059	60 cm TVD	CH	209	NA	NA	NA	< 0.01	AK99013
	WG	1	0.300	0.12	60 cm TVD	CH	209	NA	NA	NA	< 0.01	
Australia	WG	1	0.150	0.063	5–7	CH	206	NA	NA	NA	< 0.01	AK99017

SUGAR CANE FORAGE Location, year, (variety)	FL	No	kg ai/ha	kg ai/hL	GS appl	GS harv	DA T	IFT mg/ kg	RPA 202 248 mg/kg	IFT- BA mg/kg	Total mg/kg eq	Study, Trial
Jardine QLD, 1996 (Q 96) Soil: baratter cracking clay					leaves (25– 30 cm TVD)							
	WG	1	0.300	0.126	5–7 leaves (25– 30 cm TVD)	CH	206	NA	NA	NA	< 0.01	

Soil: C = clay, CL = clay loam, SaCL = sandy clay loam

Total = Total residues of IFT = measured sum of IFT, RPA 20248 and IFT-BA residues, expressed as isoxaflutole equivalents. The total residue is determined via a common moiety method which converts IFT, IFT-DKN and IFT-BA into the derivative RPA 204497

TVD = top visible dewlap

CH = commercial harvest (normal crop maturity, marketable specimens)

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data on the fate of isoxaflutole-derived residues during storage under warehouse conditions are available.

In processing

The Meeting received processing studies on soya beans, maize and sugarcane. The effect of processing on the nature of residues was not investigated since isoxaflutole related residues are generally very low.

The processing factors (residue processed commodity divided by residue RAC) were calculated based on the total isoxaflutole-derived residues (sum of IFT and IFT-DKN, expressed as isoxaflutole). For the calculation of the total isoxaflutole-derived residues any residues < LOQ were considered to be equal to the LOQ. When the total isoxaflutole-derived residues in the raw agricultural commodity were < LOQ no processing factor was derived. When the total isoxaflutole-derived residues in the processed commodity were < LOQ the calculated processing factor is reported with a "less than" (<) symbol.

Soya bean processing

A field trial was conducted in the US in 2009 [Fischer, 2010, M-368662-01-1] to measure the magnitude of isoxaflutole residues in soya bean processed commodities. An SC formulation was applied on glyphosate/HPPD resistant soya bean at an exaggerated rate of 0.525 kg ai/ha. Application spray volumes were 122–124 L/ha and Induce (0.5% v/v), AMS (2% w/w), Interlock (6 oz/A = 0.44 L/ha), and Defoamer (4 oz/100 gal = 31 mL/hL) were used as adjuvants in the tank mix. Applications were made using ground-based equipment. A bulk sample of soya bean seed was collected at DAT = 86 at the normal growth stage for commercial harvest (BBCH 89) from 12 different areas of the plot. Soya bean processing was performed using procedures that simulated commercial practices.

Aspirated grain fractions

The bulk soya bean seed sample (1463.2 lbs = 664 kg) was dried at 110–135 °F (i.e. 43–57 °C) in an oven until the moisture was between 10.0 and 13.0%. The moisture adjusted sample (1400 lbs = 635 kg) was split into two batches for dust generation. Each subsample was placed in a dust generation room containing a holding bin, two bucket conveyors, and a screw conveyor. As the sample travelled in the system for 120 minutes, aspiration removed the light impurities in the sample (grain dust, 0.7 lbs = 0.318 kg). Collected grain dust was classified on a sieve shaker equipped with the following sieves: 2360 micron (8 mesh); 2000 micron (10 mesh); 1180 micron (16 mesh); 850 micron (20 mesh); and 425 micron (40 mesh). After classification, the material through the 2360 micron sieve was recombined to produce the aspirated grain fractions (AGF, 0.172 kg).

Cleaned whole soya bean processing

Following generation of aspirated grain fractions, a representative sample of aspirated soya beans (200.0 lbs = 90.7 kg) was removed and cleaned further by aspiration and screening. Light impurities were separated from the sample using an aspirator. After aspiration, the sample was screened using a cleaner to separate large and small foreign particles (screenings) from the whole soya bean sample. Resulting fractions were cleaned whole soya beans (183.6 lbs = 83.3 kg), light impurities (0.7 lbs = 0.318 kg), small screenings (2.9 lbs = 1.32 kg) and large screenings (12.8 lbs = 5.81 kg).

Soya bean oil processing

A portion of the cleaned whole soya beans (70.0 lbs = 31.8 kg) was fed into a roller mill to crack the hull and liberate the kernel. After hulling, the material was passed through an aspirator to separate soya bean hulls and kernels. Resulting fraction were soya bean hulls (5.9 lbs = 2.68 kg) and soya bean kernels (64.1 lbs = 29.1 kg).

A portion of the soya bean kernels (30.0 lbs = 13.6 kg) was taken for further processing. The moisture content of the kernel material was determined and adjusted up to 13.5%. Moisture adjusted kernel was allowed to temper for a minimum of twelve hours prior to further processing. Moisture adjusted kernel material was heated to 160–175 °F (i.e. 71–79 °C) in a mixer and flaked in a flaking roll with a gap setting of 0.008–0.013 " (i.e. 0.20–0.33 mm). Flakes were extruded in a continuous processor, where they were turned into collets by direct steam injection and compression. Collets exited the processor at 200–250 °F (i.e. 93–121 °C). After extrusion, the collets were dried in the oven at 150–180 °F (i.e. 66–82 °C) for 30–40 minutes. Collets were placed in separate stainless steel batch extractors and submerged in 120–140 °F (i.e. 49–60 °C) hexane (solvent). After 30 minutes, the miscella (crude oil and hexane) was drained and fresh hexane was added to repeat the cycle two more times. Final two washes were for 15 minutes each. Extracted collets were desolventized in a paddle mixer by heating to 210–220 °F (i.e. 99–104 °C) and removing from the mixer. Resulting fractions were miscella (2.815 kg) and soya bean meal (21.4 lbs = 9.71 kg).

A portion of the miscella (2.0 kg) was passed through a laboratory vacuum evaporator unit to separate the crude oil and hexane. Crude oil was heated to 195–205 °F (i.e. 91–96 °C) for hexane removal and filtered. Percent free fatty acid (FFA) was determined for the crude oil. Based on the FFA, a weighed amount of crude oil and 14° Baume NaOH was placed in a water bath at 68–75 °F (i.e. 20–24 °C) and mixed for 90 minutes at high RPM, and then for 20 minutes at low RPM and 145–153 °F (i.e. 63–67 °C). Neutralized oil was then centrifuged. Refined oil was decanted and filtered. Resulting fractions were: alkali refined oil (1.85 kg) and soapstock. Soapstock was discarded.

A portion of the alkali refined oil (1.2 kg) was heated to 104–122 °F (i.e. 40–50 °C), activated bleaching earth added (1.0% by weight of oil), and placed under vacuum. Temperature was increased to 185–212 °F (i.e. 85–100 °C), and held for 10 to 15 minutes. After reducing the temperature, the bleached oil was filtered. Resulting fractions were bleached oil (1.149 kg) and spent bleaching earth.

A portion of the bleached oil (1.0 kg) was steam bathed for 28–32 minutes under vacuum and temperature held between 428–446 °F (i.e. 220–230 °C). During the cooling period a 0.5% citric acid

solution was added (1 mL per 100 grams of oil deodorized). Resulting fractions was deodorised oil (RBD oil, 0.986 kg) and deodoriser distillates.

Soymilk processing

A portion of the cleaned whole soya beans (0.70 kg) was washed and soaked in water (3.5 kg) for at least 12 hours. A portion of the soaked beans (1.67 kg) were ground and filtered to remove solids and the soymilk was cooked at 195–205 °F (i.e. 91–96 °C) for 9–11 minutes. Resulting fractions were soymilk (2.873 kg) and okara (soy pulp) (0.703 kg).

Samples of soya bean seed (RAC) were stored frozen (below 0 °C) with a maximum storage period of 153 days (5 months) until analysis. Samples of soya bean seed (RAC) were stored frozen (below 0 °C) for 193 days before being processed. Samples of processed commodities were stored frozen at -15 °C or lower with a maximum storage period of 11 days.

The soya bean seed (RAC) samples and resultant soya bean processed commodities (soya bean meal, soya bean hulls, soya bean oil, soymilk, and soya bean aspirated grain fractions) were analysed in triplicate to determine isoxaflutole and IFT-DKN by modification A of HPLC-MS-MS method IS-004-P10-01. This method is considered valid in the range 0.01–0.1 mg/kg in dry soya bean seed, soya bean meal, soya bean hulls, soya bean oil, soymilk and 0.01–0.5 mg/kg in soya bean aspirated grain fractions. Average concurrent recoveries for mixtures of IFT and IFT-DKN each at 0.01–0.1 mg/kg for soya bean seed, soya bean meal, soya bean hulls, soya bean oil, soymilk or 0.01–0.5 mg/kg for soya bean aspirated grain fractions were within 70–120% for each analyte. Levels in control samples were < 0.003 mg/kg (0.3 LOQ) for each analyte. Average concentrations of IFT, IFT-DKN (n=3 for replicate analytical portions) and corresponding processing factors are indicated in Table 57. The percent dry matter determination on soya bean seed, meal, hulls, and aspirated grain fractions was 89%, 96%, 89%, and 90%, respectively.

Note: Storage stability studies on various commodities showed that total residues (sum of IFT, IFT-DKN and IFT-BA) were stable for at least 11–20 months. Storage stability studies on various commodities showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage and IFT-DKN is stable for at least 16 months in commodities with high oil content and 6 months in all other commodities but converts to IFT-BA within 23 months of storage. Since processed soya bean commodities have been stored for less than 3 months, individual results of IFT and IFT-DKN are considered reliable. Since dry soya beans have been stored for longer than 6 months, part of the IFT may have degraded to IFT-DKN. Since dry soya beans have been stored for less than 16 months, levels of IFT-DKN are not further degraded to IFT-BA and can be considered reliable. If the residue definition includes both IFT and IFT-DKN, processing factors are considered reliable.

Table 57 Processing data on soya beans

Location, Year, (Variety)	Application details	Portion analysed	DAT	IFT mg/kg	IFT-DKN mg/kg	IFT-BA mg/kg	Total mg/kg	PF	Study Trial No
Springfield USA, 2009 (Stine FG72)	1 × 0.525 kg ai/ha at BBCH 60 SC formulation broadcast foliar spray	soya bean seed	86	< 0.01	0.042	NA	0.052	–	RAISP005 IS001-09PA
		soya bean meal	86	< 0.01	0.051	NA	0.061	1.2	
		soya bean hulls	86	< 0.01	0.031	NA	0.041	0.79	
		soya bean RBD oil	86	< 0.01	< 0.01	NA	< 0.02	< 0.4	
		soy milk	86	< 0.01	< 0.01	NA	< 0.02	< 0.4	
		soya bean aspirated grain fractions	86	0.066	0.246	NA	0.312	6.0	

PF is based on total residue (sum of IFT and IFT-DKN and expressed as IFT)

Maize processing

A processing study on maize using wet and dry milling was performed [Mickelson, 1999b, M-240664-01-1]. Since the residues in the raw agricultural commodity (maize grains) and the processed

commodities (grits, flour, meal, starch, refined) were below the LOQ (0.01 mg/kg) in all samples, processing factors could not be derived and therefore the study was not summarized.

Sugarcane processing

Six processing studies on sugarcane were performed to get juice and bagasse [Davis and Keats, 1999a/b/c/d/e/f, M-284383-01-1, M-284347-01-1, M-284356-01-1, M-284369-01-1, M-284408-01-1, M-284324-01-1]. Since the residues in the raw agricultural commodity (raw canes) and the processed commodities (juice, bagasse) were < LOQ (0.01 mg/kg) in all samples, processing factors could not be derived and therefore the study was not summarized.

Residues in the edible portion of food commodities

No data submitted.

RESIDUES IN ANIMAL COMMODITIES

Direct animal treatments

Not relevant for the present use pattern.

Farm animal feeding studies

The Meeting received information on feeding studies in dairy cows and laying hens.

Study 1

A cow feeding study was conducted in the USA in 1995 in order to determine the transfer of isoxaflutole related residues from cattle feed into milk, muscle, fat, liver and kidney [Tew, 1995a, M-192311-01-1]. The study was conducted with 14 Holstein lactating cows of 1058–1709 lbs = 480–775 kg body weight (3 to 6-years old), which were distributed in four groups. Group I was the control group and contained two animals. Groups II, III and IV contained four cows per group. The cows were orally dosed once a day in the morning following milking. Cows in group II, III and IV were dosed for 42 days using gelatine capsules fortified with the appropriate amount of isoxaflutole. Group I animals received a placebo containing cellulose powder. Individual daily doses were calculated and adjusted on a weekly basis, based on the group average feed intake from the previous week (16.1–20.2 kg dry matter per cow). Animals in Group II, III and IV were treated with isoxaflutole at actual dose levels of 4.7, 14.4, and 45.5 mg/kg dw feed, respectively, corresponding to 1×, 3×, and 10× dose groups. Equivalent mg/kg bw concentrations were not stated. Cows were milked twice each day. Pooled milk samples for analysis were collected on days 0 (24 hr before first dosing), 1, 4, 8, 11, 15, 18, 22, 25, 27, 31, 33, 36, 39 and 41. For each of these study days, the PM milk samples were refrigerated overnight and combined with the following morning's AM milk sample to get a pooled (500 g) sample in proportion with AM and PM milk production. Test animals were slaughtered within 7.5 hours after receiving their final dose. Samples of muscle (2 kg composite of thigh and loin), fat (1 kg composite of perirenal and omental), liver (1 kg composite from distal portion of each lobe) and kidney (both) were taken from each animal. The samples were stored at –15 °C or lower for 23–66 days for milk and 83–88 days for tissues.

Single milk samples were analysed for IFT, IFT-DKN, RPA 205834 and IFT-BA using HPLC-UV method RPAC #44882 (= RPA #45532 milk part). The method is considered valid in the range 0.02–2.0 mg/kg IFT, IFT-DKN, RPA 205834 and IFT-BA in milk. Average concurrent recoveries (at 0.02, 0.04 or 0.1 mg/kg) ranged between 70–120% for IFT, IFT-DKN, RPA 205834 and IFT-BA. Residue levels in control samples were either not detected or < LOQ.

Single homogenised tissue samples were analysed for IFT, IFT-DKN, RPA 205834 and RPA 207048 using an HPLC-MS-MS method RPAC #44996, version 1.0. The recovery of residues was only tested at 0.25 mg/kg level. Isoxaflutole is partially degraded during extraction to IFT-DKN and

cannot be determined on its own. Average concurrent recoveries for muscle and fat (at 0.05 mg/kg) ranged between 70–120% for each analyte. Average concurrent recoveries for kidney (at 0.05, 0.45, 0.60 mg/kg) and liver (at 0.05, 0.25, and 2.0 mg/kg) ranged between 70–120% for each analyte. It should be noted that separate recovery samples were prepared and analysed: one for IFT and one for the other compounds. Isoxaflutole is unstable and rapidly metabolizes to IFT-DKN. Therefore, IFT recovery was determined by spiking a control sample with IFT only and the recovery was based on the sum of IFT and IFT-DKN from the analysis. Residue levels in control samples were either not detected or < LOQ.

For Group III, residues in milk of IFT, IFT-DKN, RPA 205834 and IFT-BA were always found to be < 0.02 mg/kg each (Day 0, 4, 8, 22, 36, 39 and 41 analysed). Therefore, milk from Group II was not analysed. For Group IV, residues in milk are summarized in Table 58. In all milk samplings from Group IV (45.5 mg/kg in feed), IFT and IFT-BA were always < 0.02 mg/kg. No plateau was reached and therefore all residues from day 1 and onwards were taken into account for average levels in milk. The levels of isoxaflutole and its metabolites in tissues of cows dosed for 42 consecutive days are summarized in Table 59. None of the results presented in these tables have been corrected for recoveries.

Note: Storage stability studies showed that storage periods of 23–66 days for milk and 83–88 days for tissues will not result in breakdown of IFT, IFT-DKN, or RPA 205834. The results for these compounds are considered reliable. However, stability for RPA 207048 is not guaranteed and this compound may have degraded to about 50% of its original level in tissues. Levels of RPA 207048 in bovine liver at or above the LOQ were therefore multiplied by a factor of 2 to correct for possible degradation.

Note: Milk samples were not analysed for RPA 207048, although this metabolite was found at levels of 0.009 mg/kg eq in a 10 ppm metabolism study in goat (15.0% TRR as RPA 207048 and 75% TRR as IFT-DKN + RPA 205834+RPA 207048). To get total residues B (sum of IFT, IFT-DKN, RPA 205834 and RPA 207048), the sum of IFT, IFT-DKN and RPA 205834 was multiplied by a factor 1.25 to correct for this omission.

Conclusion: The cow feeding study conducted with isoxaflutole shows that residues were mainly transferred to kidney and liver and consisted of metabolites IFT-DKN and RPA 205834. In liver and kidney, there was a linear relationship between the level of isoxaflutole administered to the test animals and the resulting total residue levels.

Table 58 Isoxaflutole related residues in milk for Group IV (45.5 mg/kg in feed)

Sampling	Cow	IFT mg/kg	IFT-DKN mg/kg	RPA 205834 mg/kg	IFT-BA mg/kg	Total A mg/kg	Total B mg/kg
Day 0	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	897	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	900	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	902	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
Day 1	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	897	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	900	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	902	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
Day 4	892	< 0.02	0.020	< 0.02	NA	0.040	0.075
	897	< 0.02	0.030	< 0.02		0.050	0.087
	900	< 0.02	0.023	< 0.02		0.043	0.079
	902	< 0.02	0.027	< 0.02		0.047	0.084
Day 8	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	897	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	900	< 0.02	0.020	< 0.02	< 0.02	0.040	0.075
	902	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
Day 11	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	897	< 0.02	0.020	< 0.02	< 0.02	0.040	0.075
	900	< 0.02	0.033	0.028	< 0.02	0.053	0.10
	902	< 0.02	0.022	< 0.02	< 0.02	0.042	0.077
Day 15	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	897	< 0.02	0.022	< 0.02	< 0.02	0.042	0.077

Sampling	Cow	IFT mg/kg	IFT-DKN mg/kg	RPA 205834 mg/kg	IFT-BA mg/kg	Total A mg/kg	Total B mg/kg
	900	< 0.02	0.031	< 0.02	< 0.02	0.051	0.089
	902	< 0.02	0.023	< 0.02	< 0.02	0.043	0.079
Day 18	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	897	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	900	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	902	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
Day 22	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	897	< 0.02	0.034	< 0.02	< 0.02	0.054	0.092
	900	< 0.02	0.028	0.025	< 0.02	0.048	0.091
	902	< 0.02	0.023	< 0.02	< 0.02	0.043	0.079
Day 25	892	< 0.02	0.024	< 0.02	< 0.02	0.044	0.080
	897	< 0.02	0.035	< 0.02	< 0.02	0.055	0.094
	900	< 0.02	0.036	0.027	< 0.02	0.056	0.10
	902	< 0.02	0.023	< 0.02	< 0.02	0.043	0.079
Day 27	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	897	< 0.02	0.032	< 0.02	< 0.02	0.052	0.090
	900	< 0.02	0.024	0.026	< 0.02	0.044	0.087
	902	< 0.02	0.023	< 0.02	< 0.02	0.043	0.079
Day 31	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	897	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	900	< 0.02	< 0.02	0.023	< 0.02	< 0.04	0.079
	902	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
Day 33	892	< 0.02	0.020	< 0.02	< 0.02	0.040	0.075
	897	< 0.02	0.030	< 0.02	< 0.02	0.050	0.087
	900	< 0.02	0.024	0.029	< 0.02	0.044	0.091
	902	< 0.02	0.028	< 0.02	< 0.02	0.048	0.085
Day 36	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	< 0.075
	897	< 0.02	0.027	< 0.02	< 0.02	0.047	0.084
	900	< 0.02	0.022	0.028	< 0.02	0.042	0.087
	902	< 0.02	0.020	< 0.02	< 0.02	0.040	0.075
Day 39	892	< 0.02	0.024	< 0.02	< 0.02	0.044	0.080
	897	< 0.02	0.026	< 0.02	< 0.02	0.046	0.082
	900	< 0.02	0.025	0.021	< 0.02	0.045	0.082
	902	< 0.02	0.024	0.022	< 0.02	0.044	0.082
Day 41	892	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	0.075
	897	< 0.02	0.023	< 0.02	< 0.02	0.043	0.079
	900	< 0.02	< 0.02	0.022	< 0.02	< 0.04	0.077
	902	< 0.02	< 0.02	< 0.02	< 0.02	< 0.04	0.075
Average day 1–41	–	< 0.02	0.023	0.021	< 0.02	0.043	0.080
Highest residue	900-day 25	< 0.02	0.036	0.027	< 0.02	0.056	0.10

Total A = sum of IFT and IFT-DKN, expressed as isoxaflutole. Conversion factor of IFT-DKN to isoxaflutole equivalents is 1.00. Residues below LOQ were calculated as being at the LOQ = 0.02 mg/kg.

Total B = sum of IFT, IFT-DKN, RPA 205834 and RPA 207048, expressed as isoxaflutole. Conversion factor of IFT-DKN to isoxaflutole equivalents is 1.00; conversion factor for RPA 205834 to isoxaflutole equivalents is 359.3/361.3 = 0.994. Residues below LOQ were calculated as being at the LOQ = 0.02 mg/kg. Milk was not analysed for RPA 207048, although this metabolite was found at levels of 0.009 mg/kg eq in a 10 ppm metabolism study in goat (15.0% TRR as RPA 207048 and 75% TRR as IFT-DKN + RPA 205834+RPA 207048). The sum of IFT, IFT-DKN and RPA 205834 was therefore multiplied by a factor 1.25 to correct for this omission.

Table 59 Isoxaflutole related residues in tissues of cows

Matrix	Analyte	Group II 4.7 mg/kg in feed (dry matter)		Group III 14.4 mg/kg in feed (dry matter)		Group IV 45.5 mg/kg in feed (dry matter)	
		Animal I.D.	mg/kg	Animal I.D.	mg/kg	Animal I.D.	mg/kg
Muscle	IFT	NA		NA		892	< 0.05
						897	< 0.05
						900	< 0.05
						902	< 0.05
	IFT-	NA		NA		892	< 0.05

Matrix	Analyte	Group II 4.7 mg/kg in feed (dry matter)		Group III 14.4 mg/kg in feed (dry matter)		Group IV 45.5 mg/kg in feed (dry matter)	
		Animal I.D.	mg/kg	Animal I.D.	mg/kg	Animal I.D.	mg/kg
	DKN					897 900 902	< 0.05 < 0.05 < 0.05
	RPA 205834	NA		NA		892 897 900 902	< 0.05 < 0.05 < 0.05 < 0.05
	RPA 207048	NA		NA		892 897 900 902	< 0.05 < 0.05 < 0.05 < 0.05
	Total A	NA		NA		892 897 900 902 average	< 0.1 < 0.1 < 0.1 < 0.1 < 0.1
	Total B	NA		NA		892 897 900 902 average	< 0.2 < 0.2 < 0.2 < 0.2 < 0.2
Fat	IFT	NA		NA		892 897 900 902	< 0.05 < 0.05 < 0.05 < 0.05
	IFT- DKN	NA		NA		892 897 900 902	< 0.05 < 0.05 < 0.05 < 0.05
	RPA 205834	NA		NA		892 897 900 902	< 0.05 0.064 0.090 0.065
	RPA 207048	NA		NA		892 897 900 902	< 0.05 < 0.05 < 0.05 < 0.05
	Total A	NA		NA		892 897 900 902 average	< 0.1 < 0.1 < 0.1 < 0.1 < 0.1
	Total B	NA		NA		892 897 900 902 average	< 0.2 0.21 0.24 0.21 0.22
Kidney	IFT	NA ^a		NA ^a		892 897 900 902	< 0.05 < 0.05 < 0.05 < 0.05
	IFT- DKN	898 893 895 908	0.114 0.128 0.160 0.166	891 903 905 907	0.296 0.173 0.248 0.223	892 897 900 902	0.503 0.447 0.468 0.495
	RPA 205834	898 893 895 908	< 0.05 < 0.05 < 0.05 < 0.05	891 903 905 907	< 0.05 < 0.05 < 0.05 < 0.05	892 897 900 902	< 0.05 0.060 < 0.05 < 0.05
	RPA 207048	898 893	< 0.05 < 0.05	891 903	< 0.05 < 0.05	892 897	< 0.05 < 0.05

Matrix	Analyte	Group II 4.7 mg/kg in feed (dry matter)		Group III 14.4 mg/kg in feed (dry matter)		Group IV 45.5 mg/kg in feed (dry matter)	
		Animal I.D.	mg/kg	Animal I.D.	mg/kg	Animal I.D.	mg/kg
		895	< 0.05	905	< 0.05	900	< 0.05
		908	< 0.05	907	< 0.05	902	< 0.05
	Total A	898	0.16	891	0.35	892	0.55
		893	0.18	903	0.22	897	0.50
		895	0.21	905	0.30	900	0.52
		908	0.22	907	0.27	902	0.54
		average	0.19	average	0.28	average	0.53
	Total B	898	0.26	891	0.45	892	0.65
		893	0.28	903	0.32	897	0.61
		895	0.31	905	0.40	900	0.62
		908	0.32	907	0.37	902	0.64
		average	0.29	average	0.38	average	0.63
Liver	IFT	898	< 0.05	891	< 0.05	892	< 0.05
		893	< 0.05	903	< 0.05	897	< 0.05
		895	< 0.05	905	< 0.05	900	< 0.05
		908	< 0.05	907	< 0.05	902	< 0.05
	IFT-DKN	898	0.499	891	0.879	892	1.72
		893	0.534	903	0.475	897	1.84
		895	0.770	905	1.09	900	1.79
		908	0.696	907	0.941	902	1.70
	RPA 205834	898	0.071	891	0.299	892	0.560
		893	0.094	903	0.246	897	0.810
		895	0.082	905	0.231	900	0.750
		908	0.105	907	0.210	902	0.800
	RPA 207048	898	< 0.05	891	< 0.05	892	< 0.05
		893	< 0.05	903	< 0.05	897	< 0.05
		895	< 0.05	905	< 0.05	900	< 0.05
		908	< 0.05	907	< 0.05	902	0.136 ^b
	Total A	898	0.55	891	0.93	892	1.8
		893	0.58	903	0.52	897	1.9
		895	0.82	905	1.1	900	1.8
		908	0.75	907	0.99	902	1.8
		average	0.67	average	0.90	average	1.8
	Total B	898	0.67	891	1.8	892	2.4
		893	0.73	903	0.82	897	2.7
		895	0.95	905	1.4	900	2.6
		908	0.90	907	1.2	902	2.7
		average	0.81	average	1.2	average	2.6

Total A = sum of IFT and IFT-DKN, expressed as isoxaflutole. Conversion factor of IFT-DKN to isoxaflutole equivalents is 1.00. Residues below LOQ were calculated as being at the LOQ = 0.05 mg/kg.

Total B = sum of IFT, IFT-DKN, RPA 205834 and RPA 207048, expressed as isoxaflutole. Conversion factor of IFT-DKN to isoxaflutole equivalents is 1.00; conversion factor for RPA 205834 to isoxaflutole equivalents is 359.3/361.3 = 0.994. Conversion factor of RPA 207048 to isoxaflutole equivalents is 359.3/360.3 = 0.997. Residues below LOQ were calculated as being at the LOQ = 0.05 mg/kg.

^a NA, assumed to be < 0.05 mg/kg for calculation of total residues

^b Original value multiplied by a factor 2 to correct for possible degradation of RPA 207048 during frozen storage.

Study 2

A hen feeding study was conducted in the USA in 1995 in order to determine the transfer of isoxaflutole related residues from poultry feed into eggs, muscle, fat and liver [Tew, 1995b, M-192317-01-1]. The study was conducted with 60 laying hens of 1.1–1.8 kg bodyweight (ca. 76 week old) which were distributed in four groups (15 hens per group). Each group was subdivided into three subgroups (A, B, C) containing five hens each. Hens in Group I served as the control group and received a placebo containing cellulose powder. Hens in Groups II, III and IV were orally dosed once a day for 42 days, after the morning egg collection, using gelatine capsules fortified with the appropriate amount of isoxaflutole. Each group's daily dose was calculated and adjusted weekly based

on the previous week's feed consumption for that group (77.9–103.8 g dry matter per hen). Hens in Group II, III and IV were treated with isoxaflutole at actual dose levels of 0.18, 0.54 and 1.8 mg/kg dw feed, respectively, corresponding to 1×, 3×, and 10× dose groups. Equivalent mg/kg bw concentrations were not stated. Eggs were collected each morning and evening throughout the study and pooled by subgroup. Egg collection for analysis began with the afternoon collection prior to initial dose administration (Study Day 0) and continued until the scheduled animal slaughtering for each animal. Each day's PM egg samples were refrigerated overnight until they were pooled with the AM samples. Test animals were slaughtered within 3 hours after receiving the 42nd (final) dose. Samples of liver (entire), muscle (0.2 kg composite of breast and leg) and skin with adhering fat (0.2 kg) were collected. The samples were stored frozen at -15 °C for a maximum of 83 days for eggs and 64 days for tissues.

Eggs samples were analysed for IFT-DKN only, because preliminary work demonstrated that at high pH (the pH of egg is approx. 9) isoxaflutole degrades rapidly to IFT-DKN. Eggs were analysed using HPLC-UV method #44933. This method is considered valid in the range 0.05–0.25 mg/kg IFT-DKN. Concurrent recoveries for eggs (at 0.05 mg/kg) averaged 92% for IFT-DKN. Residues in control samples were < 0.05 mg/kg.

The tissue samples were analysed for IFT and IFT-DKN using HPLC-MS-MS method RPAC #44996, version 1.0. The recovery of residues was only tested at 0.25 mg/kg level. Concurrent recoveries for tissues (0.05, 0.45, 0.60 or 1.0 mg/kg) ranged between 70–120% for each analyte. It should be noted that separate recovery samples were prepared and analysed: one for IFT and one for IFT-DKN. Isoxaflutole is unstable and rapidly degrades to IFT-DKN. Therefore, IFT recovery was determined by spiking a control sample with IFT only and the recovery was based on the sum of IFT and IFT-DKN from the analysis. Residues in control samples were < 0.05 mg/kg for each analyte.

Egg samples from the Group IV (Days 0, 31, 33, 36, 39 and 41) were analysed for IFT-DKN and no residues (< 0.05 mg/kg) were found. Therefore, no additional egg analyses were performed.

Isoxaflutole related residues in tissues of hens dosed for 42 consecutive days are summarized in Table 60. None of the results presented in these tables have been corrected for recoveries.

Note: Storage stability studies showed that storage periods of 83 days for eggs and 64 days for tissues will not result in breakdown of IFT in tissues or IFT-DKN in eggs or tissues. Results are considered reliable.

Conclusion: The hen feeding study conducted with isoxaflutole shows that residues were mainly transferred to liver. The relationship between IFT-DKN residue levels in liver and the dose level administered is not linear. This may indicate that at the 10× dose level, residue levels have or are beginning to reach saturation.

Table 60 Isoxaflutole related residues in tissues of hens

Matrix	Analyte	Group II 0.18 mg/kg in feed (dry matter)		Group III 0.54 mg/kg in feed (dry matter)		Group IV 1.8 mg/kg mg/kg in feed (dry matter)	
		Subgroups	mg/kg	Subgroups	mg/kg	Subgroups	mg/kg
Muscle	IFT	NA		A	< 0.05	A	< 0.05
				B	< 0.05	B	< 0.05
				C	< 0.05	C	< 0.05
	IFT-DKN	NA		A	< 0.05	A	< 0.05
				B	< 0.05	B	< 0.05
				C	< 0.05	C	< 0.05
	Total A	A	< 0.1	A	< 0.1	A	< 0.1
		B	< 0.1	B	< 0.1	B	< 0.1
		C	< 0.1	C	< 0.1	C	< 0.1
		average	< 0.1	average	< 0.1	average	< 0.1
	Total B	A	< 0.1	A	< 0.1	A	< 0.1
		B	< 0.1	B	< 0.1	B	< 0.1
		C	< 0.1	C	< 0.1	C	< 0.1
		average	< 0.1	average	< 0.1	average	< 0.1
Liver	IFT	NA ^a		A	< 0.05	A	< 0.05

Matrix	Analyte	Group II 0.18 mg/kg in feed (dry matter)		Group III 0.54 mg/kg in feed (dry matter)		Group IV 1.8 mg/kg mg/kg in feed (dry matter)	
		Subgroups	mg/kg	Subgroups	mg/kg	Subgroups	mg/kg
				B	< 0.05	B	< 0.05
				C	< 0.05	C	< 0.05
	IFT-DKN	A	0.133	A	0.327	A	0.438
		B	0.159	B	0.378	B	0.645
		C	0.123	C	0.353	C	0.588
	Total A	A	0.18	A	0.38	A	0.49
		B	0.21	B	0.43	B	0.70
		C	0.17	C	0.40	C	0.64
		average	0.19	average	0.40	average	0.61
	Total B	A	0.18	A	0.38	A	0.49
		B	0.21	B	0.43	B	0.70
		C	0.17	C	0.40	C	0.64
		average	0.19	average	0.40	average	0.61
Skin with adhering fat	IFT	NA ^a		A	< 0.05	A	< 0.05
				B	< 0.05	B	< 0.05
				C	< 0.05	C	< 0.05
	IFT-DKN	NA ^a		A	< 0.05	A	< 0.05
				B	< 0.05	B	< 0.05
				C	< 0.05	C	< 0.05
	Total A	A	< 0.1	A	< 0.1	A	< 0.1
		B	< 0.1	B	< 0.1	B	< 0.1
		C	< 0.1	C	< 0.1	C	< 0.1
		average	< 0.1	average	< 0.1	average	< 0.1
	Total B	A	< 0.2	A	< 0.2	A	< 0.2
		B	< 0.2	B	< 0.2	B	< 0.2
		C	< 0.2	C	< 0.2	C	< 0.2
		average	< 0.2	average	< 0.2	average	< 0.2

Total A = sum of IFT and IFT-DKN, expressed as isoxaflutole. Conversion factor of IFT-DKN to isoxaflutole equivalents is 1.00. Residues below LOQ were calculated as being at the LOQ = 0.05 mg/kg.

Total B = sum of IFT, IFT-DKN, RPA 205834 and RPA 207048, expressed as isoxaflutole. Conversion factor of IFT-DKN to isoxaflutole equivalents is 1.00. Residues below LOQ were calculated as being at the LOQ = 0.05 mg/kg. Hen tissues were not analysed for RPA 205038 and RPA 207048, although these metabolites were found in the laying hen metabolism study in hen muscle and hen fat. The sum of IFT and IFT-DKN was therefore multiplied by a factor 1.75 in skin with adhering fat to correct for this omission. Values were then rounded up to 1 figure if below the LOQ. Results in muscle are not corrected because of low expected RPA 207048 levels. Results for liver do not need a correction.

^a NA, assumed to be < 0.05 mg/kg for calculation of total residues

NATIONAL RESIDUE DEFINITIONS

In the past, the isoxaflutole residue data in plant commodities were generated as the sum of IFT and its metabolites IFT-DKN and IFT-BA using a common-moiety method. Thus, the residue definition for monitoring and dietary risk assessment consisted of the sum of the parent IFT and its metabolites IFT-DKN and IFT-BA, expressed as isoxaflutole. Later on, in the late 1990s the residue data were generated using HPLC-MS-MS methods which allow a separate quantification of isoxaflutole, IFT-DKN and IFT-BA. IFT-BA is a common metabolite for both isoxaflutole and pyrasulfotole (another herbicide). Because, IFT-BA is not considered toxicologically relevant in the EU, Australia, USA and Canada, the residue definition for enforcement has been changed and is now described as the sum of the parent IFT and its metabolite IFT-DKN, expressed as isoxaflutole.

EU

The EU the residue definition for MRL setting and dietary risk assessment for plant and animal commodities is identical and is defined as the sum of isoxaflutole and IFT-DKN, expressed as isoxaflutole.

Australia

Since 2013, the residue definition for both plant and animal commodities is: “The sum of isoxaflutole and 2-cyclopropylcarbonyl-3-(2-methylsulfonyl-4-trifluoromethylphenyl)-3-oxopropanenitrile (i.e. IFT-DKN) expressed as isoxaflutole.

Canada

The residue definition for MRL setting is now the sum of isoxaflutole and IFT-DKN, expressed as isoxaflutole equivalents (EMRL2010-21, 24 September 2010)

USA

The residue definition for MRL setting is now the sum of isoxaflutole and IFT-DKN, expressed as isoxaflutole equivalents (Federal Register / Vol.73, No. 240 of 12 December 2008 and Federal Register / Vol.76, No. 235 of 7 December 2011). Residue definitions for dietary risk assessment are summarized in the Memorandum of 10 July 2008.

Matrix	Residues included in Risk Assessment		Residues included in Tolerance Expression
Plants	Maize	Isoxaflutole, RPA 202248	Isoxaflutole, RPA 202248
Rotational Crop	Rotational crops	Isoxaflutole, RPA 202248	Isoxaflutole, RPA 202248
Livestock	Ruminant Poultry	Isoxaflutole, RPA 202248, RPA 205834, RPA 207048	Isoxaflutole, RPA 202248

APPRAISAL

Isoxaflutole was scheduled for the evaluation as a new compound by 2013 JMPR at the Forty-fourth Session of the CCPR (2012). Isoxaflutole is a synthetic compound of the isoxazole group of chemicals used as a herbicide. The mode of action of isoxaflutole is the inhibition of the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD), which inhibits pigment formation, causing bleaching of the developing tissues of the target plants. Isoxaflutole controls a wide spectrum of grasses and broadleaf weeds by bleaching emerging or emerged weeds following herbicide uptake via the root system.

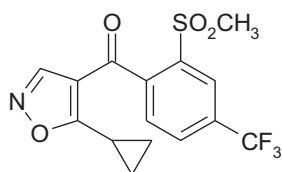
The Meeting received information from the manufacturer on identity, metabolism, storage stability, residue analysis, use patterns, residues resulting from supervised trials on sweet corn, chickpeas, glyphosate/HPPD tolerant soya beans, maize, sugar cane and poppy seed, fates of residue during processing, and livestock feeding studies.

Chemical name:

Isoxaflutole

IUPAC: 5-cyclopropyl-4-(2-methylsulfonyl-4-trifluoromethylbenzoyl)-isoxazole

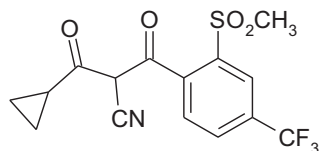
Structural formula:



Metabolites referred to in the appraisal by codes:

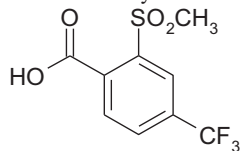
IFT-DKN
RPA 202248

Isoxaflutole diketonitrile;
IUPAC: 3-cyclopropyl-2-[2-methyl-4-(trifluoromethyl)benzoyl]-3-oxopropanenitrile;



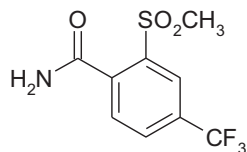
IFT-BA
RPA 203328

Isoxaflutole benzoic acid
IUPAC: 2-mesyloxy-4-(trifluoromethyl)benzoic acid;



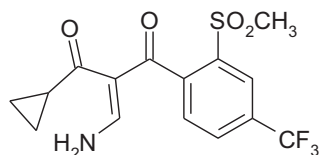
IFT-amide
(no code)

Isoxaflutole benzamide



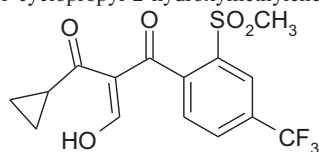
RPA 205834

IUPAC: 2-mesyloxy-4-(trifluoromethyl) benzamide
2-aminomethylene-1-cyclopropyl-3-(2-mesyloxy-4-(trifluoromethyl)phenyl)-propane-1,3-dione



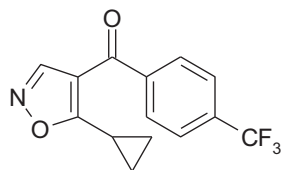
RPA 207048

1-cyclopropyl-2-hydroxymethylene-3-(2-mesyloxy-4-(trifluoromethyl)phenyl)-propane-1,3-dione



RPA 205568

5-cyclopropyl-1,2-oxazol-4-yl- α,α,α -trifluoro-p-tolyl ketone



No code

4-(trifluoromethyl) benzoic acid
 $\text{CH}_3\text{-C}_6\text{H}_4\text{-COOH}$

Animal metabolism

The Meeting received results of animal metabolism studies in lactating goats and laying hens. Experiments were carried out with [U- ^{14}C -phenyl]-isoxaflutole.

Metabolism in laboratory animals was summarized and evaluated by the WHO panel of the JMPR in 2013. Following oral administration in rats, [U- ^{14}C -phenyl]-isoxaflutole was rapidly and extensively metabolized yielding nine radioactive fractions in the urine and up to eleven in the faeces. There were no indications of any metabolites resulting from phase II (conjugation) reaction. Parent isoxaflutole was only found in the faeces of the single 100 mg/kg bw high dose group and to a lesser extent also in the urine of this group (together 5.7–8.2% of the administered dose). The major radioactive component (70–85% of the administered dose) in both urine and faeces, as well as in solvent fractions of liver was IFT-DKN for all three dose groups (single 1 mg/kg bw low dose, single 100 mg/kg bw high dose, repeated 1 mg/kg bw low dose).

The parent compound metabolized to IFT-DKN (major pathway) or RPA 205834 and subsequently further oxidized, respectively to IFT-BA (most polar, 0.6–3.5% of the administered dose) or RPA 207048. A third minor metabolic pathway includes the cleavage of the sulfonic acid group to metabolite RPA 205568 (only 1.3–2.0% of the administered dose).

Four lactating goats, orally treated twice daily for 7 consecutive days with [U-¹⁴C-phenyl]-isoxaflutole, were sacrificed 23 hours after the last dose. The four goats received low, medium (2) and high actual doses equivalent to 1.1 (goat 1), 10 (goat 2), 13 (goat 3) and 64 (goat 4) ppm dry feed (2.0, 20, 20 and 100 mg ai/kg bw, respectively). Total recovered radioactivity amounted to 97, 88, 78, and 73% of the administered dose in goat 1 to 4, respectively. Radioactivity recovered from urine and faeces ranged from 56% of the administered dose in the high dosed goat (27% in urine, 29% in faeces) to 85% in the low dosed goat (54% in urine, 31% in faeces). Radioactivity in edible tissues and organs ranged from 5.3% of the administered dose in the high dose goat to 11% in the low dose goat. Radioactivity in milk ranged from not detectable in the low dose goat to 0.54–0.60% of the administered dose in the medium to high dosed goats. Radioactivity levels in milk peaked at 0.093–0.095 mg/kg eq in goat 3 at day 4–5, 0.059–0.060 mg/kg eq in goat 2 at day 6–7 and 0.33–0.35 mg/kg eq in goat 4 at day 5–7.

Tissues (goat 3) and milk (goat 2) were subjected to further analysis. The total radioactive residues (TRR) were 2.1 mg/kg eq (liver), 0.90 mg/kg eq (kidney), 0.26 mg/kg eq (muscle), 0.069 mg/kg eq (renal fat), 0.062 mg/kg eq (omental fat) and 0.060 mg/kg eq (milk). Radioactive residues could be extracted with methanol (milk), phosphate buffer pH 7.5 (liver, kidney and fat) or phosphate buffer pH 7.5 in combination with protease treatment (muscle). The extracted radioactive residues in the medium dosed goats amounted to 95% TRR for milk, 98% TRR for liver, 94% TRR for kidney, 76% TRR for muscle, 98% TRR for omental fat and 93% TRR for renal fat.

Parent compound was not found in any of the goat commodities. In goat milk, and all tissues the metabolite IFT-DKN was the most abundant component of the residues in the primary extracts (18–86% TRR or 0.015–1.8 mg/kg eq), followed by the metabolite RPA 207048 (9.1–26% TRR or 0.10–0.016 mg/kg eq, respectively). Muscle contained 18.3% TRR free and 23% conjugated IFT-DKN as well as 9.1% free and 3.4% conjugated RPA 207048; (released as free metabolites by protease treatment). Metabolite RPA 205834 (8.1–18% TRR or 0.005–0.011 mg/kg eq) was only found in milk and fat.

Ten laying hens, orally treated once daily for 14 consecutive days with [U-¹⁴C-phenyl]-isoxaflutole, were sacrificed 23 hours after the last dose. Hens were treated at an actual dose rate of 1.1 (group A) or 11 (group B) ppm dry feed. Total recovered radioactivity amounted to 117% and 92% of the administered dose in group A and B, respectively. Radioactivity from the excreta amounted to 112% and 88% of the administered dose for group A and B, respectively. Low levels of radioactivity were recovered in the eggs (0.12–0.15% of the administered dose) or tissues (1.7% in group A and 0.20% in group B).

In the low dose group (A) the concentrations of radioactivity in egg whites were below 0.002 mg/kg eq at all-time points. The levels of radioactivity in egg yolk reached a steady state within 7 days after the first dose (0.022–0.028 mg/kg eq). In the high dose group (B) the concentration of radioactivity in egg whites reached a steady state (0.010–0.015 mg/kg eq) within 4 days. The levels of radioactivity in egg yolk were up to 16 times higher, with a steady state concentration of 0.14–0.15 mg/kg eq within 7 days of exposure.

The highest radioactivity concentrations in edible tissues were found in the liver (0.84 and 0.95 mg/kg eq for dose group A and B, respectively) and kidney (0.055 and 0.16 mg/kg eq, respectively for A and B). Radioactivity in fat and muscle was only observed in the high (B) dose group, being 0.028 and 0.035 mg/kg eq, respectively. Some radioactivity was found in skin (0.008 and 0.068 mg/kg eq in dose group A and B, respectively).

Radioactivity was characterized in tissues and eggs from the high dose group B. Radioactive residues were extracted sequentially by exhaustive extractions using hexane, methanol, acetonitrile, ethyl acetate, acidified methanol and/or water. The primary extractable residues amounted to 97%

TRR for liver, 74% TRR for kidney, 54% TRR for muscle, 93% TRR for fat, 53% TRR for skin, 66% TRR for egg yolk and 50% TRR for egg white. After treatment with protease, another 16%, 29%, 21%, 46% and 20% TRR could be released from kidney, muscle, skin, egg yolk and egg white, respectively. After extensive acid hydrolysis (6 M HCl at 95 °C for 7 days) another 1.9%, 43%, 7.4% and 20% TRR could be released from kidney, muscle, skin and egg white, respectively.

In egg yolk (0.137 mg/kg eq), the major compounds in the primary extracts represented IFT-DKN (26% TRR) and RPA 205834 (28% TRR). Parent, IFT-BA and RPA 207048 were not found. Exhaustive acid hydrolysis released additional IFT-DKN (17% TRR) from egg yolk. Residues in egg white (0.010 mg/kg eq) and the remaining fractions from egg yolk could not be identified, although two fractions in egg yolk contained considerable radioactivity (10% TRR or 0.014 mg/kg eq in the primary extract and 18% TRR or 0.025 mg/kg eq in the acid hydrolysate).

In hen liver (0.953 mg/kg eq), kidney (0.155 mg/kg eq) and skin (0.068 mg/kg eq), the major compound in the primary extracts represented IFT-DKN (93%, 74% and 37% TRR, respectively). Parent, RPA 207048 and RPA 205834 were not found. IFT-BA was found as minor metabolite in liver and kidney (3.5% TRR and 0.65% TRR, respectively). Protease digestion and exhaustive acid hydrolysis released additional IFT-DKN (18% and 7.4% TRR, respectively) from skin.

In hen muscle (0.035 mg/kg eq) the only compound identified in the primary extracts was RPA 207048 (31%TRR). Parent and RPA 205834 were not found. Exhaustive acid hydrolysis released additional RPA 207048 (17% TRR) as well low levels of IFT-DKN and IFT-BA (5.7% and 5.7% TRR, respectively) from muscle.

In hen fat (0.028 mg/kg eq) the major compounds in the primary extracts were IFT-DKN (29% TRR) and RPA 207048 (21% TRR).

The metabolic pathway of isoxaflutole in livestock involves the opening of the oxazole ring and the formation of the diketo-nitrile derivative (IFT-DKN) or the diketo-amine derivative (RPA 205834). Further degradation occurs through deamination to form the diketo-hydroxy derivative (RPA 207048) or through further cleavage to form the benzoic acid derivative (IFT-BA). Further metabolism involves conjugation of IFT-DKN, RPA 207048 and/or IFT-BA with proteins or acid cleavable compounds.

Parent compound was not found in milk, eggs, goat tissues or hen tissues. This may represent rapid metabolism within the animal or it may represent degradation during frozen storage of the samples or degradation during extraction.

The major compounds identified in goat, hen tissues, milk or eggs are: IFT-DKN, RPA 207048, RPA 205834, conjugated IFT-DKN and conjugated RPA 207048. In goats, metabolites IFT-DKN (18–86% TRR) and RPA 207048 (9.1–26% TRR) were found in all tissues and milk. Metabolite RPA 205834 (8.1–18% TRR) was only found in milk and fat. Conjugated forms of IFT-DKN (23% TRR) and RPA 207048 (3.4% TRR) were only found in goat muscle and free metabolites could be released by protease digestion. In hens, metabolite IFT-DKN (26–93% TRR) was found in eggs and all tissues, except muscle. Metabolite RPA 207048 (21–31% TRR) was only found in muscle and fat. Metabolite RPA 205834 was only found in eggs (28% TRR in egg yolk). Conjugated forms of IFT-DKN (5.7–25% TRR) were found in hen muscle, skin and eggs and free metabolites could be released by protease (skin only) or exhaustive acid hydrolysis. Conjugated forms of RPA 207048 were found in hen muscle only and free metabolites could be released by exhaustive acid hydrolysis. IFT-BA was only found as a minor metabolite in hen liver and kidney (3.5% TRR and 0.65% TRR, respectively) and as conjugate form in hen muscle (5.7% TRR).

The metabolic pathway in ruminants and poultry is identical to the metabolic pathway in rats, although in rats an additional minor pathway to RPA 205568 is found, which is not found in ruminant or poultry. All metabolites identified in livestock are also found in rats.

Plant metabolism

The Meeting received plant metabolism studies for isoxaflutole on cereals (maize and wheat), pulses/oilseeds (soya beans and poppy seeds) and sugar cane after a pre-plant, crop pre-emergence, crop post-emergence or crop foliar application.

The metabolism of [U-¹⁴C-phenyl]-isoxaflutole in outdoor grown maize was studied following pre-plant soil incorporated and pre-emergent applications. Maize forage, grains and fodder were harvested at DAT = 41, 122 and 122/138. Residue levels in maize forage, grains and fodder were 0.20–0.044–0.15 mg/kg eq, respectively, for pre-plant incorporated treatment at 0.21 kg ai/ha and 0.23–0.039–0.12 mg/kg eq, respectively, for pre-emergence treatment after 0.23 kg ai/ha. Residue levels were 0.80–0.15–0.66 mg/kg eq for pre-plant incorporated treatment at 0.66 kg ai/ha and 0.49–0.12–0.53 mg/kg eq for pre-emergence treatment at 1.1 kg ai/ha. Residue levels in maize forage, grains and fodder after pre-plant incorporated treatment were higher than those after pre-emergence treatment at the high dose rate; they were similar at the low dose rates. Exaggerated dose rates exhibited greater phytotoxicity. Radioactivity was characterized in maize from the low dose treatments. The major part of the residues could be extracted with an exhaustive range of solvents: hexane/ethyl acetate, acetonitrile, water pH 5.5, and acidified acetonitrile: 91–99% TRR in forage, 83–87% TRR in grains and 75–79% TRR in fodder. Additional residues could be released by cellulase digestion (3.0–6.5% TRR). Parent isoxaflutole was not found in any of the maize commodities. The major compound identified was free IFT-BA (61–89% TRR) in all maize commodities. Minor metabolites represented conjugated IFT-DKN (0.49–0.53% TRR in forage only) and conjugated IFT-BA (1.1–2.7% TRR in forage and fodder).

In a second study, the metabolism of [U-¹⁴C-phenyl]-isoxaflutole was studied in outdoor grown maize following post-emergent application at 0.21 kg ai/ha in the presence of the safener cyprosulfamide. Maize forage and sweet corn were harvested at DAT 75; maize grains and fodder were harvested at DAT = 106. Residue levels in maize forage, sweet corn, maize grains and fodder were 0.13–0.010–0.015–0.10 mg/kg eq, respectively after pre-plant incorporated treatment. These residue levels were similar to those from the pre-plant incorporated and pre-emergence treatments in the previous study. The major part of the residues could be extracted with acetonitrile and water: 93% TRR in forage, 97% TRR in sweet corn, 77% TRR in grains and 88% TRR in fodder. Aqueous fractions underwent base hydrolysis. Parent isoxaflutole was not found in any of the maize commodities. The major compound identified was free IFT-BA (52–63% TRR) in all maize commodities. Other identified metabolites represented free IFT-DKN (4.0–9.8% TRR in sweet corn, fodder and grain) and conjugated IFT-BA (4.1–15% TRR in forage and fodder).

The metabolism of [U-¹⁴C-phenyl]-isoxaflutole in outdoor grown wheat was studied following a post-emergent application at 0.055 kg ai/ha onto immature plants (Zadoks 30). Residue levels in wheat hay, straw and grains harvested at DAT 41, 93 and 93/99 were 0.172–0.107–0.058 mg/kg eq, respectively. The major part of the residues (86–96% TRR) could be extracted with acetonitrile/water. Parent isoxaflutole was only found in wheat hay (6.5% TRR). Major metabolites identified were free IFT-BA (65–96% TRR) in all wheat commodities and free IFT-DKN (9.9–21% TRR in forage and straw only). A small fraction of the metabolites in straw might be attributed to conjugates because 3% TRR was released through acid reflux.

The metabolism of [U-¹⁴C-phenyl]-isoxaflutole in indoor grown glyphosate/HPPD-tolerant soya was studied following a pre-plant application or a foliar application to plants in full bloom (BBCH 65, 57 days after planting) at 0.331 kg ai/ha. Soya bean forage, hay and seeds were harvested at DAT 74/17, 189/132 and 189/132, respectively, for pre-plant/foliar treatment. Residue levels in soya bean forage, hay and seeds were 0.27–0.49–0.15 mg/kg eq after pre-plant treatment and 13–1.8–0.26 mg/kg eq after foliar treatment. The major part of the residues could be extracted with acetonitrile/water: 91–100% TRR in all soya commodities. The foliar application of isoxaflutole had a significant effect on the metabolic profile. Major compounds identified in the pre-plant application were free IFT-amide (53%, 13% and 8% TRR in forage, hay and seeds, respectively), free IFT-BA (66%, 56% and 27% TRR in seeds, hay and forage, respectively) and free IFT-DKN (13–17% TRR in all soya commodities). Major compounds identified in the foliar application were parent (72% and

25% TRR in forage and hay, respectively), free IFT-BA (62%, 38% and 6% TRR in seeds, hay and forage, respectively) and free IFT-DKN (18–24% TRR in all soya commodities). Minor metabolites identified in the foliar application were free IFT-amide (3–8% TRR in hay and seeds).

FG 72 soya beans express the hppdPfW336 gene from *Pseudomonas fluorescens* and the 2mepsps gene derived from maize. These genes confer tolerance to the herbicide isoxaflutole and glyphosate-containing herbicides, respectively, via a modification of the target enzyme which makes the modified enzymes insensitive against the herbicide. Since in the FG72 soya bean variety the tolerance against glyphosate and isoxaflutole is not based on detoxification of the pesticides, the tolerance to glyphosate is not expected to modify the nature and levels of isoxaflutole-derived residues in treated soya beans. Similarly the tolerance to isoxaflutole is not expected to modify the nature and levels of glyphosate residues.

The metabolism of [U-¹⁴C-phenyl]-isoxaflutole in outdoor grown poppies was studied following a pre-emergent application (3 days after planting) at 0.11 kg ai/ha in the presence of the safener cyprosulfamide. Residue levels in poppy seeds, seed bolls and straw harvested at DAT 110 were 0.056, 0.78 and 0.72 mg/kg eq, respectively. Most of the radioactivity (92–98% TRR) could be extracted with acetonitrile/water. Parent isoxaflutole was not found in any of the samples. The major compound identified was free IFT-BA (66–94% TRR) in all commodities. Free IFT-DKN was found in low levels (2.1–3.5% TRR) in seed bolls and straw, but not in poppy seeds.

The metabolism of [U-¹⁴C-phenyl]-isoxaflutole in outdoor grown sugarcane was studied following a pre-emergent application at 0.210 kg ai/ha or a foliar application (47 days after planting) at 0.133 kg ai/ha. Residue levels in sugarcane plants harvested at DAT 81, 95 and 365 were 0.12–0.15–<0.01 mg/kg eq, respectively, for pre-emergence treatment and 0.18, <0.01 and <0.01 mg/kg eq at DAT 40, 95 and 365, respectively, for foliar treatment. Radioactivity in samples with residues >0.01 mg/kg eq was characterized. Most of the radioactivity could be extracted with acetonitrile: 66%, 79% and 84% TRR in DAT 40, 81 and 95 samples, respectively. Additional residues (9.5–24% TRR) could be released by exhaustive extraction procedures including reflux with acetonitrile, reflux with 0.1 M HCl and reflux with 0.1 M ammonia. The major compound identified in immature sugarcane (DAT 40, 81 and 95) was IFT-BA (66–93% TRR). Parent isoxaflutole (11% TRR) and IFT-DKN (2.2% TRR) were only found in the foliar treated crop harvested at DAT 40. Since initial acetonitrile extracts were combined with more exhaustive extracts, it is not clear whether the identified compounds are free or conjugated.

The effect of the safener cyprosulfamide on the metabolism of isoxaflutole was investigated in 3 day old maize seedlings grown in nutrient solution. Roots were exposed for 24 h to [U-¹⁴C-phenyl]-isoxaflutole alone or in combination with cyprosulfamide. After this period the plants were grown in blank nutrient solution for 3 days. Shoots, seeds and roots were collected and extracted with acetonitrile/water. The effect of the safener cyprosulfamide is a clear reduction of leaf damage (bleaching) and a lower ratio of IFT-DKN to IFT-BA in the shoots.

From these data it is concluded that in cereal grains, seeds of pulses/oilseeds, sugarcanes, forage and fodder of cereals or pulses/oilseeds, metabolite IFT-BA is the only residue identified at significant quantities (52–99% TRR). Parent isoxaflutole (6.5–11% TRR) is only found after post-emergent or foliar treatments in wheat hay or immature sugarcane. Minor metabolites identified were IFT-DKN (2.1–21% TRR in sweet corn, maize grain, immature sugarcane, cereal forage, cereal fodder and poppy straw), conjugated IFT-DKN (0.49–0.53% TRR in maize forage) and conjugated IFT-BA (1.1–15% TRR in maize forage and maize fodder).

Glyphosate/HPPD-tolerant soya has a somewhat different metabolic profile. Major compounds identified in the pre-plant application were free IFT-amide (53%, 13% and 8% TRR in forage, hay and seeds, respectively), free IFT-BA (66%, 56% and 27% TRR in seeds, hay and forage, respectively) and free IFT-DKN (13–17% TRR in all soya commodities). Major compounds identified in the foliar application were parent (72% and 25% TRR in forage and hay, respectively), free IFT-BA (62%, 38% and 6% TRR in seeds, hay and forage, respectively) and free IFT-DKN (18–24% TRR in all soya commodities).

The first hydrolytic step in the degradation in plants is the opening of the isoxazole ring to form IFT-DKN. Further hydrolytical cleavage of the carbonyl bridge and loss of the complete isoxazole moiety leads to the corresponding benzoic acid derivative (IFT-BA). In glyphosate/HPPD tolerant soya beans loss of the complete isoxazole moiety may also lead to the benzamide derivative (IFT-amide).

Metabolites IFT-DKN and IFT-BA are also found in rat. Metabolite IFT-amide (8–53% TRR) seems to be formed in glyphosate/HPPD tolerant soya beans only. This metabolite was not found in rat.

Environmental fate in soil

The Meeting received information on aerobic degradation in soil, soil photolysis and fate in rotational crops.

Aerobic degradation of [U-¹⁴C-phenyl]-isoxaflutole under laboratory conditions was studied at 20 °C in various soil types treated at 0.2 mg ai/kg dry soil (0.20 kg ai/ha). The half-life for isoxaflutole was estimated at 7.6–11 h in clay loam and loamy sand soils, 1.3–2.5 days for sandy loam and clay soils and 4 days for loamy soils. The major metabolites identified were IFT-DKN (max. 52–96% TAR during a period 3–10 days after treatment) and IFT-BA (max. 30–90% TAR during a period of 1–12 months after treatment). IFT-BA levels in clay loam soil were very low (max 7.1% TRR at 7 days). Carbon dioxide was formed from day 1 onwards and these levels increased with time (up to 1.8–37% TRR after 1 year). These study results show that parent isoxaflutole is unlikely to be taken up by crops (and weeds) when applied onto bare soil as pre-plant or pre-emergent application.

Using the data from these soil degradation studies, the half-life for the metabolite IFT-DKN were estimated at 20 days in a sandy loam soil, 25 days in a loam soil, 37 days in a clay soil, 41 days in a clay loam soil and 56 days in a loamy sand soil. The half-life for IFT-BA was estimated at 290 days in clay soil and 980 days in a sandy loam soil. These studies show that metabolites IFT-DKN and IFT-BA are available for take-up by the plants for a considerable period after pre-plant or pre-emergence application depending on the soil type.

Soil photolysis of [U-¹⁴C-phenyl]-isoxaflutole was studied in a sandy loam soil, surface treated at 0.645 kg ai/ha and exposed for 31 days to artificial sunlight. The half-life for isoxaflutole (DT₅₀ 23 hours) was similar to the one for the dark control (DT₅₀ 20 hours). The formation of transformation products specific for photolytic processes was insignificant. The study shows that light has no effect on the degradation of isoxaflutole on soil.

Metabolism of [U-¹⁴C-phenyl]-isoxaflutole was investigated in confined rotational crops following pre-plant incorporated soil treatment or pre-emergence treatment. A sandy loam soil was treated at a rate of 0.213 kg ai/ha under outdoor conditions. Rotational crops (radish, lettuce, mustard greens, sorghum and wheat) were sown 34, 123 and 365–375 days after application, representing first, second and third rotation. Total radioactivity for pre-plant incorporated soil treatment ranged from 0.003–0.24 mg/kg eq after first rotation, 0.001–0.030 mg/kg eq after second rotation and 0.001–0.051 mg/kg eq after third rotation. Total radioactivity for pre-emergence application ranged from 0.010–0.126 mg/kg eq after first rotation, < 0.001–0.042 mg/kg eq after second rotation and 0.001–0.030 mg/kg eq after third rotation. Total radioactivity levels above 0.05 mg/kg eq were only found in immature lettuce and sorghum commodities after the first rotation (0.126–0.24 mg/kg eq in sorghum forage, 0.13 mg/kg eq in sorghum fodder, 0.12 mg/kg in sorghum grain, 0.056 mg/kg eq in immature lettuce) and after the third rotation (0.051 mg/kg eq in sorghum forage). Parent isoxaflutole was not found in any of the rotational crops. IFT-BA represented the major compound and was present in the commodities of the first, second and third rotation at levels between < 0.001–0.11 mg/kg eq (6.9–100% TRR). IFT-DKN was only found in radish leaves and sorghum grain at levels up to 0.005 mg/kg eq (0.8–27.3% TRR) in the first rotation. RPA 205834 was detected by HPLC-MS-MS in trace amounts (< 0.001 mg/kg eq) in mature lettuce of the first rotation. A fourth metabolite (U1) was found in the commodities of the first, second and third rotation at levels between < 0.001–0.022 mg/kg eq (10–100% TRR). The polarity of this compound and the molecular weight of 192, as

determined by HPLC-MS-MS, suggests it is a carboxylic acid degradation product of IFT-BA with the structural formula $\text{CF}_3\text{-C}_6\text{H}_4\text{-COOH}$ (4-trifluoromethyl benzoic acid).

In a field rotational crop study at two different locations in the USA isoxaflutole was applied as pre-plant or pre-emergent application to maize at 0.154–0.161 kg ai/ha. Rotational crops (soya beans, sugar beets, radishes, turnips, mustard greens, wheat and sorghum) were sown 29/30, 104, 119/120, 151, 166, 180, 365 days after application, representing various rotations of maize. No residues (< 0.01 mg/kg) of parent isoxaflutole, metabolites IFT-DKN or metabolite IFT-BA were found in any of the crops at any of the rotations. Metabolite 4-trifluoromethyl benzoic acid was not analysed, but since its levels are expected to be in the same order of magnitude as IFT-BA, based on the confined rotational crop study, it is not expected to be found at levels > 0.01 mg/kg.

From these data it is concluded that the first hydrolytic step in the aerobic degradation in soil is the opening of the isoxazole ring to form IFT-DKN, which is responsible for the mode of action. Further hydrolytical cleavage of the carbonyl bridge and loss of the complete isoxazole moiety leads to the corresponding benzoic acid derivative (IFT-BA). Light has no effect on the degradation of isoxaflutole on soil. Isoxaflutole has a very short half-life of 8 h to 4 days in soil, and consequently is not found in rotational crops after pre-plant or crop pre-emergence applications. Metabolites IFT-DKN and IFT-BA have long half-lives of 20–56 and 290–980 days, respectively, in soil and consequently are the main metabolites found in plants after pre-plant, crop pre-emergence or crop post-emergence applications. Since metabolites IFT-DKN and IFT-BA were also found after foliar treatments of sugarcane and glyphosate/HPPD tolerant soya beans, it is likely that metabolites IFT-DKN and IFT-BA are also formed in plants. In confined rotational crop studies, a third metabolite (4-trifluoromethyl benzoic acid ($\text{CF}_3\text{-C}_6\text{H}_4\text{-COOH}$)) was found (10–100% TRR), formed by the loss of the methylsulfonyl moiety of IFT-BA. It is not clear whether this metabolite is formed exclusively in the plants or is formed in the soil and taken up by the plants. Metabolite 4-trifluoromethyl benzoic acid was not found in rat.

Methods of Analysis

The Meeting received description and validation data for analytical methods of isoxaflutole related residues in plant and animal commodities.

For plants, a HPLC-MS-MS method was submitted as enforcement/monitoring method for the individual determination of parent and its metabolite IFT-DKN. Plant material was extracted with acidified methanol/water followed by filtration. The Meeting considers validation sufficient for commodities with high acid content, high water content, high starch content and high oil content. The LOQ was 0.01 mg/kg for each analyte.

Several other HPLC-MS-MS methods were submitted for the determination of parent and its metabolites IFT-DKN and IFT-BA in plant material. In some trials a GC-MS method was used, where residues were extracted with methanol and converted into a common moiety IFT-methylbenzoate by hydrolysis and methylation. Most analytical methods were considered fit for purpose with LOQs ranging from 0.01 mg/kg eq for total residues or 0.01–0.03 mg/kg for individual analytes.

For animal commodities, the existing multi-residue method QuEChERS was submitted as enforcement/monitoring method. The Meeting considers this method valid for the individual determination of parent and its metabolite IFT-DKN in all animal commodities. The LOQ was 0.01 mg/kg for milk, eggs, meat, fat, liver and kidney for each analyte.

Three other analytical methods were submitted for the determination of isoxaflutole related residues in milk, eggs or animal tissues. HPLC-UV methods were used for milk and eggs. A HPLC-MS-MS method was used for tissues. Conjugates of IFT-DKN and RPA 207048 were not analysed by these methods. The reported LOQ of 0.05 mg/kg for each analyte in meat, fat, liver and kidney needs to be substantiated by additional data, since only 1–2 recoveries per matrix were provided at this level. Parent is degraded during extraction and is measured as increased IFT-DKN in these methods. Based on the validation data available, the methods are considered suitable for determination of

parent, IFT-DKN, RPA 205834 and RPA 207048 in milk at 0.02–2.0 mg/kg and 0.05–0.25 mg/kg in eggs and tissues.

Solvents used in the analytical methods were different from the extraction methods used in the metabolism studies. Extraction efficiency, using radiolabelled samples from the metabolism studies, was not verified for any of the analytical methods.

Stability of pesticide residues in stored analytical samples

The Meeting received information on the stability of isoxaflutole, IFT-DKN and IFT-BA in plant commodities or isoxaflutole, IFT-DKN, IFT-BA, RPA 205834 and RPA 207048 in animal commodities in animal commodities stored frozen.

Storage stability studies at -10 °C and -20 °C showed that total isoxaflutole residues (sum of parent, IFT-DKN and IFT-BA, measured as common moiety) were stable for at least 11 months in commodities with high protein content (chickpea seeds), 15 months in commodities with high starch content (maize grains) and straw (maize fodder) and at least 20 months in commodities with high water content (sugar canes).

Storage stability studies showed that isoxaflutole converts to IFT-DKN after 3–6 months of storage at -10 °C in commodities with high acid content (oranges), high water content (sugar canes), high protein content (dry pinto beans) and high oil content (dry soya beans). The metabolite IFT-DKN remained stable for at least 12 months at -10 °C in commodities with high acid content (oranges), high water content (sugar canes), high protein content (dry pinto beans) and at least 16 months in commodities with high oil content (poppy seeds and dry soya bean seeds). Metabolite IFT-DKN converts to IFT-BA within a period of 23 months at -20 °C in commodities with high water content (sorghum forage, lettuce and radish leaves), high starch content (radish roots), high protein content (sorghum grain) and straw (sorghum fodder).

Based on storage stability studies at -20 °C in fortified samples of animal commodities the Meeting noted that isoxaflutole was not stable. Isoxaflutole degraded rapidly to IFT-DKN in eggs and degraded after a period of 85 days in milk and muscle. Parent isoxaflutole also degrades to IFT-DKN by the extraction method used for tissue analysis in the feeding studies. Metabolite IFT-DKN is stable for a period of at least 113–130 days in liver, kidney, muscle, fat, milk and eggs. If metabolite IFT-DKN is included in the residue definition, any degradation from isoxaflutole to IFT-DKN is covered by the total residues measured.

Metabolite RPA 205834 is stable for a period of 113–131 days in kidney, muscle, fat and milk. Metabolite RPA 205834 is stable for a maximum storage period of 94 days in liver and degrades significantly thereafter (36% remaining after 130 days). Storage stability of RPA 205834 was not investigated in eggs.

Metabolite RPA 207048 is not stable in any animal commodity. RPA 207048 degrades rapidly in kidney to a level of about 45% which is maintained from 13–115 days. RPA 207048 is stable for a maximum storage period of 28 days in muscle, 40 days in liver and 84 days in fat and thereafter remains stable at a level of about 50% of the original residue level for a period up to 85–113 days. Storage stability of RPA 207048 has not been investigated in milk and eggs. Precautions need to be taken when analysing this metabolite. Besides storage conditions, also extraction conditions are critical.

In case quantitative levels of total residues based on parent, IFT-DKN, RPA 205834 and RPA 207048 are needed, samples of animal origin need to be analysed within 30 days. And even then, metabolite RPA 207048 will be underestimated in kidney.

Definition of the residue

Parent compound isoxaflutole was not found in milk, eggs or livestock tissues. Metabolites found at significant levels in livestock commodities were: IFT-DKN, conjugated IFT-DKN, RPA 205834, RPA 207048, and conjugated RPA 207048. Metabolite IFT-DKN (18–93% TRR) was found in milk, eggs, all goat and hen tissues, except hen muscle. Conjugated forms of IFT-DKN (5.7–25% TRR)

were only found in goat muscle, hen muscle, hen skin and eggs and the free metabolite could be released by protease digestion (goat muscle and hen skin) and/or exhaustive acid hydrolysis (hen muscle and eggs). Metabolite RPA 205834 (8.1–28% TRR) was found in milk, eggs (yolk) and goat fat in the metabolism studies on goat and hen, but it was also found in milk, bovine liver and bovine kidney in cow feeding study. Metabolite RPA 207048 (9.1–31% TRR) was found in milk, all goat tissues, hen muscle and hen fat. Conjugated forms of RPA 207048 (3.4% TRR) were only found in goat and hen muscle and could be released by protease digestion (goat muscle) or exhaustive acid hydrolysis (hen muscle). Further there seems to be a metabolic shift between RPA 205834 and RPA 207048 between goat and cow. In goat, RPA 207048 seems to be present in all goat tissues and at higher levels than RPA 205834, while in cow RPA 207048 is not found. This metabolic shift might be related to the shorter period between last application and slaughter time for cows (7.5 h) compared to goats (23 h).

Isoxaflutole is easily converted to IFT-DKN. Since no discrimination can be made whether isoxaflutole is metabolized within the animal, or whether it is degraded because of its sensitivity to physical chemical conditions, isoxaflutole needs to be included in the residue definition for enforcement. Any isoxaflutole degraded because of storage or extraction conditions will be measured as IFT-DKN. The sum of IFT and IFT-DKN can therefore serve as the marker residue for enforcement.

The log K_{ow} for isoxaflutole is 2.34. Isoxaflutole and its metabolite IFT-DKN are extracted with acidified aqueous solvents and highest levels of these metabolites are found in the organs kidney and liver. The sum of parent and IFT-DKN is considered not fat soluble.

Apart from isoxaflutole and IFT-DKN other metabolites found at significant levels in livestock commodities were conjugated IFT-DKN, RPA 205834, RPA 207048, and conjugated RPA 207048.

Toxicity of the free IFT-DKN, RPA 205834 and RPA 207048 is considered to be covered by toxicity studies on isoxaflutole since each of the free metabolites was found in the rat high dose group. Free IFT-DKN is the major compound found in rat urine, faeces and solvent fractions of liver, and its toxicity is considered to be similar to that of the parent compound. Since metabolites RPA 205834 and RPA 207048 have similar structures as IFT-DKN and no data are available to conclude that they are of less toxicological significance, each metabolite is considered relevant for the residue definition for dietary risk assessment. Conjugated forms of IFT-DKN and RPA 207048 are considered relevant for dietary exposure, since the free metabolites can be released during the metabolic process in humans. The Meeting proposed to include parent, IFT-DKN, conjugated IFT-DKN, RPA 205834, RPA 207048, and conjugated RPA 207048 in the residue definition for dietary risk assessment of animal commodities.

The analytical method used in the feeding study cannot determine the conjugated forms of IFT-DKN and RPA 207048. For goat muscle, conjugates represent 26.62% TRR and free compounds (IFT-DKN + RPA 205834 + RPA 207048) represent 27.43% TRR. For hen muscle, conjugates represent 22.81% TRR and free compounds represent 31.4% TRR. For hen eggs, conjugates represent 16.8% TRR and free compounds represent 54% TRR. A multiplication factor 2 for goat and hen muscle and 1.3 for hen eggs could be used on the total residues to compensate for this underestimation of dietary exposure.

In primary crops, metabolite IFT-BA is the only residue identified at significant quantities (52–99% TRR). Parent isoxaflutole is only found after post-emergent or foliar treatments in livestock feed commodities: major amounts in glyphosate/HPPD-tolerant soya bean forage and hay (25–72% TRR) and minor amounts (6.5–11% TRR) in wheat hay or immature sugarcane. Minor metabolites identified were IFT-DKN (2.1–21% TRR), conjugated IFT-DKN (0.49–0.53% TRR) and conjugated IFT-BA (1.1–15% TRR). Metabolite IFT-amide (8–53% TRR) seems only to be formed in glyphosate/HPPD tolerant soya bean (seeds, forage, hay).

Metabolite IFT-BA is the major residue and is relevant for consideration in the residue definition for enforcement. However, IFT-BA can also arise in plant commodities as a result of treatment with pyrasulfotole. For this reason IFT-BA cannot be used as a marker for isoxaflutole.

The only other compounds relevant for the residue definition for enforcement are the parent and IFT-DKN. The sum of IFT and IFT-DKN can therefore serve as the marker residue for enforcement.

Apart from isoxaflutole and IFT-DKN, other metabolites found at significant levels in plant commodities are IFT-BA (feed commodities and tolerant soya beans) and IFT-amide (tolerant soya beans only). Assessment of additional toxicological data on IFT-BA demonstrated that metabolite IFT-BA is considerably less toxic than the parent compound. Thus, from a toxicological point of view it is not necessary to include IFT-BA in the residue definition. Metabolite IFT-amide is not found in rat. But since IFT-amide is present at lower levels than IFT-BA in soya bean seeds and because of its structural similarity with IFT-BA, IFT-amide is considered not relevant for the residue definition.

The Meeting recommended the following residue definition for isoxaflutole:

Definition of the residue for compliance with the MRL and for dietary risk assessment for plant commodities: *sum of isoxaflutole and isoxaflutole diketonitrile, expressed as isoxaflutole.*

Definition of the residue for compliance with the MRL for animal commodities: *sum of isoxaflutole and isoxaflutole diketonitrile, expressed as isoxaflutole.*

The Meeting considers the residue not fat soluble.

Definition of the residue for dietary risk assessment for animal commodities: *sum of isoxaflutole, isoxaflutole diketonitrile, RPA 205834 (2-aminomethylene-1-cyclopropyl-3-(2-mesyl-4-trifluoromethylphenyl)-propane-1,3-dione) and RPA 207048 (1-cyclopropyl-2-hydroxymethylene-3-(2-mesyl-4-trifluoromethylphenyl)-propane-1,3-dione), including their conjugates, expressed as isoxaflutole.*

Results of supervised residue trials on crops

The total residue values selected for maximum residue level recommendations and dietary intake are based on the sum of isoxaflutole and IFT-DKN. In case a common moiety method is used for analysis also the IFT-BA metabolite is included. Since the relative molecular weight of IFT-DKN is identical to that of isoxaflutole, no molecular weight conversion is needed. Soil type and the addition of the safener cyprosulfamide affect the residue levels in plant commodities. Residue trials were conducted in a range of soil types, which included those with the longest half-lives.

Since IFT-DKN is included in the residue definition, any degradation from isoxaflutole to IFT-DKN is covered by the total residues measured. Since IFT-BA is not part of the residue definition, any degradation from IFT-DKN to IFT-BA means an underestimation of the original residue present in the sample. Therefore, the Meeting takes only those trials into account, where samples have been stored for a maximum of 16 months (commodities with high oil content) or 12 months (all other commodities). Also trials where IFT-BA is below LOQ can be taken into account, because it indicates that no degradation of IFT or IFT-DKN to IFT-BA occurred.

Sweet corn (corn-on-the-cob)

Field trials involving sweet corn were performed in Spain, Italy, Greece, Portugal, Germany, France, Netherlands and the United Kingdom.

Critical GAP for sweet corn in France is for a single post sowing pre-emergence treatment (BBCH 00–08) at 0.099 kg ai/ha, where the safener cyprosulfamide is added. Trials from Spain, Italy, Germany, France, Netherlands and the UK (0.099–0.10 kg ai/ha, growth stage BBCH 0–06, cyprosulfamide added) matched this GAP. For sweet corn harvested at BBCH 79, total residues were: < 0.02 (10) mg/kg (n=10).

Several trials, where isoxaflutole was applied at the same dose rate at a later growth stage (BBCH 13–14), as well as a metabolism study in sweet corn following a post-emergence treatment at 0.21 kg ai/ha, confirmed the non-residue situation.

The Meeting estimated a maximum residue level of 0.02* mg/kg on sweet corn (corn-on-the-cob). The Meeting estimated an STMR of 0 mg/kg.

Pulses

Field trials involving chick-peas (dry) were performed in Australia.

Critical GAP for chick-peas in Australia is a single post plant crop, pre-emergence application at 0.075 kg ai/ha. In trials from Australia (1×0.075 kg ai/ha post planting pre-emergent) matching this GAP, total residues were: < 0.01 (3) and $< 0.01^a$ mg/kg ($n=4$) with a common moiety method (including IFT-BA). The superscript (a) indicates the addition of an adjuvant. The addition of which did not result in a difference in total residue levels.

An additional four trials at the same locations using a single post-plant crop emergence application at a higher application rate of 0.15 kg ai/ha, as well as a metabolism study in poppy seeds after post-plant crop pre-emergence treatment at 0.11 kg ai/ha, confirmed the no residue situation.

The Meeting estimated a maximum residue level of 0.01* mg/kg on chickpea, dry and an STMR of 0 mg/kg.

Field trials involving glyphosate/HPPD tolerant soya beans (FG72) (dry) were performed in the USA and Canada.

No authorised uses were available for glyphosate/HPPD tolerant soya beans (FG72). The Meeting agreed that no recommendations could be set for soya beans.

Maize

Field trials involving maize were performed in Spain, Italy, Greece, Portugal, Germany, France, Netherlands, the United Kingdom, the USA and Canada.

Critical GAP for maize in France is a single early post emergence treatment up to 3 leaf stage of the crop (BBCH 13) at 0.099 kg ai/ha with the addition of the safener cyprosulfamide. In field trials from Spain, Italy, Greece, Portugal, Germany, France, the Netherlands and the United Kingdom (1×0.10 kg ai/ha, BBCH 13, with cyprosulfamide) matching this GAP, total residues for maize grain harvested at BBCH 89 were: < 0.02 (14) mg/kg.

The GAP for maize in the USA is a single pre-emergence treatment at 0.16 kg ai/ha without the addition of the safener cyprosulfamide or a single early post-emergence treatment at 0.105 kg ai/ha up to 2 leaf-collar growth stage of the crop (GS 12) with the addition of the safener cyprosulfamide. In field trials from the USA (1×0.15 – 0.17 kg ai/ha, pre-emergent, no adjuvants) matching the first GAP, total residues for maize grains harvested at maturity were < 0.02 (17) mg/kg. In field trials from the USA (1×0.13 kg ai/ha, post-emergent GS 12, with safener cyprosulfamide, no adjuvants) matching the second GAP, total residues for maize grains harvested at maturity were < 0.03 (17) mg/kg.

A metabolism study with mature maize grains at 0.21 kg ai/ha after pre plant or post-emergence application did not confirm the non-residue situation.

The Meeting estimated a maximum residue level of 0.02* mg/kg and an STMR of 0.02 mg/kg.

Sugar cane

Supervised residue trials on sugar cane were conducted in Australia, Mexico and Brazil.

There were no authorised uses available for Mexico and Brazil.

Critical GAP for sugar cane in Australia is a single soil directed application at 0.15 kg ai/ha when the sugar cane was at least 0.75 m high and with a PHI of 19 weeks without adjuvant. In field trials from Australia (1× 0.150 kg ai/ha, PHI 133–166 days) matching this GAP, total residues were < 0.01 (2) mg/kg with a common moiety method (including IFT-BA).

Two additional trials, at the same locations, at 1× 0.225 kg ai/ha and a PHI of 133–166 days, two trials in Brazil using two applications at 0.150 kg ai/ha and a PHI of 92–95 days and a metabolism study in mature sugar cane after soil directed application to emerged plants at 0.133 kg ai/ha, confirmed the no residue situation.

The Meeting estimated a maximum residue level of 0.01* mg/kg on sugar cane and an STMR of 0 mg/kg.

Poppy seed

Field trials involving poppy seed were performed in France, Spain, Germany, Netherlands and Hungary.

Critical GAP for poppy seed in Spain is for a single pre-emergence application at 0.060 kg ai/ha without the safener cyprosulfamide. There were no trials matching this GAP.

Critical GAP for poppy seed in Hungary is for a single pre-emergence application at 0.11 kg ai/ha with the safener cyprosulfamide. In field trials from Germany, the Netherlands and Northern France (1× 0.10 kg ai/ha, pre-emergence, with cyprosulfamide) matching this GAP, total residues poppy seeds were < 0.02 (3) mg/kg.

A metabolism study in poppy following post-plant crop pre-emergence treatment at 0.11 kg ai/ha confirmed the no residue situation.

The Meeting estimated a maximum residue level of 0.02* mg/kg in poppy seeds and an STMR of 0 mg/kg.

Legume animal feeds

Field trials involving chick-pea forage were performed in Australia.

Critical GAP for chickpeas in Australia is a single post plant crop pre-emergence application at 0.075 kg ai/ha with a PHI of 6 weeks for use as forage. There were no trials matching this GAP.

Field trials involving chick-pea fodder were performed in Australia.

Critical GAP for chick-peas in Australia is a single post plant crop pre-emergence application at 0.075 kg ai/ha. In trials from Australia (1× 0.075 kg ai/ha, post planting pre-emergent) matching this GAP, total residues were: < 0.01 (3) and < 0.01^a mg/kg (n=4) with a common moiety method (including IFT-BA). The superscript (a) indicates the addition of adjuvant. The addition of which did not result in a difference in total residue levels.

An additional trial at the same location using a single post-plant pre-emergence application at a higher application rate of 0.20 kg ai/ha did not confirm the non-residue situation.

The Meeting estimated a maximum residue level of 0.01* mg/kg on chickpea fodder, a median residue of 0.01 mg/kg and a highest residue of 0.01 mg/kg for livestock dietary burden calculations.

Forage and fodder of cereal grains and grasses

Field trials involving maize forage were performed in Spain, Italy, Greece, Portugal, Germany, France, the Netherlands, the United Kingdom, the USA and Canada.

Critical GAP for maize in France is a single early post-emergence treatment up to 3 leaf stage of the crop (BBCH 13) at 0.099 kg ai/ha with the addition of the safener cyprosulfamide. No PHI is mentioned. High total residues ranging from 1.3–16 mg/kg eq were found immediately after treatment (DAT=0). However, the Meeting considers DAT=0 irrelevant for maize forage harvest and considers

growth stage BBCH 16 or 33 (3 nodes with 6 leaves) the earliest grazing time for maize forage. In field trials from Spain, Italy, Greece, Portugal, Germany, France, Netherlands and the United Kingdom ($1 \times 0.099\text{--}0.10\text{ kg ai/ha}$, BBCH 13, with cyprosulfamide) matching the French GAP, total residues for maize forage harvested at BBCH 19 or 33–35 (DAT 40–41) were < 0.02 (11) and 0.34 mg/kg ($n=12$).

Critical GAP for maize in the USA is a single early post-emergence treatment at 0.105 kg ai/ha up to 2 leaf-collar growth stage of the crop (BBCH 14 or 32) with the addition of the safener cyprosulfamide, with or without the addition of an adjuvant. The pre-harvest interval is 45 days. In field trials from the USA ($1 \times 0.13\text{ kg ai/ha}$, PHI 43–45 days, with safener cyprosulfamide, no adjuvants) matching this GAP, total residues for early maize forage were < 0.03 (15) mg/kg .

The Meeting agreed that the dataset matching French GAP could be used to estimate a median residue of 0.02 mg/kg and a highest residue of 0.34 mg/kg for livestock dietary burden calculations.

Field trials involving maize fodder were performed in Spain, Italy, Greece, Portugal, Germany, France, Netherlands, the United Kingdom, the USA and Canada.

Critical GAP for maize in France is a single early post emergence treatment up to 3 leaf stage of the crop (BBCH 13) at 0.099 kg ai/ha with the addition of the safener cyprosulfamide. In field trials from Spain, Italy, Greece, Portugal, Germany, France, Netherlands and the United Kingdom ($1 \times 0.099\text{--}0.10\text{ kg ai/ha}$, BBCH 13, with cyprosulfamide) matching this GAP total residues for maize fodder harvested at BBCH 79 (sweet corn fodder) were < 0.02 (13) mg/kg .

Critical GAP for maize in the USA is a single pre-emergence treatment at 0.16 kg ai/ha without the addition of the safener cyprosulfamide or a single early post-emergence treatment at 0.105 kg ai/ha up to 2 leaf-collar growth stage of the crop (i.e. GS 12) with the addition of the safener cyprosulfamide, each with or without the addition of an adjuvant. In field trials from the USA ($1 \times 0.15\text{--}0.17\text{ kg ai/ha}$, pre-emergent, no adjuvants) matching the first GAP, total residues for maize fodder harvested at dent stage to maturity were < 0.02 (17) mg/kg . In field trials from the USA ($1 \times 0.13\text{ kg ai/ha}$, post-emergent GS 12, with safener cyprosulfamide, no adjuvants) matching the second GAP, total residues for maize fodder harvested at maturity were < 0.03 (14) mg/kg .

A metabolism study with mature maize fodder at 0.21 kg ai/ha after post-emergence application did not confirm the non-residue situation.

The Meeting estimated a maximum residue level of 0.02^* mg/kg , a median residue of 0.02 mg/kg and a highest residue of 0.02 mg/kg for livestock dietary burden calculations.

Miscellaneous forage and fodder crops

Supervised residue trials on sugar cane tops/fodder were conducted in Australia.

The Meeting estimated a maximum residue level of 0.01^* mg/kg on sugar cane fodder, a median residue of 0 mg/kg and a highest residue of 0.01 mg/kg for livestock dietary burden calculations.

Residues from rotational crops

Total residues above 0.01 mg/kg eq are not expected in rotational crops.

Fate of residues during processing

Processing studies with isoxaflutole were undertaken for soya beans. However, since no MRLs could be set for soya beans, no processing factors are needed.

Residues in animal commodities

The Meeting estimated the dietary burden of isoxaflutole residues on the basis of the livestock diets listed in the FAO manual appendix IX (OECD feedstuff table). Calculation from highest residue and

STMR (some bulk commodities) provides the levels in feed suitable for estimating maximum residue levels, while calculation from STMR values from feed is suitable for estimating STMR values for animal commodities. Commodities used in the dietary burden calculation are maize grains, maize forage, chickpea fodder, maize forage, maize fodder and sugar cane tops.

Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are provided in Annex 6. A mean and maximum dietary burden for livestock, based on isoxaflutole use, is shown in the table below.

Animal dietary burden for isoxaflutole total residues, expressed as ppm of dry matter diet

	US	EU	AU	JP	overall
	max	max	max	max	max
beef cattle	0.146	0.685	0.688	0.017	0.688
dairy cattle	0.394	0.518	0.688	0.436	0.688 ^{a, b}
poultry broiler	0.017	0.016	—	0.016	0.017
poultry layer	0.017	0.102	—	0.018	0.102 ^{c, d}
	mean	mean	mean	mean	mean
beef cattle	0.026	0.045	0.048	0.017	0.048
dairy cattle	0.034	0.038	0.048	0.036	0.048 ^{a, b}
poultry broiler	0.017	0.016	—	0.016	0.017
poultry layer	0.017	0.022	—	0.018	0.022 ^{c, d}

^a Highest mean and maximum dietary burden suitable for maximum residue level and STMR estimates for mammalian meat

^b Highest mean and maximum dietary burden suitable for maximum residue level and STMR estimates for milk

^c Highest mean and maximum dietary burden suitable for maximum residue level and STMR estimates for poultry meat

^d Highest mean and maximum dietary burden suitable for maximum residue level and STMR estimates for eggs

Livestock feeding studies

The Meeting received a feeding study on lactating cows and laying hens. Total residues in animal commodities for enforcement are defined as the sum of isoxaflutole and IFT-DKN, expressed as isoxaflutole equivalents. Total residues for dietary risk assessment are defined as the sum of isoxaflutole, IFT-DKN, RPA 205834 and RPA 207048, and their conjugates, expressed as isoxaflutole equivalents.

Four groups of four lactating Holstein cows were dosed once daily via capsules at levels of 0.0, 4.7, 14.4 and 45.5 ppm parent compound in dry weight feed for 42 consecutive days. Milk was collected throughout the study and tissues were collected on day 42 within 7.5 h after the last dose. Milk was not analysed for RPA 207048, but the level of RPA 207048 has been estimated based on relative levels to the other metabolites in the metabolism study. Residues found at the 4.7 ppm dose level are summarized in the residues section below.

Four groups of 15 laying hens were dosed once daily via capsules at levels of 0.0, 0.18, 0.54 and 1.8 ppm parent compound in dry weight feed for 42 consecutive days. Eggs were collected throughout the study and tissues were collected on day 42 within 3 h after the last dose. Eggs and hen tissues were not analysed for RPA 205834 and RPA 207048, but the level of these metabolites has been estimated based on relative levels to the other metabolites in the metabolism study. Residues found at the 0.18 ppm dose level are summarized in the residue section below.

Residues in animal commodities*Cattle*

For maximum residue level estimation, the highest residue in the tissues and milk were calculated by interpolating the maximum dietary burden (0.688 ppm) between the relevant feeding levels (0–4.7 ppm) from the dairy cow feeding study and using the highest tissue concentrations based on the residue definition for enforcement from individual animals within those feeding groups and using the mean milk concentration from those feeding groups (see table below).

The STMR values for the tissues and milk were calculated by interpolating the mean dietary burden (0.048 ppm) between the relevant feeding levels (0–4.7 ppm) from the dairy cow feeding study and using the mean tissue and milk concentrations based on the residue definition for dietary risk assessment from those feeding groups (see table below).

				Total residues (mg/kg eq) in			
	Feed level (ppm) for milk residues	Total residues (mg/kg eq) in milk	Feed level (ppm) for tissue residues	Muscle	Liver	Kidney	Fat
Maximum residue level—beef or dairy cattle (residue definition for enforcement)							
Feeding study ^a	4.7	NA	4.7	NA	0.82	0.22	NA
Dietary burden and residue estimate	0.688	0	0.688	0	< 0.1	< 0.1	0
STMR—beef or dairy cattle (residue definition for dietary risk assessment)							
Feeding study ^b	4.7	NA	4.7	NA	0.81	0.29	NA
Dietary burden and residue estimate	0.048	0	0.048	0	< 0.2	< 0.2	0

NA not analysed, because highest dose level of 45.5 ppm showed residues below or just above the LOQ

^a highest residues for tissues and mean residues for milk

^b mean residues for tissues and mean residues for milk

The Meeting estimated a maximum residue level for total isoxaflutole residues of 0.01* mg/kg in meat (from mammals other than marine mammals), mammalian fats (except milk fats), milks, and 0.1 mg/kg in mammalian edible offal. The residue in animal commodities is considered not fat soluble.

The Meeting estimated an STMR for total isoxaflutole residues of 0 mg/kg in meat (from mammals other than marine mammals), mammalian fats (except milk fats) and milks, and 0.2 mg/kg in mammalian edible offal.

Poultry

For maximum residue level estimation, the high residue in the tissues and eggs were calculated by interpolating the maximum dietary burden (0.102 ppm) between the relevant feeding levels (0–0.18 ppm) from the laying hen feeding study and using the highest tissue and egg concentrations based on the residue definition for enforcement from individual animals within those feeding groups (see table below).

The STMR values for the tissues and eggs were calculated by interpolating the mean dietary burden (0.022 ppm) between the relevant feeding levels (0–0.18 ppm) from the laying hen feeding study and using the mean tissue and egg concentrations based on the residue definition for dietary risk assessment from those feeding groups (see table below).

				Total residues (mg/kg eq) in			
	Feed level (ppm) for egg residues	Total residues (mg/kg eq) in egg	Feed level (ppm) for tissue residues	Muscle	Liver	Kidney	Fat
Maximum residue level—poultry broilers or layers (residue definition for enforcement)							
Feeding study ^a	0.18	NA	0.18	NA	0.21	–	NA
Dietary burden and residue estimate	0.102	0	0.102	0	0.12	–	0
STMR—poultry broilers or layers (residue definition for dietary risk assessment)							
Feeding study ^b	0.18	NA	0.18	NA	0.19	–	NA
Dietary burden and residue estimate	0.022	0	0.022	0	< 0.1	–	0

NA not analysed, because highest (1.8 ppm) and medium (0.54 ppm) dose level did not show residues

^a highest residues for tissues and eggs

^b mean residues for tissues and eggs

The Meeting estimated a maximum residue level for isoxaflutole total residues of 0.2 mg/kg in poultry edible offal, 0.01* mg/kg in poultry meat, poultry fats and poultry eggs. The residue in animal commodities is considered not fat soluble.

The Meeting estimated an STMR for isoxaflutole total residues of 0.1 mg/kg in poultry edible offal, 0 mg/kg in poultry meat and poultry fats, and eggs.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits.

Definition of the residue for compliance with the MRL and for dietary risk assessment for plant commodities: *sum of isoxaflutole and isoxaflutole diketonitrile, expressed as isoxaflutole.*

Definition of the residue for compliance with the MRL for animal commodities: *sum of isoxaflutole and isoxaflutole diketonitrile, expressed as isoxaflutole.*

The Meeting considers the residue not fat soluble.

Definition of the residue for dietary risk assessment for animal commodities: *sum of isoxaflutole, isoxaflutole diketonitrile, RPA 205834 (2-aminomethylene-1-cyclopropyl-3-(2-mesyl-4-trifluoromethylphenyl)-propane-1,3-dione) and RPA 207048 (1-cyclopropyl-2-hydroxymethylene-3-(2-mesyl-4-trifluoromethylphenyl)-propane-1,3-dione), including their conjugates, expressed as isoxaflutole.*

Summary of recommendations

CCN	Commodity name	MRL mg/kg	STMR mg/kg	HR mg/kg
VO 0447	Sweet corn (corn-on-the-cob)	0.02*	0	—
VD 0524	Chick-pea (dry)	0.01*	0	—
GC 0645	Maize	0.02*	0.02	—
GS 0659	Sugar cane	0.01*	0	—
SO 0698	Poppy seed	0.02*	0	—
AL 0524	Chick-pea fodder	0.01*	0.01 (median residue)	0.01 (highest residue)
AS 0645	Maize fodder	0.02*	0.02	0.02

CCN	Commodity name	MRL mg/kg	STMR mg/kg	HR mg/kg
			(median residue)	(highest residue)
MM 0095	Meat (from mammals other than marine mammals)	0.01*	0	—
MO 0105	Edible offal (Mammalian)	0.1	0.2	—
MF 0100	Mammalian fats (except milk fats)	0.01*	0	—
ML 0106	Milks	0.01*	0	—
PM 0110	Poultry meat	0.01*	0	—
PF 0111	Poultry fats	0.01*	0	—
PO 0111	Poultry, Edible offal of	0.2	0.1	—
PE 0112	Eggs	0.01*	0	—

Feedstuffs

Crop	Feedstuff	Highest Residue	STMR or STMR-P
Corn, field (maize)	forage/silage (forage)	0.34	0.02
Corn, field	stover	0.02	0.02
Corn, sweet (maize)	Forage	0.34	0.02
Corn, sweet	stover	0.02	0.02
Pea (chickpea)	Hay (fodder)	0.01	0.01
Sugar cane	Tops/forage	0.01	0

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDI) of for isoxaflutole was calculated from recommendations for STMRs for raw and processed commodities in combination with consumption data for corresponding food commodities. The results are shown in Annex 3 of the 2013 JMPR Report.

The IEDI of in the 13 GEMS/Food cluster diets, based on the estimated STMRs were in the range 0–1% of the maximum ADI of 0.02 mg/kg bw. The Meeting concluded that the long-term intake of residues of isoxaflutole from uses considered by the Meeting is unlikely to present a public health concern.

Short-term intake

Since no ARfD is considered necessary, no short-term intake assessment is considered necessary. The Meeting concluded that the short-term intake of residues of isoxaflutole from uses considered by the Meeting is unlikely to present a public health concern.

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M-189749-01-1	Guesnet, JL, Jendrzeczak, NH, Maestracci, MP, Ott, M & Vidal, JG	1994	Title: RPA201772—NMR, IR, MS and UV-visible spectra. Source & Testing Facility: Rhone-Poulenc Secteur Agro, Centre de Recherche de la Dargoire, Lyon, France. Date: 10 March 1994 Report No: R&D/CRLD/AN/9415238 studies no 93–184, code R014773. Published: No. Claim for Data protection: Yes.
M-213160-01-1	Guillet, M, Diot, R & Le Gren, I	1995	Title: Isoxaflutole and/or metabolites—Analytical method for the determination of residues in animal products—Method AR 109-95(E) Source & Testing Facility: Rhone-Poulenc Secteur Agro, Centre de Recherche de la Dargoire, Lyon, France. Date: 12 April 1995 Report No: R&D/CRLD/AN/bd/9515587, code C022471. Published: No. Claim for Data protection: Yes. GLP: yes.
M-162883-01-1	Hampton, RE & Pettaway, J	1995a	Title: 14C-RPA201772: Metabolic fate and distribution in corn (<i>Zea mays</i> L.)—(171–4 Nature of residue—Plants). Source: Rhone-Poulenc Ag Company, Research Triangle Park, NC, USA Testing Facility: A&L Great Lakes Laboratories, Fort Wayne, IN, USA. Date: 13 February 1995 Report No: EC-93-293 code R002551 Published: No. Claim for Data protection: Yes GLP: yes.
M-192308-01-1	Hampton, RE & Pettaway, J	1995b	Title: 14C-RPA201772: Accumulation study on confined rotational crops. Source: Rhone-Poulenc Ag Company, Research Triangle Park, NC, USA. Testing Facilities: American Agricultural Services, Inc, Lucama, NC, USA. AGVISE, Inc., Northwood, ND, USA. Date: 28 December 1995 Report No: EC 93-242, code R016766 & 439564; MRID 43904839. Published: No. Claim for Data protection: Yes. GLP: yes.
M-192325-01-1	Hampton, RE	1996	Title: Supplemental report: ¹⁴ C-RPA201772: Accumulation study on confined rotational crops. Source & Testing Facility: Rhone-Poulenc Ag Company, Research Triangle Park, NC, USA. Date: 27 November 1996 Report No: EC 93-242, code R016770; MRID: 43904839. Published: No. Claim for Data protection: Yes. GLP: yes.
M-262714-01-1	Hudson, JR, Vincent, RJ, Wells-Knecht, KJ, Seymour, RJ, Vialaneix, JP & Jones, M.	1996	Title: Method of analysis for the determination of isoxaflutole (RPA201772) and its metabolites (RPA202248, RPA207048, and RPA205834) in animal tissues. Source & Testing Facility: Rhone-Poulenc Ag Company, USA. Date: 29 January 1996 Report No: none. Published: No. Claim for Data protection: Yes. GLP: no.
M-213302-01-1	Kaune, A	2002	Independent Laboratory Validation of the method of analysis for the determination of isoxaflutole (RPA 201772) and its metabolites (RPA 202248 and RPA 205834) in milk, eggs, liver, kidney, muscle and fat tissues—version 2.0. Source & Testing Facility: Bayer CropScience GmbH, Frankfurt am Main, Germany. Date: 13 December 2002 Report No. 02F028, Code C027428. Published: No. Claim for Data protection: Yes. GLP: yes.

Code	Author	Year	Title, Institute & Report reference
M-442915-01-1	Klasmeier, BJ	2012	Title: Stability of residues of isoxaflutole and its metabolite RPA 202248 during frozen storage in several raw agricultural commodities. Source: Bayer Crop Science, Research Triangle Park, NC, USA. Testing Facility: Morse Laboratories, Sacramento, CA, USA. Date: 7 December 2012 Report No: RAISP012. Published: No. Claim for Data protection: Yes. GLP: yes.
M-360799-01-1	Klempner, A	2009	Title: Metabolism of [phenyl-UL- ¹⁴ C] isoxaflutole in poppies. Source & Testing Facility: Bayer CropScience AG, Monheim am Rhein, Germany. Date: 17 December 2009 Report No: MEF-09/499; Study no M1731775-1. Published: No. Claim for Data protection: Yes. GLP: yes.
M-366215-01-1	Klempner, A	2010	Title: Storage stability of isoxaflutole residues in poppy seeds and straw. Source & Testing Facility: Bayer CropScience AG, Monheim am Rhein, Germany. Date: 18 March 2010 Report No: MEF-10/038, Study no M9991930-0. Published: No. Claim for Data protection: Yes. GLP: yes.
M-170844-01-1	Lappin, GJ	1995a	Title: (14C)-RPA201772: Absorption, distribution, metabolism and excretion following repeated oral administration to the laying hen. Source: Rhone-Poulenc Secteur Agro, Sophia Antipolis Cedex, Valbonne, France. Testing Facility: Corning Hazleton (Europe), Harrogate, North Yorkshire, United Kingdom. Date: 30 November 1995 Report No: 198/77-1011, study no 198/77, code R005378. Published: No. Claim for Data protection: Yes. GLP: yes.
M-166744-01-2	Lappin, GJ	1995b	Title: (14C)-RPA201772: Absorption, distribution, metabolism and excretion following repeated oral administration to the dairy goat. Source: Rhone-Poulenc Secteur Agro, Sophia Antipolis, Valbonne, France. Testing Facility: Corning Hazleton (Europe), Harrogate, North Yorkshire, United Kingdom. Date: 27 December 1995 Report No: 198/78-1011, Study no 198/78. Published: No. Claim for Data protection: Yes. GLP: yes.
M-213162-01-1	Le Gren, I	1995a	Title: Isoxaflutole and/or metabolites—Analytical method for the determination of residues in animal products—Complementary report no 1—method AR109-95(E). Source & Testing Facility: Rhone-Poulenc Secteur Agro, Centre de Recherche de la Dargoire, Lyon, France. Date: 19 May 1995 Report No: R&D/CRLD/AN/fb/9515783, code C022472. Published: No. Claim for Data protection: Yes. GLP: yes. Complementary to report R&D/CRLD/AN/bd/9515587 Guillet <i>et al</i> , 1995, M-213160-01-1.
M-262409-01-1	Le Gren, I	1995b	Title: Isoxaflutole: Determination of residues in egg. Source & Testing Facility: Rhone-Poulenc Secteur Agro, Lyon, France. Date: 18 July 1995 Report No: i&D/CRLD/AN/bd/9516020, Doc no 438730. Published: No. Claim for Data protection: Yes. GLP: no.
M-213164-01-1	Le Gren, I	1995c	Title: Isoxaflutole and/or metabolites—Analytical method for the determination of residues in animal products—Complementary report no. 2—method AR109-95(E) Source & Testing Facility: Rhone-Poulenc Secteur Agro, Lyon, France. Date: 20 September 1995 Report No: R&D/CRLD/AN/fb/9516279 code C022473. Published: No. Claim for Data protection: Yes. GLP: yes. Complementary to report R&D/CRLD/AN/bd/9515587. Guillet <i>et al</i> , 1995, M-213160-01-1.
M-166734-01-2	Lopes, A, Russell, DR, Smitley, CA & Oden, KN	1998	Title: Method of analysis for the determination of isoxaflutole (RPA 201772) and its metabolites (RPA 202248 and RPA 205834) in milk, eggs, liver, kidney, muscle and fat tissues—version 2.0. Source & Testing Facility: Rhone Poulenc AG Company, Research Triangle Park, NC, USA. Date: 4 March 1998 Report No: RPAC 45532. Published: No. Claim for Data protection: Yes. GLP: No.
M-192281-01-2	Lowder, JF	1996	Title: Isoxaflutole: Storage stability of residues in dairy cow and poultry matrices. Source & Testing Facility: Rhone-Poulenc Ag Company, Research Triangle Park, USA. Date: 19 November 1996 Report No: EC-96-338, File No. 45178. Published: No. Claim for Data protection: Yes. GLP: yes.
M-432364-01-1	Lynch, A; Keats A	1999a	Title: Isoxaflutole; Formulation—Balance; Pittsworth, QLD—Australia 1999; Residues in chickpea. Source: Rhone-Poulenc Rural, Australia. Testing Facility: A-Quant Laboratories, Brisbane, Australia. Date: 20 December 1999 Report No: AK99054, protocol no 99NST26. Published: No. Claim for Data protection: Yes. GLP: no.
M-432374-01-1	Lynch, A; Keats A	1999b	Title: Isoxaflutole; Formulation—Balance; Biniguy, NSW—Australia 1999; Residues in chickpea. Source: Rhone-Poulenc Rural, Australia. Testing Facility: A-Quant Laboratories, Brisbane, Australia. Date: 22 December 1999 Report No: AK99056, protocol no 99NST26. Published: No. Claim for Data protection: Yes. GLP: no.
M-432434-01-1	Lynch, A & Keats A	2000a	Title: Isoxaflutole; Formulation—Balance; Horsham, VIC—Australia 1999; Residues in chickpea. Source: Aventis CropScience, Australia. Testing Facility: A-Quant Laboratories, Brisbane, Australia. Date: 15 February 2000 Report No: AQ00001, Protocol no 99h011. Published: No. Claim for Data protection: Yes.

Code	Author	Year	Title, Institute & Report reference
M-432441-01-1	Lynch, A & Keats A	2000b	GLP: no. Title: Isoxaflutole; Formulation—Balance; Horsham, VIC—Australia 1999; Residues in chickpea. Source: Aventis CropScience, Australia. Testing Facility: A-Quant Laboratories, Brisbane, Australia. Date: 16 February 2000 Report No: AQ00002, protocol no 99h015. Published: No. Claim for Data protection: Yes. GLP: no.
M-432444-01-1	Lynch, A & Keats A	2000c	Title: Isoxaflutole; Formulation —Balance; Bruce Rock—Australia 1999; Residues in chickpea. Source: Aventis CropScience, Australia. Testing Facility: A-Quant Laboratories, Brisbane, Australia. Date: 16 February 2000 Report No: AQ00003, protocol no 99h010. Published: No. Claim for Data protection: Yes. GLP: no.
M-268739-01-2	Meyer, BN & Ripperger, R	2006	Title: The metabolism of [phenyl-UL- ¹⁴ C]-Isoxaflutole in corn with post-emergence application. Source & Testing Facility: Bayer CropScience, Stilwell, KS, USA. Date: 27 February 2006 Report No: MEUBY003. Published: No. Claim for Data protection: Yes. GLP: yes.
M-240663-01-1	Mickelson, K	1999a	Title: Magnitude of Residue of EXP 31130A in Field Corn. Source: Rhone-Poulenc Ag Company, Research Triangle Park, NC, USA. Testing Facilities: American Agricultural Services, Inc., Cary, NC, USA. Centre Analytical Laboratories, Inc, State College, PA, USA. Date: 5 November 1999 Report No: AA98714495; RPAC file 45979, code B003643; MRID: 45655904. Published: No. Claim for Data protection: Yes. GLP: yes.
M-240664-01-1	Mickelson, K	1999b	Title: Magnitude of Residue of EXP 31130A in/on Processed Fractions of Field Corn. Source: Rhone-Poulenc Ag Company, Research Triangle Park, NC, USA. Testing Facilities: American Agricultural Services, Inc., Cary, NC, USA. Centre Analytical Laboratories, Inc, State College, PA, USA. Texas A&M University, Bryan, TX, USA. Date: 2 December 1999 Report No: AA98715447; code B003644; RPAC file no 45990, MRID: 45655905. Published: No. Claim for Data protection: Yes. GLP: yes.
M-240710-01-1	Mickelson, K	2000	Title: Isoxaflutole: Field Rotational Crop Study Using Balance WDG Herbicide. Source: Aventis CropScience, Research Triangle Park, NC, USA. Testing Facilities: American Agricultural Services, Inc., Cary, NC, USA. Centre Analytical Laboratories Inc, State College, PA, USA. Date: 7 January 2000 Report No: AA97712512, code B003705, File no 45997. Published: No. Claim for Data protection: Yes. GLP: yes.
M-020184-01-1	Nandihalli, UB	1995	Title: EXP 30953B/field corn/magnitude of residue (US93702R): Analytical method for the determination of residue of RPA 201772, RPA 202248, and RPA 203328 in corn forage, silage, grain, and fodder. Bayer CropScience Method No. 00473. Source & Testing Facility: Hazleton Wisconsin Inc., Madison, WI, USA. Date: 3 January 1995 Report No: HWI 6224-215, Study no US93702R. Published: No. Claim for Data protection: Yes. GLP: no.
M-089371-01-1	Nandihalli, UB	1996	Title: Freezer storage stability of RPA 201772 in field corn samples. Source: Rhone-Poulenc Ag Company, Research Triangle Park, NC, USA. Testing Facility: Corning Hazleton, Inc., Madison, WI, USA. Date: 7 November 1996 Report No: CHW 6224-223, code R016771. Published: No. Claim for Data protection: Yes. GLP: yes.
M-368555-01-1	Nguyen, T	2010	Title: The metabolism of [phenyl-UL- ¹⁴ C] isoxaflutole in soya bean with pre-plant and post-emergent application. Source & Testing Facility: Bayer CropScience, Stilwell, KS, USA. Date: 10 May 2010 Report No: MEISP002, MRID: 48108105. Published: No. Claim for Data protection: Yes. GLP: yes.
M-366025-01-1	Noss, G; Reineke, A	2010	Title: Determination of the residues of AE 0001789 and isoxaflutole in/on poppy after spraying of isoxaflutole & cyprosulfamide SC 480 in the field in Hungary.. Source & Testing Facility: Bayer CropScience AG, Monheim, Germany. Date: 25 March 2010 Report No: 09-2022; Lynx-ID: RAUBL007. Published: No. Claim for Data protection: Yes. GLP: yes.
M-282394-02-1	Schoening, R	2007	Title: Analytical method 01021 for the determination of residues of isoxaflutole and its metabolite RPA 202248 in/on plant material by HPLC-MS/MS. Amendment no 1. Source & Testing Facility: Bayer CropScience AG, Monheim, Germany Date: 30 January 2007 Report No: MR-06/167, project ID P682 06 4720. Published: No. Claim for Data protection: Yes. GLP: yes. Amendment no 1 to original report: MR-06/167 dated 9 January 2007.
M-280607-01-1	Schoening, R & Wolters, A	2006	Title: Modification M001 of analytical method 00985 for the determination of residues of isoxaflutole and its metabolites AEB197278-AE0540092 (RPA202248) and AE0317309-AEB197555 (RPA203328) in/on corn plant material by HPLC-MS/MS. Bayer CropScience Method No. 00985/M001. Source & Testing Facility: Bayer CropScience AG, Monheim, Germany. Date: 13 November 2006 Report No: MR-06/038. Project ID: P672064703. Published: No.

Code	Author	Year	Title, Institute & Report reference
M-210791-01-1	Schulte, W	2002	Claim for Data protection: Yes. GLP: yes. Title: Effects of safener AE 0001789 on metabolism of isoxaflutole (IFT) (RPA 201772) in maize. Source & Testing Facility: Aventis CropScience GmbH, Frankfurt am Main, Germany. Date: 16 April 2002 Report No: WS-2002-1; code C021218. Published: No. Claim for Data protection: Yes. GLP: no.
M-192304-01-2	Shaffer, SR	1995	Title: Independent laboratory validation of the Rhone-Poulenc methods entitled, "Method of analysis for the determination of isoxaflutole and its metabolites RPA203328, RPA202248, and RPA205834 in milk" and "Method of determination for isoxaflutole (RPA201772) and its metabolite RPA202248 in/on bovine and poultry tissues", version 2.0. Source: Rhone-Poulenc Ag Company, Research Triangle Park, NC, USA. Testing Facility: Horizon Laboratories, Inc., Columbia, MO, USA. Date: 22 December 1995 Report No: RPAC File #44920.EC-95-323/HL REPORT #10144. Published: No. Claim for Data protection: Yes. GLP: yes.
M-368825-01-1.	Stoughton, SM	2010a	Title: Analytical method for the determination of residues of isoxaflutole (RPA 201772) and its metabolite RPA 202248 in plant matrices using LC/MS/MS. Residue Analytical Method No. IS-004-P10-01. Source & Testing Facility: Bayer CropScience, Stilwell, KS, USA. Date: 18 February 2010 Report No: IS-004-P10-01. Published: No. Claim for Data protection: Yes. GLP: yes.
M-368826-01-1	Stoughton, SM	2010b	Title: Analytical method for the determination of residues of isoxaflutole (RPA 201772) and its metabolite RPA 202248 in plant matrices using LC/MS/MS. Residue Analytical Method No. IS-004-P10-02. Source: Testing Facility: Date: 12 May 2010 Report No: IS-004-P10-02. Published: No. Claim for Data protection: Yes. GLP: yes.
M-368828-01-1	Stoughton, SM	2010c	Title: Validation of Bayer method IS-004-P10-01 analytical method for the determination of residues of isoxaflutole (RPA 201772) and its metabolite RPA 202248 in plant matrices using LC/MS/MS. Source & Testing Facility: Bayer CropScience, Stilwell, KS, USA. Date: 12 May 2010 Report No: RAISP007; MRID: 48108107. Published: No. Claim for Data protection: Yes. GLP: yes.
M-192311-01-1	Tew, EL	1995a	Title: Isoxaflutole: magnitude of residues in milk and tissues of lactating dairy cows. Source & Testing Facility: Rhone-Poulenc Ag Company, Research Triangle Park, NC, USA. Date: 27 December 1995 Report No: US95704R; File No.: 44961 code R016767. Published: No. Claim for Data protection: Yes. GLP: yes.
M-192317-01-1	Tew, EL	1995b	Title: Isoxaflutole: magnitude of residues in tissues and eggs of laying hens. Source & Testing Facility: Rhone-Poulenc Ag Company, Research Triangle Park, NC, USA. Date: 28 December 1995 Report No: RPAC US95705R. File No.: 44981, code R016768. Published: No. Claim for Data protection: Yes. GLP: yes.
M-287038-01-1 and M-411759-02-1 (English translation)	Tornisielo, VL	2000a	Title: Determinação de resíduo de Provence 750 WG (Isoxaflutole) em colmos de cana de açúcar (Assis-SP). Source: Aventis CropScience Brasil Ltda., Sao Paulo, Brazil. Testing Facility: Universidade de Sao Paulo, Centro de Energia Nuclear na Agricultura, Laboratorio de Ecotoxicologica, Piracicaba, Brazil. Date: 10 July 2000 Report No: USP BRA98R27-2; Project no AV01/00. Published: No. Claim for Data protection: Yes. GLP: no. English translation Title: Isoxaflutole; 75 WG; sugar cane; Brazil; BBA.
M-287041-01-1 and M-411752-02-1 (English translation)	Tornisielo, VL	2000b	Title: Determinação de resíduo de Provence 750 WG (Isoxaflutole) em colmos de cana de açúcar (Cosmópolis-SP). Source: Aventis CropScience Brasil Ltda., Sao Paulo, Brazil. Testing Facility: Universidade de Sao Paulo, Centro de Energia Nuclear na Agricultura, Laboratorio de Ecotoxicologica, Piracicaba, Brazil. Date: 10 July 2000 Report No: USP BRA98R27-1; Project no AV02/00. Published: No. Claim for Data protection: Yes. GLP: no. English translation: Title: Isoxaflutole; 75 WG; sugar cane; Brazil; BBA.
M-211498-01-1	Unsworth, RH	1999	Title: (¹⁴ C)-RPA 201772: Metabolism in sugarcane. Source & Testing Facility: Rhone-Poulenc Agriculture Ltd., Ongar, Essex, United Kingdom. Date: 15 September 1999 Report No: 10316, code C026486, RPA document 201746. Published: No. Claim for Data protection: Yes. GLP: yes.
M-211481-01-1	Unsworth, RH & Clarke, DE	2000	Title: (¹⁴ C)-Isoxaflutole: Metabolism in wheat. Source & Testing Facility: Aventis CropScience, Ongar, Essex, United Kingdom. Date: 21 March 2000 Report No: 16862; code C026477, document 202392. Published: No. Claim for Data protection: Yes. GLP: yes.
M-286216-02-1	Vaughn, FC & Cosgrove D	2007	Title: Magnitude of residues in/on corn treated with one application of the herbicide IFT/1789 480 SC with a 110 day phi for grain. Source: Bayer Crops Science, Regina, UK. Testing Facility: ALS Canada Inc, Edmonton, Canada. Date: 2 April 2007 Report No: 07BAY36.REP, code RAUBP011. Published: No. Claim for Data protection: Yes. GLP: yes.
M-286215-	Wickremesinha,	1998a	Title: Method of analysis for the determination of isoxaflutole (RPA 201772) and

Code	Author	Year	Title, Institute & Report reference
01-1	E		its metabolites (RPA 202248 and 203328) in raw agricultural commodities and processed foods (Revision 1). Source: Rhone-Poulenc Agro, Lyon, France. Testing Facility: Centre Analytical Laboratories, Inc., State College, PA, USA. Date: 29 December 1998 Report No: CAL #019-03 (revision 1). Published: No. Claim for Data protection: Yes. GLP: no.
M-240820-01-1	Wickremesinha, E	1998b	Validation of method of analysis for the determination of isoxaflutole (RPA 201772) and its metabolites in raw agricultural commodities and processed foods by LC/MS/MS. Source: Rhone-Poulenc Ag Company (RPAC). Testing Facility: Centre Analytical Laboratories Inc (CAL), State College, PA, USA. Date: 22 October 1998 Report No RPAC EC-98-431, CAL 019-008, code B003824. Published: No. Claim for Data protection: Yes. GLP: no.
M-454397-01-1	Winter O & Amann S	2013	Validation of the BCS-method-01300/M009 (based on QuEChERS) for the determination of residues of isoxaflutole and its metabolite RPA 202248 in animal tissues. Source: Bayer CropScience, Monheim am Rhein, Germany. Testing facility: Eurofins Agrosiences Services Chem, Hamburg, Germany, Date 13 May 2013 Report no S12-00056 (BAY-12078V), code RAISX027. Published: No. Claim for Data protection: Yes. GLP: yes.
M-285005-01-1	Wolters, A	2007a	Title: Determination of the residues of AE 0001789, isoxaflutole and BYH 18636 in/on corn after spraying of AE 0001789 & Isoxaflutole (480 SC) and AE 0001789 & BYH 18636 (450 SC) in the field in southern France, Spain and Italy. Source & Testing Facility: Bayer CropScience AG, Monheim, Germany. Date: 8 March 2007 Report No: RA-2616/06. Published: No. Claim for Data protection: Yes. GLP: yes.
M-285014-01-1	Wolters, A	2007b	Title: Determination of the residues of AE 0001789, isoxaflutole, and BYH 18636 in/on corn after spraying of AE 0001789 & Isoxaflutole (480 SC) and AE 0001789 & BYH 18636 (450 SC) in the field in northern France, United Kingdom and Germany. Source & Testing Facility: Bayer CropScience AG, Monheim, Germany. Date: 8 March 2007 Report No: RA-2615/06. Published: No. Claim for Data protection: Yes. GLP: yes.
M-284416-01-1	Wolters, A & Erler, S	2007a	Title: Determination of the residues of AE 0001789, BYH 18636 and isoxaflutole in/on corn after spraying of BYH 18636 & IFT & AE 0001789 (465 SC) in the field in southern France, Italy and Spain. Source & Testing Facility: Bayer CropScience AG, Monheim, Germany. Date: 26 February 2007 Report No: RA-2511/06. Published: No. Claim for Data protection: Yes. GLP: yes.
M-284423-01-1	Wolters, A & Erler, S	2007b	Title: Determination of the residues of AE 0001789, BYH 18636 and isoxaflutole in/on corn after spraying of BYH 18636 & IFT & AE 0001789 (465 SC) in the field in northern France, Germany and United Kingdom. Source & Testing Facility: Bayer CropScience AG, Monheim, Germany. Date: 26 February 2007 Report No: RA-2510/06. Published: No. Claim for Data protection: Yes. GLP: yes.
M-281611-01-1	Zimmer, D	2006	Title: Determination of the residues of AE 0001789 and isoxaflutole in/on corn after spraying of AE 0001789 & isoxaflutole (480 SC) in the field in France, Spain, Italy, Greece and Portugal. Source & Testing Facility: Bayer CropScience AG, Monheim, Germany. Date: 21 December 2006 Report No: RA-2588/05. Published: No. Claim for Data protection: Yes. GLP: yes.
M-282674-01-1	Zimmer, D & Wieland, K	2007	Title: Determination of the residues of AE 0001789 and isoxaflutole in/on corn after spraying of AE 0001789 & isoxaflutole (480 SC) in the field in Germany, Northern France, United Kingdom and the Netherlands. Source & Testing Facility: Bayer CropScience AG, Monheim, Germany. Date: 23 January 2007 Report No: RA-2587/05. Published: No. Claim for Data protection: Yes. GLP: yes.

MALATHION (049)

The first draft was prepared by Professor Árpád Ambrus, Hungarian Food Chain Safety Office

EXPLANATION

Residues of malathion was evaluated by the JMPR first time in 1966 and re-evaluated several times. As part of the periodic review programme, the 1999 JMPR Meeting concluded that the residue definition for plant commodities for compliance with MRL and for consumer risk assessment was malathion. The Meeting recommended maximum residue limits for a wide range of commodities, but concluded that the supporting data was not sufficient for recommending maximum residue levels and withdrew the previous recommendation for cherries.

The manufacturer provided current US labels for ground and aerial application of malathion on sweet and tart cherries, and resubmitted the reports of supervised trials conducted in 1993 in the USA at partly higher rates than permitted by the present GAP assuming that the proportionality concept adopted by the 36th Session of CAC would be applied.

No new or additional information was provided.

RESIDUE ANALYSIS*Analytical methods*

The analytical methods used for the trials were evaluated by the 1999 JMPR Meeting. No new information was provided.

USE PATTERN

Malathion is an insecticide and acaricide used for controlling black cherry aphid, fruit tree leaf-roller, Japanese beetle, cherry fruit fly, and eye-spotted bud moth. The GAPs in the USA for cherries are summarized in Table 1.

Table 1 Registered uses of malathion on cherries (sweet and tart) in the USA

Product	Formulation Ai content %	Application				PHI (Days)
		kg ai/ha	Water L/ha	Intervals (days)	Max.No	
FYFANON® 57% EC	EC (57.0%)	1.96	Min 3740	3	4	3
FYFANON® ULV AG	ULV (96.5%)	1.37	—	7	4 (sweet cherries) 6 (tart cherries)	1
MALATHION 8 AQUAMUL (81.8% EC)	EC (81.8%)	1.96	Min 94	3	4	3

*Residues resulting from supervised trials on Cherries**Cherries*

A total of six supervised trials, three on sweet cherries and three on sour cherries were conducted in 1993 in various locations in the United States (FYF83 and FYF85). Each trial consisted of three plots, one untreated control plot, one plot treated 6–7 times 7 days apart with an EC formulation at 4.2 kg ai/ha rate by foliar airblast (ground) application, and one plot treated six times with an ULV formulation at a rate of 1.37 kg ai/ha by aerial application without carrier. In two trials, the first three or four early ground applications were made at the rate of 8.96 kg ai/ha.

In the EC formulation trials, samples of cherries were collected at 3, 7 and 14 days after the last application. In the ULV formulation trials, samples of cherries were collected at 1, 4, 7 and 14 days after the last application. Control samples were collected 1 day after the last application. Cherries were sampled to give a minimum sample weight of 0.9–2.7 kg (2–6 lb.).

Trial No., Location, Year	Crop / Variety	Method of Treatment	Application rate per treatment			No.	PHI (days)	Residues, (mg/kg)
			kg ai/ha	Total/ season (kg ai/ha)	Water (L/ha)			
No: FYF85 Trial MI1 Muskegon County, MI 1993	Tart cherry / Montmorency	Aerial	1.37	8.20	—	6	1	0.03 ^b
							4	0.02
							7	0.01
							14	< 0.01
No: FYF85 Trial MT1 Ravalli County, MT 1993	Tart cherry / Montmorency	Aerial	1.37	8.20	—	6	1	0.47
							4	0.23
							7	0.13
							14	0.05
No: FYF85 Trial NY1 Wayne County, NY 1993	Tart cherry / Montmorency	Aerial	1.37	8.20	—	6	1	0.34
							4	0.42
							7	< 0.01
							14	< 0.01

^a Number of application four (sweet cherries), six (tart cherries) minimum 7 days apart

^b Average value of duplicate analyses

RESIDUES IN ANIMAL COMMODITIES

Cherries are not animal feed items, and therefore there is no change to the dietary burden calculations evaluated at the 2005 JMPR Meeting.

APPRAISAL

The JMPR evaluated malathion residues for the first time in 1966, and several times thereafter. The compound was evaluated within the periodic review programme in 1999, and the residue was defined as malathion for compliance with MRL values as well as for consumer dietary intake assessment. An ADI of 0–0.03 mg/kg bw and an ARfD of 2 mg/kg bw were established by the 1999 and 2005 JMPRs, respectively.

The manufacturer provided current US labels for ground and aerial application of malathion on sweet and tart cherries, and resubmitted the reports of supervised trials conducted in 1993 in the USA at higher rates than permitted by the present US GAP, to be evaluated applying the proportionality concept adopted by the Thirty-sixth Session of CAC. No new information was provided.

Results of supervised trials on crops

The present US GAP specifies a maximum 4 ground treatments of cherries at 3 day intervals, a maximum dose rate of 1.96 kg/ha with a PHI of 3 days. The compound may be used for aerial application four times at seven days intervals on sweet cherries and six times on tart cherries at a maximum dose rate of 1.37 kg ai/ha with a PHI of 1 day.

Supervised trials were conducted in USA in 1993. The sweet and tart cherry plots were treated 6 or 7 times with an EC formulation at 4.2 kg ai/ha rate by foliar ground application 7 days apart. Samples were collected at 3, 7 and 14 days after the last application.

The residues in whole sweet cherries at a 3-day PHI were: 0.26, 0.45 and 1.2 mg/kg.

The residues in whole tart cherries at a 3-day PHI were: 1.1, 1.6 and 2.6 mg/kg

At the same geographical locations the cherry trees were aerially treated 6 times with an ULV formulation at a rate of 1.37 kg ai/ha 7 days apart. Samples were collected at 1, 4, 7 and 14 days after the final application.

The residues in whole sweet cherries at a 1-day PHI were: 0.02, 0.17 and 0.19mg/kg.

The residues in whole tart cherries at a 1-day PHI were: 0.03, 0.34, 0.47 mg/kg.

The Meeting noted that the last 3 ground treatments were carried out at 4.2 kg/ha rate in all trials and the early applications with 8.96 kg ai/ha did not affect the residues in harvested fruits, as the residues derived from these trials were within the residue ranges observed in other trials. As a result the Meeting agreed to apply the proportionality approach to the data set.

The residues following ground treatments were adjusted with the proportionality factor of $1.96/4.2=0.467$. This resulted in residues in sweet cherries of 0.12, 0.21 and 0.56 mg/kg, and in tart cherries of 0.51, 0.75 and 1.21mg/kg.

The Meeting noted that the aerial treatment resulted in lower residues in both commodities than the ground application, and that tart cherries contained higher residues than the sweet cherries. Since the highest and lowest residue values in the datasets overlapped the Meeting decided to use the residue data derived from ground application to estimate maximum, median and high residues.

The combined residue data in cherries in rank order were: 0.12, 0.21, 0.51, 0.56, 0.75 and 1.21 mg/kg.

The Meeting considered that residues in sweet and tart cherries properly represent various cherry fruits and estimated a median residue of 0.535 mg/kg, a HR of 1.21 mg/kg and a maximum residue level of 3 mg/kg for cherries.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

Definition of the residue (for compliance with the MRL and for estimation of dietary intake) for plant and animal commodities: malathion

The residue is fat soluble.

Commodity		Recommended MRL, mg/kg		STMR or STMR-P (mg/kg)	HR or HR-P (mg/kg)
CCN	Name	New	Previous		
FS 0013	Cherries	3	-	0.535	1.21

DIETARY RISK ASSESSMENT

Long-term intake

The evaluation of malathion resulted in recommendations for MRL and STMR values for cherries. The results are shown in Annex 3. The International Estimated Daily Intake for the 13 GEMS/Food diet based on estimated STMR value was up to 0% of the maximum ADI of 0.03 mg/kg bw. The Meeting concluded that the long-term intake of residues of malathion from cherries is unlikely to present a public health concern.

Short-term intake

The International Estimated Short-term Intake (IESTI) for malathion was calculated for cherries for which maximum residue levels and STMR values were estimated. The results are shown in Annex 4. The IESTI was 0% of the ARfD (2 mg/kg bw).

Meeting concluded that the short-term intake of residues of malathion resulting from its use on cherries is unlikely to present a public health concern.

REFERENCES

Code	Author	Year	Title, Institute, Report reference
FYF83	Bookbinder, MG	1994	Magnitude of the residue of malathion and its metabolite malaoxon in/on sweet cherries harvested after ground and aerial treatment, Report Number: AA920128, EN-CAS Analytical Laboratories, Inc., USA January 5, 1994, GLP. Unpublished.
FYF85	Bookbinder, MG	1994	Magnitude of the residue of malathion and its metabolite malaoxon in/on tart cherries harvested after ground and aerial treatment, Report Number: AA920106. EN-CAS Analytical Laboratories, Inc., USA. January 28, 1994, GLP. Unpublished.
	Prohonic, K	1993	Analytical Method for the Gas Chromatographic Determination of Malathion and Malaoxon Residues in Sweet Cherry Fruit when using Continuous Automated Sample Injections. Method No. ENC-7/93. Appended to: Bookbinder M G (1994).

MANDIPROPAMID (231)*First draft prepared by Dr. Yibing He,**Department of Science and Education, Ministry of Agriculture, China***EXPLANATION**

Mandipropamid was first evaluated by JMPR in 2008 when an ADI of 0–0.2 mg/kg bw was established and an ARfD was considered unnecessary. At the 44th Session of the CCPR, mandipropamid was scheduled for the evaluation of 2013 JMPR for additional uses on hops.

RESIDUE ANALYSIS*Analytical methods*

The Meeting received descriptions and validation data for analytical methods for residues of mandipropamid in hops and processed commodities. Methods rely on HPLC-MS/MS for analysis of mandipropamid in hops and wort.

Data collection method

Validation of Residue Analytical Method RAM 415/01 for the Determination of Residues in Crops. (Gill JP and Mound EL, 2004, NOA446510/0159)

Analyte: Mandipropamid, LC-MS/MS, Method RAM 415/01

LOQ: 0.01 mg/kg in crops

Description: Residues of mandipropamid were extracted from crop samples by homogenisation with acetonitrile:water (80:20 v/v). Extracts were centrifuged and aliquots diluted with water prior to being cleaned-up using polymeric solid-phase extraction cartridges. Residues of mandipropamid were quantified using high performance liquid chromatography with triple quadrupole mass spectrometric detection (LC-MS/MS). The transition monitored for mandipropamid was 412.1 to 327.9.

Enforcement methods

RAM 415/02 is the up-dated version of RAM 415/01 that includes the relevant modifications for the analysis of hops and has two LC-MS/MS transitions. Two MRM transitions were monitored for quantification (m/z 412.0→328.0) and confirmation (m/z 412.0→125.0). The analytical procedures were similar. The validation data on hops and hop processed fractions using method RAM 415/01 are valid for RAM 415/02.

Table 1 Recovery results obtained during validation of method RAM 415/01 for mandipropamid in hops, green and dried cones (Transition m/z = 412.0→328.0)

Matrix	Fortification (mg/kg)	Number of Analyses	Mean Recovery (%)	RSD (%)	Recovery Range (%)
Hops (Green cones)	0.01	5	103	4	98–108
	0.1	5	105	3	101–108
	Overall	10	104	4	98–108
Hops (Dried cones)	0.01	5	103	3	100–108
	0.1	5	94	3	90–97
	Overall	10	98	6	90–108

Table 2 Recovery results obtained during validation of method RAM 415/01 for mandipropamid in wort and spent hops (Transition m/z = 412.0→328.0)

Matrix	Fortification (mg/kg)	Number of Analyses	Mean Recovery (%)	RSD (%)	Recovery Range (%)
Hops (Wort)	0.01	5	110	10	99–127
	0.1	5	94	1.3	92–95
	Overall	10	102	11	92–127
Hops (Spent hops)	0.02	5	79	3.5	74–81
	0.2	5	65	7.5	58–70
	8.0	1	84	–	–
	Overall	11	73	12	58–84

Table 3 Recovery results obtained during validation of method RAM 415/01 for mandipropamid in wort and spent hops (Transition m/z = 412.0→125.0)

Matrix	Fortification (mg/kg)	Number of Analyses	Mean Recovery (%)	RSD (%)	Recovery Range (%)
Hops (Wort)	0.01	5	109	11	100–130
	0.1	5	93	1.2	92–95
	Overall	10	101	11	92–130
Hops (Spent hops)	0.02	5	90	4.6	85–95
	0.2	5	65	6.5	59–69
	8.0	1	86	–	–
	Overall	11	78	18	59–95

The S19 multi-residue method was not applicable for hops. The independent laboratory validation of RAM 415/02 was performed with fortifying mandipropamid at level of 0.5 mg/kg and 100 mg/kg. The recoveries obtained are summarized in Table 4 to Table 7.

Table 4 Recovery results obtained during an Independent Laboratory Validation of Method RAM 451/02 for mandipropamid in hops by Filtration Method (Transition m/z 412.0→328.0)

Matrix	Fortification (mg/kg)	Number of Analyses	Mean Recovery (%)	Coefficient of Variation (%)	Recovery Range (%)
Hops	0.5	5	99	3.5	95–103
	100	5	102	2.7	100–107
	Overall	10	101	3.3	95–107

Table 5 Recovery results obtained during an Independent Laboratory Validation of Method RAM 451/02 for mandipropamid in hops by Filtration Method (Transition m/z 412.0→125.0)

Matrix	Fortification (mg/kg)	Number of Analyses	Mean Recovery (%)	Coefficient of Variation (%)	Recovery Range (%)
Hops	0.5	5	94	8.3	82–102
	100	5	100	3.5	95–104
	Overall	10	97	6.7	82–104

Table 6 Recovery results obtained during an Independent Laboratory Validation of Method RAM 451/02 for mandipropamid in hops by SPE Method (Transition m/z 412.0→328.0)

Matrix	Fortification (mg/kg)	Number of Analyses	Mean Recovery (%)	Coefficient of Variation (%)	Recovery Range (%)
Hops	0.5	5	87	1.3	85–88
	100	5	111	11.9	93–125
	Overall	10	99	15.6	85–125

Table 7 Recovery results obtained during an Independent Laboratory Validation of Method RAM 451/02 for mandipropamid in hops by SPE Method (Transition m/z 412.0→125.0)

Matrix	Fortification (mg/kg)	Number of Analyses	Mean Recovery (%)	Coefficient of Variation (%)	Recovery Range (%)
Hops	0.5	5	76	14.8	64–93
	100	5	110	12.3	92–123
	Overall	10	93	22.9	64–123

Method RAM 415/02 was successfully and independently validated for the analysis of mandipropamid residues in hops. Method RAM 415/02 is suitable to be used in support of pre-registration data requirements and post-registration monitoring of hops.

Stability of residues in stored analytical samples

The Meeting received information on the stability of residues of mandipropamid in tomatoes, grapes, potatoes, lettuce, cucumbers, wheat and soya beans.

A study on the stability of mandipropamid residues in crop commodities was conducted during 2004 to 2006 (Hamilton LS, Joseph T, 2006, NOA446510/0921). Stability of mandipropamid residues was tested in both raw agricultural commodities and in processed commodities. Commodities used were tomatoes (fruit and paste), grapes (fruit and juice), potatoes (tubers and granules/flakes), lettuce, cucumbers, wheat (forage, grain and straw) and soya beans (beans, hulls, meal and oil). These include representatives of the four crop types specified in the EU guidance, i.e., predominantly water, oil, protein and starch containing materials.

Crop samples (10 g) were fortified with mandipropamid at 0.5 mg/kg. Immediately after fortification, sample sets were stored in a freezer at approximately -20 °C until analysed. At the desired storage intervals of approximately zero, three, six, twelve and twenty-four months a sample set of each substrate, consisting of a control sample, two freshly fortified samples and two freezer stored fortified samples, were analysed for residues of mandipropamid using method RAM 415/01. Analysis of the soya bean oil samples required a modification of this method, using hexane in the homogenization process instead of acetonitrile/water and replacing the solid phase extraction clean-up with a liquid-liquid partition.

Table 8 Stability of mandipropamid residues in crop commodities following storage at -20 °C (Hamilton LS, Joseph T, 2006, NOA446510/0921)

Commodity	Storage Period (Months)	Mandipropamid Concentration—Uncorrected (mg/kg)	Mean Procedural Recovery (%)
Tomatoes—Fruit	0	0.44	91
	3	0.46	97
	6	0.47	103
	12	0.42	99
	24	0.54	97
Tomatoes—Paste	0	0.45	87
	3	0.48	90
	6	0.49	104
	12	0.46	95
	24	0.48	108
Grapes—Fruit	0	0.48	95
	3	0.48	96
	6	0.47	94
	12	0.42	92
	24	0.50	84
Grapes—Juice	0	0.46	90
	3	0.47	88
	6	0.36	85
	12	0.46	88

Commodity	Storage Period (Months)	Mandipropamid Concentration—Uncorrected (mg/kg)	Mean Procedural Recovery (%)
	24	0.52	98
Potatoes—Tubers	0	0.51	100
	3	0.55	98
	6	0.57	108
	12	0.47	89
	24	0.49	104
Potatoes—Granules/ Flakes	0	0.47	90
	3	0.50	97
	6	0.48	102
	12	0.52	97
	24	0.49	108
Lettuce—Head	0	0.45	94
	3	0.44	81
	6	0.48	80
	12	0.41	102
	24	0.52	101
Cucumbers—Fruit	0	0.44	90
	3	0.49	104
	6	0.47	103*
	12	0.48	89
	24	0.59	114
Wheat—Forage	0	0.49	95
	3	0.46	88
	6	0.41	99
	12	0.41	90
	24	0.44	89
Wheat—Straw	0	0.37	82
	3	0.49	121
	6	0.58	113
	12	0.57	114
	24	0.42	80
Wheat—Grain	0	0.35	71*
	3	0.27	92
	6	0.48	100
	12	0.51	83
	24	0.52	97
Soya bean—Beans	0	0.45	91
	3	0.44	96
	6	0.46	88
	12	0.42	83
	24	0.44	109
Soya bean—Meal	0	0.46	93
	3	0.42	92
	6	0.46	99
	12	0.41	100
	24	0.55	93
Soya bean—Hulls	0	0.44	87
	3	0.47	89
	6	0.45	104
	12	0.41	94
	24	0.55	112
Soya bean—Oil	0	0.48	94
	3	0.47	94
	6	0.51	91
	12	0.41	100
	24	0.53	104

USE PATTERN

Mandipropamid is registered in the EU and the USA for the control of downy mildew on hops. The most critical Good Agricultural Practices (GAP) for the foliar application of mandipropamid on hops from Germany and USA are summarised in Table 9.

Table 9 Registered field uses of mandipropamid in Germany and USA. Labels for the following use on hops were available to the Meeting

Crop	Country or Region	Enduse product	F/G/I ^a	Method	No. per crop season min. max.	Application Min. Interval (days)	Max. Rate (g ai/ha per application)	Max. Water Volume (L/ha)	PHI [days]
Hops	Germany	SC, 250 g/L	F	spraying	2	10	400 ^b	– ^b	14
Hops	USA	SC, 250 g/L	F	spraying ^c	3	7–10	100–145	– ^d	7

^a F = field use, G = glasshouse application, I = indoor application.

^b A maximum of two applications of mandipropamid are made to hops. The rates and volumes of application are dependent upon the growth stage of the crop at the time of application. For hops, proven water application rates are 1300 to 2800 L water/ha.

^c Applied by ground, chemication or aerial application.

^d For best results, use sufficient water volume to provide thorough coverage.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised field trials for mandipropamid uses on the following crops.

Crop	Country	
Hops:	France, Germany, UK	Table 10
Hops:	USA	Table 11

Where residues were not detected, they are reported as below the LOQ. Residue data, application rates and spray concentrations have generally been rounded to two significant figures or, for residues near the LOQ, to one significant figure. Residue data are recorded unadjusted for % recovery. Multiple results are recorded in the data tables where the trial design included replicate plots and where separate samples have been identified as being from these replicate plots. Results used to estimate STMRs are double underlined.

A total of 10 residue trials were carried out according to GAP ($\pm 30\%$) in France, Germany and UK in 2005, 2006 and 2009 (Elliott, A, 2007, NOA 446510/1151; Gizler, A, Lakaschus, S, 2008, NOA 446510/1342; Lakaschus, S, Gizler, A, 2009, A12946B_10718). In all trials, mandipropamid was applied two times as an SC formulation containing 250 g ai/L at about 10 days intervals at a nominal rate of 300 g ai/ha as a foliar application to hops. The water rate was between 1500–2000 L/ha. The PHI was 14 days. The residue data from the supervised trials is summarised in Table 10.

Table 10 Results of residue trials with mandipropamid conducted as a foliar application to hops in France, Germany and UK in 2005, 2006 and 2009

HOPS	Application					PHI	Crop part	Residues mg/kg, mandipropamid	Ref. Reg.DocID. (Trail No.)
country, year (variety)	Form. (g ae/L)	kg ai/ha	water, L/ha	Growth stage	no.	days	Cones		
Germany, 2005	250 SC	0.336	2152	BBCH 75–82	2	0 ^a	green	< 0.01	NOA
(Hallertauer)		0.352	2255	BBCH 85–89		7 ^a	dried	< 0.01	446510/1151
Mittelfruher)						0 ^b	green	3.1	DE-FR-05-0353
						0	green	6.2	
						3	green	6.7	
						7	dried	23.3	

HOPS	Application					PHI	Crop part	Residues mg/kg,	Ref. Reg.DocID.
country, year (variety)	Form. (g ae/L)	kg ai/ha	water, L/ha	Growth stage	no.	days	Cones	mandipropamid	(Trail No.)
						7	green	6.0	
						10	dried	21.2	
						10	green	4.4	
						14	dried	26.0	
						14	green	7.1	
Germany, 2005	250 SC	0.310	1990	BBCH 82	2	0 ^a	green	< 0.01	NOA
(Hallertauer Tradition)		0.346	2215	BBCH 85		7 ^a	dried	< 0.01	446510/1151
						0 ^b	green	1.9	DE-FR-05-0354
						0	green	6.0	
						3	green	4.5	
						7	dried	25.6	
						7	green	5.3	
						10	dried	28.0	
						10	green	6.6	
						14	dried	19.6	
						14	green	4.6	
France, 2006	250 SC	0.370	1851	BBCH 87	2	0 ^a	green	< 0.01	NOA
(Strisselpalt)		0.366	1828	BBCH 88		7 ^a	dried	< 0.01	446510/1342
						0 ^b	green	1.6	FR-FR-06-0267
						0	green	3.5	
						3	green	3.4	
						7	dried	18.0	
						7	green	2.2	
						10	dried	15.0	
						10	green	1.4	
						14	dried	14.0	
						14	green	1.9	
France, 2006	250 SC	0.418	1851	BBCH 83–85	2	0 ^a	green	< 0.01	NOA
(Strisselpalt)		0.409	1828	BBCH 87		7 ^a	dried	< 0.01	446510/1342
						0 ^b	green	3.2	FR-FR-06-0268
						0	green	8.7	
						3	green	5.2	
						7	dried	29.0	
						7	green	4.5	
						9	dried	28.0	
						9	green	3.9	
						14	dried	26.0	
						14	green	3.5	
France, 2006	250 SC	0.379	1851	BBCH 76–81	2	0 ^a	green	< 0.01	NOA
(Perle)		0.395	1828	BBCH 81		7 ^a	dried	< 0.01	446510/1342
						0 ^b	green	3.2	FR-FR-06-0269
						0	green	6.7	
						3	green	7.3	
						8	dried	35.0	
						8	green	6.8	
						10	dried	29.0	
						10	green	3.5	
						14	dried	34.0	
						14	green	6.4	
Germany, 2006	250 SC	0.386	1851	BBCH 76–81	2	0 ^a	green	< 0.01	NOA
(Perle)		0.388	1828	BBCH 81		7 ^a	dried	< 0.01	446510/1342
						0 ^b	green	4.3	FR-FR-06-0270
						0	green	7.3	
						3	green	7.2	
						8	dried	38.0	
						8	green	5.9	
						10	dried	30.0	
						10	green	3.7	
						14	dried	31.0	
						14	green	4.3	
Germany, 2006	250 SC	0.422	1851	BBCH 75–82	2	0 ^a	green	< 0.01	NOA

HOPS	Application					PHI	Crop part	Residues mg/kg, mandipropamid	Ref. Reg.DocID. (Trail No.)
country, year (variety)	Form. (g ae/L)	kg ai/ha	water, L/ha	Growth stage	no.	days	Cones		
(Spalter)		0.408	1828	BBCH 79–85		7 ^a	dried	< 0.01	446510/1342
						0 ^b	green	3.3	FR-FR-06-0271
						0	green	6.0	
						3	green	6.3	
						8	dried	25.0	
						8	green	6.0	
						10	dried	26.0	
						10	green	3.7	
						14	dried	32.0	
						14	green	5.7	
Germany, 2006	250 SC	0.415	1851	BBCH 75–82	2	0 ^a	green	< 0.01	NOA
(Hallertauer Mittelfruher)		0.406	1828	BBCH 79–85		7 ^a	dried	< 0.01	446510/1342
						0 ^b	green	3.9	FR-FR-06-0272
						0	green	12.0	
						3	green	11.0	
						7	dried	19.0	
						7	Pre-process	27.0	
						7	Malt Grain	< 0.2	
						7	Spent Hops	3.3	
						7	Wort (cooked)	0.096	
						7	Spent Yeast	0.58	
						7	Young Beer	0.062	
						7	Beer	0.063	
						7	Malt Grain	< 0.20	
						7	Beer	0.061	
						7	Malt Grain	< 0.20	
						7	Beer	0.062	
						7	Malt Grain	< 0.20	
						7	Beer	0.049	
						7	green	6.0	
						10	dried	40.0	
						10	green	5.9	
						14	dried	34.0	
						14	green	4.8	
UK, 2006	250 SC	0.408	1540	BBCH 67	2	7 ^a	green	< 0.10	NOA
(Pioneer)		0.384	1449	BBCH 67–70		7 ^a	dried	< 0.10	446510/1342
						0	green	4.7	S09-01505-01
						3	green	7.4	
						7	green	5.5	
						7	dried	15.4	
						10	green	9.6	
						14	green	4.2	
Germany, 2009	250 SC	0.432	2267	BBCH 81–83	2	7 ^a	green	< 0.10	NOA
(Hallertauer Mittelfruher)		0.415	2180	BBCH 85–87		7 ^b	dried	< 0.10	446510/1342
						0	green	7.8	S09-01505-02
						3	green	10	
						7	green	5.7	
						7	dried	12.0	
						10	green	5.5	
						14	green	5.6	

^a Control residue value.

^b Sample taken prior to last application.

Three independent supervised trials were conducted on hops according to the US GAP in Washington state (two) and Idaho (one) during 2005 (Joseph T 2007, NOA446510/1076). The trials account for 94% of total US hops production based on acreage. In each trial, mandipropamid formulated as a suspension concentrate (SC) containing 250 g mandipropamid per litre, was applied three times at rates of 151 to 166 g ai/ha (nominally 0.135 lb ai/acre), i.e. within 25% of the nominal maximum rate of 145 g ai/ha. The application intervals were 7 days. The water volumes during applications were in the range from 235 to 433 L/ha in the trials conducted in Washington state, and about 20 L/ha in the trial conducted in Idaho to simulate an aerial application rate. Duplicate samples of fresh hop cones were collected with PHIs of 7 and 14 days from all trials. The green hops samples were kiln dried using simulated commercial technique to produce dried hops of commercial quality. Dried hops samples were analysed for residues of mandipropamid using analytical method RAM 415/01 with minor modifications. The residue data from the supervised trials is summarised in Table 11.

Table 11 Results of residue trials with mandipropamid conducted as a foliar application to hops in USA in 2005

HOPS	Application					PHI	Crop part	Residues	Ref.
country, year (variety)	Form. (g ae/L)	kg ai/ha	water, L/ha	Growth stage	no.	days	Cones	mg/kg, mandipropamid	Reg.DocID. (Trail No.)
USA, 2005 (Warrior)	250 SC	0.151	325	BBCH 79	3	0 ^a	dried	< 0.01	NOA
		0.152	327	BBCH 81–82		0	dried	1.5	446510/1076
		0.152	326	BBCH 85		3	dried	3.1	WF-FR-05-6060
						5	dried	3.6	
						7	dried	5.4	
						9	dried	3.3	
						14	dried	0.02	
						16	dried	0.5	
USA, 2005 (Warrior)	250 SC	0.153	419	immature	3	0 ^a	dried	< 0.01	NOA
		0.158	427	immature		7	dried	4.3	446510/1076
		0.155	433	Preharvest		14	dried	4.4	WF-FR-05-6061
USA, 2005 (Warrior)	250 SC	0.166	21	maturing	3	0 ^a	dried	< 0.01	NOA
		0.160	20	maturing		7	dried	10.6	446510/1076
		0.153	19	mature		14	dried	8.5	WF-FR-05-6062

^a Control residue value.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

The Meeting received information on the fate of mandipropamid residues during processing into beer.

Six residue trials were performed in Germany and northern France (Gizler, A, Lakaschus, S, 2008, NOA 446510/1342). Samples from one of the trials in Germany were taken for processing into beer. In this trial, mandipropamid formulated as a suspension concentrate (SC) containing 250 g mandipropamid per litre, was applied to hops. Two applications, at growth stages BBCH 75–82 and BBCH 79–85 and separated by an interval of 7 days, were made at 415 and 406 g ai/ha (nominal 400 g/ha for each application). Seven days after the final application, samples (approximately 2.5 kg) of treated and untreated dry hop cones were collected and transported frozen to the processing facility. The mandipropamid residues in hop cones prior to processing and in beer is presented in Table 10. The summary of processing factors was listed in Table 12.

Table 12 Summary of processing factors for mandipropamid residues

Raw agricultural commodity (RAC)	Processed commodity	Calculated processing factors	Median or best estimate
	Beer	0.002, 0.002, 0.002, 0.002	0.002

APPRAISAL

Mandipropamid was first evaluated by JMPR in 2008 when an ADI of 0–0.2 mg/kg bw was established and decided that an ARfD was unnecessary. At the Forty-fourth Session of the CCPR, mandipropamid was scheduled for the evaluation of 2013 JMPR for additional uses on hops.

Methods of analysis

The Meeting received descriptions and validation data for analytical methods for residues of mandipropamid in hops and processed hop samples.

Hop samples were extracted with acetonitrile:water (80:20 v/v). Extracts are centrifuged and aliquots diluted with water prior to being cleaned-up using polymeric solid-phase extraction cartridges. Residues of mandipropamid were quantified with HPLC-MS/MS. Validated LOQs was 0.01 mg/kg.

Stability of residues in stored analytical samples

The Meeting received information on the stability of residues in crop commodities in tomatoes, grapes, potatoes, lettuce, cucumbers, wheat and soya beans for two years.

The commodities in which stability was tested were both raw agricultural commodities and processed, such as tomatoes (fruit and paste), grapes (fruit and juice), potatoes (tubers and granules/flakes), lettuce, cucumbers, wheat (forage, grain and straw), and soya beans (beans, hulls, meal and oil). There was no significant change in the mandipropamid residue levels in any commodity during the 24 months of storage at -20 °C with any apparent losses being < 30%. These commodities contained representatives of the four crop types, i.e., predominantly water, oil, protein, and starch containing materials. Therefore, residues of mandipropamid are expected to be stable in all crop commodities including hops stored under these conditions for at least two years.

Supervised residue trials on crops

The Meeting received supervised trials data for mandipropamid uses on hops.

Hops

Ten trials were conducted on hops in Europe (maximum German GAP: 0.40 kg ai/ha, two applications, 14-day PHI) in 2005 and 2006 and in the USA (maximum USA GAP: 0.145 kg ai/ha, three applications, 7-day PHI). In eight trials conducted at the maximum German GAP, the ranked order of concentrations in dry cone, median underlined, were: 14, 20, 26(2), 31, 32 and 34(2) mg/kg. In three trials conducted at the maximum US GAP, the ranked order of concentration in the dry cones was: 4.3, 5.4 and 10.6 mg/kg.

Noting that European trials resulted in higher residues in dry cones, the Meeting estimated a maximum residue level and an STMR value for mandipropamid in hops, dry of 90 and 28.5 mg/kg on the basis of European dataset.

Fate of residues during processing

The Meeting received information on the fate of mandipropamid residues during the food processing of hops.

The processing factor for beer (0.002) was applied to the estimated STMR for dry cone (28.5 mg/kg) to produce an STMR-P value for beer (0.057 mg/kg).

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue concentrations listed below are suitable for establishing MRLs and for assessing IEDIs.

Definition of the residue (for compliance with the MRL and for estimation of dietary intake for plant and animal commodities): *mandipropamid*.

CCN	Commodity	MRL, mg/kg	STMR or STMR-P, mg/kg
DH 1100	Hops, dry	90	28.5
-	Beer	-	0.057

DIETARY RISK ASSESSMENT

Long-term intake

The Meeting noted that the new estimation of dry hops did not result in a significant change of the long term dietary intake and concluded that the long-term intake of residues of mandipropamid resulting from its uses that have been considered by JMPR is unlikely to present a public health concern.

Short-term intake

The 2008 JMPR decided that an ARfD was unnecessary. The Meeting therefore concluded that the short-term intake of mandipropamid residues is unlikely to present a public health concern.

REFERENCES

Code	Author	Year	Title, Institute, Report reference
NOA446510/0160	Crook, SJ	2004	Mandipropamid: Residue Analytical Method for the Determination of Residues of NOA446510 in Crop Samples. Final determination by LC-MS/MS. Syngenta Crop Protection AG, Basel, Switzerland. Syngenta—Jealott's Hill, Bracknell, United Kingdom, RAM415/01. Syngenta File No NOA446510/0160. Not GLP, unpublished, issued 05.11.2004.
NOA446510/1151	Elliott, A	2007	Mandipropamid: Mandipropamid (NOA446510)—Residue study on Hops (Green and Dried) in Northern France and Germany. Syngenta Crop Protection AG, Basel, Switzerland. Syngenta—Jealott's Hill International, Bracknell, Berkshire, United Kingdom, 05-6047, T020480-04. Syngenta File No NOA446510/1151. GLP, unpublished, issued 26.06.2007.
NOA446510/1342	Lakaschus, S & Gizler, A	2008	Mandipropamid: Mandipropamid (NOA446510)—Residue study on hops and brewing fractions in France and Germany in 2006. Syngenta—Jealott's Hill International, Bracknell, Berkshire, United Kingdom. Dr. Specht & Partner Chem. Laboratorien GmbH, Hamburg, Germany, T014169-05. Syngenta File No NOA446510/1342 GLP, unpublished, issued 22.01.2008.
NOA446510_10691	Crook, SJ	2009	Mandipropamid: RAM 415/02 Mandipropamid—Residue Method for the Determination of Mandipropamid in crops. Syngenta—Jealott's Hill, Bracknell, United Kingdom. Syngenta—Jealott's Hill, Bracknell, United Kingdom, RAM 415/02. Syngenta File No NOA446510_10691, not GLP, unpublished, , issued 23.01.2009.
NOA446510_10692	Eversfield, S	2009	Mandipropamid: Mandipropamid—Independent Laboratory Validation of a Method (RAM 415/02) for the Determination of Mandipropamid in Hops. Syngenta - Jealott's Hill, Bracknell, United Kingdom. CEMAS, North Ascot, United Kingdom, CEMR-4162-REG., Syngenta File No NOA446510_10692, GLP, unpublished, issued 20.01.2009.
NOA12946B_10718	Lakaschus, S & Gizler, A	2010	Mandipropamid: Mandipropamid—Residue study Hops in the UK and Germany in 2009. Syngenta—Jealott's Hill, Bracknell, United Kingdom. Eurofins—Dr Specht & Partner, Hamburg, Germany, T001044-09-REG. Syngenta File NOA12946B_10718, GLP, unpublished, issued 04.11.2010.
NOA446510/1076	Joseph, T	2007	Mandipropamid: NOA46510—Magnitude of the Residues in or on Hops. Syngenta Crop Protection, Inc., Greensboro, USA. Syngenta Crop Protection, Inc., Greensboro, USA, T000284-03. Syngenta File No NOA446510/1076, Not GLP, unpublished, issued 01.16.2007.

Code	Author	Year	Title, Institute, Report reference
NOA446510/0921	Hamilton, L & Joseph, T	2006	Mandipropamid: Mandipropamid—Residue Stability of NOA446510 Fortified into Crop Commodities under Freezer Storage Conditions. Syngenta Crop Protection AG, Basel, Switzerland. Syngenta Crop Protection, Inc., Greensboro, USA, T006170-04. Syngenta File No NOA446510/0921, GLP, unpublished, issued 06.06.2006.

PENTHIOPYRAD (253)

First draft was prepared by Mr Chritian Sieke, BfR, Germany

EXPLANATION

Penthiopyrad is a carboxamide fungicide used to control a broad spectrum of diseases on large variety of crops. Penthiopyrad inhibits fungal respiration by binding to mitochondrial respiratory complex II. It was considered for the first time by the 2011 JMPR for toxicology, establishing an acceptable daily intake (ADI) of 0–0.1 mg/kg bw and an acute reference dose (ARfD) of 1 mg/kg bw. In 2012, the Meeting evaluated uses from the USA for residues, resulting in the recommendation of various maximum residue levels for plant commodities and poultry matrices.

The present Meeting received new GAP information for penthiopyrad from Australia, Ireland, Italy, New Zealand, United Kingdom and the USA. No new data were submitted.

USE PATTERN

Penthiopyrad is a non-systemic protectant fungicide. The Meeting received information on additional uses involving foliar spray applications mainly before harvest.

Table 1 List of additional registered uses submitted to the 2013 JMPR

Crop	Country	Application detail					
		Form	Type	kg ai/ha	L/ha	No.	Pre harvest interval (PHI) in days
Alfalfa	USA	SC	foliar spray (F)	0.36	min. 140	2 (max. 0.72 kg ai/ha and year)	14
Almond	Australia		Foliar	0.3 kg ai/hL		3	14
Aubergine (field and protected)	Italy	SC	Foliar	0.04 kg ai/hL		1	3
Barley, oats	Ireland	SC	Foliar	0.25	200-300	2	Up to beginning of flowering (BBCH 61), PHI covered by growth stage
Barley, oats	UK	SC	Foliar	0.3	200-300	2	Up to end of heading (BBCH 59), PHI covered by growth stage
Berries (strawberry, blueberry)	USA	SC	foliar spray (F)	0.36	min. 140	3 (max. 1.1 kg ai/ha and year)	0
Brassica vegetables including leafy brassica	Australia		Foliar	0.3		2	0
Brassica, leafy vegetables (cabbge, broccoli, cauliflower, mustard greens)	USA	SC	foliar spray (F)	0.45	min. 140	3 (max. 1.1 kg ai/ha and year)	0
Bulb vegetables (green and dry)	USA	SC	foliar spray (F)	0.36	min. 140	3 (max. 1.1 kg ai/ha and year)	3
Chestnut	Australia		Foliar	0.3 kg ai/hL		3	14
Courgette/Zucchini (field and protected)	Italy	SC	Foliar	0.04 kg ai/hL		1	3
Cucumber (field and protected)	Italy	SC	Foliar	0.04 kg ai/hL		1	3
Cucurbits (cucumbers, melons, watermelon, squashes)	USA	SC	foliar spray (F)	0.24	min. 140	4 (max. 1 kg ai/ha and year)	1
Cucurbits (field and protected)	Australia		Foliar	0.3		2	1

Crop	Country	Application detail					
		Form	Type	kg ai/ha	L/ha	No.	Pre harvest interval (PHI) in days
Fruiting vegetables	USA	SC	foliar spray (F+G)	0.36	min. 140	3 (max. 1.1 kg ai/ha and year)	0
Fruiting vegetables (tomatoes, eggplant, peppers, field and protected)	Australia		Foliar	0.3		2	0
Hazelnut	Australia		Foliar	0.3 kg ai/hL		3	14
Leafy vegetables	Australia		Foliar	0.3		2	3
Leafy vegetables (lettuce, celery, spinach)	USA	SC	foliar spray (F)	0.36	min. 140	3 (max. 1.1 kg ai/ha and year)	3
Legume vegetables (succulent shelled or podded)	USA	SC	foliar spray (F)	0.45	min. 140	3 (max. 1.1 kg ai/ha and year)	0
Onions	Australia		Foliar	0.3		2	3
Peanut	USA	SC	foliar spray (F)	0.36	min. 140	3 (max. 1.1 kg ai/ha and year)	14
Pome fruit	Australia		Foliar	0.25 kg ai/hL		3	28
Pome fruit	New Zealand	SC	Foliar	0.25 kg ai/hL		3	Apply before 50% petal fall and/or before fruitlet formation , PHI covered by growth stage
Pome fruits	USA	SC	foliar spray (F)	0.3	min. 140	4 (max. 0.91 kg ai/ha and year)	28
Root and tuber vegetable	Australia		Foliar	0.3		2	7
Root vegetables (except sugar beets)	USA	SC	foliar spray (F)	0.45	min. 140	3 (max. 0.91 kg ai/ha and year)	0
Spring onions	Australia		Foliar	0.3		2	3
Stone fruit	Australia		Foliar	0.3 kg ai/hL		3	0
Stone fruits	USA	SC	foliar spray (F)	0.3	min. 140	4 (max. 0.91 kg ai/ha and year)	0
Strawberry	Australia		Foliar	0.35		2	0
Tomato (field and protected)	Italy	SC	Foliar	0.04 kg ai/hL		1	3
Tree nuts (incl. Pistachios)	USA	SC	foliar spray (F)	0.3	min. 140	4 (max. 0.91 kg ai/ha and year)	14
Wheat, rye, triticale	Ireland	SC	Foliar	0.25	200-300	2	Up to watery ripe stage (BBCH 71), PHI covered by growth stage
Wheat, rye, triticale	UK	SC	Foliar	0.3	200-300	2	Up to end of flowering (BBCH 69), PHI covered by growth stage

For the USA general label restrictions on rotational crops were implemented not allowing the planting of crops without authorised uses with penthiopyrad within 120 days after treatment.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

For penthiopyrad no additional residue data were submitted to the 2013 JMPR. However, for the selection of residue data for estimating maximum residue levels, STMR and HR values, supervised field trials approximating the new European labels are presented below. For a complete overview of the available data, including supervised field trials not taken into account, please refer to the 2012 JMPR Evaluation.

Table 2 Residues in summer squash following foliar application of penthiopyrad

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg (b)	
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753-A-OH	753-F-DO	DM-PCA		
Protected												
Spain, Los Palacios 2008 (Jedida) PTHIO_071	2	0.2 0.59	0.04 0.04	0a	0.021	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent:	
				0	0.19	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.23	
				1	0.29	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01		
				3	0.23	< 0.01	< 0.01	0.01	< 0.01	< 0.01	Total:	
				7	0.046	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.25	
14	0.012	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01				
France (South), Pernes-les- Fontaines 2008 (Cora) PTHIO_071	2	0.19 0.59	0.04 0.04	0a	0.014	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent :	
				0	0.2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.13
				1	0.083	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
				3	0.13	< 0.01	< 0.01	0.01	< 0.01	< 0.01	Total :	
				7	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.15
14	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01				
Outdoor												
Spain, Aguadulce 2008 (Nieve) PTHIO_072	2	0.2 0.6	0.04 0.04	3	0.12	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent :	
											0.12	
Reverse decline											Total :	
Greece, Nea Magnisia 2008 (Lorea) PTHIO_072	2	0.2 0.6	0.04 0.04	3	0.075	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent :	
											0.075	
Reverse decline											Total :	
											0.095	

^a before last treatment

^b mean of replicate samples (if applicable); total residue based on the edible portion

DALT: days after final treatment

Table 3 Residues in cucumbers following foliar application of penthiopyrad

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg b
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753-A-OH	753-F-DO	DM-PCA	
Protected											
Italy, Triginto die Mediglia 2007 (Edona) PTHIO_071	2	0.2 0.59	0.04 0.04	0 ^a	0.011	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent :
				0	0.2	< 0.01	< 0.01	0.026	< 0.01	< 0.01	0.031
				1	0.13	< 0.01	< 0.01	0.024	< 0.01	< 0.01	
				3	<u>0.031</u>	< 0.01	< 0.01	0.02	< 0.01	< 0.01	Total :
				7	0.018	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.051
14	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01					
Spain, Los Palacios 2007 (Edona) PTHIO_071	2	0.2 0.59	0.04 0.04	0 ^a	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent :
				0	0.23	< 0.01	< 0.01	0.015	< 0.01	< 0.01	0.041
				1	0.098	< 0.01	< 0.01	0.038	< 0.01	< 0.01	
				3	<u>0.041</u>	< 0.01	< 0.01	0.021	< 0.01	< 0.01	Total :
				7	0.011	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.061
14	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01					

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg b
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753- A-OH	753- F-DO	DM- PCA	
PTHIO_067				3 7 14	0.14 0.3 <u>0.38</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	
Italy, Mediglia 2007 (Naram) PTHIO_067	2	0.19 0.59	0.04 0.04	0 ^a 0 1 3 7 14	0.066 0.27 0.15 0.13 <u>0.31</u> 0.19	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	Parent : 0.31 Total : 0.33
Spain, Los Palacios 2007 (Jenaro) PTHIO_067	2	0.2 0.59	0.04 0.04	0 ^a 0 1 3 7 14	0.06 0.18 0.15 0.19 <u>0.24</u> 0.15	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	Parent : 0.24 Total : 0.26
Italy, Mediglia 2008 (Birichino) PTHIO_067	2	0.2 0.59	0.04 0.04	0 ^a 0 1 3 7 14	0.12 0.85 0.42 0.4 <u>0.55</u> 0.16	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	Parent : 0.55 Total : 0.57
Greece, Nea Magnisia 2008 (Winner F1) PTHIO_067	2	0.2 0.62	0.04 0.04	0 ^a 0 1 3 7 14	0.12 0.76 0.6 <u>0.76</u> 0.55 0.46	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	Parent : 0.76 Total : 0.78
France (South), Pact 2008 (Felicia) PTHIO_067	2	0.2 0.6	0.04 0.04	0 ^a 0 1 3 7 14	0.045 0.3 0.12 0.092 <u>0.15</u> 0.12	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	Parent : 0.15 Total : 0.17
Belgium, Eemegem 2008 (Growdena) PTHIO_067	2	0.2 0.59	0.04 0.04	0 ^a 0 1 3 7 14	0.13 1.1 0.65 0.58 0.74 <u>0.76</u>	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	Parent : 0.76 Total : 0.78
Outdoor											
Spain, Lleida 2007 (Caramba) PTHIO_068 Reverse decline	2	0.2 0.59	0.04 0.04	3	<u>0.29</u>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.29 Total : 0.31
Spain, Aguadulce 2007 (Manitu) PTHIO_068 Reverse decline	2	0.21 0.59	0.04 0.04	7	<u>0.22</u>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.22 Total : 0.24
Italy, Santa Cristina 2007 (Perfect peel) PTHIO_068	2	0.2 0.59	0.04 0.04	14	<u>0.32</u>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.32 Total : 0.34

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg _b
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753- A-OH	753- F-DO	DM- PCA	
Reverse decline											
France (South), Vaunaveys 2008 (Perfect peel) PTHIO_068 Reverse decline	2	0.2 0.6	0.04 0.04	3	<u>0.18</u>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.18 Total : 0.2
Spain, Aguadulce 2008 (Manitu) PTHIO_068 Reverse decline	2	0.2 0.6	0.04 0.04	3	<u>0.11</u>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.11 Total : 0.13

^a: before last treatment^b: mean of replicate samples (if applicable); total residue based on the edible portion

DALT: days after final treatment

Table 5 Residues in barley grain following foliar application of penthiopyrad (last application at BBCH 65–69)

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg _a
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753-A- OH	753-F- DO	DM- PCA	
UK, Aingers Green 2007 (Flagon) PTHIO_078	2	0.25	0.1	36	0.071	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.071 Total : 0.091
UK, Tranent 2007 (Oxbridge) PTHIO_078	2	0.26 0.25	0.1 0.1	49	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.01 Total : 0.03
Germany, Machern 2007 (Naomi) PTHIO_078	2	0.25	0.1	54	0.069	< 0.01	0.017	0.011	< 0.01	< 0.01	Parent : 0.069 Total : 0.089
UK, Kennoway 2007 (Rebecca) PTHIO_078	2	0.26	0.1	45	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : < 0.01 Total : < 0.01
UK, Harwich 2008 (Flagon) PTHIO_078	2	0.25	0.1	47	0.057	0.025	0.054	0.014	< 0.01	< 0.01	Parent : 0.057 Total : 0.1
Germany, Motterwitz 2008 (Laverda) PTHIO_078	2	0.26 0.25 (SC)	0.1 0.1	37	0.076	< 0.01	0.016	0.013	< 0.01	< 0.01	Parent : 0.076 Total : 0.096
Hungary, Velenca 2008 (Nelly) PTHIO_078	2	0.25 0.24 (EC)	0.1 0.1	34	0.12	< 0.01	0.011	0.014	< 0.01	< 0.01	Parent : 0.12 Total : 0.14
France (North), Senlis le Sec 2008 (Sebastian) PTHIO_078	2	0.24 0.25 (SC)	0.1 0.1	60	0.039	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.039 Total : 0.059

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg _a
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753-A-OH	753-F-DO	DM-PCA	
France (South), Charontonnay 2008 (Caravan) PTHIO 078	2	0.24 0.26 (SC)	0.1 0.1	42	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : < 0.01 Total : < 0.01
Hungary, Velence 2008 (Nelly) PTHIO 078	2	0.25 (EC)	0.1	34	0.1	< 0.01	0.01	0.013	< 0.01	< 0.01	Parent : 0.1 Total : 0.12
France (South), Pact 2008 (Franzi) PTHIO 078	2	0.24 0.25 (SC)	0.1 0.1	45	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : < 0.01 Total : < 0.01
France (South), St Martin le Chatel 2008 (Platine) PTHIO 078	2	0.25 0.24 (SC)	0.1 0.1	39	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.01 Total : 0.03
France (South), St Jean de Niost 2008 (Ketos) PTHIO 078	2	0.24 0.25 (SC)	0.1 0.1	35	0.063	< 0.01	< 0.01	0.011	< 0.01	< 0.01	Parent : 0.063 Total : 0.083

^a mean of replicate samples (if applicable); total residue based on the edible portion

DALT: days after final treatment

Table 6 Residues in wheat grain following foliar application of penthiopyrad (last application at BBCH 69–71)

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg _a
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753-A-OH	753-F-DO	DM-PCA	
UK, Colchester 2007 (Istabraq) PTHIO 077	2	0.25	0.1	44	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : < 0.01 Total : < 0.01
UK, Peaston 2007 (Robigus) PTHIO 077	2	0.24 0.25	0.1 0.1	63	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : < 0.01 Total : < 0.01
Germany, Motterwitz 2007 (Schamane) PTHIO 077	2	0.26 0.24	0.1 0.1	44	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : < 0.01 Total : < 0.01
Hungary, Velence 2007 (GK Kapos) PTHIO 077	2	0.26	0.1	18	0.081	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.081 Total : 0.1
France (North), Charmée 2007 (Apache) PTHIO 077	2	0.25 0.24	0.1 0.1	44	0.015	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.015 Total : 0.035
UK, Peaston 2008 (Consort) PTHIO 077	2	0.25 (SC)	0.1	55	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : < 0.01 Total : < 0.01
Germany, Motterwitz 2008 (Inspiration) PTHIO 077	2	0.26 0.24 (SC)	0.1 0.1	60	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : < 0.01 Total : < 0.01
Hungary, Kápolnásnyék 2008 (Petur) PTHIO 077	2	0.26 (SC)	0.1	44	0.015	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	Parent : 0.015 Total : 0.035

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg ^b
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753- A-OH	753- F-DO	DM- PCA	
France (South), St Martin le Chatel 2008 (Platine) PTHIO_078	2	0.25 0.24 (EC)	0.1	0 ^a	0.12	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Total : 3.9
				0	3.8	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				7	0.33	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				14	0.089	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				21	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				28	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
France (South), St Jean de Niost 2008 (Ketos) PTHIO_078	2	0.24 0.25 (EC)	0.1	0 ^a	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Total : 3.5
				0	3.4	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				7	0.49	0.059	< 0.05	< 0.05	< 0.05	< 0.05	
				14	0.16	0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				21	0.059	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				28	0.064	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	

^a before last treatment^b mean of replicate samples (if applicable); total residue based on the edible portion

DALT: days after final treatment

Table 8 Residues in wheat forage following foliar application of penthiopyrad (last application at BBCH 69-71)

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg ^b
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753-A- OH	753-F- DO	DM- PCA	
UK, Colchester 2007 (Istabraq) PTHIO_077	2	0.25	0.1	0 ^a	0.02	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Total : 2.2
				0	<u>2.1</u>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				7	0.57	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				14	0.54	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				21	0.53	0.05	0.055	< 0.05	< 0.05	< 0.05	
				28	0.23	< 0.05	< 0.05	0.051	< 0.05	< 0.05	
UK, Peaston 2007 (Robigus) PTHIO_077	2	0.24 0.25	0.1	0 ^a	0.03	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Total : 3.8
				0	<u>3.7</u>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				7	0.63	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				14	0.21	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				21	0.17	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				28	0.11	< 0.05	0.058	0.054	< 0.05	< 0.05	
UK, Peaston 2008 (Consort) PTHIO_077	2	0.25 (SC)	0.1	0 ^a	0.18	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Total : 5.3
				0	<u>5.2</u>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				7	0.6	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				14	0.25	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				21	0.18	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				28	0.14	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
Germany, Motterwitz 2008 (Inspiration) PTHIO_077	2	0.26 (SC)	0.1	0 ^a	1.1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Total : 5.7
				0	<u>5.6</u>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				7	0.94	0.051	< 0.05	< 0.05	< 0.05	< 0.05	
				14	0.22	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				21	0.15	0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				28	0.1	< 0.05	< 0.05	0.061	< 0.05	< 0.05	
France (South), St Trivier-sur- Moignans 2008 (Aubusson) PTHIO_077	2	0.25 (SC)	0.1	0 ^a	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Total : 4.3
				0	<u>4.2</u>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				7	0.15	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				14	0.12	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				21	0.067	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				28	0.059	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
France (South), St Martin le Chatel 2008 (Aubusson) PTHIO_077	2	0.25 (EC)	0.1	0 ^a	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Total : 3.0
				0	<u>2.9</u>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				7	0.18	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				14	0.13	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				21	0.081	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	
				28	0.065	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	

^a before last treatment

^b mean of replicate samples (if applicable); total residue based on the edible portion

DALT: days after final treatment

Table 9 Residues in barley straw following foliar application of penthiopyrad (last application at BBCH 65–69)

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg ^a
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753-A- OH	753-F- DO	DM- PCA	
UK, Aingers Green 2007 (Flagon) PTHIO_078	2	0.25	0.1	36	0.68	< 0.05	0.066	< 0.05	< 0.05	< 0.05	Parent : 0.68 Total : 0.78
UK, Tranent 2007 (Oxbridge) PTHIO_078	2	0.26 0.25	0.1 0.1	49	0.15	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Parent : 0.15 Total : 0.25
Germany, Machern 2007 (Naomi) PTHIO_078	2	0.25	0.1	54	0.28	< 0.05	0.095	< 0.05	< 0.05	< 0.05	Parent : 0.28 Total : 0.38
UK, Kennoway 2007 (Rebecca) PTHIO_078	2	0.26	0.1	45	0.051	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Parent : 0.051 Total : 0.15
UK, Harwich 2008 (Flagon) PTHIO_078	2	0.25	0.1	47	0.92	0.072	0.27	0.098	< 0.05	< 0.05	Parent : 0.92 Total : 1.0
Germany, Mottewitz 2008 (Laverda) PTHIO_078	2	0.26 0.25 (SC)	0.1 0.1	37	0.36	< 0.05	0.092	0.11	< 0.05	< 0.05	Parent : 0.36 Total : 0.46
Hungary, Velenca 2008 (Nelly) PTHIO_078	2	0.24 0.25 (SC)	0.1 0.1	34	0.28	< 0.05	0.054	< 0.05	< 0.05	< 0.05	Parent : 0.28 Total : 0.38
France (North), Senlis le Sec 2008 (Sebastian) PTHIO_078	2	0.24 0.25 (SC)	0.1 0.1	60	0.57	< 0.05	0.063	0.052	< 0.05	< 0.05	Parent : 0.57 Total : 0.67
France (South), Charontonay 2008 (Caravan) PTHIO_078	2	0.25 0.26 (SC)	0.1 0.1	42	0.13	< 0.05	0.058	< 0.05	< 0.05	< 0.05	Parent : 0.13 Total : 0.23
Hungary, Velenca 2008 (Nelly) PTHIO_078	2	0.24 0.26 (SC)	0.1 0.1	34	0.25	< 0.05	0.072	< 0.05	< 0.05	< 0.05	Parent : 0.25 Total : 0.35
France (South), Pact 2008 (Franzi) PTHIO_078	2	0.24 0.25 (SC)	0.1 0.1	45	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Parent : < 0.05 Total : < 0.05
France (South), St Martin le Chatel 2008 (Platine) PTHIO_078	2	0.25 0.24 (SC)	0.1 0.1	39	0.11	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Parent : 0.11 Total : 0.21
France (South), St Jean de Niost 2008 (Ketos) PTHIO_078	2	0.24 0.25 (SC)	0.1 0.1	35	0.2	< 0.05	0.051	< 0.05	< 0.05	< 0.05	Parent : 0.2 Total : 0.3

^a mean of replicate samples (if applicable); total residue based on the edible portion

DALT: days after final treatment

Table 10 Residues in wheat straw following foliar application of penthiopyrad (last application at BBCH 69–71)

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg ^a
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753-A- OH	753-F- DO	DM- PCA	
UK, Colchester 2007 (Istabraq) PTHIO_077	2	0.25	0.1	44	<u>0.26</u>	< 0.05	0.076	0.1	< 0.05	< 0.05	Parent : 0.26 Total : 0.36
UK, Peaston 2007 (Robigus) PTHIO_077	2	0.24 0.25	0.1 0.1	63	<u>0.059</u>	< 0.05	0.058	0.054	< 0.05	< 0.05	Parent : 0.059 Total : 0.16
Germany, Motterwitz 2007 (Schamane) PTHIO_077	2	0.26 0.24	0.1 0.1	44	<u>0.13</u>	< 0.05	0.067	0.082	< 0.05	< 0.05	Parent : 0.13 Total : 0.23
Hungary, Velence 2007 (GK Kapos) PTHIO_077	2	0.26	0.1	18	<u>2.3</u>	<u>0.17</u>	0.27	0.16	0.071	< 0.05	Parent : 2.3 Total : 2.6
France (North), Charmée 2007 (Apache) PTHIO_077	2	0.25 0.24	0.1 0.1	44	<u>1.1</u>	< 0.05	0.13	0.39	< 0.05	< 0.05	Parent : 1.1 Total : 1.2
UK, Peaston 2008 (Consort) PTHIO_077	2	0.25 (SC)	0.1	55	<u>0.05</u>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Parent : 0.05 Total : 0.15
Germany, Motterwitz 2008 (Inspiration) PTHIO_077	2	0.26 (SC)	0.1	60	<u>0.067</u>	< 0.05	0.084	0.16	< 0.05	0.15	Parent : 0.067 Total : 0.17
Hungary, Kápolnásnyék 2008 (Petur) PTHIO_077	2	0.26 (EC)	0.1	44	<u>0.75</u>	< 0.05	0.1	0.15	< 0.05	< 0.05	Parent : 0.75 Total : 0.85
France (North), Douai 2008 (Bermude) PTHIO_077	2	0.25 (SC)	0.1	58	<u>0.21</u>	< 0.05	< 0.05	0.28	< 0.05	< 0.05	Parent : 0.21 Total : 0.31
France (South), Charantonay 2008 (Garcia) PTHIO_077	2	0.24 0.25 (SC)	0.1 0.1	49	<u>0.077</u>	< 0.05	< 0.05	0.06	< 0.05	< 0.05	Parent : 0.077 Total : 0.18
France (South), St Jean di Niost 2008 (Aubusson) PTHIO_077	2	0.24 (EC)	0.1	43	<u>0.052</u>	< 0.05	< 0.05	0.066	< 0.05	< 0.05	Parent : 0.052 Total : 0.15
France (South), St Trivier-sur- Moignans 2008 (Aubusson) PTHIO_077	2	0.25 (SC)	0.1	36	<u>0.12</u>	< 0.05	0.05	0.074	< 0.05	< 0.05	Parent : 0.12 Total : 0.22

Location, Year (variety) Reference	Application			DALT	Residues, mg/kg						Selected residue mg/kg ^a
	n	kg ai/ha	kg ai/hL		parent	PAM	PCA	753-A- OH	753-F- DO	DM- PCA	
France (South), St Martin le Chatel 2008 (Aubusson) PTHIO_077	2	0.25 (SC)	0.1	47	0.16	< 0.05	0.05	0.096	< 0.05	< 0.05	Parent : 0.16 Total : 0.26

^a mean of replicate samples (if applicable); total residue based on the edible portion

DALT: days after final treatment

APPRAISAL

Penthiopyrad (ISO common name) is a carboxamide fungicide used to control a broad spectrum of diseases on a large variety of crops. Penthiopyrad inhibits fungal respiration by binding to mitochondrial respiratory complex II. It was considered for the first time by the 2011 JMPR for toxicology, establishing an acceptable daily intake (ADI) of 0–0.1 mg/kg bw and an acute reference dose (ARfD) of 1 mg/kg bw. In 2012, the Meeting evaluated uses from the USA for residues, resulting in the recommendation of various maximum residue levels for plant and poultry commodities.

However, the Meeting estimated a maximum and mean dietary burden for beef and dairy cattle above the highest dose level administered in livestock animal feeding studies on cows and concluded, that no recommendations on mammalian animal products and milk could be made based on the available data. The maximum and mean dietary burden was calculated based on the Australian diet for beef and dairy cattle (main contributor: soya bean hay).

The Forty-fifth Session of the CCPR scheduled penthiopyrad for the evaluation of additional labels from Australia, Ireland, Italy, New Zealand, United Kingdom and the USA. In addition, following official communication from Australia that no fodder crops are imported, a re-evaluation of the dietary burden for livestock animals was requested. No additional residue data were provided to the 2013 Meeting.

Results of supervised residue trials on crops

As indicated the present Meeting did not receive additional supervised trial data for penthiopyrad. New European GAPs residue data was previously presented in the 2012 Evaluation for penthiopyrad, which at the time could not be taken into account as label authorisations had not been finalised.

For the new labels registered for penthiopyrad in Australia, New Zealand and the USA the Meeting noted that none of the GAPs involves higher application rates or shorter PHIs than evaluated in 2012. Since no additional supervised field trial data were submitted, no re-evaluation of these uses was conducted by the 2013 JMPR.

For dietary intake assessment the residue is defined as the sum of penthiopyrad and PAM, expressed as penthiopyrad (referred to as “total”). Since residue data were expressed in mg of the specific analyte per kg sample, PAM needs to be converted into penthiopyrad equivalents. The corresponding factor is: PAM → penthiopyrad = 359.42 g/mol ÷ 193.13 g/mol = 1.86. In supervised field trials PAM residues were normally found at much lower levels than parent penthiopyrad. As a result, no adjustment of PAM or addition of LOQs was conducted, if both analytes were below the LOQ. For all other purposes of calculation < LOQ values were handled as their numeric value (e.g., < 0.01 mg/kg as 0.01 mg/kg).

This is illustrated below:

Penthiopyrad [mg/kg]	PAM [mg/kg]	Total [mg/kg]* (Sum of penthiopyrad and PAM, expressed as penthiopyrad equivalents)
< 0.01	< 0.01	< 0.01
0.1	< 0.01	0.12 (0.1 + 1.86 × 0.01)
< 0.01	0.1	0.2 (0.01 + 1.86 × 0.1)
0.1	0.1	0.29 (0.1 + 1.86 × 0.1)

* rounded to two significant figures above the LOQ

Cucurbits with edible peel

In Italy penthiopyrad is registered for the use on cucumber and summer squash (zucchini) with one foliar application of 0.04 kg ai/hL with a 3 day PHI. Supervised field trial data on courgettes (zucchini) and cucumbers involving two treatments at the registered spray concentration were available for glasshouse use (Belgium, France, Greece, Italy and Spain) and field application (France, Greece, Italy and Spain). The analysis of samples collected directly before the second treatment indicates a contribution by the previous application of < 25% to the final residue, making these trials acceptable for evaluation.

For the purposes of MRL estimation penthiopyrad residues in protected summer squash were (n=2): 0.13 and 0.23 mg/kg.

For the dietary intake purposes the total residues in protected summer squash were (n=2): 0.15 and 0.25 mg/kg.

For the purposes of MRL estimations penthiopyrad residues in field summer squash were (n=2): 0.075, 0.12 mg/kg.

For the dietary intake purposes the total residues in field summer squash were (n=2): 0.095 and 0.14 mg/kg.

For the purposes of MRL estimations penthiopyrad residues in protected cucumber were (n=4): 0.031, 0.041, 0.053, 0.058 mg/kg.

For the dietary intake purposes the total residues in protected cucumber were (n=4): 0.051, 0.061, 0.073, 0.078 mg/kg.

For the purposes of MRL estimations penthiopyrad residues in field cucumber were (n=5): 0.013, 0.019, 0.082, 0.13, 0.3 mg/kg.

For the dietary intake purposes the total residues in field cucumber were (n=5): 0.033, 0.039, 0.1, 0.15, 0.32 mg/kg.

The Meeting decided that the previous recommendation for a maximum residue level of 0.5 mg/kg for penthiopyrad in fruiting vegetables, cucurbits also covered residues in cucumber and summer squash resulting from the new uses considered.

Tomato and eggplants

In Italy penthiopyrad is registered for the use on tomato and eggplants with one foliar application of 0.04 kg ai/hL with a 3 day PHI. Supervised field trial data on tomato involving two treatments at the registered spray concentration were available for glasshouse (Belgium, France, Greece, Italy, Spain) and field application (France, Greece, Italy, Spain). The analysis of samples collected directly before the second treatment indicates a contribution by the previous application of < 25% to the final residue, making these trials acceptable for evaluation.

For the purposes of MRL estimations penthiopyrad residues in protected tomato were (n=7): 0.15, 0.24, 0.31, 0.38, 0.55, 0.76, 0.76 mg/kg.

For the dietary intake purposes the total residues in protected tomato were (n=7): 0.17, 0.26, 0.33, 0.4, 0.57, 0.78, 0.78 mg/kg.

For the purposes of MRL estimations penthiopyrad residues in field tomato were (n=5): 0.11, 0.18, 0.22, 0.29, 0.32 mg/kg.

For the dietary intake purposes the total residues in field tomato were (n=5): 0.13, 0.2, 0.24, 0.31, 0.34 mg/kg.

The Meeting recognized that residue data on tomato can also be extrapolated to eggplants.

The Meeting decided that the previous recommendation for a maximum residue level of 2 mg/kg for penthiopyrad in fruiting vegetables, other than cucurbits, except sweet corn and mushrooms also covers residues in tomatoes and eggplants resulting from the new uses considered.

Barley and oats

In Ireland and the UK penthiopyrad is registered for the use on barley and oats with two foliar application up to 0.3 kg ai/ha each. The PHI is covered by a specified growth stage (BBCH 61). Supervised residue trials approximating this GAP were submitted to the 2012 Meeting from France, Germany, Hungary and the UK.

For the purposes of MRL estimations penthiopyrad residues in barley grain were (n=14): < 0.01(3), 0.01, 0.01, 0.039, 0.057, 0.063, 0.069, 0.071, 0.076, 0.1, 0.12 mg/kg.

For the dietary intake purposes the total residues in barley grain were (n=14): < 0.01(3), 0.03, 0.03, 0.059, 0.083, 0.089, 0.091, 0.096, 0.1, 0.12, 0.14 mg/kg.

The Meeting recognized that barley and oats share an identical GAP and decided to extrapolate residue data from barley to oats.

The Meeting estimated a maximum residue level and an STMR of 0.2 mg/kg and 0.086 mg/kg for penthiopyrad in barley and oats, respectively, replacing its previous recommendation of a maximum residue level of 0.15 mg/kg for barley and oats.

Wheat, rye and triticale

In Ireland and the UK penthiopyrad is registered for the use on rye, triticale and wheat with two foliar application up to 0.3 kg ai/ha each. The PHI is covered by a specified growth stage (BBCH 71). Supervised residue trials approximating this GAP were submitted to the 2012 Meeting from France, Germany, Hungary and the UK.

For the purposes of MRL estimations penthiopyrad residues in wheat grain were (n=13): < 0.01(9), 0.013, 0.015, 0.015, 0.081 mg/kg.

For the dietary intake purposes the total residues in wheat grain were (n=13): < 0.01(9), 0.033, 0.035, 0.035, 0.1 mg/kg.

The Meeting recognized that wheat, rye and triticale share an identical GAP and decided to extrapolate residue data from wheat to rye and triticale.

The Meeting estimated a maximum residue level of 0.1 mg/kg and confirmed its previous estimate of an STMR of 0.01 mg/kg for penthiopyrad in wheat, rye and triticale, respectively, replacing its previous recommendation of a maximum residue level of 0.04 mg/kg for wheat, rye and triticale.

Animal feeds

Barley, oats, rye, triticale and wheat forage

In Ireland and the UK penthiopyrad is registered for the use on barley, oats, rye, triticale and wheat with two foliar application up to 0.3 kg ai/ha each. The PHI is covered by specified growth stages (BBCH 61 & 71). Supervised residue trials approximating this GAP were submitted to the 2012 Meeting from France, Germany, Hungary and the UK.

For the calculation of the livestock animal dietary burden total residues in barley forage (fresh) were (n=6): 2.0, 3.5, 3.9, 3.9, 4.0 and 4.5 mg/kg.

For the calculation of the livestock animal dietary burden total residues in wheat forage (fresh) were (n=6): 2.2, 3.0, 3.8, 4.3, 5.3 and 5.7 mg/kg.

The Meeting decided that the previously estimated median and highest residues in barley, oats, rye, triticale and wheat forage (fresh) of 10 mg/kg and 17 mg/kg, respectively, covered residues resulting from the new uses considered by the present Meeting.

Barley, oats, rye, triticale and wheat straw and fodder of cereals

In Ireland and the UK penthiopyrad is registered for the use on barley, oats, rye, triticale and wheat with two foliar application up 0.3 kg ai/ha each. The PHI is covered by specified growth stages (BBCH 61 & 71). Supervised residue trials approximating this GAP were submitted to the 2012 Meeting from France, Germany, Hungary and the UK.

For the purposes of MRL estimations penthiopyrad residues in barley straw (fresh) were (n=12): < 0.05, 0.051, 0.11, 0.13, 0.15, 0.2, 0.25, 0.28, 0.28, 0.36, 0.57 and 0.68 mg/kg.

For the calculation of the livestock animal dietary burden total residues in barley straw (fresh) were (n=12): < 0.05, 0.15, 0.21, 0.23, 0.25, 0.3, 0.35, 0.38, 0.38, 0.46, 0.67, 0.78 and 1.0 mg/kg.

For the purposes of MRL estimations penthiopyrad residues in wheat straw (fresh) were (n=13): 0.05, 0.052, 0.059, 0.067, 0.077, 0.12, 0.13, 0.16, 0.21, 0.26, 0.75, 1.1 and 2.3 mg/kg.

For the calculation of the livestock animal dietary burden total residues in wheat straw (fresh) were (n=13): 0.15, 0.16, 0.16, 0.17, 0.18, 0.22, 0.23, 0.26, 0.31, 0.36, 0.85, 1.2 and 2.6 mg/kg.

The Meeting decided that the previously estimated maximum residue level, median and highest residue in barley, oats, rye, triticale and wheat straw of 80 mg/kg (DM based), 21 mg/kg and 54 mg/kg, respectively, covered residues resulting from the new uses considered by the present Meeting.

Fate of residues during processing

The Meeting estimated new maximum residue levels for barley, oats, rye, triticale and wheat and a new STMR for barley and oats.

The estimation of maximum residue levels is based on the parent substance only, whereas for the dietary intake assessment the total residue needs to be taken into account. Based on the processing factors derived by the 2012 Meeting the following residues in processed products were estimated:

Commodity	Processing factor	Processing factor (median or best estimate)	MRL / STMR (mg/kg)	MRL, STMR-P (mg/kg)
Barley beer	Total: < 0.11, < 0.36	Total: < 0.24	STMR: 0.086	STMR-P: 0.021
Pot barley	Total: 0.67, 0.68	Total: 0.68	STMR: 0.086	STMR-P: 0.058
Wheat bran	Penthiopyrad: 1.8	Penthiopyrad: 1.8	MRL: 0.1	MRL: 0.2
Wheat germ	Penthiopyrad: 2.1	Penthiopyrad: 2.1	MRL: 0.1	MRL: 0.2

For wheat processed into wheat bran and wheat germ the Meeting estimated maximum residue levels of 0.2 mg/kg, respectively, and agreed to withdraw its previous recommendations of 0.1 mg/kg.

Residues in animal commodities

Livestock dietary burden

Livestock feeding studies involving administration of penthiopyrad to lactating cows and laying hens were reported in the 2012 JMPR Report.

Estimated maximum and mean dietary burdens of livestock

Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are presented in Annex 6.

The Meeting received official communication from Australia that no fodder crops are imported. The Meeting therefore decided to make a refined calculation of the livestock dietary burden based using the following parameters:

For the Australian diet only feed commodities corresponding to Australian authorisations plus globally traded non-fodder commodities are taken into account (e.g., grains and seeds).

For US-Canada, EU and Japan the calculation was conducted according to the usual procedure described in FAO Manual and amended by the new estimated median residue of 0.086 mg/kg for barley and oats. However, in contrast to 2012, forage crops were only included in the dietary burden for regions with corresponding labels (e.g. barley, oats, rye, triticale and wheat forage for Europe).

The dietary burdens were estimated using the OECD diets listed in Appendix IX of the 2009 edition of the FAO Manual.

	Livestock dietary burden, total residue*, ppm of dry matter diet							
	US-Canada		EU		Australia		Japan	
	max.	mean	max.	mean	max.	mean	max.	mean
Beef cattle	12	4.5	23	12	1.3	1.3	1.9	0.46
Dairy cattle	55 ^{a c}	26 ^{b d}	30	13	1.1	1.1	4.6	0.9
Poultry - broiler	0.2	0.2	0.19	0.19	0.19	0.19	0.17	0.17
Poultry - layer	0.2	0.2	22 ^e	11 ^f	0.19	0.19	0.14	0.14

^a Highest maximum beef or dairy cattle burden suitable for MRL estimates for mammalian meat

^b Highest mean beef or dairy cattle burden suitable for STMR estimates for mammalian meat

^c Highest maximum dairy cattle burden suitable for MRL estimates for milk

^d Highest mean dairy cattle burden suitable for STMR estimates for milk

^e Highest maximum broiler or laying hen burden suitable for MRL estimates for poultry products and eggs

^f Highest mean broiler or laying hen burden suitable for STMR estimates for poultry products and eggs

* total residue: sum of penthiopyrad and PAM, expressed as penthiopyrad

Animal commodities, MRL estimation

For beef and dairy cattle maximum and mean dietary burdens of 55 ppm and 26 ppm were estimated, respectively. The calculation to estimate highest total residues for use in estimating maximum residue levels, STMR and HR values were shown below.

Penthiopyrad feeding study	Feed level	Total residue				
	(ppm)	(mg/kg) in milk	(mg/kg) in muscle	(mg/kg) in kidney	(mg/kg) in liver	(mg/kg) in fat
Maximum residue level: dairy cattle						
Feeding study	21.4	< 0.01	< 0.01	0.03	0.04	0.03
	74.6	0.042	0.036	0.07	0.08	0.04
Dietary burden and residue estimate	55	0.03	0.026	0.055	0.065	0.036
STMR dairy cattle						
Feeding study	21.4	< 0.01	< 0.01	0.03	0.04	0.03
	74.6	0.042	0.036	0.07	0.08	0.04
Dietary burden and residue estimate	26	0.013	0.012	0.033	0.043	0.031

For beef and dairy cattle the Meeting estimated HR values for penthiopyrad (total residue) of 0.026 mg/kg in muscle, of 0.065 mg/kg in edible offal (based on liver) and of 0.036 mg/kg in fat. STMR values were estimated at levels of 0.013 mg/kg for milk, 0.012 mg/kg for meat, 0.043 mg/kg for edible offal (based on liver) and 0.031 mg/kg for fat.

The Meeting also estimated the following maximum residue levels: milk 0.04 mg/kg, meat (mammalian except marine mammals) 0.04 mg/kg, mammalian fat 0.05 mg/kg and edible offal 0.08 mg/kg.

For poultry the mean and maximum dietary burden differed insignificantly compared to the calculation by the 2012 Meeting (Max/Mean; 2012: 22 ppm/10ppm; 2013: 22 ppm/11ppm). The previous recommendations for penthiopyrad in poultry tissues and eggs are confirmed.

RECOMMENDATIONS

The Meeting estimated the STMR, HR and MRL values shown below.

Definition of the residue for compliance with MRL for plant commodities: *penthiopyrad*

Definition of the residue for compliance with MRL for animal commodities and for the estimation of dietary intake for plant and animal commodities: *sum of penthiopyrad and 1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide (PAM), expressed as penthiopyrad*

The residue is not fat-soluble.

Maximum residue levels and dietary intake

Commodity		MRL, mg/kg		STMR or STMR-P, mg/kg	HR, mg/kg
CCN	Name	New	Previous		
GC 0640	Barley	0.2	0.15	0.086	
MO 0105	Edible offal (mammalian)	0.08		0.043	0.065
MF 0100	Mammalian fats (except milk fats)	0.05		0.031	0.036
MM 0095	Meat (from mammals other than marine mammals)	0.04		0.012	0.026
ML 0106	Milks	0.04		0.013	
GC 0647	Oats	0.2	0.15	0.086	
GC 0650	Rye	0.1	0.04	0.01	
GC 0653	Triticale	0.1	0.04	0.01	
GC 0654	Wheat	0.1	0.04	0.01	
CM 0654	Wheat, bran	0.2	0.1	0.018	
CF 1210	Wheat, germ	0.2	0.1	0.019	

Dietary intake only

Commodity		MRL, mg/kg		STMR or STMR-P, mg/kg	HR, mg/kg
Name		New	Previous		
	Barley, beer			0.021	
	Barley, pearl			0.058	

DIETARY RISK ASSESSMENT***Long-term intake***

The WHO Panel of the 2011 JMPR established an Acceptable Daily Intake (ADI) of 0-0.1 mg/kg bw/day for penthiopyrad.

The 2013 evaluation of penthiopyrad resulted in new recommendations for MRLs and STMR values for barley, oats, rye, triticale, wheat and mammalian animal products. Where data on consumption were available for the listed food commodities evaluated in 2012 or 2013, dietary intakes were calculated for the 13 GEMS/Food Consumption Cluster Diets. The results are shown in Annex 3 of the 2013 JMPR Report.

The IEDIs in the thirteen Cluster Diets, based on the estimated STMRs were 0-6% of the maximum ADI (0.1 mg/kg bw). The Meeting concluded that the long-term intake of residues of penthiopyrad from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The WHO Panel of the 2011 JMPR established an Acute Reference Dose (ARfD) of 1 mg/kg bw for penthiopyrad.

The International Estimated Short-Term Intake (IESTI) for penthiopyrad was calculated for the food commodities for which STMRs or HRs were estimated by the present Meeting and for which consumption data were available. The results are shown in Annex 4 of the 2013 JMPR Report. The IESTI for children and for the general population was 0% of the ARfD.

The Meeting concluded that the short-term intake of residues of penthiopyrad resulting from uses that have been considered by the 2013 JMPR is unlikely to present a public health concern.

PROPICONAZOLE (160)

The first draft was prepared by Professor Eloisa Dutra Caldas

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EXPLANATION

The triazole fungicide propiconazole was first evaluated by the JMPR in 1987 and has been reviewed for residues in 1991, 1994, and within the periodic review programme in 2007, when a number of maximum residue levels being recommended. Propiconazole has an ADI of 0–0.07 mg/kg bw and an ARfD of 0.3 mg/kg bw. The compound was scheduled at the Fort-fourth Session of the CCPR (2012) for the evaluation of residues in additional crops by the 2013 JMPR. Information and data on citrus, stone fruits and tomato following post-harvest applications of propiconazole were submitted.

Residue definition for plant and animal commodities is *propiconazole* for compliance with the MRL, and *propiconazole plus all metabolites convertible to 2,4-dichlorobenzoic acid, expressed as propiconazole* for the estimation of the dietary intakes.

METHODS OF RESIDUE ANALYSIS***Stability of pesticide residues in stored analytical samples***

A storage stability study was conducted with citrus (IR-4 PR 09715), with samples fortified with 5 mg/kg propiconazole and stored at -20 °C. The results are shown in Table 1.

Table 1 Stability of propiconazole residues in citrus fruit and processed fractions, and cherries and of total residues in tomato stored under frozen conditions (-20 °C)

Matrix	Fortification (mg/kg)	Storage interval (days)	% remaining
Citrus fruit	5	207	87, 91, 90
Orange juice	5	155	96, 95, 95
Dried orange pulp	5	154	104, 102, 105
Orange oil	5	224	102, 97, 108
Cherries without pits and stems	0.5	189	108, 89, 93
Tomato ^a	0.5	160	84, 86, 81

^a measured by the common moiety method.

USE PATTERN

The post-harvest trials on citrus fruits, stone fruits, and tomato submitted in this dossier were conducted in the United States. The recommended use patterns in the US for post-harvest applications of propiconazole on the commodities relevant for this submission are summarized in Table 2.

Table 2 Registered post-harvest use of propiconazole (WP, 45%) in the USA

Commodity	Application			PHI (days)
	Method	No.	Rate	
Citrus ^b	In-Line Dip/Drench ^a	2	0.027-0.054 kg a.i./ 100 L	NA
	In-line aqueous or fruit coating spray	2	0.90-1.8 g ai/1000 kg fruits	NA
Stone fruit	In-Line Dip/Drench ^a	1	0.067-0.0135 kg ai/100 L	NA
	In-line aqueous or fruit coating spray	1	0.28-0.56 g ai/1000 kg fruits	NA
Tomato	In-Line Dip/Drench ^a	1	0.014-0.27 g ai/100 L	NA
	High volume (dilute spray) application	1	2.2-4.5 g ai/1000 kg fruit	NA

^a dip fruits for a minimum of 30 seconds and allow to drain;

^b treat fruit once before storage and once after storage, just prior to marketing

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

Supervised residue trials conducted with propiconazole in Canada and USA were submitted to the Meeting. Studies were conducted according to GLP, and concurrent determination of residues in untreated crops gave residues < LOQ, unless specified otherwise. Residues of propiconazole arising from use patterns with the rate or PHI within $\pm 25\%$ of the GAP are underlined and were considered for estimation of maximum residue levels and STMRs. All the trials were conducted using a WP formulation.

Residues of propiconazole were analysed by LC-MS/MS. Samples were analysed within a storage period that was shown not to impact the residue levels, according to storage stability studies evaluated previously by the JMPR.

Citrus fruits

A total of twelve post-harvest trials on citrus were conducted in 2006 in the United States. Fruits were treated with the first application, allowed to dry, then the second application was made. Except for trials CA131, CA134, CA135, CA136, the samples were washed before the second application. Table 3 summarizes the results.

Table 3 Propiconazole residues in citrus fruit from post-harvest treatments from trials conducted in USA in 2006 using (IR-4 PR 09715)

State	Crop (variety)	Treatment	Rate, kg ai/hL	no.	Propiconazole [mean]	Trial
Florida,	Orange (Orlando Tangelo)	Dip for 30 sec.	0.048	2	0.96, 0.77 [0.87]	09715.06-FL42
California	Orange (Washington Navel)	Dip for 30 sec	0.048	2	2.16, 2.33 [2.2]	09175.06-CA131
California	Orange (Valencia)	Dip for 30 sec	0.048	2	5.66, 4.15 [4.9]	09175.06-CA 132
California	Orange (Valencia)	Dip for 30 sec	0.048	2	2.18, 2.49 [2.3]	09175.06-CA 133
Florida	Orange (Roberts mandarin)	Dip for 30 sec	0.048	2	2.38, 2.40 [2.4]	09175.06-FL43
California	Orange (W. Murcott mandarin)	Dip for 30 sec	0.048	2	3.40, 3.36 [3.4]	09175.06-CA134
California	Orange (W. Murcott mandarin)	Dip for 30 sec	0.048	2	2.41, 2.50 [2.5]	09175.06-CA135
California	Orange (Dancy mandarin)	Dip for 30 sec	0.048	2	2.48, 4.90 [3.7]	09175.06-CA136
Texas,	Grapefruit (Red Rio)	Dip for 30 sec	0.048	2	0.93, 0.90 [0.9]	09175.06-TX41
California	Grapefruit (Marsh)	Dip for 30 sec	0.048	2	1.17, 1.44 [1.3]	09175.06-CA137
California	Lemon (Eureka)	Dip for 30 sec	0.048	2	3.19, 2.79 [3.0]	09175.06-CA138
California	Lemon (Eureka)	Dip for 30 sec	0.048	2	1.92, 2.29 [2.1]	09175.06-CA 140
California,	Orange (W. Murcott mandarin)	In-line fruit coating spray	1.7 + 1.6 g ai/ 1000 kg fruit	2	2.32, 2.24 [2.3]	09175.06-CA135
California	Orange (Dancy mandarin)	In-line fruit coating spray	1.7 + 1.6 g ai/ 1000 kg fruit	2	1.18, 1.51 [1.3]	09175.06-CA136
California	Grapefruit (Marsh)	In-line fruit coating spray	1.6 + 1.7 g ai/ 1000 kg fruit	2	1.41, 1.19 [1.3]	09175.06-CA137
California	Lemon (Eureka)	In-line fruit coating spray	1.7 + 1.6 g ai/ 1000 kg fruit	2	1.10, 1.14 [1.1]	09175.06-CA138
California	Lemon (Eureka)	In-line fruit coating spray	1.6 + 1.6 g ai/ 1000 kg fruit	2	0.92, 0.94 [0.9]	09175.06-CA 140

Note: For risk assessment purposes, following the residue definition, total residues were calculated by applying a factor of 1.1 to convert propiconazole only residues to total residues of propiconazole and metabolites convertible to 2,4-DCBA.

Stone fruits

A total of nine post-harvest trials on stone fruits were conducted in 2007 in the United States. Propiconazole was applied to harvested mature fruits either as a high-volume spray, low-volume spray or dipped for 30 seconds. Fruit wax was included in each of the tank mixes, except in the dip in the GA*17 peach trial. Fruits were allowed to air dry following treatment. The results are shown in Table 4.

Table 4 Propiconazole residues in stone fruits without stone from post-harvest treatments from trials conducted in USA using WP formulation in 2007/2008 (IR-4 PR 09787)

State	Crop (variety)	Treatment Method	Rate	no.	Propiconazole only	Total residues	Trial
California	Peach (Flavorcrest)	Dip for 30 seconds	0.014 kg/hL	1	1.68, 1.77 [1.7]	2.52 c=0.06	09787.07-CA88
New Jersey	Peach (Blake)	Dip for 30 seconds	0.014 kg/hL	1	1.16, 1.18 [1.2]	0.73 c=0.05	09787.07-NJ30
Georgia	Peach (Organic)	Dip for 30 seconds	0.014 kg/hL	1	2.17, 2.04 [2.1]	2.35, 2.23 [2.3] c=0.07	09787.08-GA*17
California	Peach (O'Henry)	Dip for 30 seconds	0.014 kg/hL	1	1.24, 1.46 [1.4]	1.06 c=0.07	09787.07-CA116
California,	Plum (Friar)	Dip for 30 seconds	0.014 kg/hL	1	0.16, 0.20 [0.18]	0.11	09787.07-CA86,
California	Plum (Casselman)	Dip for 30 seconds	0.014 kg/hL	1	0.22, 0.18 [0.20]	0.13	09787.07-CA87,
Michigan	Cherry (Hedelfingen)	Dip for 30 seconds	0.014 kg/hL	1	1.0, 0.70 [0.85]	2.23	09787.07-MI14,
Oregon	Cherry (Lapins)	Dip for 30 seconds	0.014 kg/hL	1	0.65, 0.69 [0.67]	0.78	09787.07-OR14,
California	Peach (Flavorcrest)	High volume in-line spray application	0.60 g ai/1000 kg fruit	1	0.14, 0.14 [0.14]	0.33 c=0.06	09787.07-CA88
		Low volume in-line spray application	0.57 g ai/1000 kg fruit	1	0.46, 0.52 [0.49]	0.43	
California	Peach (O'Henry)	High volume in-line spray application	0.57 g ai/1000 kg fruit	1	0.19, 0.20 [0.20]	0.13 c=0.07	09787.07-CA116
		Low volume in-line spray application	0.57 g ai/1000 kg fruit	1	0.43, 0.56 [0.50]	0.42 c=0.07	
California	Plum (Friar)	Low volume in-line spray application	0.57 g ai/1000 kg fruit	1	0.16, 0.15 [0.16]	0.13	09787.07-CA86
California	Plum (Casselman)	Low volume in-line spray application	0.58 g ai/1000 kg fruit	1	0.18, 0.20 [0.19]	0.40	09787.07-CA87,
California	Cherry (Bing)	High volume in-line spray application	0.56 g ai/1000 kg fruit	1	0.17, 0.16 [0.17]	0.24	09787.07-CA89,

c= residues in control samples

Tomato

A total of six post-harvest trials on tomato were conducted in the United States in 2009. Mature tomatoes were collected from the field, rinsed with water, allowed to dry, and treated with propiconazole and fludioxonil in a tank mix, except in two trials. In the NC19 and NC32 trials, the tomatoes were collected and placed in storage at 14 to 20 °C until treatment within 1 to 3 days; the tomatoes were not rinsed prior

to treatment. For the dip application, the fruit was dipped in the test solution for approximately 30 seconds and drained. For the drench application, the test solution was applied with either a watering can or a drench plate. For the spray application, the test solution was applied as the fruit passed under the nozzle on brush rollers. The fruit was allowed to air dry following treatment. The results are shown in Table 5.

Table 5 Propiconazole residues in tomato from post-harvest treatments from trials conducted in USA in 2009 using WP formulation (IR-4 PR 10182)

Location	Variety	Treatment Method	Rate	no.	Propiconazole only [Mean]	Total residues ¹	
New York	Polbig	Dip for 30 seconds	27 g ai/100L	1	0.532, 0.412 [0.47]	0.515, 0.331 [0.42]	10182.09-NY12
Florida	AGRI-SET 761	Dip for 30 seconds	27 g ai/100L	1	0.654, 0.948 [0.80]	0.631, 0.621 [0.63]	10182.09-FL06
North Carolina (Amelia)		Dip for 30 seconds	27 g ai/100L	1	0.541, 0.573 [0.56]	0.583, 0.572 [0.58]	10182.09-NC19
		Drenching	27 g ai/100L	1	0.765, 0.965 [0.87]	1.13, 0.958 [1.0]	
California	Shady Lady	Dip for 30 seconds	27 g ai/100L	1	0.474, 0.464 [0.47]	0.436, 0.555 [0.50]	10182.09-CA98
		Drenching	27 g ai/100L	1	0.394, 0.520 [0.46]	0.331, 0.426 [0.38]	
Florida	IL-7108	Dip for 30 seconds	27 g ai/100L	1	0.784, 0.806 [0.80]	0.800, 0.840 [0.82]	10182.09-FL68
North Carolina	Red Cherry	Dip for 30 seconds	27 g ai/100L	1	1.12, 1.11 [1.1]	1.23, 1.02 [1.1]	10182.09-NC32
		Drenching	27 g ai/100L	1	1.50, 1.26 [1.4]	1.35, 1.52 [1.4]	
North Carolina	Amelia	In-line spray	4.5 g ai/1000 kg fruit	1	0.677, 0.809 [0.74]	0.752, 0.678 [0.72]	10182.09-NC19
California	Shady Lady	In-line spray	4.5 g ai/1000 kg fruit	1	0.324, 0.407 [0.37]	0.364, 0.284 [0.32]	10182.09-CA98
North Carolina	Red Cherry	In-line spray	4.5 g ai/1000 kg fruit	1	1.4, 1.53 [1.5]	1.25, 1.76 [1.5]	10182.09-NC32

FATE OF RESIDUES IN STORAGE AND PROCESSING

Effect of processing on the nature of the residues

The hydrolytic stability of [triazolyl-¹⁴C]-propiconazole was investigated in aqueous buffer solutions at three pH values and temperatures to simulate processing practices (Adam D., 2008; Report No. T005078). The study was performed at pH 4 and 90 °C to simulate pasteurisation, pH 5 and 100 °C to simulate baking/brewing/boiling and at pH 6 and 120 °C to simulate sterilisation.

Buffer solutions containing [triazolyl-¹⁴C]-propiconazole at an initial concentration of 1.7 mg/L (significantly less than its water solubility of 100 mg/L at 20 °C) were incubated in closed high-pressure glass vessels in oil baths. The temperatures were maintained constant throughout incubation time (max ± 0.2 °C) and no significant variation of the pH values were observed in the buffered solutions. At time 0 and after 20 or 60 minutes incubation, duplicate samples per pH value (except at time 0) were taken, measured for total radioactivity by liquid scintillation counting (LSC), and analysed to determine the nature of degradates by high-performance liquid chromatography (HPLC). Selected samples were additionally analysed by two-dimensional thin layer chromatography (2D-TLC) to confirm the HPLC results. Mean recoveries of applied radioactivity were 99.0±1.3% (pH 4), 99.9% (pH 5) and 99.8±0.5% (pH 6). The results from analysis of the buffer solutions following incubation are summarised in Table 6.

Table 6 Analysis of ^{14}C -propiconazole in buffer solutions before and after incubation

Duplicate	Percentage of initial radioactivity (mg parent equivalents/litre solution)					
	pH 4 (90°C)		pH 5 (100°C)		pH 6 (120°C)	
	0 min	20 min	0 min	60 min	0 min	20 min
A	100 (1.696)	98.8 (1.675)	100 (1.676)	99.4 (1.666)	100 (1.673)	100.2 (1.675)
B	100 (1.696)	97.2 (1.647)	100 (1.676)	100.3 (1.682)	100 (1.673)	99.0 (1.656)
Mean	100 (1.696)	98.0 (1.661)	100 (1.676)	99.9 (1.674)	100 (1.673)	99.6 (1.666)

RESIDUES IN PROCESSED COMMODITIES

Orange samples collected in trial 06-CA133 (Table 3) were processed to oil, juice and dried pomace using procedures simulating commercial practice.

Oranges were washed, peeled by abrasion and a cold water mist was sprayed into the peeler to trap the highly volatile oil. The resulting emulsion of water and oil was treated with 0.2% of a pectinase enzyme preparation and allowed to react overnight at approximately 20 °C. The oil emulsion was passed through a screen separator, the peels were resuspended to extract any clinging oil and then passed through a centrifuge to separate solids, water, and the oil stream. The oil stream was centrifuged, kept frozen for at least 16 hours, filtered, anhydrous sodium sulfate added, and filtered again to obtain the oil.

Oranges were processed through a juice extractor, the juice processed through a finisher equipped with a 0.051-cm screen to remove coarse pulp and peel pieces, and then heated in a small steam jacketed kettle to 90 °C.

The peel from the juice extraction process was shredded and ground, combined with the other peel solid fractions (from oil separation) and blended with lime slurried water. The neutralized peel/pulp fraction was passed through a continuous screw press, resulting in fractions of expressed liquid and wet pulp. The wet pulp was spread on stainless steel trays and dried at 65 to 75 °C until reaching approximately 92% dry matter (dried orange pomace).

All processed samples were shipped frozen to the analytical laboratory within 85 days of processing for analysis of propiconazole. The results are shown in Table 7.

Table 7 Residues of propiconazole in orange processed fractions

Matrix	Residues of propiconazole (mg/kg)	Processing factor
Orange (RAC)	0.94	-
Juice	<0.01	<0.011
Dried Pulp	1.29	1.4
Oil	174	185

APPRAISAL

Propiconazole was evaluated by the JMPR for residues in 1987, 1991, 1994, and within the periodic review program in 2007, when a number of maximum residue levels were recommended. Propiconazole has an ADI of 0–0.07 mg/kg bw and an ARfD of 0.3 mg/kg bw. Information and residue trial data on citrus, stone fruits and tomato following post-harvest applications of propiconazole were submitted to current Meeting.

The residue definition for plant and animal commodities is *propiconazole* for compliance with the MRL and *propiconazole plus all metabolites convertible to 2,4-dichlorobenzoic acid, expressed as propiconazole* for the estimation of the dietary intakes.

Methods of analysis

Methods of analysis evaluated by the 2007 JMPR are divided into two groups. Methods where only propiconazole is analysed involves mostly LC-MS/MS detection, with LOQ of 0.01 mg/kg for citrus and tomato and of 0.05 mg/kg for stone fruits. The common moiety method measure all residues convertible to 2,4-dichlorobenzoic (2,4-DCBA) and are performed using mostly GC-MSD (after derivatisation of 2,4-DCBA to its methyl ester) with an LOQ of 0.05 mg/kg.

Stability of residues in stored analytical samples

A study to investigate the stability of residues in analytical samples in peach submitted to the 2007 JMPR showed that residues of propiconazole in peach samples are stable up to 36 months after frozen storage. New studies evaluated by the present Meeting have shown that propiconazole residues were stable for up to 207 days in orange, 154 days in juice and dried pulp, and 224 days in orange oil and 189 days in cherries. Propiconazole residues measured using the common moiety method in tomato (fortified with propiconazole at 0.5 mg/kg level) were stable up to 160 days, and the samples in the residue trials were analysed within this period. No storage stability study for total residues was performed in stone fruits (samples were stored for at least 560 days).

Results from supervised residue trials on crops

The 2007 JMPR agreed that, based on metabolism study, a factor of 3 needs to be applied to convert parent residues to total residues (all residues convertible to 2,4-DCBA and expressed as propiconazole). Data evaluated by the present Meeting are from post harvested uses, and it is unlikely that propiconazole metabolites are formed between treatment and sample preparation for analysis. Furthermore, residues of propiconazole will be used for dietary exposure assessment, without using the factor of 3.

Citrus fruits

In USA, propiconazole can be applied twice as post-harvest treatment as in line dip/drench twice at up to 0.054 kg ai/hL or in-line aqueous or fruit coating spray at up to 1.8 g ai/1000 kg fruit. Seventeen post-harvest trials on citrus were conducted in 2006 in USA according to GAP rate, but in eight trials the samples were washed before the second application.

In four trials conducted in orange using dip application conducted according to GAP, residues of propiconazole were 2.2, 2.5, 3.4 and 3.7 mg/kg (highest level of duplicate sample was 4.9 mg/kg).

The Meeting estimates a maximum residue level of 9 mg/kg, a STMR of 2.95 mg/kg and a HR of 4.9 mg/kg for propiconazole in oranges.

Stone fruits

In USA, propiconazole can be applied once as post-harvest treatment in stone fruits using in line dip/drench twice at up to 0.014 kg ai/hL or in-line aqueous or fruit coating spray at up to 0.56 g ai/1000 kg fruit. Nine post-harvest trials on stone fruits were conducted in 2007 in USA according to GAP. In all trials, fruits without stone was analysed, but the Meeting agreed that the residues found in whole fruit is within 10% (higher) of that found in the fruits without the stones and consider the data appropriate.

Residues of propiconazole from trials conducted using dip application were 1.2, 1.4, 1.7 and 2.1 mg/kg in peaches (highest value of duplicate samples of 2.2 mg/kg), 0.18 and 0.20 mg/kg in plums (highest value of duplicate samples of 0.22 mg/kg) and 0.67 and 0.85 mg/kg in cherry.

Residue of propiconazole in fruits without stone from trials conducted using in-line aqueous application were 0.14, 0.20, 0.49 and 0.50 mg/kg in peaches, 0.16 and 0.19 mg/kg in plum and 0.17 mg/kg in cherry.

The Meeting agreed that trials conducted using dip application in peach gave the highest residues and recommends a maximum residue level of 5 mg/kg (Po), a STMR of 1.55 mg/kg and a HR of 2.2 mg/kg for propiconazole in peaches.

Residues in plums from dip and spray application are similar and can be grouped as 0.16, 0.18, 0.19 and 0.20 mg/kg. The Meeting recommends a maximum residue level of 0.6 mg/kg, a STMR of 0.185 mg/kg and a HR of 0.22 mg/kg for propiconazole in plums.

The Meeting agreed that there is not enough trials to estimate a maximum residue level for cherry.

Tomato

In USA, propiconazole can be used in tomato as a post-harvest treatment in line dip or drench at up to 0.27 kg ai/hL or high volume spray application at 4.5 g ai/1000 kg fruit. Nine post-harvest trials on tomato were conducted in 2009 in USA according to GAP.

In six trials using dip or drench application, residues of propiconazole in tomatoes were 0.47 (2), 0.80 (2), 0.87 and 1.4 mg/kg. In three trials using in-line spray, residues were 0.37, 0.74 and 1.5 mg/kg.

The Meeting agreed that the dip/drench and the in-line spray trials gave similar results that can be grouped as (n=9) 0.37, 0.47 (2), 0.74, 0.80 (2), 0.87 and 1.4 and 1.5 mg/kg (highest level among the samples was 1.5 mg/kg)

The Meeting estimates a maximum residue level of 3 mg/kg, a STMR of 0.80 mg/kg and a HR of 1.5 mg/kg for propiconazole in tomato.

Fate of residues in storage and processing

Effect on the nature of the residues during processing

The hydrolytic stability of [triazolyl-U-¹⁴C]-propiconazole was investigated in aqueous buffer solutions at three pH values and temperatures to simulate processing practices. The study was performed at pH 4 and 90 °C for 20 minutes to simulate pasteurisation, pH 5 and 100 °C for 60 min to simulate baking/brewing/boiling, and at pH 6 and 120 °C for 20 min to simulate sterilisation. Only the parent compound was detected in the buffer solutions throughout the study, indicating that propiconazole is hydrolytically stable under the conditions of the tests.

Residues in processed commodities

In one study, orange were processed to oil, juice and dried pomace using procedures simulating commercial practice. Residues of propiconazole in oranges were 0.94 mg/kg, not detected in juice (< 0.01 mg/kg), 1.29 mg/kg in dried pulp and 174 mg/kg in oil, giving processing factors of < 0.011 for orange juice and of 184 for orange oil.

Based on a STMR of 1.95 mg/kg in oranges, the Meeting estimated a STMR-P of 0.02 mg/kg in orange juice.

Residues in animal commodities

Dried orange fruit can contribute to animal diets and is listed on the OECD animal diet. However, in commercial practice, post-harvest treatment is normally reserved for high value commodities and is unlikely that dried fruit from treated fruits would be fed to livestock. The Meeting considered that the estimations for propiconazole in orange will not change the dietary burden calculated by the 2007 JMPR meeting, and confirms its previous recommendations for animal commodities

RECOMMENDATIONS

Residues: For plant and animal commodities is *propiconazole* for compliance with the MRL and *propiconazole plus all metabolites convertible to 2,4-dichlorobenzoic acid, expressed as propiconazole* for the estimation of the dietary intakes.

CCN	Commodity name	Recommended maximum residue level (mg/kg)		STMR (P) mg/kg	HR (P) mg/kg
		New	Previous		
FS 0247	Peach	5 (Po)		1.55	2.2
FS 0014	Plums (including prunes)	0.6 (Po)		0.185	0.22
FC 0004	Oranges, Sweet, Sour (including Ordange-like hybrids): several cultivars	9 (Po)		2.95	4.9
JF 0004	Orange juice			0.02	
VO 0448	Tomato	3 (Po)		0.80	1.5

DIETARY RISK ASSESSMENT

Long-term intake

The IEDI of propiconazole based on the STMRs estimated by this and previous Meetings for the 13 GEMS/Food regional diets were 1–20% of the maximum ADI of 0–0.07 mg/kg bw (see Annex 3 of the 2013 Report). The Meeting concluded that the long-term dietary intake of residues of propiconazole is unlikely to present a public health concern.

Short-term intake

The ARfD for propiconazole is 0.3 mg/kg bw. The International Estimated Short-Term Intake (IESTI) for propiconazole was calculated for the plant commodities for which STMRs, HRs and maximum residue levels were estimated by the current Meeting and for which consumption data were available. The results are shown in Annex 4 of the 2013 Report. The IESTI represented a maximum of 100% of the ARfD for oranges (children 2–6 years). The Meeting concluded that the short-term intake of propiconazole residues from uses considered by the current Meeting were unlikely to present a public health concern.

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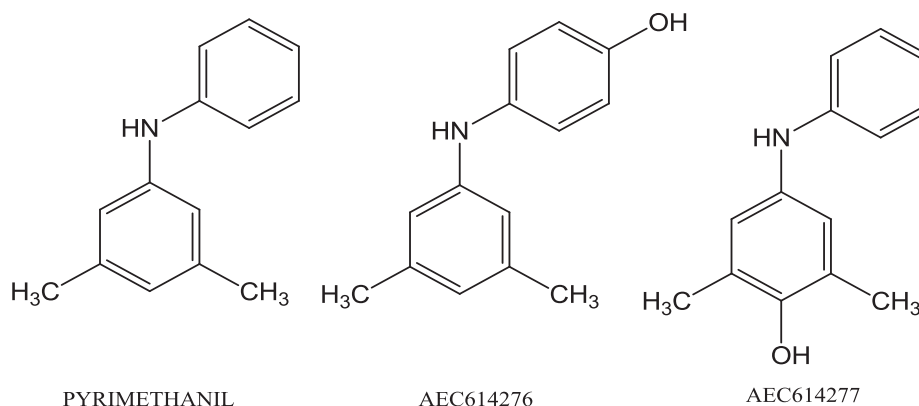
PYRIMETHANIL (226)

The first draft was prepared by Dr Michael Doherty, Office of Pesticide Programs, United States Environmental Protection Agency

EXPLANATION

Pyrimethanil is an anilinopyrimidine fungicide that was first reviewed by the JMPR in 2007. During this review, maximum residue levels for commodities from field and post-harvest uses were recommended and subsequently adopted by the Codex Alimentarius Commission as Codex MRLs. Among these were maximum residue levels for pre-harvest uses on apricot, plums and peach and on post-harvest uses on pome fruit and cherries.

The sponsors (Janssen and IR-4) have since provided additional studies on the properties of pyrimethanil in a motion to re-evaluate the maximum residue levels of pyrimethanil on pome and stone fruits. Further, preharvest residue data on lemon and ginseng have also been submitted.

Structural Formulae**RESIDUE ANALYSIS***Description of analytical methods*

A number of analytical methods developed to determine pyrimethanil residues in plant matrices, including those used in pre- and post-harvest trials on pome fruit and stone fruit, were submitted and reviewed by JMPR in 2007. For plant commodities, methods consisted of organic solvent extraction (acetone or methanol), clean-up, and analysis by either gas chromatography with mass spectrometric detection (GC/MS), or by high performance liquid chromatography with ultraviolet detection (HPLC/UV). The HPLC/UV method was validated for apples with an LOQ of 0.05 mg/kg. The GC/MS method was validated for apples, peaches, and plums with an LOQ of 0.05 mg/kg. Multiresidue methods (US FDA and DFG S 19) were also reported for pyrimethanil and validated with an LOQ of 0.05 mg/kg. The JMPR concluded that adequate analytical methods exist for both data collection and enforcement purposes for pyrimethanil residues in plant commodities.

The new field trial studies used analytical methods similar to those reviewed by the 2007 JMPR. Among the new field trial data submitted to the 2013 JMPR, ginseng is the only new crop for which no data were submitted to the 2007 JMPR. Ginseng samples were analysed for pyrimethanil residues via GC/MS after an acetone homogenization/extraction step, an acid/base partitioning procedure, and additional clean up by silica SPE column. The method LOQ was 0.05 mg/kg; at this spiking level, method validation recoveries were $101 \pm 8\%$ (n=6).

Method validation and procedural recoveries

A summary of the method validation and procedural recoveries for the new pome and stone fruit studies for 2013 JMPR review are provided in Table 1. Average method and concurrent recoveries were all within the acceptable range of 70–120%, with relative standard deviations (RSD) below 20%.

Table 1 Summary of Method Validation and Procedural Recoveries

Analyte	Crop	Fortification mg/kg	n	Range Recovery (%)	Mean recovery (%)	% RSD	Method	Reference
Method Validation								
Pyrimethanil	Apple	0.05-5.0	15	92-109	97	4.6	GC/MSD	06001
Pyrimethanil	Apple	0.05-5.0	18	87-131	106	12	GC/MSD	AGR 406
Pyrimethanil	Pear	0.05-5.0	18	85-113	98	8.7	GC/MSD	AGR 406
Pyrimethanil	Apple	0.2-1.2	6	90-110	101	8.6	HPLC/UV	AGR 521
Pyrimethanil	Pear	0.2-2.3	6	87-96	91	3.4	HPLC/UV	AGR 521
Pyrimethanil	Cherry	0.05-5.0	11	81-100	92	6.1	GC/MSD	PR 08701
Procedural Recoveries								
Pyrimethanil	Apple	0.05; 0.5	2	95.9, 96.3	96	-	GC/MSD	AGR 511
Pyrimethanil	Apple	2.2	3	101-107	104	2.9	LC/MS	AGR 1234
Pyrimethanil	Pear	2.2	3	105-116	112	5.4	LC/MS	AGR 1234
Pyrimethanil	Cherry	0.5; 15	5	87-93	91	2.8	GC/MSD	PR 08701

Storage Stability Studies

The 2007 JMPR received data for pyrimethanil demonstrating adequate residue stability for at least one year in the following crop matrices held in frozen storage: apple, grape, tomato, lettuce, carrot, pea, peach, and plum. Ginseng samples were stored frozen for a maximum of 259 days in the field trials. The supporting storage stability study showed recoveries of 80, 89, and 90% (86% average) after 259 days of storage at < -20 °C, for control samples spiked at 0.50 mg/kg.

USE PATTERN

Pyrimethanil may be applied both pre-harvest and post-harvest for disease control in a range of crops. The various national GAPs relevant to the pre-harvest treatment and post-harvest treatment studies reported herein are summarized in Table 2 and in Table 3, respectively. For pome fruit, a combination of pre-harvest and post-harvest applications can be followed by a thermofog treatment except in the situation where a dip/drench treatment has already been made. For stone fruit, combinations of pre-harvest and post-harvest treatments are permitted, but no thermofog treatments have been registered.

Table 2 Summary of Pre-harvest GAP Uses of Pyrimethanil in/on Pome and Stone Fruit, Ginseng and Lemon^a

Crop	Country	Formulation	Application				PHI (Days)
			Method	kg ai/ha	kg ai/hL	No. or max (kg ai/ha/season)	
Pome Fruit	Belgium	400 g/L SC	Foliar	0.45	0.22	5	28
	France	400 g/L SC	Foliar		0.02	4	28
	Germany	400 g/L SC	Foliar		0.03	5	--
	Greece	400 g/L SC	Foliar		0.08	2	28
	Italy	400 g/L SC	Foliar		0.03-0.04	5	14
	Netherlands	400 g/L SC	Foliar		0.03	5	28
	UK	400 g/L SC	Foliar		0.04	5	--
	USA	600 g/L SC	Foliar		--	1.8	72
Stone Fruit (except cherry)	USA	600 g/L SC	Foliar	0.8	--	2.4	2
Ginseng	USA	600 g/L SC	Foliar	0.78	--	2.35	30
Lemon	USA	600 g/L SC	Foliar	0.78	--	0.78	7

^a All submitted to 2007 JMPR except ginseng and lemon.

Table 3 Summary of Post-harvest GAP Uses of Pyrimethanil in/on Pome Fruit and Stone Fruit ^a

Crop	Country	Formulation (Pyrimethanil content)	Application			
			Method	Time (minutes)	Rate, kg ai/hL	No. (max)
Dip, drench, aqueous line spray, wax line spray						
Apple, Pear	Chile	400 g/L SC	Dipping	1	0.05–0.1	1
			Drench	1	0.05–0.1	1
			Aqueous line spray	1	0.1	1
			Wax line spray	1	0.2	1
Apple, pear	Uruguay	200 g/L SC	Dipping		0.05	2
			Drench		0.05	2
Cherry	Chile	400 g/L SC	Dipping	0.5-1	0.04	1
			Wax line spray	0.5-1	0.04	1
Peach, Plum, Nectarines	Chile	400 g/L SC	Aqueous line spray	1	0.1	1
			Wax line spray	1	0.2–0.3	1
Pear	Belgium	200 g/L SC	Dip		0.03	1
			Drench		0.03	1
Pear	Italy	200 g/L SC	Dipping	0.3-0.5	0.03	1
			Drench	0.3-0.5	0.03	1
Pear	Netherlands	200 g/L SC	Dipping		0.03	1
			Aqueous line spray		0.03	1
Pear	South Africa	200 g/L SC	Dipping	1	0.03	1
Pear	Spain	200 g/L SC	Drench		0.04	1
Pome fruit	Argentina	400 g/L SC	Dipping	1	0.05-0.1	1
			Drench	1	0.05-0.1	1
			Aqueous line spray	1	0.1	1
			Wax line spray	1	0.2	1
Pome fruit	USA	400 g/L SC	Dipping	1	0.05–0.1	Up to maximum combination of 2 methods: (1) drench + dip; (2) drench + wax; (3) drench + aq. Spray; (4) dip + wax; (5) dip + aq. Spray; (6) aq. Spray + wax
			Drench	1	0.05–0.1	
			Aqueous line spray	1	0.1	
			Wax line spray	1	0.2	
Dip, drench, aqueous line spray, wax line spray						
Stone fruit	USA	400 g/L SC	Dip tanks	0.5	0.05	1
			high volume line application	0.5	0.05	1
			low volume line application (except cherry)	0.5	0.2	1
Thermofogging						
Apple	Belgium	160 g/L NH	Thermofogging		5.6-8 g ai/ 1000 kg fruit	1
Apple, pear	Italy	160 g/L NH	Thermofogging		8 g ai/1000 kg fruit	1
Apple, pear	Chile	160 g/kg NH	Thermofogging		6.4-9.6 g ai/ 1000 kg of fruit	1
Pome fruit	South Africa	160 g/L NH	Thermofogging		9.6 g ai/1000 kg fruit	1
Pome fruit	USA	160 g/L NH	Thermofogging		9.6 g ai/1000 kg of fruit	1 Do not apply to fruit already treated via drench or dip/wash applications

^a Submitted to 2007 JMPR, but additional trials and complete GAPs submitted for 2013 JMPR consideration [In 2007, the only thermofog GAP was from Chile as a proposed use on pome fruit].

RESIDUES FROM SUPERVISED TRIALS ON CROPS

Pre-harvest Lemon Trials

The 2013 Meeting received data reflecting residues of pyrimethanil on lemons following foliar spray according to the USA GAP (600 g/L SC, single foliar application at 0.78 kg ai/ha).

Table 4 Pyrimethanil Residues in Lemon following Pre-Harvest Treatment (Reference PR 09085)

Lemon Year Variety	Application Rate (kg ai/ ha)	Number of Applications	DAT	Pyrimethanil Residue (mg/kg) Whole Fruit [Average]
GAP, USA	0.78	1	7	--
2004 04-CA73: Porterville, CA (Pryor)	0.69	1	7	0.26 0.27 [0.265]
2004 04-CA77: Ivanhoe, CA (Lisbon)	0.817	1	7	0.22 0.19 [0.205]
2004 04-CA74: Orange Cove, CA (Lisbon)	0.711	1	7	0.068 0.095 [0.815]
2004 04-CA76 : Orange Cove, CA (Lisbon)	0.707	1	7	0.12 0.24 [0.180]
2005 04-CA75: Riverside, CA (Lisbon)	0.703	1	7	0.22 0.31 [0.265]

Pome fruits

A number of pre- and post-harvest supervised trials on pome fruit were submitted and reviewed by the JMPR in 2007. Those data are included in the table below.

Table 5 Summary of pyrimethanil/pome fruit residue data reviewed by 2007 JMPR

Application	Crop	GAP	Residues (mg/kg)
Pre-harvest	Apple	USA	<0.05 (7), 0.06, 0.10, 0.12, 0.15, 0.16
	Apple	Italy	0.56
	Pear	USA	<0.05 (6)
Post harvest- aq. spray, wax spray	Apple	Spain	1.2, 1.3, 2.0, 2.1
		Belgium	0.57, 1.7
		USA	0.27, 0.28, 0.33, 0.39, 0.64, 0.70, 1.1, 1.1, 1.2, 1.5
	Pear	Belgium	0.32, 0.55
		Spain	0.57, 0.66
		USA	0.13, 0.18, 0.32, 0.45, 0.56, 0.86, 1.1, 1.1
Post-harvest, dip, drench	Apple	Belgium	0.53, 0.81, 0.89, 0.89, 0.92, 1.0, 1.3, 1.5, 1.9, 1.9, 2.0, 2.1, 2.3, 3.1, 3.3
	Pear	Belgium	0.61, 0.96, 2.1, 1.5, 1.0, 1.1, 1.1, 1.2, 2.8, 3.6
Post-harvest, dip + spray	Apples	USA	0.44, 0.51, 0.55, 0.67, 0.76, 0.79, 0.86, 1.0, 1.1, 1.2, 1.2, 1.4, 1.5, 1.5
	Pear	USA	0.36, 0.43, 0.56, 0.84, 0.86, 0.91, 1.5, 1.8, 1.9, 2.0, 2.5
Post-harvest, thermofogging	Apple	USA	0.43
		Belgium	1.1, 1.4, 1.4, 1.5, 1.6, 4.9, 6.4, 7.1
	Pear	Belgium/Italy	1.0, 1.6, 1.8, 3.5

New Post-Harvest Trials on Pome Fruits

The 2013 Meeting received new and updated labels for post-harvest uses of pyrimethanil. In addition, 15 post-harvest dipping/drenching trials on apples and 10 on pears conducted from 2001-2005 in Australia, Italy, France, Spain and Belgium, as well as 7 thermofogging trials from the USA (2007)

and Belgium (2001) were submitted. All dip/drench trials followed the GAP in Belgium (200 g ai/L SC, dip/drench at the rate of 0.03 kg ai/hL). Note: Netherlands and Italy have similar GAPs. Table 6 summarizes the post-harvest trials on pome fruit, with residues according to GAP underlined.

Table 6 Pyrimethanil residues in pome fruit resulting from post-harvest treatments

POME	Postharvest Application					Residues	Reference
country, year (variety)	Form. (pyrimethanil content)	Treatment Method	Rate (kg ai/hL)	No.	Sampling (day)	mg/kg (mean)	
APPLES							
GAP, Belgium	200 g/L EC	Dip/drench	0.03	1			
Belgium, 2001 Apple/ Golden Delicious	LAg 2001 334 100 g/L EC	Dipping for 30 seconds	0.01	1	0	0.35, 0.39 (0.37)	AGR 406
					7 months	0.27, 0.33 (0.30)	
			0.02	1	0	0.49, 0.54 (0.52)	
					7 months	0.44, 0.52 (0.48)	
			0.03	1	0	0.54, 0.52 (0.53)	
					7 months	0.50, 0.49 (0.50)	
Belgium, 2001 Apple/ Golden Delicious	LAg 2001 206 150 g/L EC	Dipping for 30 seconds	0.03	1	0	0.91, 0.81 (0.86)	AGR 406
					7 months	0.89	
			0.04	1	0	1.2, 1.5 (1.4)	
					7 months	1.2	
			0.06	1	0	1.3, 1.9 (1.6)	
					7 months	1.7	
Belgium, 2001 Apple/ Jonagold	LAg 2001 206 150 g/L EC	Dipping for 30 seconds	0.03	1	0	1.4, 1.3 (1.4)	AGR 406
					7 months	1.9	
			0.04	1	0	1.7, 1.8 (1.8)	
					7 months	2.0	
			0.06	1	0	2.3, 2.9 (2.6)	
					7 months	2.2	
Trial 2132 AN1 France, 2002 Apple/ Golden	LAg 2002 258 200 g/L SC	Pre-harvest only	-	-		0.15	AGR 511
		Pre + post- harvest dip for 30 sec	0.03	1	0	0.76	
		Dip for 30 sec	0.03	1	0	1.0	
Trial 2132 AN2 France, 2002 Apple/ Golden	LAg 2002 258 200 g/L SC	Pre-harvest only	-	-		0.21	AGR 511
		Pre + post- harvest dip for 30 sec	0.03	1	0	0.63	
		Dip for 30 sec	0.03	1	0	0.92	
AGR 521 Italy, 2002 Apple/ Golden	LAg 2002 228 150 g/L EC	Drenching for 1 min	0.03	1	1	1.8	AGR 521
					14	1.5	
					36	1.9	
					59	2.3	
					72	2.3	
AGR 521 Italy, 2002 Apple/ Stark	LAg 2002 228 150 g/L EC	Drenching for 1 min	0.03	1	1	1.6	AGR 521
					14	1.6	
					36	1.6	
					59	2.0	
					72	1.8	

POME	Postharvest Application					Residues	Reference
country, year (variety)	Form. (pyrimethanil content)	Treatment Method	Rate (kg ai/hL)	No.	Sampling (day)	mg/kg (mean)	
AGR 521 Italy, 2002 Apple/ Pink Lady	LAg 2002 228 150 g/L EC	Drenching for 1 min	0.03	1	1 14 36 59 72	1.9 1.2 1.2 1.8 1.9	AGR 521
AGR 521 Italy, 2002 Apple/ Fuji	LAg 2002 228 150 g/L EC	Drenching for 1 min	0.03	1	1 14 36 59 72	1.9 1.7 1.8 2.1 1.8	AGR 521
AGR 521 Italy, 2002 Apple/ Golden	LAg 2002 258 200 g/L SC	Drenching for 1 min	0.03	1	1 14 36 59 72	0.69 1.3 1.2 1.1 0.98	AGR 521
AGR 521 Italy, 2002 Apple/ Stark	LAg 2002 258 200 g/L SC	Drenching for 1 min	0.03	1	1 14 36 59 72	0.58 0.78 0.75 0.82 0.89	AGR 521
AGR 521 Italy, 2002 Apple/ Pink Lady	LAg 2002 258 200 g/L SC	Drenching for 1 min	0.03	1	1 14 36 59 72	0.65 0.56 0.70 0.71 0.81	AGR 521
AGR 521 Italy, 2002 Apple/ Fuji	LAg 2002 258 200 g/L SC	Drenching for 1 min	0.03	1	1 14 36 59 72	0.80 1.1 1.1 1.1 1.5	AGR 521
AGR 1234 Australia, 2005 Apple/ Fuji	LAg 2002 258 200 g/L SC	Dipping for 30 seconds	0.03	1	0 day: Whole fruit Peel Pulp	3.1 17 0.7	AGR 1234
AGR 1234 Australia, 2005 Apple/ Fuji	LAg 2002 258 200 g/L SC	Dipping for 30 seconds	0.03	1	0 day: Whole fruit Peel Pulp	3.3 12 0.7	AGR 1234
PEAR							
AGR 521 Italy, 2002 Pear/ Decana	LAg 2002 228 150 g/L EC	Drenching for 1 min	0.03	1	1 14 36 59 72	0.73 0.80 0.93 0.94 0.96	AGR 521
AGR 521 Italy, 2002 Pear/Kaiser	LAg 2002 228 150 g/L EC	Drenching for 1 min	0.03	1	1 14 36 59 72	1.7 1.9 2.1 1.8 1.8	AGR 521
AGR 521 Italy, 2002 Pear/Abate	LAg 2002 228 150 g/L EC	Drenching for 1 min	0.03	1	1 14 36 59 72	1.2 1.4 1.5 1.4 1.4	AGR 521
AGR 521 Italy, 2002 Pear/ Conference	LAg 2002 228 150 g/L EC	Drenching for 1 min	0.03	1	1 14 36 59 72	1.0 1.0 0.95 0.98 0.91	AGR 521

POME	Postharvest Application					Residues	Reference
country, year (variety)	Form. (pyrimethanil content)	Treatment Method	Rate (kg ai/hL)	No.	Sampling (day)	mg/kg (mean)	
AGR 521 Italy, 2002 Pear/ Decana	LAg 2002 258 200 g/L SC	Drenching for 1 min	0.03	1	1 14 36 59 72	0.38 0.34 0.61 0.33 0.50	AGR 521
AGR 521 Italy, 2002 Pear/Kaiser	LAg 2002 258 200 g/L SC	Drenching for 1 min	0.03	1	1 14 36 59 72	1.2 0.91 0.96 1.0 0.94	AGR 521
AGR 521 Italy, 2002 Pear/Abate	LAg 2002 258 200 g/L SC	Drenching for 1 min	0.03	1	1 14 36 59 72	0.83 0.83 1.1 0.90 0.91	AGR 521
AGR 521 Italy, 2002 Pear/ Conference	LAg 2002 258 200 g/L SC	Drenching for 1 min	0.03	1	1 14 36 59 72	0.91 0.76 1.1 0.81 1.0	AGR 521
AGR 1234 Australia, 2005 Pear/ De Malines	LAg 2002 258 200 g/L SC	Dipping for 30 seconds	0.03	1	0 day: Whole fruit Peel Pulp	2.8 11 0.2	AGR 1234
AGR 1234 Australia, 2005 Pear/ De Malines	LAg 2002 258 200 g/L SC	Dipping for 30 seconds	0.03	1	0 day: Whole fruit Peel Pulp	3.6 18 0.3	AGR 1234

One thermofogging trial was conducted in the US in 2007, following the GAP there (160 g/ai/L HN, one application at 9.6 kg ai/1000 kg fruits) (Report 06001). Three of the five thermofogging trials were carried out in Belgium in 2001 following the GAP ($\pm 25\%$) in the country (160 g ai/L HN, one application at the rate of 5.6 to 8 kg ai/1000 kg fruits). The trials are summarized in Table 7, with residues according to GAP underlined.

Table 7 Pyrimethanil residues in pome fruit resulting from thermofogging

POME	Postharvest Application					Residues	Reference
country, year (variety)	Form.	Treatment Method	Rate (g ai/1000 kg fruit)	No.	Sampling (day)	mg/kg	
APPLES							
GAP, USA	160 g/kg HN	thermofogging	9.6	1	1		
Trial 06001 USA, 2007 Apple/ Red Delicious	160 g/kg HN	Thermofogging	9.6	1	1	0.26, 0.88, 0.25, 0.34 (0.43)	06001
GAP, Belgium	160 g/kg HN	thermofogging	5.6-8	1			
Belgium, 2001 Apple/ Golden; Jonagold	160 g/kg HN	Thermofogging	4.7	1	0 7 months	4.8, 3.3, 6.2, 1.7 (4.0) 4.8, 4.2, 6.8, 1.7 (4.4)	AGR 406
Belgium, 2001 Apple/ Golden; Jonagold	160 g/kg HN	Thermofogging	8	1	0 7 months	5.7, 4.3, 8.6, 4.7 (5.8) 5.5, 5.7, 8.7 (6.4)	AGR 406
Belgium, 2001 Apple/ Golden;	160 g/kg HN	Thermofogging	10	1	0	5.0, 4.9, 5.4, 7.9 (5.9)	AGR 406

POME	Postharvest Application					Residues	Reference
country, year (variety)	Form.	Treatment Method	Rate (g ai/1000 kg fruit)	No.	Sampling (day)	mg/kg	
Jonagold					7 months	5.4, 6.8, 6.5, 9.5 (7.1)	
Belgium, 2001 Apple/ Golden ; Jonagold	150 g/L HN	Aerobrume (= thermofog)	2.3	1	0	1.2, 2.8, 3.1, 2.9 (2.5)	AGR 406
					7 months	1.3, 3.4, 4.0, 2.7 (2.9)	
Belgium, 2001 Apple/ Golden; Jonagold	150 g/L HN	Aerobrume (= thermofog)	4.0	1	1	7.4, 3.0, 2.8, 4.2 (4.4)	AGR 406
					7 months	7.1, 3.5, 3.3, 6.8 (4.4)	
Belgium, 2001 Apple/ Golden; Jonagold	LAg 2001 206 (150 g/L HN)	Aerobrume (= thermofog)	6.4	1	1	6.6, 2.8, 3.3, 3.9 (4.2)	AGR 406
					7 months	6.5, 3.9, 3.6, 5.7 (4.9)	

Stone fruits

A number of pre- and post-harvest supervised trials on stone fruit were submitted and reviewed by the JMPR in 2007. Those data are included in the table below.

Table 8 Summary of pyrimethanil/stone fruit residue data reviewed by 2007 JMPR

Application	Crop	GAP	Residues (mg/kg)
Pre-harvest	Apricot	USA	0.6, 0.64, 0.94, 1.3, 1.7
	Peach	USA	1.5, 0.38, 0.54, 0.94, 0.99, 1.1, 1.2, 1.3, 1.3, 1.5, 1.6, 2.6
	Plum	USA	1.2, 0.05, 0.44, 0.58, 0.59, 0.59, 0.61, 0.62
Post-harvest, dip	Cherry	Chile	0.82, 1.0, 1.1, 1.2, 1.4, 1.4, 1.4, 1.5

New post-harvest trials on cherry

Five post-harvest trials on sweet cherry were conducted in the USA during 2006, in support of the GAP in the US (400 g ai/L SC, 0.05 kg ai/hL for dip and high volume line application and 0.2 kg ai/hL for low volume line application (Report PR 080701). At each trial, fruit samples were dipped for approximately 30 seconds in a pyrimethanil solution containing 400 g ai/378 litres (0.11 kg ai/hL). Two other treatments were examined at a high-volume application of 1000 kg fruits, applied at a spray concentration of 0.1 kg ai/hL. Fruit wax was added to the mixtures in all treatments. The trials are summarized below.

Table 9 Pyrimethanil residues in cherries resulting from post-harvest treatments

CHERRY	Postharvest Application					Residues	Reference
country, year (variety)	Form. (pyrimethanil content)	Treatment Method	Rate (kg ai/hL)	No.	Sampling (day)	mg/kg (mean)	
GAP, USA	400 g/L SC	Dip, 30 sec	0.05	1			
		High volume applic, 30 sec	0.05	1			
Trial 06-CA 100 USA, 2006 Cherry/Bing	Penbotec 400 SC (400 g/L SC)	Dipping with wax for 30 seconds	0.11	1	0	2.2, 2.1 (2.2)	PR 08701
Trial 06-WA10 USA, 2006 Cherry/Bing	Penbotec 400 SC (400 g/L SC)	Dipping with wax for 30 seconds	0.11	1	0	12, 13 (13)	PR 08701

CHERRY	Postharvest Application					Residues	Reference
country, year (variety)	Form. (pyrimethanil content)	Treatment Method	Rate (kg ai/hL)	No.	Sampling (day)	mg/kg (mean)	
Trial 06-MI40 USA, 2006 Cherry/Bing	Penbotec 400 SC (400 g/L SC)	Dipping with wax for 30 seconds	0.11	1	0	5.4, 5.9 (5.7)	PR 08701
Trial 06-CA 100 USA, 2006 Cherry/Bing	Penbotec 400 SC (400 g/L SC)	High volume spray with wax	0.11	1	0	1.2, 1.2 (1.2)	PR 08701
Trial 06-WA10 USA, 2006 Cherry/Bing	Penbotec 400 SC (400 g/L SC)	High volume spray with wax	0.11	1	0	12, 12 (12)	PR 08701

Pre-harvest Ginseng trials

The 2013 Meeting received data reflecting residues of pyrimethanil on ginseng following foliar spray according to the USA GAP (600 g/L SC, foliar application at 0.78 kg ai/ha on a 7 to 14-day interval, seasonal maximum of 2.35 kg ai/ha). Three-year old ginseng plants were treated and the roots were harvested 29 days after the last application. The roots were dried in a commercial drying facility. Untreated and treated roots were placed on separate racks at opposite ends of a grower's commercial drying room. The roots were dried at approx. 18–27 °C from 10/3 to 10/06 and at approx. 90–115 °F from 10/6 to 10/17/2007 when they were sampled.

Table 10 Pyrimethanil Residues in Dried Ginseng following Pre-Harvest Treatment (Reference PR 09707)

Ginseng Year Variety	Application Rate (kg ai/ ha)	Number of Applications	Total Rate (kg ai/ ha)	RTI (days)	DAT	Pyrimethanil Residue (mg/kg) Whole, Dried Root [Average]
2007 MI11: Edgar, WI (American Ginseng)	0.78	3	2.372	6	29	0.35 0.47 [0.41]
2007 MI12: Nutterville, WI (American Ginseng)	0.78	3	2.391	6	29	0.11 0.088 [0.099]
2007 MI13: Mosinee, WI (American Ginseng)	0.78	3	2.377	6	29	0.48 0.69 [0.585]

APPRAISAL

Pyrimethanil was most recently evaluated for toxicology and residues by the JMPR in 2007. The Meeting derived an ADI of 0.2 mg/kg bw per day and decided that an ARfD is unnecessary.

In 2007 the Meeting agreed that the residue definition for both enforcement and dietary intake for plant commodities is parent pyrimethanil. The Meeting further concluded that the residue definition for both enforcement and dietary exposure considerations for milk is the sum of pyrimethanil and 2-anilino-4,6-dimethylpyrimidin-5-ol, expressed as pyrimethanil; and for livestock tissues (excluding poultry) is the sum of pyrimethanil and 2-(4-hydroxyanilino)-4,6-dimethylpyrimidine, expressed as pyrimethanil.

The compound was listed by the Forty-fourth Session of the CCPR for the evaluation of additional MRLs. The 2013 JMPR received residue data for pome fruit, stone fruit, lemons and ginseng.

Methods of analysis

The Meeting received information on the analytical methods used for determination of pyrimethanil residues in samples obtained from supervised trials on pome fruit, stone fruit, lemon, and ginseng. The residues were measured using GC/MS or HPLC/UV with LOQs of 0.05 mg/kg. The methods were reviewed by the JMPR in 2007, which concluded that adequate analytical methods for pyrimethanil exist for both data collection and enforcement purposes. The methods used in the trials submitted to the 2013 Meeting are essentially identical to those accepted at the 2007 Meeting.

Stability of residues in stored analytical samples

Detailed information from the 2007 JMPR showed that pyrimethanil residues are stable (> 70% remaining) in frozen storage for at least 12 months in the tested commodities, i.e., apple, grape, tomato, lettuce, carrot, pea, peach, and plum. Concurrent storage stability studies were submitted with the ginseng trials and demonstrated residue stability for at least 259 days.

The periods of demonstrated stability cover the frozen storage intervals in the residue studies.

Results of supervised residue trials on crops

The 2007 JMPR received supervised trials for many crops, including pre- and post-harvest uses of pome and stone fruit. However, due to incomplete GAP information, pome fruit thermofog data were not included in the pome fruit MRL recommendation. The 2013 JMPR received complete GAP information for pome and stone fruits, as well as expanded post-harvest residue data. For completeness, all relevant pome and stone fruit supervised trial data for pyrimethanil are considered in the following sections. The USA GAP allows for pre- and post-harvest applications of pyrimethanil to pome and stone fruit; however, few trials reflect residues from the combined pre- and post-harvest applications.

Lemon

In the USA, pyrimethanil is registered for use on lemons for up to 4 treatments at a rate of 1.7 kg ai/ha, with a PHI and a retreatment interval of 7 days. Five supervised field trials are available at this GAP from the USA.

Rank-order pyrimethanil residues in lemon were (n=5): 0.18, 0.21, 0.27 (2), and 0.82 mg/kg.

The Meeting noted that there is a current MRL for citrus fruit at 7 mg/kg based on post-harvest uses and concluded that the current MRL for citrus is adequate to cover the submitted pre-harvest-use lemon data. Therefore, the Meeting confirms its previous recommendation.

Pome fruits

In 2007, the Meeting reviewed residue values on pome fruits from pre-harvest and post-harvest trials according to Belgium, France, Germany, Greece, Italy, Netherlands, United Kingdom, and USA GAPs. Residues from post-harvest GAPs were higher and served as the basis for the previous recommendations for maximum residue level, STMR, and HR estimates of 7(Po), 0.7, and 3.8 mg/kg, respectively.

The 2013 Meeting has evaluated data from the USA and Europe matching a new GAP for uses of pyrimethanil as a post-harvest thermofog treatment. Although the GAP for thermofog uses in the US has a higher application rate than the GAPs in European countries (one application at 9.6 kg ai/1000 kg fruits vs. one application at the rate of 5.6 to 8 kg ai/1000 kg fruits), the residues resulting from the trials conducted according to the GAP in Europe were approximately 10-fold higher than the trial conducted according to the US GAP; therefore, the meeting selected data according to GAP in Europe.

Residues from post-harvest trials in apples (n=8, new data in bold) were: 1.1, 1.4 (2), 1.5, 1.6, 4.9, 6.4, and 7.1 mg/kg.

Residues from post-harvest trials in pears (n=4) were: 1.0, 1.6, 1.8, and 3.5 mg/kg.

As the residue data from apples and pears are from the same population, they were combined to give the following residues (n=12, median underlined): 1.0, 1.1, 1.4 (2), 1.5, 1.6 (2), 1.8, 3.5, 4.9, 6.4, and 7.1 mg/kg. The Meeting agreed to replace its previous maximum residue level recommendation of 7 mg/kg with a new estimated STMR of 1.6 mg/kg and a maximum residue level of 15 (Po) mg/kg for pome fruit.

Stone fruits

In 2007, the Meeting recommended an STMR of 1.3 mg/kg and a maximum residue level of 4 (Po) for cherries based on the post-harvest GAP for Chile. The 2013 Meeting received new information on the post-harvest GAP in the USA. Post-harvest trials were conducted at 2× the USA GAP. Since post-harvest data may not be adjusted via proportionality, there are no new data for the Meeting to use for a recommendation. Therefore, the Meeting confirmed its prior recommendations.

Berries and other small fruits

From the 2007 JMPR:

“Eight trial were conducted on the foliar application of pyrimethanil to strawberries in the USA, where the GAP is 600 g/L SC, 0.8 kg ai/ha, 2.4 kg ai/ha/season, 1 day PHI. All trials were at maximum GAP, and the residues in ranked order (median underlined) were: 0.79, 0.93, 0.99, 1.1, 1.2, 1.3(2), and 2.3 mg/kg. The Meeting estimated an STMR of 1.2 mg/kg and a maximum residue level of 3 mg/kg for strawberries.”

The current Meeting was asked to extrapolate the strawberry field trial data to Berries and Other Small Fruits [Subgroup 004E, Low Growing Berries (including Bakeapple; Cranberry (FB 0265); Cloudberry (FB 0277); Muntries (FB 0283); Partridge berry; Squaw vine; Strawberry (FB 0275); Strawberries, wild (FB 0276); Strawberry, Musky)], reflecting the USA label allowing use on the Low Growing Berry Crop Subgroup 13-07G.

Taking into account the available historic data showing that pesticide residues in strawberry are generally comparable to or higher than residues in other low-growing berries, the Meeting agreed to extrapolate the residue estimates for strawberry to commodities comprising the low-growing berries subgroup. Therefore, for the low-growing berries subgroup (Subgroup 004E, FB 2009) the Meeting recommended a maximum residue level of 3 mg/kg and estimated an STMR of 1.2 mg/kg. The Meeting agreed to withdraw its previous recommendation of 3 mg/kg for strawberry.

Ginseng

In the USA, pyrimethanil is registered for use on ginseng for up to 3 treatments at a rate of 0.78 kg ai/ha, with a PHI of 30 days and a retreatment interval of 7 days. Three supervised field trials were available at this GAP from the USA.

Rank-order pyrimethanil residues in dried ginseng were (n=3): 0.099, 0.41, and 0.59 mg/kg.

The Meeting estimated an STMR value of 0.41 mg/kg and a maximum residue level value of 1.5 mg/kg for ginseng, dried.

Fate of residue during processing

In 2007, the Meeting estimated the following STMR-Ps for citrus juice, citrus pulp (dried) and citrus oil, respectively: 0.028 mg/kg; 1.3 mg/kg; 56 mg/kg. As these estimates adequately cover residues in lemon, the Meeting confirmed its prior recommendations for citrus.

The 2007 Meeting estimated a processing factor of 0.45 for apple juice, 0.37 for apple puree, and 4.1 for wet apple pomace. Applying these processing factors to the estimated STMR for pome fruit (1.6 mg/kg) resulted in STMR-P estimates of 0.72 mg/kg for apple juice, 0.59 mg/kg for apple puree, and 6.6 mg/kg for wet apple pomace. The Meeting agreed these values should replace the estimates made in 2007.

Residues in animal commodities

Dietary burden calculations for beef cattle and dairy cattle are provided below. The dietary burdens were estimated using the OECD diets listed in Appendix IX of the 2009 edition of the FAO Manual.

Potential cattle feed items include: apple pomace, almond hulls, carrot culls, citrus pulp, grape pomace, pea seed and pea straw. Pyrimethanil residues in all these feed items were as estimated by the 2007 JMPR except for apple pomace, which has a revised STMR-P of 6.6 mg/kg (the previous estimate was 2.9 mg/kg).

Summary of livestock dietary burdens (ppm of dry matter diet)

	US-Canada		EU		Australia		Japan	
	max	mean	max	mean	max	mean	max	mean
Beef cattle	0.14	0.14	4.3	3.6	4.6 ^a	3.9 ^c	0.0	0.0
Dairy cattle	2.5	2.1	2.8	2.1	4.1 ^b	3.4 ^d	0.0	0.0

^a Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian meat

^b Highest maximum dairy cattle dietary burden suitable for MRL estimates for mammalian milk

^c Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat.

^d Highest mean dairy cattle dietary burden suitable for STMR estimates for milk.

Animal commodity maximum residue levels

The calculations used to estimate residues in animal commodities based on comparisons of the dietary burden to results of the bovine feeding study, for use in estimating maximum residue levels, STMR and HR values, are shown below.

Pyrimethanil feeding study	Feed level	Residues	Feed level	Residues (mg/kg) in			
	(ppm) for milk residues	(mg/kg) in milk	(ppm) for tissue residues	Muscle	Liver	Kidney	Fat
MRL beef or dairy cattle							
Feeding study ^a	3	< 0.01	3	< 0.05	< 0.05	0.08	< 0.05
	10	0.017	10	< 0.05	< 0.05	0.13	< 0.05
Dietary burden and high residue	4.1	< 0.01	4.6	< 0.05	< 0.05	0.09	< 0.05
STMR beef or dairy cattle							
Feeding study ^b	3	< 0.01	3	< 0.05	< 0.05	0.066	< 0.05
	10	0.017	10	< 0.05	< 0.05	0.12	< 0.05
Dietary burden and residue estimate	3.4	< 0.01	3.9	< 0.05	< 0.05	0.07	< 0.05

^a highest residues for tissues and mean residues for milk

^b mean residues for tissues and mean residues for milk

Residue estimates in animal commodities are unchanged relative to those recommended in 2007; therefore, the Meeting confirmed its prior recommendations: an STMR of 0.01 mg/kg for milk and estimated a maximum residue level of 0.01 mg/kg for milk. The Meeting estimated STMRs of 0.0 mg/kg for each of meat and fat and maximum residue levels of 0.05 (*) mg/kg for meat. The Meeting estimated an STMR of 0.07 mg/kg for edible offal based on the STMR value for beef cattle kidney.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

Definition of the residue (for compliance with MRL and dietary intake) for plant commodities: *pyrimethanil*.

The residue is not fat-soluble.

Commodity		MRL, mg/kg		STMR, mg/kg	HR, mg/kg
CCN	Name	New	Previous		
FP 0009	Pome fruits	15 Po	7	1.6	
FB 2009	Low Growing Berries	3		1.2	
FB 0275	Strawberry	W	3		
DV 0604	Ginseng	1.5		0.41	
JF 0226	Apple, Juice			0.72	

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDIs) of pyrimethanil were calculated for the 13 GEMS/Food cluster diets using STMRs/STMR-Ps estimated by the current Meeting. The ADI is 0–0.2 mg/kg bw and the calculated IEDIs were 0–5% of the maximum ADI (0.2 mg/kg bw). The Meeting concluded that the long-term intakes of residues of pyrimethanil, resulting from the uses considered by the current Meeting, are unlikely to present a public health concern.

Short-term intake

The 2007 JMPR decided that an ARfD was unnecessary and concluded that the short-term intake of pyrimethanil residues is unlikely to present a public health concern.

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AGR 659	Martos, C	2004	Magnitude of Residue: R215559 and R023979 Residues in apple resulting from post-harvest treatment. Field: TrialCamp, Spain (TRC03-12), Analytical: Lisec, Belgium (RA-080), Janssen Pharmaceutica, N.V., Belgium Reference ID: AGR 659, Date: 26.05.2004 GLP : Yes, Unpublished
ISPaVe-PRM-IML-T-15/02	Pompi, V	2004	Pyrimethanil Imazalil: determination of the residues in different crops after post-harvest trials (thermonebulization). Istituto

Report No	Author	Year	Title
PR 08700	Thompson, D	2007	Sperimentale per la Patologia Vegetale, Italy. Report No. ISPaVe-PRM-IML-T-15/02 Date: 16.09.2004., GLP: Yes Unpublished Pyrimethanil: Magnitude of the Residue on Peach (Post-Harvest). 111 pgs. Generated by: IR-4 Project Headquarters. Rutgers, The State University of New Jersey. Report No. IR-4 PR No. 08700. Analytical Laboratory Identification Number 08701.05-CAR17 Date: 16.08.2007., GLP: Yes, Unpublished
PR 08701	Thompson, D	2008	Pyrimethanil: Magnitude of the Residue on Cherry, Sweet (Post-Harvest) IR-4 Project Headquarters. Rutgers, The State University of New Jersey. Report No. IR-4 PR No. 08701. Analytical Laboratory Identification Number 08701.05-CAR11, Date: 31.03.2008, GLP: Yes, Unpublished
PR 08702	Thompson, D	2007	Pyrimethanil: Magnitude of the Residue on Plum (Post-Harvest). 107 pgs. Generated by: IR-4 Project Headquarters. Rutgers, The State University of New Jersey. Report No. IR-4 PR No. 08702., Analytical Laboratory Identification Number 08701.05-CAR16 Date: 16.08.2007., GLP: Yes, Unpublished
PR 09085	Thompson, D	2007	Pyrimethanil: Magnitude of the Residue on Lemon 109 pgs. IR-4 Project Headquarters. Rutgers, The State University of New Jersey. Report No. IR-4 PR No. 09085. Analytical Laboratory Identification Number 09085.04-CAR06, Date: 20.12.2007., GLP: Yes, Unpublished
PR 09707	Corley, J.	2009	Pyrimethanil: Magnitude of the Residue on Ginseng. 101 pgs. Generated by: IR-4 Project Headquarters. Rutgers, The State University of New Jersey. Report No. IR-4 PR No. 09707. Analytical Laboratory Identification Number 09707.07-CAR13, Date: 30.04.2009., GLP: Yes, Unpublished
XDA-G007-02	Loriau, P	2007	Magnitude of residue of pyrimethanil in/on pome fruit in storage following one post harvest thermofogging application of Xedathane-A HN. France 2007., Field: Redebel S.A., Belgium, Report No. XDA-G002-07 Analytical: Capinov, France (E-07-01), 06.02.2007 GLP Unpublished

SPIROTETRAMAT (234)

The first draft was prepared by Professor Mi-Gyung Lee, Andong National University Republic of Korea

EXPLANATION

Spirotetramat was evaluated by the JMPR in 2008 for the first time for toxicology and residues. The Meeting derived an ADI of 0–0.05 mg/kg bw and an ARfD of 1.0 mg/kg bw and recommended maximum residue levels for a range of crops. In 2011 and 2012, the JMPR recommended additional MRLs. The compound was again listed by the Forty-fourth Session of CCPR for the evaluation of 2013 JMPR for additional MRLs.

Residue definitions established by the 2008 JMPR are:

- For compliance with the MRL for plant commodities: *spirotetramat plus spirotetramat enol, expressed as spirotetramat.*
- For dietary intake estimation for plant commodities: *spirotetramat plus the metabolites enol, ketohydroxy, enol glucoside, and monohydroxy, expressed as spirotetramat.*
- For compliance with the MRL and for dietary intake estimation for animal commodities: *spirotetramat enol, expressed as spirotetramat.*

The residue is not fat soluble.

The present Meeting received supervised field trial data for berries and other small fruits (blueberries and cranberries), assorted tropical and sub-tropical fruits (bananas, pineapples and pomegranates), bulb vegetables (bulb onions and spring onions), watercress, globe artichokes and coffee beans. Information on analytical methods, storage stability testing results (bananas and coffee) and residue levels in processed products (pineapple juice and process residue, roasted bean coffee and freeze-dried coffee) was also received.

METHODS OF RESIDUE ANALYSIS***Analytical methods***

The Meeting received information on analytical methods used for the determination of spirotetramat and its major metabolites in the submitted residues trials. In all trials, method 00857 (Shōning *et al.*, 2005) or modified 00857 (Coopersmith, 2009) was used as a reference method. These methods are based on LC-MS/MS using isotopically labelled internal standards. Method 00857 was previously reported and evaluated by the 2008 and 2011 JMPR.

Further modifications of the reference method were made and applied to determine spirotetramat, the metabolites spirotetramat-enol, spirotetramat-ketohydroxy, spirotetramat-monohydroxy and spirotetramat-enol-glucoside (enol-Glc) in blueberries, cranberries, bananas, pineapples (including juice and processing residues), pomegranates, bulb onions, spring onions, watercress, globe artichokes and coffee beans (including roasted beans and freeze-dried coffee). Residues in samples were extracted with 0.22 mL of formic acid (88%) or 0.20 mL formic acid (98%) in 4:1 acetonitrile:water. The extract was filtered (using Celite or polyethylene frit) or non-filtered (pineapple juice) and cleaned up with C18 SPE cartridge or in tandem with an Envi-Carb SPE (or HLB SPE). Quantitation was made by LC-MS/MS. Conversion factors to parent equivalents were used as follows: enol, $\times 1.239$; ketohydroxy, $\times 1.177$; monohydroxy, $\times 1.231$; and enol-glucoside, $\times 0.806$.

Except in some cases (enol-Glc in roasted coffee beans and all analytes in freeze-dried coffee), recovery tests for all analytes in all matrices were conducted at the fortification levels of ≥ 0.01 mg/kg (as parent equivalents). With the exception of enol-Glc in pineapple juice and the process residues, the recoveries were within 70–120% (RSD below 20%) and the limits of

quantitation were 0.01 mg/kg (as parent equivalents) for each analyte and 0.05 mg/kg for total spirotetramat equivalents. The average recoveries of enol-Glc in pineapple juice and process residues were 134% (range, 98–161%) and 137% (range, 102–159%), respectively, at the fortification levels of 0.01 mg/kg, therefore the method was not considered suitable for the pineapple products.

For enol-Glc in roasted coffee beans, recovery tests were conducted at the fortification levels of ≥ 0.05 mg/kg (as parent equivalents). The average recovery was 98% (range, 82–121%) and the limit of quantification was 0.05 mg/kg.

In recovery tests for each analyte (parent and four metabolites) in freeze-dried coffee, the lowest spiking level was 0.1 mg/kg (as parent equivalents). Some recoveries of parent and enol-Glc were 50, 59 and 67%, and 130, 133 and 139%, respectively, at the fortification level. Overall, the method performance was not considered acceptable.

Results of the method validation and procedural recoveries for commodities for which residues trials are reported are summarized in Table 1.

Table 1 Recovery percentage of spirotetramat and its metabolites obtained with method 00857

Sample	Analyte	Fortification, mg/kg	No.	Range of recoveries, %	Mean recovery, %	Recovery, SD
Blueberries	Spirotetramat	0.01–1.0	15	93–103	99	3
	Enol	0.01–1.0	15	86–103	96	6
	Ketohydroxy	0.01–1.0	15	80–97	86	10
	Monohydroxy	0.01–1.0	15	85–109	95	6
	Enol-Glc	0.01–1.0	15	93–106	99	4
Cranberry	Spirotetramat	0.01–0.50	12	89–103	97	4
	Enol	0.01–0.50	12	91–107	99	5
	Ketohydroxy	0.01–0.50	12	74–91	85	6
	Monohydroxy	0.01–0.50	12	95–111	101	5
	Enol-Glc	0.0–0.50	12	91–101	95	3
Banana ,with peel	Spirotetramat	0.01–5.0	16	79–101	91	6
	Enol	0.01–5.0	16	79–101	92	7
	Ketohydroxy	0.01–5.0	16	80–106	95	6
	Monohydroxy	0.01–5.0	16	88–106	97	5
	Enol-Glc	0.01–5.0	16	76–115, 122	95	12
Banana ,without peel	Spirotetramat	0.01–5.0	15	82–105	94	7
	Enol	0.01–5.0	15	79–104	94	8
	Ketohydroxy	0.01–5.0	15	93–108	98	5
	Monohydroxy	0.01–5.0	15	84–110	100	8
	Enol-Glc	0.01–5.0	14	71–122	95	15
Pineapple	Spirotetramat	0.01	6	95–108	99	5
		0.1	3	99–102	101	2
		1.0	5	101–105	103	2
	Enol	0.01	6	95–98	96	1
		0.1	3	96–101	99	3
		1.0	5	74–95	87	10
	Ketohydroxy	0.01	6	89–115	97	10
		0.1	3	92–99	95	4
		1.0	5	101–111	105	4
	Monohydroxy	0.01	6	86–97	91	4
		0.1	3	101–103	102	1
		1.0	5	85–103	98	7
	Enol-Glc	0.01	6	64, 93–120	100	20
		0.1	3	86–99	93	7
		1.0	5	77–106	96	11
Pineapple, juice	Spirotetramat	0.01	6	93–111	102	9
		0.1	3	99–100	100	1
		1.0	4	101–105	104	2
	Enol	0.01	6	88–102	96	5
		0.1	3	97–99	98	1
		1.0	4	81–94	89	5

Sample	Analyte	Fortification, mg/kg	No.	Range of recoveries, %	Mean recovery, %	Recovery, SD
	Ketohydroxy	0.01	6	81–101	91	7
		0.1	3	100–106	103	3
		1.0	4	93–109	104	7
	Monohydroxy	0.01	6	84–115	96	15
		0.1	3	96–104	101	4
		1.0	4	92–105	98	6
	Enol-Glc	0.01	6	98–116, 138, 143, 149, 161	134	23
		0.1	3	100–111	107	6
		1.0	4	88–97	92	4
Pineapple, process residue	Spirotetramat	0.01	6	87–100	91	5
		0.1	3	92–100	97	4
		1.0	4	97–101	100	2
	Enol	0.01	6	86–101	92	6
		0.1	3	93–95	94	1
		1.0	4	86–87	87	1
	Ketohydroxy	0.01	6	88–100	91	5
		0.1	3	93–96	95	2
		1.0	4	100–106	103	3
	Monohydroxy	0.01	6	89–101	94	4
		0.1	3	94–97	96	2
		1.0	4	96–105	100	4
	Enol-Glc	0.01	6	102, 129, 134, 138, 157, 159	137	21
		0.1	3	100–106	104	3
		1.0	4	80–105	95	11
Pomegranate	Spirotetramat	0.01–2.0	14	93–102	98	3
	Enol	0.01–2.0	14	74–107	92	10
	Ketohydroxy	0.01–2.0	14	73–107	92	11
	Monohydroxy	0.01–2.0	14	87–110	98	7
	Enol-Glc	0.01–2.0	14	70–111	98	12
Bulb onion	Spirotetramat	0.01–1.0	12	85–97	93	3
	Enol	0.01–1.0	12	86–97	92	4
	Ketohydroxy	0.01–1.0	12	85–101	93	4
	Monohydroxy	0.01–1.0	12	78–101	89	7
	Enol-Glc	0.01–1.0	12	89–115	97	7
Spring onion	Spirotetramat	0.01–0.5	12	91–97	94	2
	Enol	0.01–0.5	12	71–96	80	10
	Ketohydroxy	0.01–0.5	12	71–93	82	8
	Monohydroxy	0.01–0.5	12	91–100	95	3
	Enol-Glc	0.01–0.5	12	92–101	96	3
Watercress	Spirotetramat	0.01	9	88–100	92	5
		0.1	5	90–97	93	3
		1	3	94–99	97	3
	Enol	0.01	9	87–104	94	6
		0.1	5	85–95	91	5
		1	3	92–96	94	3
	Ketohydroxy	0.01	9	78–92	88	4
		0.1	5	93–100	95	3
		1	3	96–105	100	5
	Monohydroxy	0.01	9	84–106	93	8
		0.1	5	83–97	92	6
		1	3	90–97	94	4
	Enol-Glc	0.01	6	76–103	89	10
		0.1	5	84–92	87	3
		1	3	88–91	88	3
Artichoke, globe	Spirotetramat	0.01–0.5	12	91–95	92	1
	Enol	0.01–0.5	12	91–102	98	4
	Ketohydroxy	0.01–0.5	12	91–105	97	4

Sample	Analyte	Fortification, mg/kg	No.	Range of recoveries, %	Mean recovery, %	Recovery, SD
	Monohydroxy	0.01–0.5	12	99–110	103	3
	Enol-Glc	0.01–0.5	12	87–106	97	5
Green bean coffee	Spirotetramat	0.01–1.0	19	86–94	91	2
	Enol	0.01–1.0	19	72–94	85	7
	Ketohydroxy	0.01–1.0	19	78–92	87	4
	Monohydroxy	0.01–1.0	19	70–97	87	6
	Enol-Glc	0.01–1.0	19	74–113	91	10
Roasted coffee bean	Spirotetramat	0.01–1.0	18	72–92	84	7
	Enol	0.01–1.0	18	76–103	89	9
	Ketohydroxy	0.01–1.0	18	75–111, 135	93	14
	Monohydroxy	0.01–1.0	18	61, 80–105	88	10
	Enol-Glc	0.05–1.0	15	82–121	98	11
Freeze-dried coffee	Spirotetramat	0.1–1.0	15	50 ^a , 59 ^a , 67 ^a , 71–98	80	14
	Enol	0.1–1.0	15	70–120, 132	109	16
	Ketohydroxy	0.1–1.0	15	66–122	101	15
	Monohydroxy	0.1–1.0	15	77–116	91	12
	Enol-Glc	0.1–1.0	15	70–118, 130 ^a , 133 ^a , 139 ^a	103	20

Method 00857 (Shöning *et al.*, 2005; Coopersmith, 2009) was further modified for matrices.

For bananas, pineapples, pomegranates, watercress and coffee beans, concurrent recoveries were included.

^a Recoveries at fortification levels of 0.1 mg/kg.

Stability of residues in stored analytical samples

Storage stability studies were performed on bananas with peel, peeled bananas, green bean coffee, roasted coffee bean and freeze-dried coffee for days 771, 770, 418, 438 and 448, respectively. Actual storage periods of the samples are shown in Table 2. For others, storage periods were as follows: blueberries - 587 days, cranberries - 483 days, pineapples without crown/juice/process residues - 179/119/114 days, pomegranates - 412 days, bulb onions - 434 days, spring onions - 550 days, watercress - 472 days and globe artichokes - 500 days.

As shown in Table 2, the results demonstrated that the residues in the samples are stable for the testing period. In addition, the 2008 JMPR reported frozen storage (-18 °C) stabilities of spirotetramat and its metabolites up to 2 years on various plant commodities. These cover storage stability for the samples in this evaluation.

Table 2 Storage stability of spirotetramat and its metabolites in banana and coffee

Crop	Analyte	Fortification level, mg/kg	Days of storage testing	Actual storage days	Remaining, %	Average spirotetramat equivalents ^a mg/kg
Banana with peel	Spirotetramat	0.1	771	363	0, 0, 0	
	Enol	0.1	771	363	137, 137, 144	0.0487
	Ketohydroxy	0.1	771	363	141, 129, 128	0.033
	Monohydroxy	0.1	771	363	124, 119, 127	0.0287
	Enol-Glc	0.1	771	363	101, 93, 98	< 0.01
Banana, peeled	Spirotetramat	0.1	770	357	0, 0, 0	
	Enol	0.1	770	357	95, 89, 117	< 0.01
	Ketohydroxy	0.1	770	357	151, 164, 161	0.0693
	Monohydroxy	0.1	770	357	133, 120, 133	0.0353
	Enol-Glc	0.1	770	357	100, 108, 108	< 0.01
Green bean coffee	Spirotetramat	1.0	418	355	78, 80, 81	
	Enol	1.0	418	355	68, 73, 74	< 0.01
	Ketohydroxy	1.0	418	355	69, 78, 80	< 0.01
	Monohydroxy	1.0	418	355	97, 1104, 107	< 0.01
	Enol-Glc	1.0	418	355	82, 85, 88	< 0.01

Crop	Analyte	Fortification level, mg/kg	Days of storage testing	Actual storage days	Remaining, %	Average spirotetramat equivalents ^a mg/kg
Roasted coffee bean	Spirotetramat	1.0	438	181	67, 66, 64	
	Enol	1.0	438	181	93, 94, 87	< 0.01
	Ketohydroxy	1.0	438	181	79, 67, 64	< 0.01
	Monohydroxy	1.0	438	181	96, 94, 91	< 0.01
	Enol-Glc	1.0	438	181	104, 89, 100	< 0.05
Freeze-dried coffee	Spirotetramat	1.0	448	174	52, 55, 51	
	Enol	1.0	448	174	117, 113, 120	0.211
	Ketohydroxy	1.0	448	174	95, 87, 81	< 0.1
	Monohydroxy	1.0	448	174	112, 90, 115	0.0738
	Enol-Glc	1.0	448	174	82, 76, 100	< 1

^a Spirotetramat converted to its metabolites after fortification.

USE PATTERN

Spirotetramat is a systemic insecticide used for the control of a broad spectrum of sucking insects. The authorized uses of spirotetramat on crops, submitted for evaluation by the present JMPR, are summarized in Table 3.

Table 3 Registered use of spirotetramat 240 SC formulation on some crops

Crop	Country	Application ^a			PHI, days
		Rate, kg ai/ha	Interval, days	Total/season, kg ai/ha	
Bush berry (blueberries) and low growing berry (cranberry) ^b	Canada	0.053–0.20	7	0.44	7
Banana and plantain	USA	0.18–0.28	14	1.4	1
Pineapple	USA	0.18	14	0.36	1
Pomegranate	USA	0.15–0.18	14	0.36 per 12-month period	1
Bulb vegetables (bulb onion)	USA	0.090	7	0.18	3
Bulb vegetables (spring onion)	USA	0.090	7	0.18	7
Watercress	USA	0.067–0.22	7	0.45	3
Artichoke, globe	USA	0.090–0.15	7	0.56	3
Coffee	USA	0.15–0.18	21	0.53	14

^a The spirotetramat 240 SC, w/w, 22.4% (240 g/L) formulation must be tank-mixed with a spray adjuvant /additive.

In trees, tropical and vine crops, minimum application volumes of water are 470 L/ha for conventional ground airblast sprayer, 280 L/ha for high air velocity, low volume or air curtain sprayers and 94 L/ha for aerial application.

In vegetable and potato crops, minimum application volumes of water are 140 L/ha by ground and 47 L/ha by aerial application. The formulation may also be applied through overhead irrigation systems. If needed, repeat application at a 7- to 10 day interval.

^b Usage is registered as 220–585 mL/ha/application and 1.833 L/ha/crop season.

Apply 200–3000 L total volume/ha by ground. For chemigation (cranberry only), the higher rate of the 240 SC formulation and a maximum spray volume of 3000 L total volume are recommend.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

Supervised residue trials were conducted in the USA and Canada according to GLP principles under IR-4 programmes of the USA. The results of the supervised trials are shown in the following tables:

Crop group	Commodity	Table No.
Berries and other small fruits	Blueberries	4
	Cranberry	5
Assorted tropical and sub-tropical fruits—inedible peel	Banana	6
	Pineapple	7

Crop group	Commodity	Table No.
	Pomegranate	8
Bulb vegetables	Onion, bulb	9
	Spring onion	10
Leafy vegetables (including Brassica leafy vegetables)	Watercress	11
Stalk and stem vegetables	Artichoke, globe	12
Seed for beverages and sweets	Coffee beans	13

Where two replicate field samples were taken and residues were determined in each, a mean value was calculated for estimating a maximum residue level. From trials carried out side-by-side, the higher residue was chosen.

Total spirotetramat equivalents are the sum of all components converted to spirotetramat equivalents by multiplying by the following conversion factors: enol $\times 1.239$, ketohydroxy $\times 1.177$, monohydroxy $\times 1.231$ and enol-glucoside $\times 0.806$. Where a component is reported as '<value', the '<value' is added into the calculation of the total equivalents. The following example illustrates this.

Residues as spirotetramat equivalents (mg/kg)

Spirotetramat	enol	keto-hydroxy	mono-hydroxy	enol-glucoside	total residue	Spirotetramat + enol
0.15	0.30	< 0.012	< 0.012	< 0.008	0.48	0.45
0.55	0.68	0.012	0.022	0.010	1.3	1.2
< 0.01	< 0.012	< 0.012	< 0.012	< 0.008	< 0.055	< 0.022

Berries and other small fruits

Blueberries

Eleven residue trials were conducted in the USA (seven trials) and Canada (four trials) during the 2009 growing season. Four trials were conducted on low-bush blueberries and seven trials were conducted on high-bush blueberries. Spirotetramat 240 SC (240 g/L) was applied to blueberry as three foliar applications ranging from 0.17–0.19 kg ai/ha, with re-treatment intervals of 5 to 8 days. The total seasonal application rate ranged from 0.52 to 0.56 kg ai/ha. A non-ionic surfactant was included in the spray mixtures at 0.25% with the exception of Trial ID#132 (non-ionic surfactant of 1%) and the spray volume of 115–573 L/ha was used. The blueberry samples were harvested 6 to 8 days after the final application. One decline trial was conducted, with blueberry samples harvested at 1, 3, 7, and 10 days after the last application, to assess the decline in potential residues over time.

Table 4 Spirotetramat and its metabolites in blueberries from 240 SC foliar applications in the USA and Canada (IR-4 PR No. 10194)

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spir o + enol
GAP, Canada	0.20		7	0.44	7							
Sainte- Anne-de- Kent, NB, Canada 2009	0.17 –0.18	3	5–8	0.52	8	0.33 0.30 0.31 (mean)	0.37 0.37 0.37	0.39 0.37 0.38	0.11 0.11 0.11	0.035 0.033 0.034	1.2 1.2 1.2	0.68

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spir o + enol
(Lowbush, Wild type) Trial ID #131												
Jonesboro, ME , USA 2009 (Lowbush, Wild type) Trial ID #132	0.17– 0.18	3	6–7	0.52	7	0.10 0.16 0.13	0.19 0.29 0.24	0.21 0.21 0.21	0.044 0.075 0.060	0.011 0.021 0.016	0.56 0.76 0.66	0.37
Chatsworth, NJ, USA 2009 (Highbush, Bluecrop) Trial ID #133	0.17– 0.18	3	7	0.53	7	0.24 0.27 0.25	0.067 0.050 0.059	0.11 0.10 0.11	0.019 0.019 0.019	< 0.01 < 0.01 < 0.01	0.45 0.45 0.45	0.31
Sheffield Mills, NS, Canada 2009 (Lowbush, Wild type) Trial ID #134	0.17– 0.18	3	7	0.53	1	0.065 0.061 0.063	0.27 0.26 0.27	0.18 0.19 0.19	0.038 0.050 0.044	< 0.01 < 0.01 < 0.01	0.56 0.56 0.56	0.33
					3	0.041 0.034 0.038	0.21 0.20 0.21	0.18 0.19 0.19	0.053 0.045 0.049	< 0.01 < 0.01 < 0.01	0.49 0.48 0.49	0.25
					7	0.042 0.029 0.036	0.092 0.12 0.11	0.21 0.17 0.19	0.033 0.040 0.037	< 0.01 < 0.01 < 0.01	0.38 0.38 0.38	0.14
					10	0.025 0.031 0.028	0.096 0.094 0.095	0.18 0.17 0.18	0.051 0.046 0.049	0.015 0.013 0.014	0.36 0.36 0.36	0.12
Rawdon Gold Mines, NS, Canada 2009 (Lowbush, Wild type) Trial ID #135	0.17– 0.18	3	6–7	0.52	7	0.083 0.073 0.078	0.082 0.095 0.089	0.21 0.22 0.21	0.046 0.050 0.048	0.011 0.012 0.012	0.43 0.45 0.44	0.17
Fennville, MI, USA 2009 (Highbush, Rubel) Trial ID #136 ^b	0.18	3	7	0.54	7	0.27 0.18 0.23	0.071 0.060 0.066	0.17 0.14 0.15	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.53 0.40 0.46	0.30
Fennville, MI, USA 2009 (Highbush, Rubel) Trial ID #137 ^b	0.18	3	7	0.54	7	0.44 0.47 0.46	0.067 0.064 0.066	0.15 0.14 0.14	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.68 0.70 0.69	0.53

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spir o + enol
Jordan Station, ON, Canada 2009 (Highbush, Patriot) Trial ID #138	0.18	3	7	0.54	7	0.10 0.13 0.12	0.41 0.40 0.41	0.82 0.82 0.82	0.17 0.17 0.17	0.036 0.040 0.038	1.5 1.6 1.6	0.53
Aurora, OR, USA 2009 (Highbush, Bluecrop) Trial ID #139	0.18– 0.19	3	7	0.56	7	0.33 0.50 0.41	0.28 0.28 0.28	0.25 0.26 0.25	0.094 0.097 0.096	0.026 0.029 0.028	1.0 1.2 1.1	0.69
Castle Hayne, NC, USA 2009 (Highbush, Croatan) Trial ID #140	0.17– 0.18	3	7–8	0.52	6	0.08 0.11 0.10	0.098 0.12 0.11	0.21 0.25 0.23	0.030 0.041 0.036	0.014 0.020 0.017	0.43 0.54 0.49	0.21
Castle Hayne, NC, USA 2009 (Highbush, Summit) Trial ID#141	0.17– 0.18	3	7	0.53	6	0.30 0.28 0.29	0.097 0.097 0.097	0.18 0.18 0.18	0.027 0.023 0.025	< 0.01 0.011 0.011	0.61 0.59 0.60	0.39

^a Mean value of residues is expressed in bold

^b The two trials were conducted at the same site with the same variety, on 1st application 8 days apart, thus they were not independent.

Cranberry

Six trials were conducted in the USA (five trials) and Canada (one trial) during the 2009 growing season. Five trials were conducted in the US and one trial in Canada. Spirotetramat 240 SC formulation was applied to cranberries as three foliar applications ranging from 0.17 to 0.19 kg ai/ha, with re-treatment intervals of 6 to 8 days. The total seasonal application rate ranged from 0.52 to 0.55 kg ai/ha. A non-ionic surfactant was included in all spray mixtures at a rate of 0.25% and the spray volume of 240–555 L/ha was used. One decline trial was conducted, with cranberry samples harvested at 1, 4, 7 and 11 days after the last application, to assess the decline in potential residues over time.

Table 5 Spirotetramat and its metabolites in cranberry from 240 SC foliar applications in the USA and Canada (IR-4 PR No. 10198)

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
GAP, Canada	0.20		7	0.44	7							
Chatsworth, NJ, USA 2009 (Early Black) Trial ID#143 ^b	0.17– 0.18	3	7	0.53	7	0.014 0.016 0.015	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.054 0.056 0.055	0.025
Plymouth, MA, USA 2009 (Stevens) Trial ID#144	0.17– 0.18	3	7–8	0.53	7	0.036 0.033 0.035	0.011 0.011 0.011	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.077 0.074 0.076	0.046
Warrens, WI, USA 2009 (Ben Lear) Trial ID#145	0.18	3	7–8	0.55	8	0.012 0.013 0.013	< 0.01 < 0.01 < 0.01	0.011 0.011 0.011	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.053 0.054 0.054	0.023
Warrens, WI, USA 2009 (Stevens) Trial ID#146	0.18– 0.19	3	7–8	0.55	7	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.05 < 0.05 < 0.05	< 0.02
Langley, BC, Canada 2009 (Stevens) Trial ID#14	0.18	3	7–8	0.54	1	0.23 0.28 0.26	0.042 0.043 0.043	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.30 0.35 0.33	0.30
					4	0.24 0.21 0.23	0.048 0.045 0.047	0.024 0.027 0.026	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.33 0.30 0.32	0.28
					7	0.077 0.084 0.081	0.040 0.039 0.040	0.015 < 0.01 < 0.013	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.15 0.15 0.15	0.12
					11	0.057 0.067 0.062	0.038 0.037 0.038	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.13 0.13 0.13	0.10
Langlois, OR, USA 2009 (Pilgrim) Trial ID#148	0.17	3	6–8	0.52	8	0.044 0.036 0.040	0.018 0.017 0.018	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.092 0.083 0.088	0.058

^a Mean value of residues expressed in bold

*Assorted tropical and sub-tropical fruits - Inedible peel**Banana*

Spirotetramat is used to control banana aphids (*Pentalonia nigronervosa*) in banana production. In Hawaii, USA, five trials (HI05, HI06, HI09, HI10 and HI14) were conducted during the 2008 and 2009 growing seasons. In each trial, the test substance (spirotetramat 240 SC) was applied in five foliar directed applications of approximately 0.28–0.30 kg ai/ha each, for a total of approximately 1.4–1.5 kg ai/ha. An organosilicone surfactant was included in each tank mix and the spray volume of approximately 500 L/ha was used.

The test substance was applied to bagged bunches in the HI05 trial. The bunches were not bagged in the other trials. All applications were made approximately 14 days apart and timed so that marketable-sized bananas could be collected 1 day after the final application. For decline determination, banana samples were collected additionally from HI14 trial at 3, 7, and 14 days after last application. In HI06 and HI10 trials, the bananas were cut in half lengthwise, retaining one half as samples for the banana fruit with peel samples. From the HI06 trial, the samples were additionally collected at 1-day PHI to determine residues in peeled fruits where a whole fruit was peeled and retained as a sample.

Table 6 Spirotetramat and its metabolites in banana from 240 SC foliar applications in the USA ^a (IR-4 PR No. 10042)

Location Year (Variety) Trial No.	Application				PHI (d)	Matrix	Residue (mg/kg) expressed as spirotetramat equivalents						
	kg ai/ha		Int. days	Total/ season, kg ai /ha			spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
GAP, USA	0.28	1	14	1.4									
Hilo, HI 2008 (Williams) 08-HI05 ^b	0.28– 0.30	1		1.5		Whole fruit	0.035 0.044 0.040	0.12 0.12 0.12	0.016 0.018 0.017	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.20	0.16
Waialua, HI 2009 (Williams) 08-HI06	0.28– 0.29	5		1.4	1	Whole fruit	0.38 0.20 0.29	0.28 0.24 0.26	0.060 0.046 0.053	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.62	0.55
Waialua, HI 2009 (Williams) 08-HI06						Pulp	0.013 0.017 0.015	0.12 0.12 0.12	0.033 0.033 0.033	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.19	0.14
Waianae, HI 2009 (Brazilian Dwarf Apple) 08-HI09	0.28	5		1.4	1	Whole fruit	1.5 0.97 1.2	0.55 0.42 0.49	0.068 0.034 0.051	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	1.8	1.7
Hilo, HI 2009 (Williams) 08-HI10	0.28– 0.29	5		1.4	1	Whole fruit	0.51 0.37 0.44	0.59 0.61 0.60	0.092 0.081 0.087	< 0.01 < 0.01 < 0.01	0.014 0.015 0.015	1.2	1.0
Waimanalo, HI 2009 (Dwarf Apple) 09-HI14	0.29– 0.30	5		1.4	1	Whole fruit	0.97 1.3 1.1	0.21 0.30 0.26	0.035 0.061 0.048	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	1.4	1.4
					3	Whole fruit	0.88 1.0 0.94	0.19 0.32 0.26	0.056 0.102 0.079	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	1.3	1.2
					7	Whole fruit	0.27 0.28 0.28	0.16 0.15 0.16	0.040 0.035 0.038	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.50	0.44
					14	Whole fruit	0.50 0.35	0.093 0.10	0.114 0.058	< 0.01 < 0.01	< 0.01 < 0.01		

Location Year (Variety) Trial No.	Application				PHI (d)	Matrix	Residue (mg/kg) expressed as spirotetramat equivalents						
	kg ai/ha		Int. days	Total/ season, kg ai /ha			spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
							0.43	0.097	0.086	< 0.01	< 0.01	0.63	0.53

^a Mean value of residues was expressed as a bold letter. Portion analysed was a whole banana with peel.

^b Test substance was applied to bagged bunches. In the other trials, the bunches were not bagged.

Pineapple

Spirotetramat is needed to control grey mealybugs and pink mealybugs (vectors of pineapple mealybug wilt virus) in pineapple production. Five field trials (HI01-HI05) were conducted in Hawaii, USA during 2011. At each trial, two foliar broadcast applications of the test substance (spirotetramat 240 SC) 13–14 days apart were made. The application rates were in the range 0.17–0.18 kg ai/ha per application for a total rate range of 0.35–0.36 kg ai/ha per season. All applications were made using appropriate spray equipment with an adjuvant in the tank mix, and the spray volumes of 830–1900 L/ha were sufficient to provide adequate dispersal of the test substance.

At the HI02 trial, duplicate samples were collected 0, 3, 7, and 14 days after the last application. Additional samples taken from the HI01 trial were subjected to processing into pineapple juice and process residue.

HI01, HI02 and HI05 trials were conducted on different plantations at the same site with the same variety, the 1st application 36–106 days apart. HI03 and HI04 were also conducted on different plantations at the same site with the same variety, the 1st application 40 days apart. These five trials were considered as independent.

At all trials, samples were harvested one day after the last application. Crowns were removed from the sampled fruit and were cut into quarters longitudinally, retaining one quarter of each for the sample. In field site, sample size reduction should be avoided. These trials are not appropriate for evaluation.

Table 7 Spirotetramat and its metabolites in pineapple from 240 SC foliar applications in the USA (IR-4 PR No. 10635)

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a							
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono-OH	enol -Glc	total spiro	spiro + enol	
GAP, USA	0.18		14	0.36	1								
Wahiawa, HI 2011 (Tropical Gold, MG-3) HI01	0.17– 0.18	2	14	0.36		0.038 0.045 0.042	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.082	0.052	
Wahiawa, HI 2011 (Tropical Gold, MG-3) HI02	0.18	2	14	0.36	0	0.034 0.039 0.037	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.077	0.047	
					1	0.015 0.013 0.014	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.054	0.024	
					3	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.05	0.02	

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono-OH	enol -Glc	total spiro	spiro + enol
					7	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.05	0.02
					14	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.05	0.02
Makawao, HI 2011 (Maui Gold) HI03	0.18	2	14	0.35	1	0.065 0.054 0.060	0.016 0.016 0.016	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.11	0.076
Makawao, HI 2011 (Maui Gold) HI04	0.18	2	14	0.36	1	0.023 0.017 0.020	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.060	0.030
Wahiawa, HI 2011 (Tropical Gold, MG-3) HI05	0.17– 0.18	2	13	0.35	1	0.030 0.030 0.030	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.070	0.040

^a Mean value of residues was expressed in bold. Portion analysed was fruit crown removed.

Pomegranate

Spirotetramat is used to control aphids, whiteflies, and grape mealybug in pomegranate production. In California, USA, four field trials were conducted during the 2009 growing season. In each trial, the test substance (spirotetramat 240 SC) was applied in two foliar directed applications of approximately 0.35–0.36 kg ai/ha each, for a total of approximately 0.17–0.18 kg ai/ha. An adjuvant was included in each tank mix and the spray volume of 550–1060 L/ha was applied. The applications were made 14 days apart and timed so that marketable-sized pomegranates could be collected 1 day after the final application. Additional samples for decline determination were collected from one trial, CA69 at 3, 7, and 14 days. Each fruit was cut into quarters, retaining opposite quarters as samples. Cutting of samples in field site was not appropriate.

Table 8 Spirotetramat and its metabolites in pomegranate from 240 SC foliar applications in the USA (IR-4 PR No. 10113)

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono-OH	enol -Glc	total spiro	spiro + enol
GAP, USA	0.18		14	0.36 per 12- month	1							
Gridley, CA 2009 (Wonderful) 09-CA71 ^b	0.17– 0.18	2	14	0.35	1	0.058 0.061 0.060	0.079 0.066 0.073	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.024 0.019 0.022	0.18	0.13
Gridley, CA 2009 (Wonderful) 09-CA72 ^b	0.17– 0.18	2	14	0.35	1	0.041 0.052 0.047	0.055 0.085 0.070	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.018 0.021 0.020	0.16	0.12
Reedley, CA 2009 (Wonderful) 09-CA69 ^c	0.18	2	14	0.35	1	0.13 0.090 0.11	0.038 0.027 0.033	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.011 < 0.01 0.011	0.17	0.14
					3	0.096	0.028	< 0.01	< 0.01	< 0.01		

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono-OH	enol -Glc	total spiro	spiro + enol
						0.10 0.098	0.025 0.027	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	0.16	0.13
					7	0.10 0.075 0.088	0.025 0.020 0.023	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.14	0.11
					14	0.035 0.016 0.026	0.021 0.015 0.018	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.013 < 0.01 0.012	0.076	0.044
Reedley, CA 2009 (Wonderful) 09-CA70 ^c	0.18	2	14	0.36	1	0.032 0.025 0.029	0.019 0.015 0.017	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.076	0.046

^a Mean value of residues was expressed in bold

^b The two trials were conducted at the same site with the same variety, on the same dates of application. Thus they were not independent.

^c The two trials were conducted at the same site with the same soil type and maintenance, with the same variety, on 1st application 21 days apart. They were not considered as independent.

Bulb vegetables

Onion, bulb

Twelve field trials were conducted in Canada (four trials) and in the USA (eight trials) during 2008 and 2009 growing season. Two foliar broadcast applications of spirotetramat 240 SC formulation were made at a rate of application ranged from 0.084 to 0.094 kg ai/ha. The spray volumes ranged from approximately 205 to 533 L/ha and the PHI was 2 to 4 days, with a 6 to 8 day retreatment interval between applications. A non-ionic surfactant (Agral 90 or Dyne-Amic), at the target rate of 0.25% v/v in the spray mixture was included with each application. Two residue decline trials were conducted with samples collected at 1, 6–7, and 9–10 days after the last application, in addition to the samples collected at the target PHI of 3 to 4 days.

Table 9 Spirotetramat and its metabolites in bulb onion from 240 SC foliar applications in the USA and Canada (IR-4 PR No. 09983)

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
GAP, USA	0.09		7	0.18	3							
Delhi, ON, Canada 2008 (Nebula) #141	0.092– 0.093	2	7	0.18	3	< 0.01 < 0.01 < 0.01	0.068 0.062 0.065	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.11	0.075
Delhi, ON, Canada 2008 (Milestone) #142	0.091– 0.093	2	8	0.18	4	< 0.01 < 0.01 < 0.01	0.087 0.083 0.085	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.13	0.095
Sainte-Clotilde, QC, Canada 2008 (Hybrid Centennial) #143 ^b	0.086– 0.088	2	7	0.17	1	< 0.01 < 0.01 < 0.01	0.20 0.17 0.19	0.013 < 0.01 0.012	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.23	0.20
					3	< 0.01 < 0.01 < 0.01	0.22 0.21 0.22	0.014 0.013 0.014	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.26	0.23
					6	< 0.01 < 0.01	0.21 0.19	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01		

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
						< 0.01	0.20	< 0.01	< 0.01	< 0.01	0.24	0.21
					9	< 0.01 < 0.01 < 0.01	0.22 0.21 0.22	0.014 < 0.01 0.012	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.26	0.23
Sainte-Clotilde, QC, Canada 2008 (Hybrid Champlain) #144 ^b	0.084– 0.094	2	7	0.18	3	< 0.01 < 0.01 < 0.01	0.24 0.30 0.27	0.014 0.016 0.015	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.32	0.28
Freeville, NY, USA 2008 (Patterson) #589	0.085– 0.089	2	6	0.17	2	< 0.01 < 0.01 < 0.01	0.045 0.050 0.048	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.088	0.058
Arlington, WI, USA 2008 (Stutgard yellow) #590	0.090– 0.094	2	7	0.18	3	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.05	< 0.02
Weslaco, TX, USA 2008 (Super Star F1) #591	0.091– 0.090	2	7	0.18	3	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.05	< 0.02
Greeley, CO, USA 2008 (Talon, yellow) #592	0.094– 0.092	2	6	0.19	1	< 0.01 < 0.01 < 0.01	0.032 0.033 0.033	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.073	0.043
					4	< 0.01 < 0.01 < 0.01	0.037 0.048 0.043	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.083	0.053
					7	< 0.01 < 0.01 < 0.01	0.051 0.042 0.047	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.087	0.057
					10	< 0.01 < 0.01 < 0.01	0.037 0.046 0.042	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.082	0.052
Salem, OR, USA 2008 (Red Bull) #593	0.091	2	7	0.18	2	< 0.01 < 0.01 < 0.01	0.036 0.035 0.036	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.076	0.046
Holtville, CA, USA 2009 (Serengeti) #594	0.089– 0.092	2	7	0.18	4	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.05	< 0.02
Parlier, CA, USA 2008 (Candy) #595	0.092– 0.093	2	7	0.18	3	< 0.01 < 0.01 < 0.01	0.041 0.041 0.041	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.081	0.051
Parma, ID, USA 2008 (Granero) #596	0.089– 0.089	2	8	0.18	4	< 0.01 < 0.01 < 0.01	0.014 0.019 0.016	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.056	0.026

^a Mean value of residues was expressed in bold

^b The trials were conducted at the same site with the same variety, on the same dates of application.

Spring onion

Two field trials were conducted during the 2009 growing season in Ontario and Quebec of Canada. Spirotetramat 240 SC formulation was applied to green onions as two foliar applications ranging from 0.090 to 0.092 kg ai/ha each, with re-treatment intervals of six to seven days, for maximum seasonal rates of 0.18 kg ai/ha. A non-ionic surfactant was included at 0.25% in the spray mixtures and the spray volume of approximately 300 L/ha was applied. Samples were harvested 6 to 7 days after the final application. One decline trial was conducted with additional samples harvested at 1, 4, and 11

days following the last application to assess the decline pattern of spirotetramat and its metabolites residues.

Table 10 Spirotetramat and its metabolites in spring onion from 240 SC foliar applications in Canada (IR-4 PR No. 10942)

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
GAP, USA	0.09		7	0.18	7							
Harrow, ON 2009 (Emerald Isle) #113	0.090– 0.091	2	7	0.18	1	0.24 0.27 0.26	0.26 0.35 0.31	0.12 0.11 0.12	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.71	0.57
					4	0.14 0.16 0.15	0.20 0.18 0.19	0.080 0.084 0.082	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.44	0.34
					6	0.098 0.099 0.096 0.10 0.098	0.13 0.12 0.16 0.15 0.14	0.075 0.056 0.064 0.063 0.064	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.32	0.24
					11	0.053 0.059 0.056	0.067 0.062 0.065	0.039 0.034 0.037	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.18	0.12
St-Jeansur- Richelieu, QC 2009 (Parade)	0.091– 0.092	2	6	0.18	7	0.043 0.040 0.040 0.035 0.039	0.046 0.060 0.064 0.047 0.054	0.059 0.050 0.044 0.046 0.050	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.16	0.093

^a Mean value of residues was expressed in bold

Leafy vegetables (including Brassica leafy vegetables)

Watercress

Three field trials were conducted in the USA (Florida and Maryland) during 2008 (Trial FL38, FL39, MD27). In the FL39 and MD27 trials, the plots received two applications of spirotetramat 240 SC formulation using conventional broadcast sprayers at the rate of 0.21–0.22 kg ai/ha. In the FL38 trial, additionally, two chemigation applications were made in the different plot using overhead mini-sprinklers at the rate of 0.22 kg ai/ha. The organo-silicone surfactant Dyne-Amic was used with all applications (except application 1 at the FL39 trial) at all the field trials. Applications of the test substance were made at 7–8 day intervals when the watercress was in the vegetative stage with the last application 3 days before the harvest. The foliage (leaves and stems) was cut with a knife/pruners and placed directly into sample bags. Samples were taken from at least 12 separate areas within each plot. For chemigation application of FL38 trial, half of each sample was taken from the plot area where the sprinkler spray overlapped and the other half was taken from areas where the spray did not overlap.

Table 11 Spirotetramat and its metabolites in watercress from 240 SC foliar applications in the USA (IR-4 PR No. 09948)

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
GAP, USA	0.22		7	0.45	3							
Fellsmere, FL 2008 (B&W 1)	0.22	2	8	0.44	3	< 0.01 < 0.01	0.13 0.14	0.077 0.083	< 0.01 < 0.01	< 0.01 < 0.01		

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
FL38 ^b						< 0.01	0.14	0.080	< 0.01	< 0.01	0.25	0.15
						< <i>0.01</i>	<i>0.25</i>	<i>0.21</i>	< <i>0.01</i>	< <i>0.01</i>		
						< <i>0.01</i>	<i>0.23</i>	<i>0.18</i>	< <i>0.01</i>	< <i>0.01</i>		
						< 0.01	0.24	0.20	< 0.01	< 0.01	0.47	0.25
Fellsmere, FL 2008 (B&W 1) FL39 ^b	0.22	2	7	0.44	3	0.044 0.054 0.049	0.19 0.22 0.21	0.21 0.24 0.23	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.51	0.26
Rocktown, MD 2008 (B&W 47)	0.21	2	7	0.42	3	0.014 0.016 0.015	0.27 0.33 0.30	0.22 0.22 0.22	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.56	0.32

^a Mean value of residues was expressed in bold. Italic values mean residues from chemigation application using overhead mini-sprinklers.

^b FL 38 trials using backpack sprayer and mini-sprinkler were conducted at the same site with the same variety on the same dates of application. FL38 and FL 39 trials were conducted at the same site and soil type with the same variety, on 1st application 13 days apart. These trials were not considered as independent.

Stalk and stem vegetables

Artichoke, globe

Five trials were conducted in the USA (three trials) and Canada (two trials) during the 2009 and 2010 growing season. Spirotetramat 240 SC formulation was applied to artichoke as four foliar applications ranging from 0.13 to 0.15 kg ai/ha, with re-treatment intervals of 5 to 9 days, and the last application timed for a 3 ± 1 day PHI. The total seasonal application rate ranged from 0.56 kg ai/ha. A non-ionic surfactant was included at 0.25% in the spray mixtures and the spray volumes ranged from 92 to 708 L/ha. The artichoke samples were harvested 2 to 3 days after the final application. One decline trial was conducted, with artichoke samples harvested at 1, 3, 7 and 10 days after the last application, to assess the potential decline in residues over time.

Table 12 Spirotetramat and its metabolites in globe artichoke from 240 SC foliar applications in the USA and Canada (IR-4 PR No. 10243)

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
GAP, USA	0.15		7	0.56	3							
L'Acadie QC, Canada 2009 (Imperial Star) #125	0.14	4	6-8	0.56	1	0.051 0.058 0.055	0.16 0.13 0.15	0.077 0.056 0.067	< 0.01 < 0.01 < 0.01	0.025 0.018 0.022	0.30	0.21
					3	0.020 0.012 0.016	0.11 0.11 0.11	0.073 0.066 0.069	< 0.01 < 0.01 < 0.01	0.027 0.024 0.026	0.23	0.13
					7	< 0.01 < 0.01 < 0.01	0.044 0.043 0.044	0.038 0.025 0.032	< 0.01 < 0.01 < 0.01	0.021 0.015 0.018	0.11	0.054
					10	< 0.01 < 0.01 < 0.01	0.025 0.022 0.024	0.028 0.016 0.022	< 0.01 < 0.01 < 0.01	0.021 0.011 0.016	0.081	0.034
Agassiz, BC, Canada 2010 (Imperial Star) #126	0.13- 0.15	4	5-8	0.56	3	0.046 0.038 0.042	0.17 0.14 0.16	0.099 0.11 0.10	< 0.01 < 0.01 < 0.01	0.031 0.026 0.028	0.34	0.20

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
Castroville, CA, USA 2009 (F1 1855) #128	0.14	4	7-8	0.56	3	0.25 0.38 0.31	0.13 0.19 0.16	0.071 0.10 0.087	< 0.01 < 0.01 < 0.01	0.020 0.051 0.035	0.60	0.47
Marina, CA, USA 2009 (Green Globe) #129	0.14	4	6-8	0.56	3	0.052 0.074 0.063	0.21 0.21 0.21	0.095 0.095 0.095	< 0.01 < 0.01 < 0.01	0.033 0.033 0.033	0.41	0.27
Castroville, CA, USA 2009 (Green Globe) #130	0.14	4	6-9	0.56	2	0.28 0.28 0.28	0.23 0.19 0.21	0.19 0.14 0.17	< 0.01 < 0.01 < 0.01	0.042 0.026 0.034	0.70	0.49

^a Mean value of residues was expressed as a bold letter.

Seed for beverages and sweets

Coffee beans

Spirotetramat is used to control green scale (*Coccus viridis*) in coffee production. Five field trials were conducted in Hawaii, USA during the 2009 growing season. In each trial, the test substance (spirotetramat 240 SC) was applied in three foliar directed applications of approximately 0.18–0.19 kg ai/ha each, for a total of approximately 0.54–0.57 kg ai/ha. An organosilicone surfactant was included in each tank mix and the spray volumes ranged from 240 to 470 L/ha.

The applications were made 20 to 22 days apart in HI09, HI10, and HI13 trials. The interval between the second and third application was shortened to 13 days and 7 days, respectively, in HI11 and HI12 because the beans were ripening earlier than expected. Ripe coffee bean “cherries” were collected 13 to 14 days after the final application in all but HI11, where samples were collected at 7 days HI11 because the crop was maturing faster than expected. Additional samples for decline determination were collected from HI13 at 1, 7, and 21 days.

At the field facility, the coffee bean cherries were run through a mechanical pulper and demulsilager to remove the flesh from the bean. The beans were then dried in an oven at 50 °C for up to 2 days, hulled, and winnowed. The green bean coffee samples from HI12 were further processed into roasted coffee beans and freeze-dried coffee at a processing facility.

Table 13 Spirotetramat and its metabolites in coffee beans from 240 SC foliar applications in the USA (IR-4 PR No. 10041)

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
GAP, USA	0.18		21	0.53	14							
Kealakekua, HI 2009 (Guatemalan) 09-HI09 ^b	0.18– 0.19	3	21–22	0.56	13	< 0.01 < 0.01 < 0.01	0.033 0.022 0.028	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.016 0.012 0.014	0.072	0.038
Lahaina, HI 2009 (Yellow Caturra) 09-HI10	0.18	3	20	0.54	14	< 0.01 < 0.01 < 0.01	0.025 0.016 0.021	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.011 < 0.01 0.011	0.062	0.031
Kealakekua, HI 2009 (Guatemalan) 09-HI11 ^b	0.19	3	13 ^c – 21	0.57	7 ^d	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.05	< 0.02

Location Year (Variety) Trial No.	Application				PHI (d)	Residue (mg/kg) expressed as spirotetramat equivalents ^a						
	kg ai/ha	n	Int. days	Total/ season, kg ai /ha		spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
Kauai, HI 2009 (Red Caturra) 09-HI12	0.18	3	7 ^c -21	0.54	14	< 0.01 < 0.01 < 0.01	0.012 < 0.01 0.011	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.05	0.02
Kauai, HI 2009 (Yellow Caturra) 09-HI13	0.18	3	20	0.54	1	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.05	< 0.02
					7	< 0.01 < 0.01 < 0.01	0.012 < 0.01 0.011	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.051	0.021
					14	< 0.01 < 0.01 < 0.01	0.020 < 0.01 0.015	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.010 < 0.01 0.010	0.055	0.025
					21	< 0.01 < 0.01 < 0.01	0.021 0.015 0.018	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	0.011 < 0.01 0.011	0.059	0.028

^a Mean value of residues was expressed in bold. Analysed sample is green bean coffee.

^b Trials were conducted at the sites within 3 km with the same variety, 1st application 22 days apart. They were not considered as independent.

^c Interval between the second and third application was shortened due to an earlier ripening of coffee beans.

^d Harvested earlier due to the faster maturing of coffee beans.

FATE OF RESIDUES IN STORAGE AND PROCESSING+-

Magnitude of residue in processing

The Meeting received information on the residue levels on the processed products of pineapple and green bean coffee. They are summarized in Table 14.

Pineapple (juice and process residue)

One processing study for pineapple was carried out in Hawaii, USA (HI01, IR-4 PR No. 10635). The trial plot received two foliar broadcast applications with the test substance (spirotetramat 240 SC) 14 days apart. The application rates were in the range 0.17–0.18 kg ai/ha per application for a total rate range of 0.36 kg ai/ha per season. The spray solutions included adjuvant in the tank mix. The fruit samples were harvested one day after the last application.

Crowns were removed from the sampled fruit and the fruits without crown were processed into juice and process residue as follows. Both ends of the fruits were cut and peeled. The peeled fruit, scraped flesh from peels and end cuts were juiced using a commercial juicer. Juice and pulp were collected separately. Antifoam agent was added into the separated juice, mixed and heated in a water bath to 88 °C. The juice was cooled to 8 °C. For preparing process residue, the retained pineapple peels were chopped in a food cutter. Pulp left over from juicing was added and stirred to mix thoroughly. Juice and process residue samples were placed in the freezer until shipment to the residue laboratory.

From the results, processing factors for juice and process residue, based on total spirotetramat residues, could not be calculated as valid LOQ values at or below 0.01 mg/kg for enol glucoside were not provided.

Coffee beans (roasted coffee bean and freeze-dried coffee)

One processing study was conducted in Hawaii, USA (09-HI12, IR-4 PR No. 10041). Spirotetramat 240 SC formulation was applied in three foliar directed applications of approximately 0.18 kg ai/ha

each, for a total of approximately 0.54 kg ai/ha. An organosilicone surfactant was included in each tank mix. The applications were made 7 to 21 days apart and ripe coffee bean “cherries” were collected 14 days after the final application.

At the field facility, the coffee bean cherries were run through a mechanical pulper and demusilager to remove the flesh from the bean. The beans were then dried in an oven at 50 °C for up to 2 days, hulled, and winnowed. The green bean coffee (RAC) samples were further processed into roasted coffee beans and freeze-dried coffee at a processing facility.

The green beans were roasted to light to medium roast in the coffee roaster set at 208 °C. The roasted beans were thoroughly mixed and a portion was moved to freezer storage. The remaining roasted beans were ground fine in a small burr grinder, added to boiling water, steeped at least 10 minutes brewing (1600 g ground coffee per 10 litre water), and filtered. The filtered coffee extract was cooled in an ice water bath and then placed on a tray in a freezer set at approximately -50 °C and frozen overnight. The following day, the frozen coffee grounds were placed in a prepared freeze-dryer for 3 days (shelf temperature, 35 °C; vacuum chamber pressure, approximately 100 m Torr). Freeze-dried coffee samples were placed in frozen storage until shipment to the analytical laboratory.

No spirotetramat or spirotetramat equivalent residues were observed in coffee green bean (RAC), except spirotetramat enol, 0.011 mg/kg. However, this value is very close to the LOQ (< 0.01 mg/kg). Further, the high LOQ values for enol-Glc in roasted coffee bean and all analytes in freeze-dried coffee made an estimation of processing factors for total spirotetramat residues impossible.

Table 14 Residues on pineapple and coffee processed fractions from the foliar application of spirotetramat (IR-4 PR No. 10635, IR-4 PR No. 10041)

Location Year (Variety) Trial No.	Application				PHI (d)	Portion analysed	Residue (mg/kg) expressed as spirotetramat equivalents						
	kg ai/ha	n	Int. (d)	Total/ season, kg ai /ha			spiro	enol	keto -OH	mono- OH	enol -Glc	total spiro	spiro + enol
Pineapple													
GAP, USA	0.18	(2)	14	0.36	1								
Wahiawa, HI 2011 (Tropical Gold, MG-3) HI01	0.17– 0.18	2	14	0.36	1	Fruit without crown	0.042	< 0.01	< 0.01	< 0.01	< 0.01	0.082	0.052
						Juice	0.019	< 0.01	< 0.01	< 0.01	< 0.01 ^a		0.029
						Process residue	0.050	0.015	< 0.01	< 0.01	< 0.01 ^a		0.065
Coffee bean													
GAP, USA	0.18	(3)	21	0.53	14								
Kauai, HI 2009 (Red Caturra) 09-HI12	0.18	3	7– 21	0.54	14	Green bean	< 0.01	0.011	< 0.01	< 0.01	< 0.01	0.05	0.021
						Roasted bean	< 0.01	0.018	< 0.01	< 0.01	< 0.05		0.028
						Freeze- dried coffee	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1		

^a The analytical method performance was not acceptable due to high recoveries.

APPRAISAL

Spirotetramat was evaluated for the first time by the JMPR in 2008 for toxicology and residues. The Meeting derived an ADI of 0–0.05 mg/kg bw and an ARfD of 1.0 mg/kg bw and recommended

maximum residue levels for a range of crops. In 2011 and 2012, the JMPR recommended additional maximum residue levels. The residue is defined as follows.

For compliance with the MRL for plant commodities: *spirotetramat plus spirotetramat enol, expressed as spirotetramat*.

For dietary intake estimation for plant commodities: *spirotetramat plus the metabolites enol, ketohydroxy, enol glucoside, and monohydroxy, expressed as spirotetramat*.

For compliance with the MRL and for dietary intake estimation for animal commodities: *spirotetramat enol, expressed as spirotetramat*.

The residue is not fat soluble.

The present Meeting evaluated supervised field trial data for various crops including their analytical methods, stability of frozen sample and stability tests, and processing studies.

Methods of analysis

Analytical methods used in raw agricultural commodities from field trials were suitable for quantifying spirotetramat residues including the metabolites spirotetramat enol, spirotetramat ketohydroxy, spirotetramat monohydroxy and spirotetramat enol glucoside in the various plant commodities. The methods were based on LC-MS/MS and the reference method used was evaluated by the Meeting in 2008 and 2011. The limits of quantitation for the raw commodities are 0.01 mg/kg (parent equivalents) for each analyte and 0.05 mg/kg for total spirotetramat equivalents.

For the processed products of pineapple and coffee bean, overall, the method performance was not acceptable. In pineapple juice and processing by-products, average recoveries of enol glucoside (0.01 mg/kg as parent equivalents) were not in the allowable range.

In roasted coffee bean, a limit of quantitation for enol glucoside was as high as 0.05 mg/kg. For freeze-dried coffee, the LOQ levels for spirotetramat enol, -ketohydroxy and - monohydroxy were 0.1 mg/kg, i.e., the fortification levels were not sufficiently low enough, further, some recoveries of parent and enol glucoside at the indicated LOQ level were outside the acceptable range, as a result the method performance was not considered satisfactory.

Stability of residues in stored analytical samples

Storage stability studies were performed with banana with peel, peeled banana, green coffee bean, roasted coffee bean and freeze-dried coffee. They indicated that the residues were stable during the frozen storage intervals of field trial samples. Stabilities of residues in commodities not assessed by the present Meeting are covered by the storage stability data evaluated by the 2008 JMPR, which demonstrated stability of all analytes for up to 2 years for a diverse range of commodities.

Results of supervised residue trials on crops

The Meeting received supervised residue trial data for the foliar application of spirotetramat as a suspension concentrate formulation (SC) to a variety of crops, i.e., blueberries, cranberry, banana, pineapple, pomegranate, blub onion, spring onion, watercress, globe artichoke and coffee.

In the discussions below, spirotetramat plus enol residues considered first for the estimation of maximum residue levels followed by total residues (spirotetramat plus the metabolites enol, ketohydroxy, monohydroxy, and enol glucoside, expressed as spirotetramat) for estimation of STMR and HR values for the dietary risk assessments.

Berries and other small fruits

Blueberries

In Canada, spirotetramat is registered at a rate of 0.20 kg ai/ha, a 7-day retreatment interval, a total seasonal rate of 0.44 kg, and a 7-day PHI. Eleven residue trials were conducted in the USA (7) and

Canada (4) with three applications at a rate of 0.17–0.19 kg ai/ha, total seasonal rate of 0.52–0.56 kg ai/ha, 5–8 days retreatment intervals and 6–8 days PHIs. Of the trials, two were not considered independent as they were conducted at the same site, with the same variety at very close dates of application.

Residues of spirotetramat plus enol from the trials were (n=10): 0.14, 0.17, 0.21, 0.31, 0.37, 0.39, 0.53, 0.53, 0.68 and 0.69 mg/kg.

Total residues of spirotetramat from the trials were (n=10): 0.38, 0.44, 0.45, 0.49, 0.60, 0.66, 0.69, 1.1, 1.2 and 1.6 mg/kg.

The Meeting estimated a maximum residue level of 1.5 mg/kg and an STMR of 0.63 mg/kg and an HR of 1.6 mg/kg for bush berries as blueberry is a representative crop of the subgroup.

Cranberry

In Canada, spirotetramat is registered for the use on cranberry at a rate of 0.20 kg ai/ha, a 7-day retreatment interval, a total seasonal rate of 0.44 kg, and a 7-day PHI. Six residue trials were conducted in the USA and Canada with three applications at a rate of 0.17–0.19 kg ai/ha, total seasonal rate of 0.52–0.55 kg ai/ha, 6–8 days retreatment intervals and 7–8 days PHIs, approximating the Canadian GAP.

Residues of spirotetramat plus enol from the trials were (n=6): < 0.02, 0.023, 0.025, 0.046, 0.058 and 0.12 mg/kg.

Total residues of spirotetramat from the trials were (n=6): < 0.05, 0.054, 0.055, 0.076, 0.088 and 0.15 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.066 mg/kg and an HR of 0.15 mg/kg for cranberry.

Assorted tropical and sub-tropical fruits-inedible peel

Banana

Five residue trials were conducted using five applications in Hawaii, USA, according to the USA GAP (rate of 0.28 kg ai/ha, 14-day retreatment interval, total seasonal rate of 1.4 kg ai/ha, and 1-day PHI). In one trial, application was made on bagged banana. For the other four trials, banana bunches were not bagged, however, residues in pulp were not analysed, except one trial.

From the trials, residues of spirotetramat plus enol in unbagged whole banana were (n=4): 0.16 0.55, 1.0, 1.4 and 1.7 mg/kg.

From the trials, total residues of spirotetramat in unbagged whole banana were (n=4): 0.2, 0.62, 1.2, 1.4 and 1.8 mg/kg.

In the one trial, residues in pulp were 0.14 mg/kg (0.55 mg/kg for whole) for spirotetramat plus enol and 0.19 mg/kg (0.62 mg/kg for whole) for total spirotetramat.

The Meeting could not estimate a maximum residue level for banana as the number of trials was considered insufficient.

Pineapple

Five trials were conducted in Hawaii, USA with two applications, according to the USA GAP (rate of 0.18 kg ai/ha, 14-day retreatment interval, total seasonal rate of 0.36 kg ai/ha, and 1-day PHI). In these trials the preparation of samples did not comply with the relevant FAO guidelines, i.e., samples underwent cutting/quarterming at the field site.

As the handling of samples did not comply with the relevant FAO guidelines on sample preparation, the Meeting decided that residue data could not be used for the estimation of a maximum residue level.

Pomegranate

Four trials were conducted in the USA with two applications, complying with the GAP of the USA (rate of 0.18 kg ai/ha, 14-day retreatment interval, 0.36 kg ai/ha/12-month, and a 1-day PHI). In these trials the preparation of samples did not comply with the relevant FAO guidelines, i.e., samples underwent cutting/quartering at the field site. As a result the residue data could not be used in estimating a maximum residue level.

*Bulb vegetables,**Onion, bulb*

Twelve trials were performed in Canada and USA with two applications, according to the USA GAP (rate of 0.09 kg ai/ha, 7-day retreatment interval, total seasonal rate of 0.18 kg ai/ha, and 3-day PHI). Two trials were not independent as they were conducted at the same site with the same variety with the same dates of application.

Residues of spirotetramat plus enol from the trials were (n=11): < 0.02, < 0.02, < 0.02, 0.026, 0.046, 0.051, 0.057, 0.058, 0.075, 0.095 and 0.28 mg/kg.

Total residues of spirotetramat from the trials were (n=11): < 0.05, < 0.05, < 0.05, 0.056, 0.076, 0.081, 0.087, 0.088, 0.11, 0.13 and 0.32 mg/kg.

Based on the residue values, the Meeting estimated a maximum residue level of 0.4 mg/kg.

The 2011 JMPR recommended a maximum residue level of 0.4 mg/kg, an STMR of 0.11 mg/kg and an HR of 0.27 mg/kg, based on the residues from trials in Australia matching GAP (2 applications at 0.048 kg ai/ha with a PHI of 7 days).

The Meeting therefore confirmed its previous maximum residue level recommendation of 0.4 mg/kg for onion, bulb.

Spring onion

Two trials were performed in Canada with two applications, matching the USA GAP (rate of 0.09 kg ai/ha, 7-day retreatment interval, total seasonal rate of 0.18 kg ai/ha, and 7-day PHI). The residues were 0.093 and 0.24 mg/kg as spirotetramat plus enol, 0.16 and 0.32 mg/kg as total residues.

The Meeting considered the number of trials insufficient to estimate a maximum residue level.

Watercress

Three trials were performed in the USA with two applications, according to GAP of the country (rate of 0.22 kg ai/ha, 7-day retreatment interval, total seasonal rate of 0.45 kg ai/ha, and 3-day PHI).

Two trials were not independent as they were conducted at the same site with the same variety, with dates of application 13 days apart. In addition, in one trial, two methods of application were utilized, i.e., using a backpack sprayer and overhead mini-sprinkler in a separate plot. These treatments were considered replicates of the trial. As a result one residue value was selected from each of the trials.

Residues from the trials were 0.26 and 0.32 mg/kg for spirotetramat plus enol, 0.51 and 0.56 mg/kg for total residues. The Meeting could not estimate a maximum residue level due to insufficient residue data.

The Meeting noted that the residues from the trials were covered by the previously recommended maximum residue level for leafy vegetables.

Artichoke, globe

Five trials were conducted in Canada and the USA with four applications, according to the USA GAP (rate of 0.15 kg ai/ha, 7-day retreatment interval, total seasonal rate of 0.56 kg ai/ha, and 3-day PHI).

Residues of spirotetramat plus enol from the trials were (n=5): 0.13, 0.20, 0.27, 0.47 and 0.49 mg/kg.

Total residues of spirotetramat from the trials were (n=5): 0.23, 0.34, 0.41, 0.60 and 0.70 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.41 mg/kg and an HR of 0.70 mg/kg for artichoke, globe.

Coffee beans

Five trials were conducted in Hawaii, USA with three applications, according to the GAP of that country (rate of 0.18 kg ai/ha, 21-day retreatment interval, total seasonal rate of 0.53 kg ai/ha, and 14-day PHI). Exceptionally, in one trial, a retreatment interval between the second and third application was 7 days due to an earlier ripening of coffee beans. The Meeting considered such a divergence from GAP would have little impact on the final residue level. Two trials were not considered independent as they were carried out at geographically close sites on the same variety within the same growing season.

Residues of spirotetramat plus enol from the four trials available were: 0.020, 0.028, 0.031 and 0.038 mg/kg; and 0.050, 0.059, 0.062 and 0.072 mg/kg for total residues of spirotetramat.

The Meeting considered the number of trials insufficient to estimate a maximum residue level.

Animal feeds

Residue information on animal feeds was not available for this Meeting.

Fate of residues during processing

One processing study for pineapple juice and pineapples processing by-products, roasted coffee bean and freeze-dried coffee were made available. However, the estimation of processing factors was not required as maximum residue levels could not be recommended for pineapple and coffee beans.

Residues in animal commodities

From the evaluations by the present Meeting, no feed items were added to the feed list evaluated by the 2011 JMPR. The Meeting retained the residue levels for animal commodities estimated by the 2011 and 2012 JMPR.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue concentrations listed below are suitable for establishing MRLs and for assessing IEDIs and IESTIs.

Definition of the residue (for compliance with MRL for plant commodities: Spirotetramat and its enol metabolite, 3-(2,5-dimethylphenyl)-4-hydroxy-8-methoxy-1-azaspiro[4.5]dec-3-en-2-one, expressed as spirotetramat.

Definition of the residue (for estimation of dietary intake)for plant commodities: Spirotetramat, enol metabolite 3-(2,5-dimethylphenyl)-4-hydroxy-8-methoxy-1-azaspiro[4.5]dec-3-en-2-one, ketohydroxy metabolite 3-(2,5-dimethylphenyl)-3-hydroxy-8-methoxy-1-azaspiro[4.5]decane-2,4-dione, monohydroxy metabolite cis-3-(2,5-dimethylphenyl)-4-hydroxy-8-

methoxy-1-azaspiro[4.5]decan-2-one, and enol glucoside metabolite glucoside of 3-(2,5-dimethylphenyl)-4-hydroxy-8-methoxy-1-azaspiro[4.5]dec-3-en-2-one, expressed as spirotetramat.

Definition of the residue (for compliance with MRL and estimation of dietary intake) for animal commodities: Spirotetramat enol metabolite, 3-(2,5-dimethylphenyl)-4-hydroxy-8-methoxy-1-azaspiro[4.5]dec-3-en-2-one, expressed as spirotetramat.

The residue is not fat-soluble.

CCN	Commodity	Recommended MRL mg/kg		STMR or STMR-P mg/kg	HR or HR-P mg/kg
		New	Previous		
VS 0620	Artichoke, globe	1		0.41	0.70
FB 2006	Bush berries	1.5		0.63	1.6
FB 0265	Cranberry	0.2		0.066	0.15

DIETARY RISK ASSESSMENT

Long-term intake

The ADI for spirotetramat is 0–0.05 mg/kg bw. The International Estimated Daily Intakes (IEDIs) for spirotetramat were estimated for the 13 GEMS/Food Consumption Cluster Diets using the STMR or STMR-P values estimated by the previous and present JMPR. The results are shown in Annex 3 of the 2013 Report. The IEDIs ranged 2–20% of the maximum ADI. The Meeting concluded that the long-term intake of residues of spirotetramat from uses considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The ARfD for spirotetramat is 1.0 mg/kg bw. The International Estimate Short Term Intakes (IESTIs) for difenoconazole were calculated for the food commodities for which STMRs or HRs were estimated by the present Meeting and for which consumption data were available. The results are shown in Annex 4 of the 2013 Report. The IESTIs varied from 0–2% of the ARfD for children and 0–1% for general population.

The Meeting concluded that the short-term intake of residues of spirotetramat from other uses that have been considered by the present Meeting is unlikely to present a public health concern.

REFERENCES

Code	Author	Year	Title, Institute, Report reference
	Coopersmith, H	2009	An Analytical Method for the Determination of Residues of BYI08330, BYI08330-enol, BYI08330-ketohydroxy, BYI08330-mono-hydroxy and BYI08330-enol-Glc Metabolites in/on Crop Matrices Using LC/MS/MS. Bayer CropScience, Bayer Method No. FN-007-P08-01, June 5, 2009.
09948	Corley, J	2010	Spirotetramat: Magnitude of the Residue on Watercress. IR-4 Project HQ, Rutgers, The State University of New Jersey, Princeton, NJ 08540; dated: 20 September, 2010.
10042	Dorschner, K	2011	Spirotetramat: Magnitude of the Residue on Banana. IR-4 Project HQ, Rutgers, The State University of New Jersey, Princeton, NJ 08540; dated: 21 November 2011.
10041	Dorschner, K	2011	Magnitude of the Residue on Coffee. IR-4 Project HQ, Rutgers, The State University of New Jersey, Princeton, NJ 08540; dated: 2 December, 2011.
10113	Dorschner, K	2011	Spirotetramat: Magnitude of the Residue on Pomegranate. IR-4 Project HQ, Rutgers, The State University of New Jersey, Princeton, NJ 08540; dated: 29 September, 2011.

Code	Author	Year	Title, Institute, Report reference
10635	Dorschner, K	2011	Spirotetramat: Magnitude of the Residue on Pineapple. IR-4 Project HQ, Rutgers, The State University of New Jersey, Princeton, NJ 08540; dated: 7 December, 2011.
10234	Lonsbary, S	2011	Spirotetramat: Magnitude of the Residue on Artichoke, Globe. Minor Use Pesticide Program, Pest Management Centre, Agriculture and Agri-Food Canada, Ottawa, ON K1A 0C6; dated: 1 December, 2011.
10194	Lonsbary, S	2011	Spirotetramat: Magnitude of the Residue on Blueberry, Lowbush and Highbush. Minor Use Pesticide Program, Pest Management Centre, Agriculture and Agri-Food Canada, Ottawa, ON K1A 0C6; dated: 25 November, 2011.
10198	Lonsbary, S	2011	Spirotetramat: Magnitude of the Residue on Cranberry. Minor Use Pesticide Program, Pest Management Centre, Agriculture and Agri-Food Canada, Ottawa, ON K1A 0C6; dated: 1 December, 2011.
09983	Lonsbary, S	2011	Spirotetramat: Magnitude of the Residue on Onion, Dry Bulb. Minor Use Pesticide Program, Pest Management Centre, Agriculture and Agri-Food Canada, Ottawa, ON K1A 0C6; dated: 7 July, 2011.
10924	Lonsbary, S	2011	Spirotetramat: Magnitude of the Residue on Onion, Green. Minor Use Pesticide Program, Pest Management Centre, Agriculture and Agri-Food Canada, Ottawa, ON K1A 0C6; dated: 1 December, 2011.
	Schöning, R and Wolters, A	2007	Storage stability of BYI08330 and its metabolites BYI08330-enol, BYI08330-ketohydroxy, BYI08330-mono-hydroxy and BYI08330-enol-glucoside in/on tomato (fruit), tomato (paste), potato (tuber), lettuce (head), climbing French bean (bean with pod), and almond (nutmeat) for 24 months. Bayer CropScience AG, Monheim, Germany, Bayer Report No.: MR-07/268. June 21, 2007.
	Schöning, R, Stuke, S and Billian, P	2005	Analytical Method 00857 for the Determination of Residues of BYI08330 (Parent Compound and Total Residue of BYI08330), BYI08330-enol, BYI08330-ketohydroxy, BYI08330-mono-hydroxy and BYI08330-enol-Glc Metabolite in/on Plant Material by HPLC-MS/MS. Bayer CropScience AG, Monheim, Germany, Bayer Report No. MR-099/04. June 17, 2005.

TOLFENPYRAD (269)*First draft was prepared by Prof. Dr. Árpád Ambrus**National Food Chain Safety Office, Hungary***EXPLANATION**

Tolfenpyrad is a broad spectrum pyrazole class insecticide and a miticide, with contact activity against target pests on eggs, larvae, nymphs and adults. It also has anti-feeding activity on larvae of lepidopteran insects. It has activity against several economically important insect pests of vegetables, fruits, nuts, vines and row crops.

At the Forty-fourth Session of the CCPR (2012), it was scheduled for toxicological and residue evaluation as a new compound by 2013 JMPR.

The residue studies were submitted by the manufacturers to support the following commodities: almonds, cantaloupes, cauliflowers, cherries, cucumbers, cotton seed, grapes (table), grapefruits, lemons, oranges, peaches, pears, pecans, peppers, plums, potatoes, summer squash, tea and tomatoes.

IDENTITY

ISO common name: tolfenpyrad

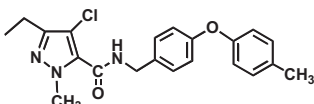
IUPAC name: 4-chloro-3-ethyl-1-methyl-N-[4-(p-tolyloxy)benzyl]pyrazole-5-carboxamide

Chemical Abstract name: 4-chloro-3-ethyl-1-methyl-N-[[4-(4-methylphenoxy)phenyl]methyl]-1H-pyrazole-5-carboxamide

CAS No.: 129558-76-5

Synonyms: OMI-88

Molecular Formula: C₂₁H₂₂ClN₃O₂

Structural Formula: 

Molecular Weight: 383.9

PHYSICAL AND CHEMICAL PROPERTIES

Chemical/physical property	Guideline(s)	Results	Reference
Physical properties	830.6302, 830.6303, 830.6303	White, solid powder at 20 °C with no discernible odour (99.33% pure)	Comb, A (2008b)
Melting point	OECD 102 830.7050	87.8–88.2 °C (99.85% pure) 85.5–88.5 °C (99.9% pure)	Ikeda, Y (1995) Comb, A (2008a)
Boiling point	OECD 103 830.7220	Decomposed above 250 °C without boiling	Koike, N (2001) Comb, A (2008a)
Chemical stability	830.6313	Chemically stable (99.33% pure)	Comb, A (2008b)
Oxidation/reduction	830.6314	Non-reactive (99.33% pure)	Comb, A (2008b)
Relative density	830.7300	1.25 at 20 °C (99.33% pure)	Comb, A (2008b)

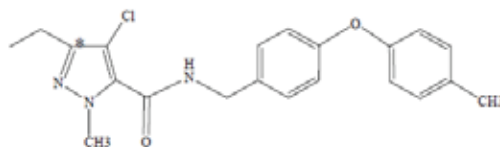
Chemical/physical property	Guideline(s)	Results	Reference
Vapour pressure	830.7950	4×10^{-5} Pa at 25 °C (99.9% pure)	Comb, A (2008b)
Flammability	830.6315	Not highly flammable (99.33% pure)	Comb, A (2008b)
Explosive properties	830.6316	Not explosive (99.33% pure)	Comb, A (2008b)
Viscosity	830.7100	Not applicable	Comb, A (2008b)
pH (1% suspension)	830.7000	5.1 (99.33% pure)	Comb, A (2008b)
Solubility in water	OECD 105	0.087 mg/L at 25 °C (99.1% pure)	Nakanome, T (1996)
	830.7840	0.061 mg/L at 20 °C (99.9% pure)	Comb, A (2008a)
Aqueous photolysis		pH 7 daylight DT ₅₀ :21.9–25.6 days	Ponte, M 2008
Solubility in organic solvents	OECD 105	at 25 °C (99.1% pure) hexane: 7.41 g/L toluene: 366 g/L dichloromethane: > 500 g/L methanol: 59.6 g/L acetone: 368 g/L ethyl acetate: 339 g/L	Nakanome, T 1996
	830.7840	at 20 °C (99.33% pure) n-heptane: 6.92 g/L xylene: 218 g/L 1,2-dichloethane: > 250 g/L methanol: 50.8 g/L n-octanol: 43.7 g/L acetone: > 250 g/L ethyl acetate: > 250 g/L	Comb, A. (2008b)
Partition coefficient	830.7570	Log P _{ow} 4.3 (99.9% pure)	Comb, A (2008a)
Dissociation constant	830.7370	Does not dissociate	Comb, A (2008a)

Formulation

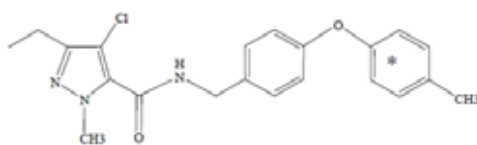
Tolfenpyrad is formulated as a 15% SC and a 15% EC.

METABOLISM AND ENVIRONMENTAL FATE

Metabolism and fate studies in livestock, agriculture crops and soil were carried out with pyrazol-¹⁴C tolfenpyrad.



And [tolyl ring-U-¹⁴C] tolfenpyrad.

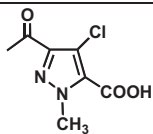
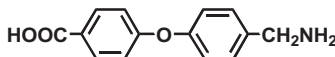
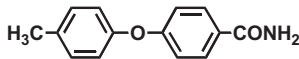
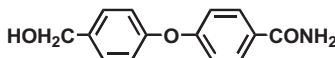
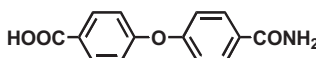
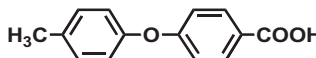
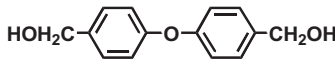
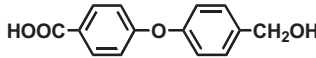
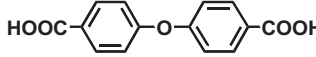
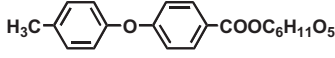


The codes, chemical names and structure of metabolites and the matrices in which they were found are given in Table 1.

Table 1 Metabolites of tolfenpyrad in animal, plant, soil and water/sediment

Code Name	Chemical name	Structure	Matrices
Tolfenpyrad (OMI-88)	4-chloro-3-ethyl-1-methyl-N-[4-(<i>p</i> -toloxy)benzyl]pyrazole-5-carboxamide		Active ingredient
OH-PT	4-chloro-3-(1-hydroxyethyl)-1-methyl-N-[4-(<i>p</i> -toloxy)benzyl]pyrazole-5-carboxamide		rat, plant
CO-PT	3-acetyl-4-chloro-1-methyl-N-[4-(<i>p</i> -toloxy)benzyl]pyrazole-5-carboxamide		plant
PT-OH	4-chloro-3-ethyl-N-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		rat, plant, soil, photodecomposition
PT-CHO	4-chloro-3-ethyl-N-[4-[4-(formylphenoxy)benzyl]-1-methylpyrazole-5-carboxamide		rat, plant, soil, photodecomposition
PT-CA	4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		rat, plant, soil
OH-PT-OH	4-chloro-3-(1-hydroxyethyl)-N-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		rat, plant
CO-PT-OH	3-acetyl-4-chloro-N-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		plant
OH-PT-CA	4-[4-[(4-chloro-3-(1-hydroxyethyl)-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		rat, plant
CO-PT-CA	4-[4-[(3-acetyl-4-chloro-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		plant

Code Name	Chemical name	Structure	Matrices
CA-PT	[4-chloro-1-methyl-5-[<i>N</i> -(<i>p</i> -toloxybenzyl)carbamoyl]pyrazol-3-yl]acetic acid		rat, plant
CA-PT-OH	[4-chloro-5-[<i>N</i> -(4-(4-hydroxymethyl)phenoxy)benzylcarbamoyl]-1-methylpyrazol-3-yl]acetic acid		rat, plant
CA-PT-CA	4-[4-[3-(carboxymethyl-4-chloro-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		rat, plant
DM-PT	4-chloro-3-ethyl- <i>N</i> -(4-(<i>p</i> -toloxy)benzyl)pyrazole-5-carboxamide		plant
DM-PT-OH	4-chloro-3-ethyl- <i>N</i> -(4-[4-(hydroxymethyl)phenyl]benzyl) pyrazole-5-carboxami		plant
PT-CA-TA	2-[4-[4-(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]phenylcarbonylamino]ethane-1-sulfonic acid		rat
PT-CA-GA	Glucuronic acid conjugate of 4-[4-[4-(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy] benzoic acid		rat
PT-CA-Glu	Glucose conjugate of 4-[4-[4-(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		plant
PT-CA-Me	4-[4-[4-(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy] benzoate		rat
Sul-OH-PT-CA	4-[4-[4-(4-chloro-1-methyl-3-(1-sulfoethyl)pyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		rat
PT(A)-4OH	4-chloro-3-ethyl- <i>N</i> -(4-hydroxybenzyl)-1-methylpyrazol-5-carboxamide		soil
PAM	4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide		rat, plant, soil
OH-PAM	4-chloro-3-(1-hydroxyethyl)-1-methylpyrazole-5-carboxamide		rat, plant, soil
CO-PAM	3-acetyl-4-chloro-1-methylpyrazole-5-carboxamide		soil
PCA	4-chloro-3-ethyl-1-methylpyrazole-5-carboxylic acid		plant, soil

Code Name	Chemical name	Structure	Matrices
CO-PCA	3-acetyl-4-chloro-1-methylpyrazole-5-carboxylic acid		soil
CA-T-NH ₂	4-[4-(aminomethyl)phenoxy]benzoic acid		photodecomposition
T-AM	[4-(<i>p</i> -tolxyloxy)benzamide		plant
OH-T-AM	4-[4-(hydroxymethyl)phenoxy] benzamide		plant
CA-T-AM	4-(4-carbamoylphenoxy)benzoic acid		plant
T-CA	4-(<i>p</i> -tolxyloxy)benzoic acid		rat, plant
OH-T-OH	<i>bis</i> [4-(hydroxymethyl)phenyl]ether		plant
OH-T-CA	4-[4-(hydroxymethyl)phenoxy] benzoic acid		rat, plant
CA-T-CA	4,4'-oxydibenzoic acid		rat, plant
T-CA-Glu	glucose conjugate of 4-(<i>p</i> -tolxyloxy) benzoic acid		plant

Animal metabolism

The Meeting received information on the fate of [¹⁴C] tolfenpyrad in lactating goats and laying hens. Metabolism in laboratory animals are summarized and evaluated by the WHO panel of the present JMPR.

Lactating goats

[Pyrazole-¹⁴C]-tolfenpyrad and [tolyl-¹⁴C]-tolfenpyrad were administered orally (in gelatine capsules) to two lactating goats of 51–53 kg (one for each label) once daily for five consecutive days (Quistad, GB, Kovatchev, A, 2007b, Report no. R-10160). The administered daily dose was 12.3–12.5 mg/kg feed/day. Milk was collected twice daily and excreta were collected once daily. Goats were sacrificed approximately 21–22 hours after the last dose administration and samples of muscle, liver, kidney, fat, bile and gastrointestinal tracts with contents were collected for analysis.

Milk samples were extracted with ethyl acetate and portions of the combined extracts were cleaned up on a silica gel column for removal of fat. Each sample extract aliquot (1–2 g) was loaded in hexane on a 2-g silica gel SPE column that was eluted with hexane / ethyl acetate (9:1, 10 mL, then 5:1, 10 mL), ethyl acetate (10 mL), and methanol (10 mL). Milk samples with highest residues for each radiolabel were used for TLC analysis. Additional subsamples of milk (about 2 mL each) were added to scintillation cocktail for determination of the TRR.

Sample aliquots of muscle, liver and kidney were extracted twice with acetonitrile / water and once with acetonitrile by high speed homogenisation. The post extraction solids (PES) were separated by centrifugation. The clear water / acetonitrile extracts were evaporated for analysis by HPLC and TLC. The post extraction solid (PES) (except tolyl-label in kidney) was treated with 24% KOH, acidified, and partitioned into ethyl acetate. The ethyl acetate extract was analysed by LSC (muscle) and HPLC (liver and kidney). For the pyrazole-treated liver and kidney, 24% KOH treatment was preceded by treatment with 0.1 M KOH and 1.0 M KOH.

Fat samples were extracted by shaking the fat/solvent mixtures on a wrist-action shaker and the solids were separated by centrifugation. The fat was extracted sequentially twice with acetone / hexane and once with acetone. The TRR of each extract was determined by LSC. A representative composite was made of all three extracts and aliquots were evaporated to dryness and reconstituted in hexane. This sample was cleaned up by silica gel SPE eluted with hexane / ethyl acetate and ethyl acetate. The ethyl acetate fraction was subjected to TLC (pyrazole) or HPLC analysis.

Tissues including gastrointestinal tracts were homogenised in the presence of dry ice. For determination of the total radioactive residue (TRR) by liquid scintillation counting (LSC), tissues (liver, kidney, muscle and fat) were solubilised with Soluene™ tissue solubiliser and aliquots of milk were directly mixed with scintillation cocktail. Samples of faeces and gastrointestinal tract were analysed after combustion.

All samples were analysed within 51 days.

Total residue

The total recovery of radiolabel was 76.1% and 96.3% of the administered dose for the pyrazole-label and tolyl-label, respectively. Most of the administered dose (66.4% for the pyrazole-label and 82.7% for the tolyl-label) was recovered in the excreta and gastrointestinal tracts at sacrifice (Table 2).

Table 2 Total radioactive residues in tissues and excreta

Matrix	Pyrazole-labelled Tolfenpyrad		Tolyl-labelled Tolfenpyrad	
	mg/kg	% of dose	mg/kg	% of dose
Tissues				
Liver	16.99	8.5	25.22	12.2
Kidney	6.11	0.8	6.93	0.7
Muscle	0.09	0.1	0.14	0.2
Fat	0.27	0.1	0.36	0.4
Bile	6.93	0.04	8.72	0.02
Excreta				
Urine ^a		3.5		5.9
Faeces ^a		43.3		43.9
Gastro-Intestinal-Tract		19.2		32.6
Cage Wash		0.4		0.2
Total		76.1		96.3

^a Sum of recovered radioactivity during the study period

The concentration of TRR in milk samples is given in Table 3.

Table 3 Total radioactive residues in milk samples

		¹⁴ C- pyrazole]-tolfenpyrad		¹⁴ C-tolyl-tolfenpyrad	
		mg/kg	% of dose	mg/kg	% of dose
Day 1	AM	nd		nd	
	PM	< 0.01	0.00		
Day 2	AM	0.01	0.00	< 0.01	0
	PM	0.05	0.00	0.03	0.01
Day 3	AM	0.10	0.02	0.05	0.01
	PM	0.16	0.01	0.10	0.03

		¹⁴ C- pyrazole]-tolfenpyrad		¹⁴ C-tolyl-tolfenpyrad	
		mg/kg	% of dose	mg/kg	% of dose
Day 4	AM	0.14	0.03	0.14	0.01
	PM	0.17	0.01	0.13	0.03
Day 5	AM	0.16	0.04	0.15	0.02
	PM	0.15	0.02	0.17	0.04
Day 6	AM	0.14	0.03	0.17	0.02
Total			0.18		0.19

Of the total administered dose 3.48% and 5.93% were excreted in urine and 43.3% and 43.9% in faeces for pyrazole and tolyl labelled compounds, respectively.

Characterisation of residues

In milk

Two milk samples with the highest concentrations for each radiolabel were selected for characterisation of the radioactive residues by TLC on silica gel. Most of the radioactivity (95 and 97%) was extracted (Table 4).

Table 4 Characterisation and identification of radioactive residues in milk

Fraction /metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.17	100	0.17	100
Solvent extractable	0.16	94.8	0.17	97.1
Tolfenpyrad	< 0.01	4.1	< 0.01	2.9
PT-CA	0.01	7.6	0.01	5.9
OH-PT-CA	0.03	16.9	0.01	7.6
Lipid conjugates	0.11	62.2	0.13	75.8
Ethyl acetate fraction after KOH 24%	0.11	62.2	0.12	70.6
PT-CA (conjugated)	0.06	32.0	0.08	48.2
CA-T-NH ₂ (conjugated)	–	–	0.03	19.4
PCA (conjugated)	0.02	12.2	–	–
Remaining conjugates	0.02	11.0	nd	nd
Unidentified	0.02	8.7	< 0.01	4.7
Fat fraction	0.02	11.0	nd	nd
PES (aqueous)	0.01	6.4	< 0.01	2.9
Total identified		72.8		84.0

nd = Not detected

The amount of radioactive residue remaining in the aqueous phase (liquid + PES) was small (< 0.01–0.01 mg/kg and 2.9–6.4 % of TRR) and was not further characterised. Most of the radioactivity (95 and 97%) was extracted.

In muscle

Table 5 Characterisation and identification of radioactive residues in muscle

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.09	100	0.14	100
Solvent extractable	0.08	92.2	0.11	81.2
Tolfenpyrad	< 0.01	10.0	0.01	10.1
PT-CA	0.06	67.8	0.09	63.8
OH-PT-CA	< 0.01	8.9	< 0.01	3.6
max other single	< 0.01	2.2	< 0.01	3.6

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
PES	0.01	11.1	0.02	15.9
KOH (24%) extract of PES	< 0.01	10.0	0.02	10.9
Ethyl acetate fraction	< 0.01	4.4	< 0.01	3.6
Aqueous fraction	< 0.01	5.6	0.01	7.2
Total identified		86.7		77.5

In liver

Table 6 Characterisation and identification of radioactive residues in liver

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	16.99	100	25.22	100
Solvent extractable	13.65	80.4	22.48	89.2
Tolfenpyrad	nd	nd	nd	nd
PT-CA	6.99	41.1	13.06	51.8
OH-PT-CA	3.21	18.9	6.79	26.9
max other single	1.12	6.6	0.58	2.3
PES	not reported		3.58	14.2
KOH (24%) extract	2.23	13.1	2.76	11.0
Ethyl acetate fraction	1.94	11.4	2.13	8.4
OH-PT-CA	0.21	1.2	0.19	0.8
PT-CA	1.52	9.0	1.74	6.9
other single	0.06	0.3	0.06	0.3
PES	0.05	0.3	not reported	
Total identified		70.2		86.4

nd = Not detected

In kidney

Table 7 Characterisation and identification of radioactive residues in kidney

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	6.11	100	6.93	100
Solvent extractable	5.45	89.2	6.36	91.9
Tolfenpyrad	nd	nd	nd	nd
PT-CA	3.56	58.2	4.33	62.6
OH-PT-CA	1.01	16.5	1.34	19.3
max other single	0.25	4.1	0.32	4.6
KOH (24%) extract	0.43	7.1	not performed	
Ethyl acetate fraction	0.28	4.6		
OH-PT-CA	0.02	0.3		
PT-CA	0.21	3.5		
other single	0.04	0.6		
PES	0.02	0.3	0.49	7.1
Total identified		78.5		81.9

nd = Not detected

In fat

Radiolabel was readily extractable from fat (94–95% of TRR). TLC analysis showed two zones of radiolabels.

Table 8 Characterisation and identification of radioactive residues in fat

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.27	100	0.36	100
Solvent extractable	0.26	95.2	0.34	94.1
after SPE	0.20	72.9	0.25	69.0
Tolfenpyrad	0.04	13.6	0.06	17.3
PT-CA	nd	nd	nd	nd
OH-PT-CA	nd	nd	nd	nd
Lipid conjugates	0.16	59.3	0.19	51.7
Ethyl acetate fraction after KOH 24%	0.18	65.9	0.20	55.6
PT-CA (conjugated)	0.09	34.1	0.11	31.0
CA-T-NH ₂ (conjugated)	–	–	0.02	5.3
PCA (conjugated)	0.08	28.6	–	–
Fat fraction	0.06	22.7	0.03	8.7
PES	0.02	8.4	0.01	2.8
Total identified		76.3		53.6

nd = Not detected

Proposed metabolic/degradation pathway

Tolfenpyrad is oxidized at the tolyl-methyl group to PT-CA. Further oxidation at the pyrazole ethyl group of PT-CA produces OH-PT-CA. Both PT-CA and OH-PT-CA occur as free metabolites in milk, liver, kidney, and muscle. PT-CA and its hydrolysis metabolites (PCA and CA-T-NH₂) are converted into nonpolar lipids in milk and fat. Saponification of the lipid conjugates releases PT-CA, PCA, and CA-T-NH₂. The metabolic pathway for tolfenpyrad in goats is shown in Figure 1.

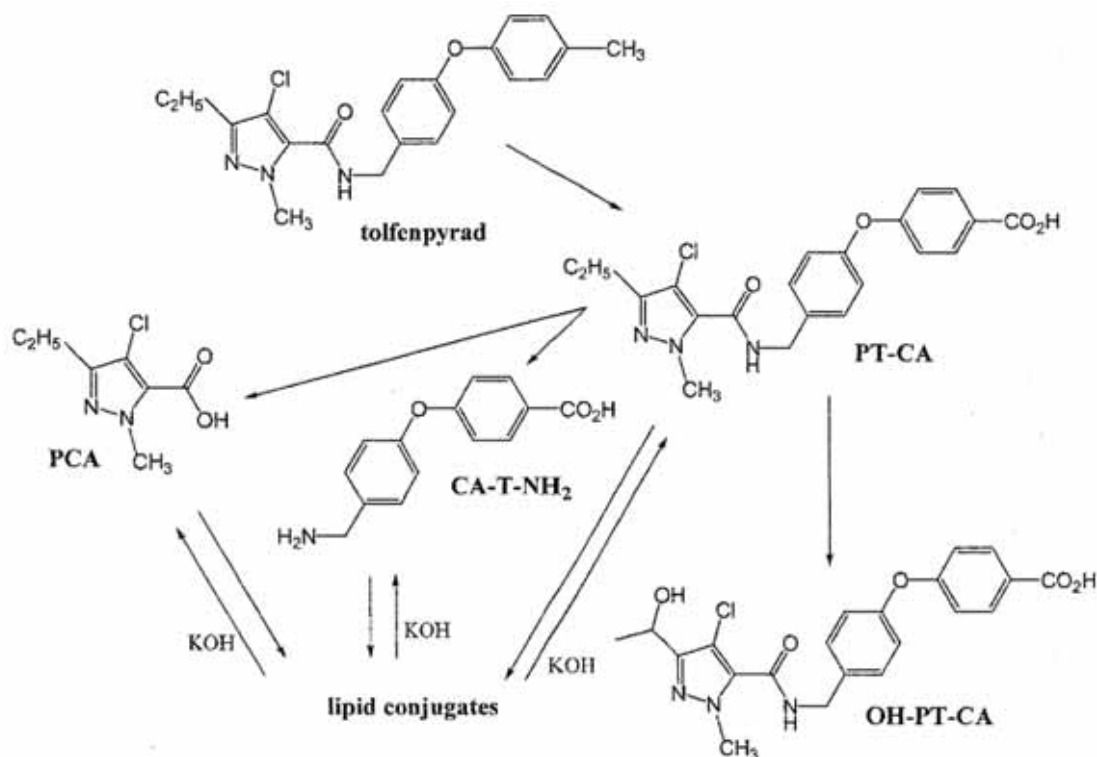


Figure 1 Proposed metabolic pathway of active substance in lactating goat

Laying hens

[Pyrazole-¹⁴C]-tolfenpyrad and [tolyl-¹⁴C]-tolfenpyrad were administered orally in gelatine capsules to two separate groups of hens comprised of 10 birds each once daily for seven consecutive days (Quistad, GB, Kovatchev, A, 2007b Report no. R-10161). The administered daily dose was 12.6–13.5 mg/kg feed/day. Eggs were collected twice daily and excreta were collected once daily. Hens were sacrificed approximately 22–23 hours after the last dose administration, and liver, muscle, fat and gastrointestinal tracts with contents were collected for analysis.

Tissues including gastrointestinal tracts were homogenised in the presence of dry ice. For determination of the total radioactive residue by liquid scintillation counting (LSC), tissues (liver, egg, muscle and fat) were solubilised with Soluene™ tissue solubiliser. Samples of faeces and gastrointestinal tract were analysed after combustion. The results are shown in Table 9.

Table 9 Total radioactive residues in tissues and excreta

Matrix	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of dose	mg/kg	% of dose
Tissues				
Liver	1.64	0.7	1.94	0.8
Muscle	0.13	0.1	0.11	0.1
Fat	0.43	0.1	0.44	0.1
Eggs	–	0.3	–	0.3
Excreta				
Faeces		81.9		87.7
Gastro-Intestinal-Tract		2.3		2.4
Total		85.4		91.4

Table 10 Excretion of radio-labelled compounds as function of time

Day	1	2	3	4	5	6	7	8	G.I.T	total
	% of total dose									
Pyrazole-label	nd	8.6	10.4	12.6	13.3	12.5	12.1	12.3	2.3	84.2
Tolyl-label	nd	8.5	10.8	13.2	14.0	13.3	12.6	15.3	2.4	90.1

nd = Not determined

Table 11 Total radioactive residues (TRRs) in egg as function of time

Egg		Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
		mg/kg	% of dose	mg/kg	% of dose
Day 1	AM	nd		nd	
	PM	nd		nd	
Day 2	AM	0.02	< 0.01	0.01	0.01
	PM	0.03	< 0.01	0.02	< 0.01
Day 3	AM	0.04	0.02	0.03	0.01
	PM	0.07	< 0.01	0.04	< 0.01
Day 4	AM	0.06	0.02	0.05	0.01
	PM	0.09	0.01	0.07	0.01
Day 5	AM	0.08	0.02	0.08	0.02
	PM	0.11	0.02	0.09	0.01
Day 6	AM	0.10	0.03	0.10	0.03
	PM	0.14	0.02	0.16	0.01
Day 7	AM	0.13	0.03	0.14	0.03
	PM	0.15	0.02	0.15	0.03
Day 8	AM	0.17	0.07	0.16	0.07

Egg	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of dose	mg/kg	% of dose
Total	n.a.	0.3	n.a.	0.3

nd = Not detected

n.a. = Not applicable

Characterisation and identification of residues

Eggs were extracted sequentially with acetonitrile/water, acetonitrile and ethyl acetate. The PES was extracted with ethyl acetate (2 × 50 mL). All extracts were combined. For removal of fat, an aliquot was cleaned up by a silica column by elution with ethyl acetate and methanol. All fractions were evaporated to dryness and reconstituted in acetonitrile for TLC and HPLC analysis. A portion of the ethyl acetate fraction was evaporated to dryness and lipid conjugates were hydrolysed with 24% KOH. After acidification and partitioning into ethyl acetate, released acids were analysed by HPLC.

Muscle and liver were extracted with acetonitrile / water and acetonitrile. The post extraction solids (PES) were removed by centrifugation. The acetonitrile / water extracts were concentrated by rotary evaporation and analysed by HPLC and TLC. The remaining PES were weighed and their radioactive residues determined. The PES from liver was also treated with 24% KOH, acidified, and partitioned into ethyl acetate. The ethyl acetate extract was analysed by HPLC. For liver and muscle, the acetonitrile / water extracts were analysed by TLC and HPLC, the ethyl acetate fractions resulting from the partitioning of the alkaline extraction of the PES were analysed by HPLC.

Fat samples were extracted with acetone / hexane and acetone and the PES was separated by centrifugation. The four extracts were combined and the radioactive residue determined by LSC. A composite of the extracts was cleaned-up on silica gel SPE by elution with hexane / ethyl acetate, ethyl acetate and methanol. A portion of the ethyl acetate fraction was also saponified with 24% KOH. The hexane / ethyl acetate, ethyl acetate and methanol fractions eluting from the SPE clean-up were analysed by TLC.

All samples were analysed within 53 days

Two egg samples with the highest concentrations for each radiolabel (Day 8 AM for pyrazole-label, Day 6 PM for tolyl-label) were selected for characterisation of the radioactive residues. The characterisation of tolfenpyrad residues in eggs is summarized in Table 12.

Table 12 Characterisation and identification of radioactive residues in eggs

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.17	100	0.16	100
Solvent extractable	0.16	92.8	0.15	93.3
Tolfenpyrad	< 0.01	2.4	< 0.01	1.2
PT-CA	0.03	19.8	0.07	40.5
OH-PAM	0.02	12.6	—	—
OH-PT-CA	nd	—	—	—
Lipid conjugates	0.09	53.9	0.07	41.1
Ethyl acetate fraction after KOH 24%	0.09	50.9	0.06	38.0
PT-CA (conjugated)	0.05	28.7	0.04	23.9
PCA (conjugated)	0.02	14.4	—	—
Unidentified	—	—	< 0.01	1.8
Fat fraction	0.03	18.0	—	—
PES	< 0.01	5.4	< 0.01	4.9
Total identified		77.9		65.6

nd = Not detected

In muscle

Table 13 Characterisation and identification of radioactive residues in muscle

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.13	100	0.11	100
Solvent extractable	0.12	89.1	0.11	93.8
Tolfenpyrad	< 0.01	0.8	< 0.01	1.8
PT-CA	0.09	69.8	0.10	84.8
OH-PAM	0.02	12.4	–	–
OH-PT-CA	< 0.01	1.6	< 0.01	2.7
max other single	< 0.01	2.3	< 0.01	0.9
PES	< 0.01	7.0	< 0.01	7.1
Total identified		84.6		89.3

In liver

Table 14 Characterisation and identification of radioactive residues in liver

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	1.64	100	1.94	100
Solvent extractable	1.49	90.8	1.74	89.5
Tolfenpyrad	< 0.01	0.2	< 0.01	0.2
PT-CA	1.30	79.0	1.35	69.4
OH-PAM	–	–	–	–
OH-PT-CA	0.09	5.2	0.09	4.8
max other single	0.05	2.8	0.13	6.6
KOH (24%) extract	0.19	11.8	0.21	11.0
Ethyl acetate fraction	0.19	11.4	0.19	9.9
PT-CA	0.19	11.4	0.19	9.9
aqueous fraction	< 0.01	0.4	0.01	0.7
PES	0.24	1.5	0.06	3.0
Total identified		95.8		84.3

In fat

Table 15 Characterisation and identification of radioactive residues in fat

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.43	100	0.44	100
Solvent extractable	0.40	92.1	0.40	91.2
Tolfenpyrad	0.06	14.7	0.06	12.9
PT-CA	0.06	14.2	0.07	15.0
OH-PAM	–	–	–	–
OH-PT-CA	–	–	–	–
Lipid conjugates	0.22	50.3	0.20	46.0
Ethyl acetate fraction after KOH 24%	0.21	48.0	0.18	41.0
PT-CA (conjugated)	0.14	32.4	0.15	34.5
PCA (conjugated)	0.05	11.2	–	–
Unidentified	0.04	8.9	0.03	6.3
Fat fraction	0.10	23.3	0.08	18.1
PES	< 0.01	0.7	< 0.01	1.1
Total identified		72.5		62.4

nd = Not detected

The metabolic pathway for tolfenpyrad in hens is shown in Figure 2.

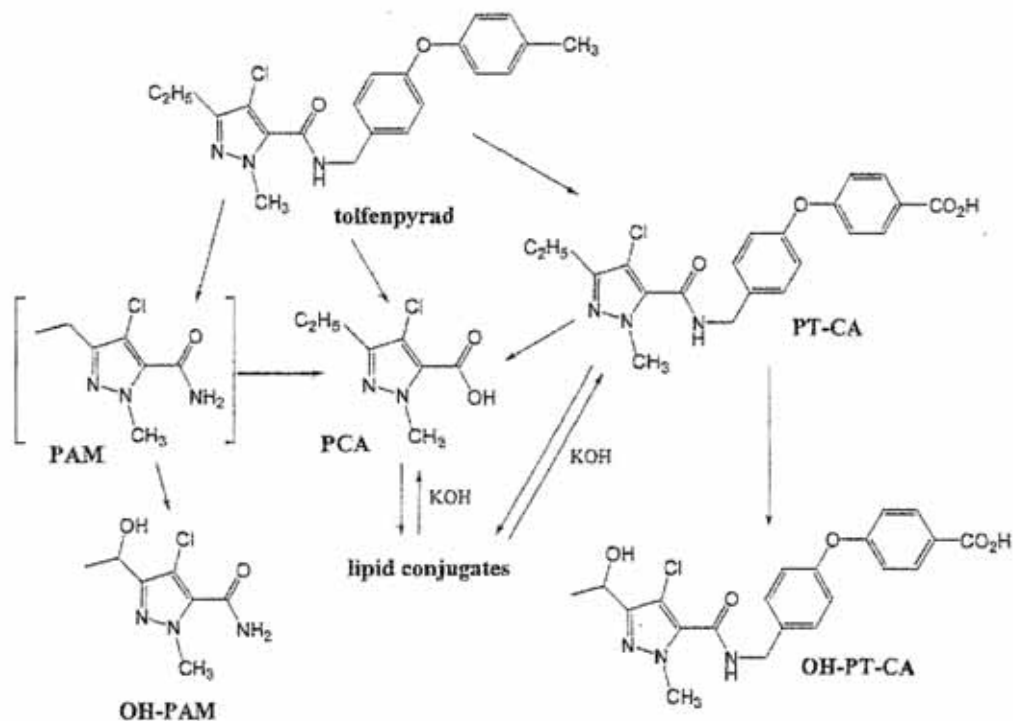


Figure 2 Proposed metabolic pathway of tolfenpyrad in poultry

Plant metabolism

Metabolism studies were carried out on cabbages, peaches and radishes applying tolyl and pyrazole ring labelled tolfenpyrad.

Cabbage

[Tolyl-¹⁴C]-tolfenpyrad was applied to individual cabbage plants in separate pots in a spray chamber (Ogawa, K and Koyama, T, 2000a Report no. R-10001). One application was made at a rate of 15 mg ai/m² plant surface corresponding to 750 g ai/ha.

Single cabbages in separate pots were sampled immediately after drying of the test formulation, and after 7, 14 and 28 days of application. The head and outer leaves of each cabbage were weighed and then subjected to analysis.

Each plant part (outer leaves and head) was cut into pieces and extracted with methanol by high-speed homogenisation. The homogenate was partitioned into the organo-soluble (OS), water-soluble (WS) and unextractable (PES) fractions. The WS fraction was diluted 1/10 with acetonitrile and partitioned into the acetonitrile-soluble (WS/OS) and aqueous (WS/WS) fractions.

TRRs in the soluble fractions were directly analysed by LSC, the PES was analysed by LSC after combustion. The distribution of tolfenpyrad equivalents in each plant part was calculated.

Organo-soluble (OS) and acetonitrile-soluble (WS/OS) extracts were analysed by HPLC with β -radiation detector or UV detection using the available reference standards for co-chromatography. The polar metabolites were analysed after acid hydrolysis treatment and β -glucosidation. Portions of the sample solutions were analysed after methylation with diazomethane or acetylation with acetic anhydride.

The samples were analysed within approximately seven months, nonetheless no storage stability test was carried out.

The TRRs found at different times after application are shown in Tables 16–17.

Table 16 Distribution of total radioactive residues (TRRs) in cabbage following one application of [^{14}C] tolfenpyrad

Crop part	TRR (mg tolfenpyrad equiv./kg) ^a							
	0 DAT		7 DAT		14 DAT		28 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Outer leaves	12.78	90.6	12.05	98.5	9.29	98.8	8.39	99.7
Head	2.61	9.4	0.51	1.5	0.25	1.2	0.03	0.3
Total	15.39	100.0	12.56	100.0	9.54	100.0	8.42	100.0

^a Values determined as sum of extracted and unextracted radiocarbon

DAT: = Days after treatment

Table 17 Extractability of TRR in cabbage following the application of [^{14}C] tolfenpyrad

Crop part / Fraction	mg tolfenpyrad equiv./kg							
	0 DAT		7 DAT		14 DAT		28 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Outer leaves (total)	12.78	90.6	12.05	98.5	9.29	98.8	8.39	99.7
organosoluble	12.36	87.6	10.95	89.5	8.60	91.4	6.62	78.7
water-soluble	0.41	2.9	1.03	8.4	0.56	6.0	1.34	15.9
PES	0.01	0.1	0.07	0.6	0.13	1.4	0.43	5.1
Head (total)	2.61	9.4	0.51	1.5	0.25	1.2	0.03	0.3
organosoluble	2.53	9.1	0.41	1.2	0.17	0.8	0.01	0.1
water-soluble	0.08	0.3	0.10	0.3	0.08	0.4	0.02	0.2
PES	< 0.03	< 0.1	< 0.03	< 0.1	< 0.02	< 0.1	< 0.01	< 0.1
Total		100.0		100.0		100.0		100.0

DAT = Days after treatment

In total, thirty-three metabolite signals together with unchanged tolfenpyrad were detected in cabbage samples (outer leaves and head). Twenty of them were identified as presented in Tables 18–19.

Table 18 Identification of metabolites in cabbage leaves

Metabolite ^a	TRR in (%) and (mg/kg)							
	0 DAT		7 DAT		14 DAT		28 DAT	
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
	total	total	total	total	total	total	total	total
parent	89.2	12.59	74.8	9.15	78.3	7.37	55.0	4.63
OH-T-AM	nd	–	0.7	0.09	0.8	0.08	1.9	0.16
CA-T-AM	nd	–	0.4	0.05	0.7	0.07	2.4	0.20
OH-T-OH	nd	–	1.0	0.12	1.4	0.13	3.7	0.31
OH-T-CA	nd	< 0.01	0.7	0.09	1.1	0.10	3.9	0.33
OH-PT-OH	nd	–	0.7	0.09	0.6	0.06	1.5	0.13
CA-T-CA	nd	< 0.01	1.0	0.12	0.5	0.05	0.9	0.08
OH-PT-CA	< 0.1	< 0.01	0.5	0.06	0.3	0.03	0.5	0.04
CA-PT-OH	nd	–	0.2	0.02	0.2	0.02	0.3	0.03
CO-PT-OH	nd	–	0.5	0.06	0.7	0.07	1.2	0.10
CO-PT-CA	< 0.1	< 0.01	1.3	0.16	nd	–	0.9	0.08
CA-PT-CA	nd	–	nd	–	0.1	0.01	0.3	0.03
PT-OH	0.1	0.01	0.7	0.09	0.6	0.06	0.4	0.03
PT-CA	nd	–	0.2	0.02	nd	–	0.3	0.03
DM-PT-OH	nd	–	0.5	0.06	0.2	0.02	0.5	0.04
T-CA	nd	–	0.2	0.02	< 0.1	< 0.01	0.3	0.03
OH-PT	0.1	0.01	5.2	0.64	4.6	0.43	6.4	0.54
PT-CHO	nd	–	0.4	0.05	nd	–	nd	–

Metabolite ^a	TRR in (%) and (mg/kg)							
	0 DAT		7 DAT		14 DAT		28 DAT	
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
	total	total	total	total	total	total	total	total
DM-PT	nd	–	0.4	0.05	0.3	0.03	0.1	0.01
CO-PT	< 0.1	< 0.01	0.5	0.06	0.3	0.03	0.3	0.03
unknown	1.1	0.16	8.0	0.98	6.7	0.60	13.8	1.13
Total	90.5		97.9		97.4		94.6	

^a For identification of abbreviation see Table 1

DAT = Days after treatment

OS = Organo-soluble fraction

WS = Water-soluble fraction

nd = Not detected

The proportion of the parent tolfenpyrad expressed as TRR% in organo-soluble and water fractions was 86.4, 2.8; 74.4, 0.1; 77.4, 0.9 and 52.4, 2.6 at days 0, 7, 14 and 28, respectively

Table 19 Identification of metabolites in cabbage head

Metabolite ^a	TRR in (%) and (mg/kg)							
	0 DAT		7 DAT		14 DAT		28 DAT	
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
	total	total	total	total	total	total	total	total
parent	9.2	2.56	1.1	0.38	0.8	0.17	nd	< 0.01
OH-T-AM	nd	–	< 0.1	< 0.03	nd	–	nd	–
OH-T-OH	nd	–	nd	< 0.03	< 0.1	< 0.02	nd	–
OH-T-CA or OH-PT-OH	< 0.1	< 0.03	< 0.1	< 0.03	nd	–	nd	–
CO-PT-CA	0.1	0.03	0.1	0.03	nd	–	nd	–
OH-PT	< 0.1	< 0.03	0.1	0.03	0.1	0.02	nd	–
DM-PT	nd	–	< 0.1	< 0.03	< 0.1	< 0.02	nd	–
unknown	0.1	0.03	0.2	0.07	0.3	0.06	0.3	0.03
Total	9.4	2.61	1.5	0.51	1.2	0.25	0.3	0.03

Notes: see Table 18

Study 2

In the second study [pyrazole-¹⁴C]-tolfenpyrad was applied once to individual cabbage plants, at the head formation stage, in separate pots in a spray chamber at a rate of 15 mg ai/m² plant surface corresponding to 750 g ai/ha (Ogawa, K 1999c, Report no. R-10002). Cabbage samples were collected on one occasion, 28 days after application. Head and outer leaves were collected; each part was weighed and then subjected to analysis.

Each plant part (outer leaves and head) was cut into pieces and extracted with methanol by high-speed homogenisation. The homogenate was partitioned into the organosoluble (OS), water-soluble (WS) and unextractable (PES) fractions. The WS fraction was partitioned into acetonitrile resulting in an organosoluble (WS/OS) and an aqueous (WS/WS) fraction.

Chlorophyll was removed from the organosoluble (OS) fraction by coagulation with an aqueous ammonium chloride / phosphoric acid solution. After removal of chlorophyll, radioactive residues were extracted with ethyl acetate.

TRRs in the soluble fractions were directly analysed by LSC, the PES was analysed by LSC after combustion. The distribution of tolfenpyrad equivalents in each plant part was calculated.

Organosoluble (OS) and acetonitrile-soluble (WS/OS) extracts were analysed by HPLC with β radiation detection or UV detection using the available reference standards for co-chromatography.

The polar metabolites were analysed after acid hydrolysis treatment. Portions of the sample solutions were analysed after methylation with diazomethane and acetylation with acetic anhydride.

All samples were analysed within 6 months of sampling. Of the 33 metabolites detected 19 compounds were consistent with authentic reference standards based on HPLC retention times and GC/MS analysis. The others were estimated based on their relative retention time. The results are summarized in Tables 20–22.

Table 20 Distribution of total radioactive residues (TRRs) in cabbage following one application of [^{14}] -tolfenpyrad

Crop part	TRR (mg tolfenpyrad equiv./kg) ^a at 28 DAT	
	mg/kg	%TRR
Outer leaves	9.22	97.2
Head	0.23	2.8
total	9.45	100.0

^a Values were determined as sum of extracted and unextracted radiocarbon

DAT = Days after treatment

Table 21 Extractability of residues in cabbage 28 days after treatment with [^{14} C] tolfenpyrad

Crop part / Fraction	TRR (mg tolfenpyrad equiv./kg)	
	mg/kg	%TRR
Outer leaves (total)	9.22	97.2
organosoluble fraction	6.67	70.3
water-soluble fraction	1.09	11.4
distributed into acetonitrile	0.74	7.8
aqueous remainder	0.34	3.6
PES	1.47	15.5
Head (total)	0.23	2.8
organosoluble fraction	0.05	0.6
water-soluble fraction	0.06	0.7
distributed into acetonitrile	0.02	0.3
aqueous remainder	0.04	0.5
PES	0.12	1.5
total	9.45	100.0

Table 22 Identification of metabolites in cabbage leaves and heads 28 days after treatment with [^{14} C] tolfenpyrad

Metabolite ¹⁾	TRR in (%) and (mg/kg)							
	Cabbage leaves				Cabbage heads ^a			
	% TRR			mg/kg	% TRR			mg/kg
	OS	WS	total		OS	WS	total	
parent	48.5	1.3	49.8	4.71	0.4	0.02	0.4	0.03
OH-PAM	nd	0.5	0.5	0.05	nd	0.1	0.1	0.01
PAM	0.8	nd	0.8	0.07				
PCA	1.3	0.8	2.1	0.20	nd	0.1	0.1	0.01
OH-PT-OH	0.7	2.7	3.4	0.32	nd	0.1	0.1	0.01
OH-PT-CA	1.1	1.9	2.9	0.27	nd	0.1	0.1	0.01
CO-PT-OH	0.8	0.1	1.0	0.09				
PT-OH	0.5	0.4	0.9	0.08				
PT-CA	0.5	nd	0.5	0.05				
OH-PT	7.6	0.3	7.9	0.75	0.007	0.001	0.01	0.01
CO-PT	0.4	nd	0.4	0.04				
unknown	8.2	3.4	11.5	0.90	0.1	0.3	0.4	0.02
Total	70.3	11.4	81.7	7.53	0.6	0.7	1.3	0.11

^a Distribution rates of any metabolites did not exceed 0.1%

OS = Organosoluble fraction

WS = Water-soluble fraction

nd = Not detected.

Peach

Study 1

[Tolyl-¹⁴C]-tolfenpyrad was applied to individual peach plants in separate pots in a spray chamber. One application was made at a rate corresponding to 750 g ai/ha (Ogawa, K and Koyama, T 2000b Report no. R-10003). Four peach plants were treated for use in the metabolism study. One branch with one fruit was treated from each plant. A fifth plant was treated by direct application on the leaves for examination of translocation in the leaves by autoradiography.

Leaves stem and the fruit of the treated branch of the plant were collected on four occasions following application; immediately after treatment and then 14, 28 and 56 days after treatment. Untreated leaves were also collected on the latter three occasions. The fruit collected 56 DAT was divided into peel, pulp and stone. After collection, each part was weighed and then subjected to analysis.

Each plant part (leaves, stem and whole fruit) and processed fraction of the fruit (peel, pulp and stone) was cut into pieces and extracted with methanol by high-speed homogenisation. The homogenate was partitioned into the organo-soluble (OS), water-soluble (WS) and unextractable (PES) fractions. The WS fraction was diluted 1/10 with acetonitrile and partitioned into the acetonitrile-soluble (WS/OS) and aqueous (WS/WS) fractions.

TRRs in the soluble fractions were directly analysed by LSC, the post extraction solid (PES) was analysed by LSC after combustion. The distribution of tolfenpyrad equivalents in each plant part was calculated.

Organo-soluble (OS) and acetonitrile-soluble (WS/OS) extracts were analysed by HPLC with β radiation detection. Analysis of unidentified and overlapping signals was enhanced by derivatization of functional groups by methylation with diazomethane or acetylation with acetic anhydride and subsequent analysis by HPLC. Identification was performed by comparing the HPLC chromatograms obtained with β radiation scanner and with UV detection using the available reference standards for co-chromatography. Some fractions containing polar metabolites were analysed after acid hydrolysis treatment and β -glucosidation. Portions of the sample solutions were analysed after methylation with diazomethane or acetylation with acetic anhydride.

Structural identification of main metabolites was performed by GC/MS.

Samples were analysed within 95 days.

The results of the analyses are summarized in Tables 23–28.

Table 23 Distribution of total radioactive residues (TRRs) in peaches following the application of [¹⁴C] tolfenpyrad

Crop part	TRR (mg tolfenpyrad equiv./kg)							
	0 DAT		14 DAT		28 DAT		56 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Leaves (treated)	100.1	83.5	57.0	73.1	58.1	90.3	51.5	83.1
Leaves (untreated)	–	nd	–	< 0.1	–	< 0.1	–	< 0.1
Stem	19.3	11.8	26.7	12.7	12.6	6.4	17.6	7.5
Fruit	2.97	4.7	4.43	14.2	0.53	3.3	1.03	9.3
Total	n.a.	100.0	n.a.	100.0	n.a.	100.0	n.a.	100.0

DAT = Days after treatment

The recovered radioactivity was 32.6%, 31.5%, 37.8% and 32.8% of the applied doses at days 0, 14, 28 and 56, respectively.

Table 24 Extraction summary for peach leaves, stem and fruit following the application of [¹⁴C] tolfenpyrad

Crop part / Fraction	TRR (mg tolfenpyrad equiv./kg)							
	0 DAT		14 DAT		28 DAT		56 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Leaves (total)	100.1	83.5	57.0	73.1	58.2	90.3	51.5	83.1
organosoluble	98.1	81.8	52.2	67.0	47.6	74.0	33.8	54.4
water-soluble	2.0	1.7	3.2	4.1	8.8	13.7	7.8	12.7
PES	< 0.1	< 0.1	1.6	2.0	1.7	2.6	9.9	16.0
Stem (total)	19.3	11.8	26.7	12.7	12.6	6.4	17.6	7.5
organosoluble	19.3	11.8	26.3	12.5	12.0	6.1	16.2	6.9
water-soluble	< 0.2	< 0.1	0.2	0.1	0.2	0.1	0.5	0.2
PES	< 0.2	< 0.1	0.2	0.1	0.4	0.2	0.9	0.4
Fruit (total)	2.97	4.7	4.43	14.2	0.53	3.3	1.03	9.3
organosoluble	2.78	4.4	4.24	13.6	0.48	3.0	0.93	8.4
water-soluble	0.19	0.3	0.16	0.5	0.03	0.2	0.06	0.5
PES	< 0.06	< 0.1	0.03	0.1	0.02	0.1	0.04	0.4
Total	n.a.	100.0	n.a.	100.0	n.a.	100.0	n.a.	100.0

DAT - Days after treatment

n.a. = Not applicable

Table 25 Distribution of TRR in peach peel, pulp and stone 56 days after application of [¹⁴C] tolfenpyrad

Fraction	TRR (mg tolfenpyrad equiv./kg) at 56 DAT							
	Peel		Pulp		Stone		total	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Fruit (organo-soluble)	39.9	8.2	0.01	0.1	—	—	0.93	8.4
Fruit (water-soluble)	0.97	0.2	0.03	0.3	—	—	0.06	0.5
PES	not determined						0.04	0.4
total	42.7	8.8	0.04	0.4	0.2	0.1	1.03	9.3

DAT = Days after treatment;

The TRR in the non-treated leaves was less than 0.1% throughout the study. Therefore parent tolfenpyrad and its metabolites show a very low tendency to transfer into any other part of the plant.

Table 26 Identification of metabolites in peach fruits

Metabolite ^a	TRR in (%) and (mg/kg)							
	0 DAT		14 DAT		28 DAT		56 DAT	
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
Parent	100	2.97	89.4	3.95	69.7	0.37	77.4	0.79
CA-T-CA	nd	nd	nd	nd	nd	nd	2.2	0.02
T-AM	nd	nd	2.8	0.12	nd	< 0.02	1.1	0.01
PT-OH	nd	nd	1.4	0.06	nd	nd	nd	nd
PT-CA ^b	nd	nd	1.4	0.06	nd	nd	nd	nd
T-CA ^b	nd	nd	nd	nd	6.1	0.03	nd	nd
unknown	nd	nd	4.2	0.21	21.2	0.11	14	0.17
PES	< 0.1	< 0.06	0.7	0.03	3.0	0.02	4.3	0.04
Total	100	2.97	99.9	4.43	100	0.53	99.0	1.02

^a For identification see Table 1^b Sum of free and conjugated

DAT = Days after treatment

nd = Not detected

The parent compound was mainly present in the organic fraction and amounted to the 93.6%, 88.7%, 69.7% and 77.4% of applied radioactivity. The portion of radioactive residues of the total

radioactivity in the water soluble fraction was 6.4% on day 0, and $\leq 1\%$ at the following sampling days.

Table 27 Identification of metabolites in peach leaves

Metabolite ^a	TRR in (%) and (mg/kg)							
	0 DAT		14 DAT		28 DAT		56 DAT	
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
parent	100	100.1	63.3	36.0	41.4	24.1	24.1	12.4
CA-T-CA ^b	nd	nd	3.3	1.9	10.7	6.3	11.0	5.7
T-AM	nd	nd	2.2	1.2	2.9	1.7	2.4	1.2
PT-OH	nd	nd	0.8	0.5	1.0	0.6	1.0	0.5
PT-CA ^b	nd	nd	8.5	4.9	8.5	5.0	11.0	5.6
T-CA ^b	nd	nd	5.1	2.9	7.9	4.6	6.1	3.2
OH-PT	nd	nd	0.3	0.2	0.4	0.3	nd	nd
PT-CHO	nd	nd	0.3	0.2	0.3	0.2	nd	nd
CO-PT	nd	nd	0.4	0.2	0.6	0.3	0.4	0.2
OH-T-CA	nd	nd	0.3	0.2	0.3	0.2	0.5	0.2
OH-PT-CA	nd	nd	0.5	0.3	1.8	1.0	1.6	0.8
unknown	nd	nd	12.3	7.0	21.3	12.5	22.8	10.7
PES	< 0.1	< 0.3	2.7	1.5	2.9	1.4	19.3	9.9
Total	100	100.1	100	57.0	100	58.2	100	51.5

^a For identification see Table 1

^b Sum of free and conjugated

DAT = Days after treatment

nd = Not detected

The parent compound was mainly present in the organic fraction and amounted to the 98%, 62.9%, 41.2% and 24.1% of applied radioactivity. The proportion of radioactive residues in the water soluble fraction was $\leq 2\%$ of the total radioactivity at the corresponding sampling days.

Table 28 Identification of metabolites in peach stem

Metabolite ^a	TRR in (mg/kg) ^c			
	0 DAT	14 DAT	28 DAT	56 DAT
parent	19.3	25.2	11.1	14.4
CA-T-CA				
T-AM		0.2		
PT-OH				
PT-CA ^b		0.4	0.8	1.2
T-CA ^b				
OH-PT		0.2		
PT-CHO				
CO-PT				
unknown		0.5	0.3	1.1
PES	< 0.2	0.2	0.4	0.9
Total	19.3	26.7	12.6	17.6

Notes: see Table 26

Study 2

In the second study [pyrazole-¹⁴C]-tolfenpyrad was applied to individual peach plants in separate pots in a spray chamber. One application was made at a rate corresponding to 750 g ai/ha (Ogawa, K 1999d, Report no. R-10004). Treated leaves and stem of the treated branch were collected 56 days after treatment. The treated fruit was collected at day 53 and divided into peel, pulp and stone. After collection, each part was weighed and then subjected to analysis. The analytical procedures were practically the same as described under the study with ¹⁴C-tolyl-tolfenpyrad. All samples were analysed within 6 months after sampling. The results are summarized in Tables 29–32.

Table 29 Distribution of total radioactive residues (TRRs) in peach following application of [^{14}C] tolfenpyrad

Crop part	TRR (mg tolfenpyrad equiv./kg) ^a	
	mg/kg	% AD
Leaves (56 DAT)	64.53	86.1
Stem (56 DAT)	9.93	7.3
Fruit (53 DAT)	0.77	6.6
Total	n.a.	100.0

^a Values determined as sum of extracted and unextracted radiocarbon

DAT = Days after treatment

n.a. = Not applicable

Table 30 Distribution of total radioactive residues (TRRs) in peach fruit following application of [^{14}C] tolfenpyrad

Crop part	TRR (mg tolfenpyrad equiv./kg) ^a		
	mg/kg	%TRR of whole branch	adjusted to fruit
Peel	11.01	5.7	86.4
Pulp	0.12	0.8	12.7
Stone	0.09	0.1	0.9
Total	0.77	6.6	100.0

Notes: see Table 30

Table 31 Distribution of TRR in peach leaves, stem and fruit following application of [^{14}C] tolfenpyrad

Crop part / Fraction	TRR (mg tolfenpyrad equiv./kg)	
	mg/kg	%TRR
Leaves at 56 DAT (total)	64.53	86.1
organo-soluble	38.04	50.7
water-soluble	24.13	32.2
PES	2.36	3.2
Stem at 56 DAT (total)	9.93	7.3
organo-soluble	8.88	6.5
water-soluble	0.70	0.5
PES	0.35	0.3
Fruit at 53 DAT (total)	0.77	6.6
organo-soluble	0.60	5.2
water-soluble	0.11	1.0
PES	0.05	0.5
Total	n.a.	100.0

n.a. = Not applicable

Table 32 Distribution of TRR in peach peel, pulp and stone 53 days after application of [^{14}C] tolfenpyrad

Fraction	Residues (mg tolfenpyrad equiv./kg) at 53 DAT							
	Peel		Pulp		Stone		total	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Fruit (organo-soluble)	9.51	5.0	0.04	0.3	< 0.01	< 0.01	0.60	5.2
Fruit (water-soluble)	0.77	0.4	0.07	0.5	0.03	0.02	0.11	1.0
PES	0.73	0.4	0.01	0.04	0.06	0.04	0.05	0.5
Total	11.01	5.7	0.12	0.8	0.09	0.06	0.77	6.6

DAT = Days after treatment

n.a. = Not applicable

In total 25 metabolite signals together with unchanged tolfenpyrad were detected in peaches (leaves, stem and fruits). Nine of them were identified by co-chromatography with reference standards. After β -glucosidation, one metabolite was identified to be a glucose conjugate of PT-CA. (Tables 33–35).

Table 33 Identification of pyrazole [^{14}C] tolfenpyrad metabolites in peach fruits 53 days after treatment

Compounds ^a	TRR (%)							mg/kg
	Pulp ^b			Peel ^b			Total	
	OS	WS	Total	OS	WS	Total		
parent	0.3	nd	0.3	62.1	2.6	64.7	65.0.	0.53
OH-PAM	2.3	1.7	4.0	nd	nd	nd	4.0	0.03
PAM	nd	nd	nd	0.9	nd	0.9	0.9	0.01
OH-PT-OH	0.3	nd	0.3	0.6	nd	0.6	0.9	0.01
OH-PT-CA	0.3	nd	0.3	nd	nd	nd	0.3	< 0.01
PT-CA-Glu	nd	nd	nd	0.3	nd	0.3	0.3	nd
PT-OH	nd	nd	nd	0.6	nd	0.6	0.6	0.01
PT-CA	nd	nd	nd	0.2	nd	0.2	0.2	< 0.01
PT-CHO	nd	nd	nd	0.5	nd	0.5	0.5	< 0.01
CO-PT	0.2	nd	0.2	0.8	nd	0.8	1.0	0.01
unknown	0.5	6.5	7.0	8.6	3.4	12.0	19.0	0.16
PES	—	—	0.6	—	—	5.7	6.3	0.05
total	—	—	12.7	—	—	86.3	99.0	—

^a For identification see Table 1

^b The figures represent % of TRR in the fruits

OS = Organo-soluble fraction;

WS = Water-soluble fraction

nd = Not detected

Table 34 Identification of pyrazole [^{14}C] tolfenpyrad metabolites in peach leaves 56 days after treatment

Metabolite ^a	TRR% ^b			mg/kg
	OS	WS	total	
parent	32.5	0.2	32.7	21.06
OH-PAM	0.5	8.6	9.1	5.82
PAM	1.5	0.7	2.2	1.40
PCA	0.6	nd	0.6	0.37
OH-PT-OH	nd	0.3	0.3	0.21
OH-PT-CA	1.4	1.9	3.3	2.06
PT-CA-Glu	1.5	nd	1.5	0.94
PT-OH	3.0	1.4	4.4	2.83
PT-CA	14.1	1.4	15.5	10.01
CO-PT	0.8	nd	0.8	0.52
unknown	3.0	22.9	25.9	16.95
PES	–	–	3.7	2.36
Total	–	–	100	64.53

^a For identification see Table 1

^b The figures represent % of TRR in leaves

OS = Organo-soluble fraction

WS = Water-soluble fraction

nd = Not detected

Table 35 Identification of pyrazole [^{14}C] tolfenpyrad metabolites in peach stem 56 days after treatment

Metabolite ^a	TRR % ^b			mg/kg
	OS	WS	total	total
parent	70.9	not determined	70.9	7.04
OH-PAM	nd		nd	nd
PAM	3.4		3.4	0.34
PCA	nd		nd	nd
OH-PT-OH	1.1		1.1	0.11
OH-PT-CA	0.8		0.8	0.08
PT-CA-Glu	6.3		6.3	0.63
PT-OH	0.4		0.4	0.04
PT-CA	2.3		2.3	0.23
CO-PT	1.0		1.0	0.10
unknown	3.2		10.2	1.01
PES	–	–	3.6	0.35
Total	–	–	100	9.93

^a For identification see Table 1

^b The figures represent % of TRR in stem

OS = Organo-soluble fraction

WS = Water-soluble fraction

nd = Not detected

Radish

[Tolyl- ^{14}C]-tolfenpyrad or [pyrazole- ^{14}C]-tolfenpyrad were applied to separate plots of radishes located outdoors. Each plot received two applications, 14 days apart, at a nominal rate of 230 g ai/ha (Quistad, GB and Kovatchev, A 2008, Report no. R-10172

Samples of radish foliage and root were harvested at maturity, 1 day after last application. Mature radishes were pulled from the soil and the loose soil was removed. The tops were cut from the roots and the tap root and remaining top was snapped off.

Samples were transferred under deep frozen conditions to the analytical laboratory, where they were blended in the presence of dry ice. After sublimation of the dry ice, processed samples were stored in plastic bags under frozen conditions.

The pre-homogenised processed sample (20 g) was weighed into a centrifuge bottle. The sample was extracted twice with 80 mL of acetonitrile each by shaking on a wrist-action shaker for 20 minutes. Samples of radish foliage and root were harvested at maturity, 1 day after last application. Mature radishes were pulled from the soil and the loose soil was removed. The tops were cut from the roots and the tap root and remaining top was snapped off.

Samples were transferred under deep frozen conditions to the analytical laboratory, where they were blended in the presence of dry ice. After sublimation of the dry ice, processed samples were stored in plastic bags under frozen conditions. The sample was centrifuged, the supernatant was separated and, after combination of the extracts, an aliquot was taken for liquid scintillation counting (LSC). Extraction of the PES was repeated twice using 80 mL of acetonitrile/hydrochloric acid 0.2 M (1/1; v/v) and an aliquot was taken for LSC as mentioned above. Finally, the PES was extracted once using 80 mL of acetonitrile/KOH 0.2 M (1/1; v/v) and once with 80 mL of KOH (24% in water) by shaking and centrifugation as mentioned above.

For determination of soluble residues by HPLC or TLC all fractions obtained so far were combined using representative portions of each extract. Combined extracts were concentrated. For certain samples e.g. radish roots, a clean-up over silica gel SPE was performed. Extracts were analysed by TLC and/or HPLC using the available reference standards for co-chromatography. The presence of known metabolites was confirmed by TLC.

The samples were analysed within 62 days.

Table 36 Distribution of total radioactive residues (TRRs) in radish following two applications of [^{14}C] tolfenpyrad

Crop part	Pyrazole-label				Tolyl-label			
	by combustion		sum of fractions		by combustion		sum of fractions	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Radish root	0.44	4.9	0.44	5.9	0.59	5.2	0.53	4.6
Radish foliage	8.58	95.1	6.96	94.1	10.77	94.8	10.95	95.4

Extraction with acetonitrile removed 79.7–90.0% of the TRR and acetonitrile/0.2 M HCl (1:1) removed an additional 8.3–12.9%. After further alkaline extraction with acetonitrile/0.2 M KOH (1:1) and 24% KOH that removed in total 1.1–4.6%, the post extraction solids (PES) contained only 0.6–2.9% of the TRR.

Table 37 Identification of metabolites in radish (root and foliage)

Metabolite	Foliage (HPLC)				Root (TLC)			
	Pyrazole-label		Tolyl-label		Pyrazole-label		Tolyl-label ^a	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
TRR	6.96	100.0	10.95	100.1	0.44	99.9	0.53	100.1
Solvent and acid extractable	6.79	97.6	10.76	98.3	0.41	94.9	0.49	92.6
Tolfenpyrad	5.74	82.4	9.31	85.0	0.24	54.0	0.22	42.2
PT-CA	–	–	–	–	0.04	10.1	0.11	21.5
PAM	0.15	2.1	–	–	0.04	9.9	–	–
OH-PT-OH	0.27	3.8	0.36	3.2	–	–	–	–
OH-PAM (free and conj.)	–	–	–	–	0.02	3.4	–	–
OH-PCA	–	–	–	–	0.03	6.4	–	–
Unknown and conjugate	0.12	1.8	0.19	1.8	0.01	1.8	0.03	5.9
0.2M KOH in acetonitrile	0.07	1.0	0.08	0.7	0.02	3.9	0.01	2.5
KOH (24% aqu.)	0.05	0.7	0.05	0.4	0.01	1.8	0.01	2.1
PES	0.05	0.7	0.06	0.6	0.01	1.6	0.02	2.9

^a The maximum of any other single metabolite was 0.03 mg/kg, 5.9% of TRR.

The metabolic pathways of tolfenpyrad in three different crops were essentially the same (Figure 3) and the metabolism of tolfenpyrad in all three crops is considered comparable.

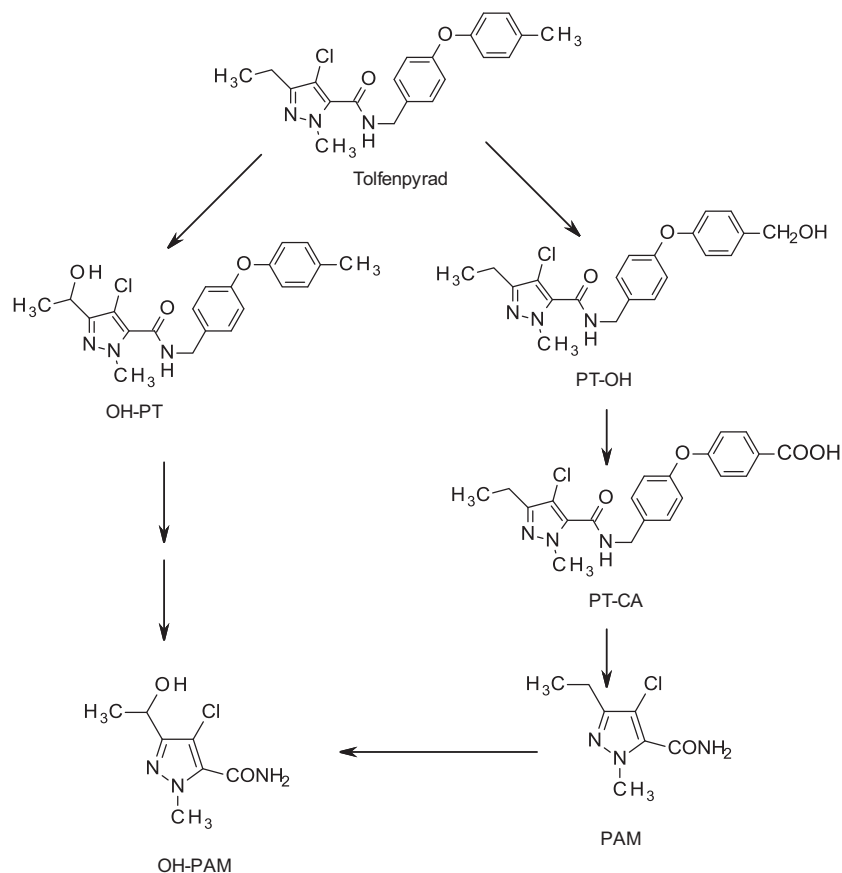


Figure 3 Main metabolic pathways of tolfenpyrad in plants

Environmental fate in Soil and Water

The Meeting received information on photolysis on soil, aerobic degradation in soil, aqueous photolysis and confined and field rotational crop studies.

Soil photolysis

A photolysis study of [^{14}C] tolfenpyrad was conducted on a viable sandy loam soil from California (Ponte, M, 2008b. report no. E-10008). Artificial light (xenon lamp equipped with a UV filter at 290 nm) was applied continuously for 13 days (equivalent to 32 days of alternating day/night exposure) to the test substance. The soil was sieved through 2 mm sieve, placed in quartz containers of 50 mm diameter and treated at approximately double field rate (28.8 $\mu\text{g/g}$ soil). The temperature was maintained at $25 \pm 2^\circ\text{C}$. The samples were sealed and purged continuously with a gentle flow of sterile moisturised air into a series of traps including ethylene glycol and two 10% aqueous NaOH solutions. Samples were collected at time 0 and following approximately 2, 3, 4, 6, 9 and 13 days exposure. Concurrent dark control samples were maintained under equivalent conditions.

The soils were extracted with acetonitrile /0.01 M HCl (4:1). The extracts were analysed with HPLC and TLC, and the residual soil was combusted. The radiocarbon was quantified with LSC.

Half-life of tolfenpyrad was calculated based on its percent present in the soil extracts at each sampling interval, using pseudo-first order kinetics.

Sample set	$t_{1/2}$ (hours)	Solar equivalent $t_{1/2}$ (Days)	DT_{90} (days)	R^2
Pyrazole-label	624	64.0	2074	0.919
Tolyl-label	444	45.6	1476	0.907

Table 38 Summary of transformation pyrazole labelled tolfenpyrad during 13 days exposure

Metabolites	% of Applied Radioactivity													
	Exposure Time (hours)													
	0	44.6		68.8		91.6		144.5		213		310.3		
	–	Light	Dark	Light	Dark	Light	Dark	Light	Dark	Light	Dark	Light	Dark	
Tolfenpyrad	93.6	85.5	92.0	86.6	94.4	84.0	91.5	80.7	92.9	73.2	89.2	65.3	93.4	
OH-PAM	0.0	0.1	0.0	0.2	0.0	0.3	0.0	1.3	0.0	2.0	0.0	3.5	0.0	
PAM	0.0	2.1	0.5	2.4	0.7	3.0	0.6	5.0	0.8	7.5	0.9	11.3	0.9	
PT-OH	0.0	0.8	0.1	0.7	0.1	0.8	0.1	0.7	0.0	0.9	0.2	1.3	0.1	
PT-CHO	0.1	4.2	1.3	3.3	0.3	3.6	0.0	2.8	0.0	4.2	0.0	6.6	0.3	
PT-CA	0.0	0.3	0.3	0.4	0.6	0.5	0.5	0.7	0.2	0.6	0.5	1.1	2.0	
Others	2.5	3.5	1.6	3.3	2.5	3.3	2.2	3.7	2.5	4.4	2.0	4.6	2.2	
Bound	0.7	1.7	0.9	1.4	1.5	1.3	1.5	1.9	1.9	2.3	1.6	3.2	0.9	
CO ₂	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.2	0.0	0.5	0.0	0.9	0.0	
Organic Volatiles	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.2	0.0	
Total Recoveries	96.9	98.4	96.7	98.4	100.1	96.9	96.4	97.0	98.3	95.7	94.4	98.0	99.8	

Table 39 Summary of transformation tolyl labelled tolfenpyrad during 13 days exposure

Metabolites	% of Applied Radioactivity													
	Exposure Time (hours)													
	0	47		70.5		94		145.5		218.5		313.5		
	–	Light	Dark	Light	Dark	Light	Dark	Light	Dark	Light	Dark	Light	Dark	
Tolfenpyrad	94.5	85.4	91.4	79.0	88.4	81.0	90.4	75.3	91.3	65.9	88.6	56.7	86.9	
PT-OH	0.0	0.9	0.1	1.2	0.2	0.6	0.1	1.3	0.2	0.0	0.2	0.0	0.2	
PT-CHO	0.3	2.0	0.0	1.9	0.1	0.9	0.3	1.9	0.1	0.5	0.1	0.5	0.1	
PT-CA	0.0	0.1	0.4	1.0	0.4	2.0	0.7	5.9	3.3	10.5	3.9	13.0	4.7	
TD-1	0.0	0.5	1.0	2.1	1.1	3.8	1.3	3.0	1.7	5.3	2.2	5.5	1.9	
Others	3.9	5.2	3.3	5.2	3.0	4.7	2.8	6.3	2.6	6.2	2.5	6.4	2.7	
Bound	0.5	1.5	1.0	3.0	1.2	4.1	1.1	4.2	1.3	5.9	2.7	10.7	2.4	
CO ₂	0.0	0.1	0.0	0.3	0.0	0.5	0.0	2.0	0.0	3.3	0.0	4.7	0.1	
Organic Volatiles	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.2	0.0	0.3	0.0	
Total Recoveries	99.2	95.7	97.2	93.7	94.4	97.7	96.7	100.0	100.5	97.8	100.2	97.8	99.0	

Aerobic soil metabolism

An aerobic soil metabolism study was conducted on a California sandy loam soil using [¹⁴C] tolfenpyrad (Ponte, M 2008, report no. E-10010). Approximately 50.55 g of the soil (50.00 g dry weight equivalent) were weighed into 120 mL amber bottles, deionized water was added to the soils to achieve 75% ± 10% field moisture capacity (FMC) at 1/3 bar, then the bottles were capped and placed in the Hotpack constant temperature chamber and pre-incubated at 25 ± 1 °C with a CO₂-free air flow for approximately 2–3 weeks prior to dosing. Individual samples were treated with pyrazole- and tolyl labelled [¹⁴C] tolfenpyrad at 0.681 mg/kg soil and 0.662 mg/kg soil, respectively. The bottles of treated soil were connected to the trapping system and maintained at 25 ± 1 °C and incubated in the dark at 25 °C for periods up to 365 days. All samples were aerated/ trapped continuously during the incubation period. Samples were collected immediately after treatment (time 0) and after 1, 2, 3, 8, 14, 21, 30, 63, 90, 181, and 365 days of exposure.

At sampling, the total soil sample weight was recorded, and the soil sample was transferred to a pre-weighed 250 mL centrifuge bottle. An aliquot (100 mL) of the extraction solvent (acetonitrile:0.01 M HCl, 4:1 v/v) was added to the bottle, with some of the solvent used to rinse the original sample container. The samples were placed on a Wrist-Action shaker for 60 minutes followed by centrifugation for 10 minutes at 2500 rpm. The supernatant soil extract was decanted and the extraction repeated twice more with fresh aliquots (75 mL) of extraction solvent. The soil extracts were combined, the total volume was measured and aliquots (3 × 1 mL) were taken for radio-assay.

For HPLC analysis an aliquot of soil extract was evaporated under nitrogen to remove acetonitrile.

All samples were extracted on the same day of collection, and initial HPLC analysis was performed within 48 hours of collection.

Table 40 Summary of aerobic soil metabolism of [PYR-¹⁴C] tolfenpyrad

Incubation (days)	% of Applied Dose ^a or mg/kg ^b								
	Tolfenpyrad	PT-CA	PAM	PCA	PT(A)-4OH	Others ^c	Bound Residues	Organic Volatiles	CO ₂
Day 0	95.0	0.0	0.1	0.0	0.0	4.7	0.7	NA	NA
Day 1	87.0	6.7	1.7	0.0	0.0	1.6	1.4	0.0	0.0
Day 2	74.8	16.7	1.6	0.5	0.4	1.5	2.1	0.0	0.1
Day 3	74.8	17.2	1.6	0.6	0.3	1.3	2.7	0.0	0.1
Day 8	45.4	32.9	3.3	6.2	1.7	1.4	8.4	0.0	0.1
Day 14	66.3	16.6	1.6	5.2	0.0	0.7	7.2	0.0	0.2
Day 21	30.0	36.2	3.5	11.5	2.9	2.3	10.8	0.0	0.1
Day 30	19.4	30.1	3.4	19.4	4.3	2.7	17.6	0.0	0.4
Day 30	0.132	0.205	0.023	0.132	0.029	0.018	0.120	0.000	0.003
Day 63	5.8	7.8	1.6	34.0	2.5	7.7	36.3	0.1	3.5
Day 90	3.5	6.5	3.8	26.6	1.1	4.6	44.4	0.1	7.7
Day 180	1.7	3.2	0.1	15.4	1.4	5.8	54.8	0.0	17.7
Day 365	1.6	2.0	0.0	3.1	0.7	3.2	48.2	0.1	31.6
Day 365	0.011	0.013	0.000	0.021	0.005	0.022	0.328	0.000	0.215

^a Average of two measurements

^b The mg/kg values are printed in bold face

^c This column is comprised of multiple components, none representing > 3.7% of dose.

Table 41 Summary of aerobic soil metabolism of [tolyl-¹⁴C] tolfenpyrad

Incubation (days)	% of Applied Dose ^a or mg/kg ^b							
	Tolfenpyrad	PT-CA	PT-OH	U-1	Others ^c	Bound Residues	Organic Volatiles	CO ₂
Day 0	102.3	0.0	0.0	0.0	0.0	0.6	NA	NA
Day 1	93.8	7.1	0.2	0.0	0.0	1.4	0.0	0.3
Day 2	83.6	13.1	0.0	0.0	0.0	2.0	0.0	0.6
Day 3	72.5	20.0	0.1	0.0	0.3	3.5	0.0	1.3
Day 8	43.7	36.5	0.0	1.0	0.8	10.5	0.0	5.3
Day 14	61.2	18.7	0.1	0.6	0.9	9.3	0.0	6.4
Day 21	38.4	30.1	0.0	1.1	0.5	13.9	0.0	11.2
Day 30	17.1	36.9	0.0	1.9	1.3	19.3	0.0	15.4
Day 30	0.113	0.244	0.000	0.013	0.008	0.127	0.000	0.102
Day 63	7.9	13.1	0.0	2.2	0.5	28.0	0.0	40.2
Day 90	6.8	11.5	0.0	2.3	0.1	27.0	0.0	44.6
Day 180	4.0	6.0	0.0	1.5	0.2	26.0	0.0	52.1
Day 365	2.8	2.6	0.0	0.9	0.2	21.8	0.0	59.4
Day 365	0.019	0.017	0.000	0.006	0.001	0.144	0.000	0.393

^a Average of two measurements

^b The mg/kg values are printed in bold face

^c This column is comprised of multiple components, none representing > 3.7% of dose.

Confined Rotational Crop Studies

Study 1

A confined rotational crop study was conducted in Porterville, California, USA, in 2006–2008 (Quistad, GB, Kovatchev, A and Hilter, RL 2008) applying pyrazole [¹⁴C] tolfenpyrad and tolyl [¹⁴C]

tolfenpyrad evenly on bare sandy loam soil at a nominal rate of 350 g ai/ha, using an SC formulation containing 15% tolfenpyrad. There were eight treated test plot boxes of 1 m² each created for this study, four for each label. Lettuce, radish and wheat were planted at intervals of 30, 120 and 365 days after soil treatment representing crop failure conditions, a typical harvest interval and following year rotation.

Samples of lettuce, radish (foliage and roots) and wheat (forage, hay, grain and straw) were taken at appropriate harvest time, analysed by combustion to determine the total radioactive residue (TRR) and for residue determination of the post-extraction solid (PES). The pre-homogenised processed crop sample was weighed into a centrifuge bottle. Straw was soaked in water before extraction (20 mL, 30 min). The sample was extracted twice with acetonitrile (100 mL) by shaking on a wrist action shaker for one hour, then centrifuged or filtered, and an aliquot of the clear solution was taken for liquid scintillation counting (LSC). Extraction of the PES was repeated once or twice using a hydrochloric acid / acetonitrile-solution (1/1; v/v) by shaking on a wrist action shaker for one hour, then centrifuged or filtered, and an aliquot of the clear solution was taken for LSC.

When residues in PES were > 0.01 mg/kg (or > 10% TRR) a two-step alkaline extraction was performed with aqueous 0.2 N KOH/acetonitrile-solution (1/1; v/v) followed by 24% KOH-solution (50–100 mL each). In certain cases, these basic extracts were acidified and partitioned into ethyl acetate. The ethyl acetate fraction was analysed by HPLC as needed.

Representative portions of extracts were combined prior to analysis. The combined organic extracts were evaporated to dryness. Where required, samples were cleaned up by C₁₈-SPE. Samples with or without clean-up were reconstituted in acetonitrile/water and analysed by HPLC and TLC. Aliquots of the PES at the end of each extraction step were combusted to determine the radioactive residue.

The results are summarized in Tables 42–50.

Table 42 Intervals between soil treatment and harvest of crops

	Interval between soil treatment and sampling ^a		
	30 PBI	120 PBI	365 PBI
Lettuce	124	176	415
Radish	83	169	404
Wheat forage	83	175	415
Wheat hay	209	230	524
Wheat straw	230	237	562
Wheat grain	230	237	562

^a All analyses were completed within 2 months of sampling

Table 43 Summary of TRRs in lettuce, radish and wheat at each planting interval

Crops	TRR (mg tolfenpyrad equiv./kg) ^a					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Lettuce	0.08 (87.8)	0.05 (90.6)	0.03 (91.9)	0.04 (81.3)	0.02 (93.8)	< 0.01
Radish (foliage)	0.13 (84.5)	0.12 (92.4)	0.05 (97.9)	0.04 (109.4)	0.01 (66.7)	< 0.01
Radish (roots)	0.06 (103.5)	0.06 (109.1)	0.01 (73.3)	0.02 (80.0)	< 0.01 (100.0)	< 0.01
Wheat forage	0.54 (89.5)	0.26 (95.3)	0.19 (97.0)	0.01 (100.0)	< 0.01	< 0.01
Wheat hay	0.66 (96.4)	0.74 (86.2)	0.26 (97.8)	0.02 (105.6)	0.02 (105.6)	< 0.01
Wheat straw	1.24 (85.5)	0.78 (85.8)	0.30 (109.1)	0.02 (100.0)	0.02 (131.3)	< 0.01
Wheat grain	0.06 (96.6)	0.05 (97.9)	< 0.01 (88.9)	0.01 (84.6)	< 0.01	< 0.01

^a Values in parenthesis represent % radioactive residue recovered during extraction vs. combustion

PBI = Plant back interval—planting days after treatment

Table 44 Identification of tolfenpyrad residues in lettuce

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	n.d	< 0.01 —	no extraction
OH-PAM conjugates (Met-1)	0.02 (24.1)	< 0.01 (16.7)	0.01 (32.4)	—	—	
OH-PAM	< 0.01 (3.8)	incl. in Met-2	incl. in Met-2	—	—	
OH-PCA conjugates (Met-2)	0.02 (26.6)	0.01 (29.2)	< 0.01 (14.7)	—	—	
OH-PCA	0.02 (20.3)	0.01 (27.1)	< 0.01 —	—	—	
PAM	< 0.01 (5.1)	< 0.01 (8.3)	< 0.01 (8.8)	—	—	
OH-T-CA	—	—	—	nd	nd	
CA-T-CA	—	—	—	nd	nd	
OH-PT-CA	—	—	—	nd	nd	
PT-CA	—	—	—	nd	< 0.01 (13.3)	
others (sum)	< 0.01 (10.0)	< 0.01 (10.4)	0.01 (38.2)	0.02 (48.7)	< 0.01 (40.0)	
maximum others (single)	< 0.01 (2.5)	< 0.01 (2.1)	0.006 (17.6)	< 0.01 —	< 0.01 (6.7)	
unanalysed fractions	< 0.01 (8.8)	—	—	0.01 (28.2)	< 0.01 (33.4)	
PES	< 0.01 (1.3)	< 0.01 (8.3)	< 0.01 (5.9)	< 0.01 (23.1)	< 0.01 (13.3)	
total	0.08 (100.0)	0.05 (100.0)	0.03 (100.0)	0.04 (100.0)	0.02 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 45 Identification of tolfenpyrad residues in radish foliage

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	< 0.001 —	nd	no extraction
OH-PAM conjugates (Met-1)	0.03 (20.0)	0.01 (11.6)	< 0.01 (15.2)	—	—	
OH-PAM	0.02 (14.4)	incl. in Met-2	incl. in Met-2	—	—	
OH-PCA conjugates (Met-2)	0.03 (24.0)	0.01 (8.3)	< 0.01 (6.5)	—	—	
OH-PCA	< 0.01 (4.0)	< 0.01 (2.5)	< 0.01 (2.2)	—	—	
PAM	0.02 (12.0)	0.01 (8.3)	< 0.01 (4.3)	—	—	
OH-T-CA	—	—	—	nd	nd	
CA-T-CA	—	—	—	< 0.01 (2.9)	nd	
OH-PT-CA	—	—	—	< 0.01 (—)	nd	

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
PT-CA	< 0.01 (2.4)	–	–	< 0.01 (5.7)	< 0.01 (16.7)	
others (sum)	0.02 (16.0)	0.08 (62.8)	0.03 (65.3)	0.02 (48.6)	< 0.01 (33.3)	
maximum others (single)	0.01 (3.2)	0.04 (28.9)	0.03 (56.5)	< 0.01 (8.6)	< 0.01 (8.3)	
unanalysed fractions	no extraction			0.01 (28.6)	no extract.	
PES	< 0.01 (7.2)	< 0.01 (6.6)	< 0.01 (6.5)	< 0.01 (14.3)	< 0.01 (50.0)	
total	0.13 (100)	0.12 (100.0)	0.05 (100.0)	0.04 (100.0)	0.01 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 46 Identification of tolfenpyrad residues in radish roots

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	nd	nd	no extraction
OH-PAM conjugates (Met-1)	nd	nd	nd	–	–	
OH-PAM	< 0.01 (8.5)	incl. in Met-2	incl. in Met-2	–	–	
OH-PCA conjugates (Met-2)	0.02 (27.1)	< 0.01 (8.3)	< 0.01 (9.1)	–	–	
OH-PCA	< 0.01 (1.7)	nd	nd	–	–	
PAM	0.02 (25.4)	0.02 (30.0)	< 0.01 (27.3)	–	–	
OH-T-CA	–	–	–	< 0.001 (–)	()	
CA-T-CA	–	–	–	< 0.01 (6.3)	()	
OH-PT-CA	–	–	–	< 0.001 (–)	()	
PT-CA	–	–	–	< 0.001 (–)	()	
others (sum)	0.01 (17.0)	0.03 (48.4)	< 0.01 (63.6)	< 0.01 (50.0)	< 0.01 (62.5)	
maximum others (single)	< 0.01 (3.4)	0.01 (20.0)	< 0.01 (45.5)	< 0.01 (6.3)	< 0.01 (12.5)	
unanalysed fractions	< 0.01 (15.2)	no extraction		< 0.01 (31.3)	no extract.	
PES	< 0.01 (5.1)	< 0.01 (13.5)	< 0.001 (–)	< 0.01 (12.5)	< 0.01 (37.5)	
total	0.06 (100.0)	0.06 (100.0)	0.01 (100.0)	0.02 (100.0)	< 0.01 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 47 Identification of tolfenpyrad residues in wheat forage

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	nd	no extraction	no extraction

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
OH-PAM conjugates (Met-1)	0.16 (29.7)	0.05 (19.5)	0.15 (77.1)	—		
OH-PAM	0.03 (5.0)	0.02 (8.4)	nd	—		
OH-PCA conjugates (Met-2)	0.17 (32.3)	0.08 (30.3)	nd	—		
OH-PCA	0.09 (17.5)	0.05 (17.6)	< 0.01 (2.1)	—		
PAM	< 0.01 (1.1)	nd	nd	—		
OH-T-CA	—	—	—	—		
CA-T-CA	—	—	—	—		
OH-PT-CA	—	—	—	—		
PT-CA	—	—	—	—		
others (sum)	0.05 (10.1)	0.04 (14.2)	0.03 (14.6)	< 0.01 (23.1)		
maximum others (single)	0.01 (2.6)	0.01 (5.0)	0.01 (5.2)	—		
unanalysed fractions	no extract.	0.02 (9.2)	no extract.	< 0.01 (61.6)		
PES	0.02 (4.3)	< 0.01 (0.8)	0.01 (6.3)	< 0.01 (15.4)		
total	0.54 (100.0)	0.26 (100.0)	0.19 (100.0)	0.01 (100.0)	< 0.01 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 48 Identification of tolfenpyrad residues in wheat hay

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	nd	nd	no extraction
OH-PAM conjugates (Met-1)	0.26 (38.4)	0.23 (31.6)	0.04 (16.4)	—	—	
OH-PAM	0.05 (6.8)	0.04 (5.5)	nd	—	—	
OH-PCA conjugates (Met-2)	0.09 (12.8)	0.22 (30.3)	0.10 (36.3)	—	—	
OH-PCA	0.03 (5.1)	0.08 (10.2)	0.02 (5.7)	—	—	
PCA	< 0.01 (0.2)	< 0.01 (0.1)	nd	—	—	
OH-T-CA	—	—	—	nd	—	
CA-T-CA	—	—	—	nd	—	
OH-PT-CA	—	—	—	nd	—	
PT-CA	—	—	—	< 0.01 (5.3)	—	
others (sum)	0.22 (32.8)	0.15 (20.4)	0.10 (37.8)	< 0.01 (47.3)	—	
maximum others (single)	0.04 (6.0)	0.08 (10.7)	< 0.01 (3.4)	< 0.01 (15.8)	—	
unanalysed fractions	—	—	—	< 0.01 (5.3)	< 0.01 (33.3)	
PES	0.03 (4.1)	0.01 (1.9)	0.01 (3.8)	< 0.01 (42.1)	0.01 (66.7)	

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
total	0.66 (100.0)	0.74 (100.0)	0.26 (100.0)	0.02 (100.0)	0.02 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 49 Identification of tolfenpyrad residues in wheat straw

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	nd	nd	no extraction
OH-PAM conjugates (Met-1)	0.40 (32.1)	0.20 (25.4)	0.06 (19.7)	—	—	
OH-PAM	0.14 (11.5)	0.06 (8.2)	< 0.001 (—)	—	—	
OH-PCA conjugates (Met-2)	0.16 (12.7)	0.17 (21.4)	0.13 (41.8)	—	—	
OH-PCA	0.11 (8.5)	0.04 (5.6)	0.02 (6.7)	—	—	
PCA	< 0.01 (0.2)	< 0.01 (0.3)	nd	—	—	
OH-T-CA	—	—	—	no extraction		
CA-T-CA	—	—	—			
OH-PT-CA	—	—	—			
PT-CA	—	—	—			
others (sum)	0.39 (31.2)	0.26 (33.1)	0.09 (28.8)	—	—	
maximum others (single)	0.13 (10.6)	0.06 (7.8)	0.01 (4.7)	—	—	
unanalysed fractions	—	—	—	< 0.01 (40.0)	0.02 (76.2)	
PES	0.05 (4.0)	0.05 (6.0)	< 0.01 (3.0)	< 0.01 (60.0)	< 0.01 (23.8)	
total	1.24 (100.0)	0.78 (100.0)	0.30 (100.0)	0.02 (100.0)	0.02 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 50 Identification of tolfenpyrad residues in wheat grain

Metabolite	Metabolite (mg tolfenpyrad equiv./kg) ^a					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	nd	no extraction	no extraction
OH-PAM conjugates (Met-1)	< 0.01 (7.1)	< 0.01 (19.6)	< 0.01 (12.5)	—		
OH-PAM	incl. in Met-2	incl. in Met-2	incl. in Met-2	—		
OH-PCA conjugates (Met-2)	< 0.01 (14.3)	0.01 (23.9)	< 0.01 (12.5)	—		
OH-PCA	< 0.01 (10.7)	< 0.01 (2.2)	nd	—		
PAM	nd	nd	nd	—		
OH-T-CA	—	—	—	no extraction		
CA-T-CA	—	—	—			
OH-PT-CA	—	—	—			
PT-CA	—	—	—			

Metabolite	Metabolite (mg tolfenpyrad equiv./kg) ^a					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
others (sum)	0.02 (35.7)	0.02 (32.6)	< 0.01 (50.0)	–		
maximum others (single)	< 0.01 (12.5)	< 0.01 (10.9)	< 0.01 (25.0)	–		
unanalysed fractions	0.02 (32.1)	< 0.01 (4.3)	–	< 0.01 (18.2)		
PES	nd	< 0.01 (17.4)	< 0.01 (25.0)	< 0.01 (81.8)		
total	0.06 (100.0)	0.05 (100.0)	< 0.01 (100.0)	0.01 (100.0)	< 0.01 (100.0)	< 0.01 (100.0)

^a Values in brackets represent % TRR

Study 2

Two trials were carried on mustard greens as the primary crop grown in the USA in 2009. Two treatments with a 15EC formulation were made at 0.299 kg ai/ha with an interval of 14 days resulting in a maximum seasonal application rate of about 0.598 kg ai/ha (Carringer SJ, Report no. R-10218). The primary crop was removed from the trials at normal harvest with a PHI of one day after last application. Rotational crops (radish, lettuce and sorghum) were planted at intervals of 14, 28–30 and 58–60 days after last application.

The samples were analysed for parent tolfenpyrad and its metabolites OH-PAM, OH-PCA and PAM. The limit of quantification for each analyte in each matrix (radish, lettuce and sorghum) was 0.01 mg/kg and the limit of detection was 0.003 mg/kg.

From sampling to extraction, specimens were stored for up to 112 days for radish roots, 141 days for radish tops, 139 days for lettuce, 105 days for sorghum forage and grain and 85 days for sorghum stover. The results of storage stability test are presented in section on Stability of pesticide residue in stored analytical samples.

At normal harvest of the rotational crops, no residues of tolfenpyrad, OH-PAM, OH-PCA and PAM above the LOQ were found in radish roots, lettuce and sorghum forage, grain and stover. Residues of OH-PAM and OH-PCA at the LOQ (0.01 mg/kg) were found at rotational intervals of 14 and 30 days after last application only in radish tops from one trial site.

RESIDUE ANALYSIS

Analytical methods

Analytical methods have been developed for determination of residues of tolfenpyrad and its metabolites in plant and animal matrices. Each method has been validated at the stated LOQ.

Plant commodities

Tolfenpyrad and OH-PT were separated on the HPLC column and quantified with MS/MS.

The specificity of the detection was assured by monitoring of two mass transitions. Quantification by external standard was performed using the mass transitions $m/z = 384 \rightarrow 197$ (confirmation by $m/z = 384 \rightarrow 154$) for tolfenpyrad and $m/z = 400 \rightarrow 197$ (confirmation by $m/z = 400 \rightarrow 382$) for OH-PT. Linearity of detector response was demonstrated using five concentrations of external standard across the range of 0.01–0.2 ng/ml, with correlation coefficients in the range of 0.9934–1.0000 for both, tolfenpyrad and OH-PT. The LOQ was 0.01 mg/kg for both compounds, except tea (0.05 mg/kg).

The methods applied in supervised trials are briefly described hereunder.

Citrus-Method Meth-183, rev. 2 (Wyatt, DR, 2008a)

Residues of tolfenpyrad and its OH-PT metabolite were extracted from the sample with methanol using triplicate extractions. The crude extract from each extraction was vacuum filtered, then combined. The combined filtrates were brought to a final known volume. An aliquot of the combined extract was purified by means of an Oasis[®] HLB solid phase extraction (SPE) clean-up. The purified extract was evaporated to dryness, reconstituted in methanol, and then submitted to HPLC analysis. For the citrus oil samples, the extraction and Oasis[®] HLB SPE clean-up steps were eliminated and replaced with a direct dilution of the sample with methanol to a suitable sample concentration. The diluted samples were filtered then submitted to HPLC analysis. Determination and quantitation for both tolfenpyrad and its OH-PT metabolite were conducted with LC-MS/MS.

Apple, pear—Method Meth-183, rev. 2 (Carringer, SJ, 2009a)

Residues of tolfenpyrad and its OH-PT metabolite were extracted from the sample with methanol using triplicate extractions. The crude extract from each extraction was vacuum filtered, then combined. The combined filtrates were brought to a final known volume. An aliquot of the combined extract was purified with Oasis[®] HLB SPE clean-up. The purified extract was evaporated to dryness, reconstituted in methanol. Determination and quantitation of tolfenpyrad and OH-PT were conducted with HPLC-MS/MS.

Tree nuts and stone fruits—Method Meth-183, rev. 2 (Greenland, RG, 2009a)

The method allows for the quantitative determination of residues of tolfenpyrad and OH-PT in or on almond nutmeat, almond hulls and pecan nut meat samples. It is based on Meth-183, (rev. 2). An aliquot of the homogenised sample (approximately 5 g) was transferred to a 250 mL Nalgene[®] bottle and methanol (60 mL) and Celite (10 g) were added. The sample was allowed to sit for 15 minutes then blended using a high speed homogenizer for one minute. The sample was centrifuged. The supernatant was decanted and vacuum filtered into a 250 mL graduated cylinder. Sample extraction was repeated twice as mentioned above; all extracts were combined and brought to volume (200 mL) with methanol. For determination of residues by HPLC-MS/MS, the sample was diluted with methanol (1:5; v/v).

Stone fruit (sweet cherries, peaches and plums)—Method Meth-183, rev. 2 (Greenland, RG, 2009b)

The method is effectively the same as described for tree nuts.

Potatoes—Method Meth-183, rev. 2 (Carringer, SJ, 2008)

The method is effectively the same as described for apples and pears.

Fruiting vegetables (tomatoes and processed fractions, pepper) Method Meth-183, rev. 2 (Carringer, SJ, 2009b)

The method is effectively the same as described for apple and pear.

Fruiting vegetables (cucumbers, cantaloupes and summer squash) Method Meth-183, rev. 2 (Greenland, RG, 2009c)

The method is effectively the same as described for tree nuts.

Tea (Yabusaki, T, 2010a and 2010b)

After swelling with water, residues of tolfenpyrad were extracted from the sample with acetone by high speed homogenisation and mechanical shaking. After filtration the combined extracts were brought to volume and an aliquot was rotary evaporated to an aqueous remainder. After addition of acetone, a coagulation reagent and Celite 545 the solution was briefly mixed and filtrated. The sample solution was diluted with an aqueous sodium chloride solution and residues were partitioned into

hexane. The solvent was exchanged with acetone and the sample was cleaned up over ENVI-Carb and subsequently over Sep-Pak Plus silica after a second solvent exchange with hexane. Finally the sample solution was evaporated to dryness and residues were re-dissolved in acetone for final determination by GC-NPD.

Oilseeds (cotton seed) Method Meth-183, rev. 2 (Wyatt, DR, 2008b)

The method is practically the same as described for apples and pears with exception of refined oil. Refined oil samples were extracted four times with methanol. Extracts were combined without filtration and further processed as stated in the analytical method for apples and pears.

A summary of recoveries obtained during method validation and procedural recoveries for commodities included in this evaluation are summarized in Table 51.

Table 51 Summary of method validation and concurrent recovery data

Analyte	Crop	Fortification (mg/kg)	n	Range Recovery	Mean Recovery	% RSD	Method	Reference
Method Validation								
Tolfenpyrad	Orange (whole fruit)	0.01–1.0	14	70–94	82	9.1	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–1.0	14	70–109	87	11		
Tolfenpyrad	Grapefruit (whole fruit)	0.01–0.5	8	75–100	86	10	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–0.5	8	84–118	103	12		
Tolfenpyrad	Lemon (whole fruit)	0.01–1.0	8	83–102	90	6.1	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–1.0	8	77–98	90	7.8		
Tolfenpyrad	Almond (nut meat)	0.01–5.0	6	88–98	95	4.3	Meth-183, rev. 2	SARS-08-01
OH-PT		0.01–5.0	6	89–102	97	4.6		
Tolfenpyrad	Almond (hulls)	0.01–5.0	6	90–115	98	9.6	Meth-183, rev. 2	SARS-08-01
OH-PT		0.01–5.0	6	96–113	102	6.0		
Tolfenpyrad	Pecan (nut meat)	0.01–5.0	6	81–119	94	15	Meth-183, rev. 2	SARS-08-02
OH-PT		0.01–5.0	6	100–109	104	3.2		
Tolfenpyrad	Sweet Cherry	0.01–5.0	6	92–103	99	5.1	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	93–100	97	3.1		
Tolfenpyrad	Peach	0.01–5.0	6	92–108	100	6.7	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	91–99	97	3.2		
Tolfenpyrad	Plum	0.01–5.0	6	96–105	99	3.5	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	95–101	98	2.4		
Tolfenpyrad	Prune (processed)	0.01–5.0	6	91–100	96	3.3	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	94–100	97	1.8		
Tolfenpyrad	Cucumber	0.01–10	6	73–99	88	13.1	Meth-183, rev. 2	SARS-08-10
OH-PT		0.01–10	6	93–101	95	5.3		
Tolfenpyrad	Cantaloupe	0.01–10	6	88–99	93	4.2	Meth-183, rev. 2	SARS-08-11
OH-PT		0.01–10	6	95–101	98	2.1		
Tolfenpyrad	Summer Squash	0.01–10	6	89–100	95	5.3	Meth-183, rev. 2	SARS-08-12
OH-PT		0.01–10	6	92–98	96	3.3		
Procedural Recoveries								
Tolfenpyrad	Orange (juice)	0.01–0.5	2	70–85	78	–	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–0.5	2	98–105	102	–		
Tolfenpyrad	Orange (dried pulp)	0.01–10	3	88–97	93	4.5	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–10	2	89–103	96	–		
Tolfenpyrad	Orange (oil)	0.01–80	3	91–118	108	15	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–80	2	115–118	116	–		
Tolfenpyrad	Almond (nut meat)	0.01–5.0	6	77–107	92	12	Meth-183, rev. 2	SARS-08-01
OH-PT		0.01–5.0	6	90–96	93	2.1		
Tolfenpyrad	Almond (hulls)	0.01–5.0	6	76–96	88	8	Meth-183, rev. 2	SARS-08-01
OH-PT		0.01–5.0	6	89–100	95	4.3		
Tolfenpyrad	Pecan (nut meat)	0.01–5.0	4	97–103	100	2.7	Meth-183, rev. 2	SARS-08-02
OH-PT		0.01–5.0	4	88–104	97	7.3		
OH-PT		0.01–4.0	2	99–111	105	–		
Tolfenpyrad	Pear	0.01–1.0	10	70–98	83	9.3	Meth-183, rev. 2	TCI-08-196
OH-PT		0.01–1.0	10	70–100	85	8.1		

Analyte	Crop	Fortification (mg/kg)	n	Range Recovery	Mean Recovery	% RSD	Method	Reference
Tolfenpyrad	Sweet Cherry	0.01–5.0	6	87–101	95	5.6	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	88–105	99	6.4		
Tolfenpyrad	Peach	0.01–5.0	6	81–112	90	13	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	89–117	99	9.4		
Tolfenpyrad	Plum	0.01–5.0	6	90–106	95	6.6	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	93–100	98	2.8		
Tolfenpyrad	Prune (processed)	0.01–5.0	2	100	100	–	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	2	89–98	93	–		
Tolfenpyrad	Potato	0.01–0.5	16	67–101	81	9.7	Meth-183, rev. 2	TCI-07-163
OH-PT		0.01–0.5	16	79–116	100	9.8		
Tolfenpyrad	Potato (flakes)	0.01–0.5	2	77–85	81	–	Meth-183, rev. 2	TCI-07-163
OH-PT		0.01–0.5	2	86–89	88	–		
Tolfenpyrad	Potato (chips)	0.01–0.5	2	85–92	88	–	Meth-183, rev. 2	TCI-07-163
OH-PT		0.01–0.5	2	77–97	87	–		
Tolfenpyrad	Potato (wet peel)	0.01–0.5	2	70–91	80	–	Meth-183, rev. 2	TCI-07-163
OH-PT		0.01–0.5	2	75–80	78	–		
Tolfenpyrad	Tomato	0.01–1.0	18	70–101	81	8.2	Meth-183, rev. 2	TCI-07-164
OH-PT		0.01–1.0	18	71–115	99	11		
Tolfenpyrad	Tomato (puree)	0.01–0.5	2	71–80	76	–	Meth-183, rev. 2	TCI-07-164
OH-PT		0.01–0.5	2	99–103	101	–		
Tolfenpyrad	Tomato (paste)	0.01–0.5	2	87–102	94	–	Meth-183, rev. 2	TCI-07-164
OH-PT		0.01–0.5	2	99–120	110	–		
Tolfenpyrad	Pepper	0.01–0.5	8	71–90	78	6.3	Meth-183, rev. 2	TCI-07-164
OH-PT		0.01–0.5	8	92–112	103	6.7		
Tolfenpyrad	Cucumber	0.01–10	6	71–110	92	17	Meth-183, rev. 2	SARS-08-10
OH-PT		0.01–10	6	84–108	98	9.6		
Tolfenpyrad	Cantaloupe	0.01–10	4	96–107	99	5.3	Meth-183, rev. 2	SARS-08-11
OH-PT		0.01–10	4	87–99	96	6.0		
Tolfenpyrad	Summer Squash	0.01–10	4	86–111	99	14	Meth-183, rev. 2	SARS-08-12
OH-PT		0.01–10	4	88–98	93	4.9		
Tolfenpyrad	Cauliflower	0.01–5.0	8	75–119	89	16	Meth-183, rev. 2	SARS-07-07
OH-PT		0.01–5.0	8	87–104	95	5.4		
Tolfenpyrad	Cabbage	0.01–5.0	6	78–104	91	10	Meth-183, rev. 2	SARS-07-08
OH-PT		0.01–5.0	6	81–102	95	8.2		
Tolfenpyrad	Mustard Greens	0.01–20	5	80–90	85	6.0	Meth-183, rev. 2	SARS-07-09
OH-PT		0.01–20	5	86–102	96	6.4		
Tolfenpyrad	Leaf Lettuce	0.01–20	5	72–110	94	19	Meth-183, rev. 2	SARS-07-03
OH-PT		0.01–20	5	93–101	96	3.3		
Tolfenpyrad	Head Lettuce	0.01–10	8	81–104	91	7.9	Meth-183, rev. 2	SARS-07-04
OH-PT		0.01–10	8	87–106	97	6.5		
Tolfenpyrad	Celery	0.01–10	4	91–117	104	10	Meth-183, rev. 2	SARS-07-05
OH-PT		0.01–10	4	89–99	95	4.6		
Tolfenpyrad	Spinach	0.01–20	4	81–94	89	6.5	Meth-183, rev. 2	SARS-07-06
OH-PT		0.01–20	4	90–100	94	4.6		
Tolfenpyrad	Cotton (undelinted)	0.01–5.0	13	77–110	96	10	Meth-183, rev. 2	TCI-07-165
OH-PT		0.01–0.5	12	84–112	101	8.1		
Tolfenpyrad	Cotton (gin trash)	0.01–10	9	82–98	91	6.7	Meth-183, rev. 2	TCI-07-165
OH-PT		0.01–0.5	8	107–119	113	4.7		
Tolfenpyrad	Cotton Seed (hulls)	0.01–0.5	2	72–94	83	–	Meth-183, rev. 2	TCI-07-165
OH-PT		0.01–0.5	2	80–99	90	–		
Tolfenpyrad	Cotton Seed (meal)	0.01–0.5	2	85–98	92	–	Meth-183, rev. 2	TCI-07-165
OH-PT		0.01–0.5	2	114–120	117	–		
Tolfenpyrad	Cotton Seed (refined oil)	0.01–0.5	2	70	70	–	Meth-183, rev. 2	TCI-07-165
OH-PT		0.01–0.5	2	71–96	84	–		
Tolfenpyrad	Tea (green)	1.6–16	8	84–98	91	5	not specified ^a	R-10027

Analyte	Crop	Fortification (mg/kg)	n	Range Recovery	Mean Recovery	% RSD	Method	Reference
Tolfenpyrad	Tea (green)	0.05–100	12	85–118	99	11	not specified ^a	R-10097

^a Japan Food Research Laboratories owned method implemented in compliance with the official residue test method notified by Ministry of Environment (Japan)

The Method-183, rev-2 was subject to independent laboratory validation with undelinted cotton seed matrix (Boatwright, MT 2007, study no: 070269). The precision and accuracy data are summarized in Table 52.

Table 52 Precision and accuracy data for the determination of tolfenpyrad and OH-PT in undelinted cotton seed

Compound	Mass transition	Fortification (mg/kg)	Replicates	Recovery range (%)	Mean recovery (%)	RSD
Tolfenpyrad	384 → 197	0.01	5	92–110	102	7.4
		0.10	5	81–92	87	5.7
		All levels	10	81–110	95	11
OH-TP	400 → 197	0.01	5	93–108	102	6.1
		0.10	5	91–104	97	5.6
		All levels	10	91–108	99	6.0

The validation of analytical method no. 1898W for tolfenpyrad, OH-PAM, OH-PCA, and PAM in plant material (radish, lettuce and grain sorghum) was performed as part of the field rotational crop study (Carringer SJ 2010, Report no. R-10218). The samples were extracted with 100 mL and 2 × 50 mL 5:1methanol:water. Citric acid was added to an aliquot of the concentrated extracts the residues were partitioned into ethyl acetate, concentrated and subjected to SPE on ENVITM-Carbo Pack. A further aliquot of the sample solution was evaporated to dryness and reconstituted in hydrochloric acid (6 N, 5.0 mL). Samples were hydrolysed over night at 50 °C. After reaction the sample was transferred into a separating funnel by rinsing with 10 mL water, and then partitioned into ethyl acetate (20 mL) four times. The organic layers were combined, evaporated to dryness and reconstituted in ethyl acetate (10 mL). The sample was subjected to SPE-clean-up as mentioned above and subjected to HPLC-MS/MS analysis. Quantification and confirmation by external standard was performed using the following mass transitions.

Table 53 Mass transitions used for identification and quantification

Tolfenpyrad	OH-PAM	OH-PCA	PAM
384 → 198	204 → 144	203 → 159 ^a	188 → 118
384 → 154	204 → 107	203 → 88	188 → 145
	414 → 145	203 → 73 ^b	

^a Not used for stover analysis

^b Used for stover analysis only

For each analyte the sum of the response for each ion transition was monitored. The precision and accuracy data are given in Tables 54–57.

Table 54 Tolfenpyrad—precision and accuracy data

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
Radish Roots (without Hydrolysis)	0.01	3	92–129	106	19
	0.1	3	85–91	88	4
	All levels	6	85–129	97	16
Radish Roots (with Hydrolysis)	0.01	3	97–112	102	8
	0.1	3	91–93	92	1
	All levels	6	91–112	97	8

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
Lettuce (without Hydrolysis)	0.01	3	79–97	86	11
	0.1	3	85–88	87	2
	All levels	6	79–97	86	7
Lettuce (with Hydrolysis)	0.01	3	47–66	58	17
	0.1	3	59–63	61	3
	All levels	6	47–66	59	11
Sorghum Forage (without Hydrolysis)	0.01	3	86–102	92	10
	0.1	3	86–90	87	3
	All levels	6	86–102	90	7
Sorghum Forage (with Hydrolysis)	0.01	3	75–88	83	8
	0.1	3	53–65	57	12
	All levels	6	53–88	70	21
Sorghum Stover (without Hydrolysis)	0.01	3	82–85	84	2
	0.1	3	73–76	74	2
	All levels	6	73–85	79	7
Sorghum Stover (with Hydrolysis)	0.01	3	74–82	78	5
	0.1	3	61–69	65	6
	All levels	6	61–82	71	11
Sorghum Grain (without Hydrolysis)	0.01	3	63–65	64	2
	0.1	3	65–68	66	2
	All levels	6	63–68	65	3
Sorghum Grain (with Hydrolysis)	0.01	3	55–63	60	7
	0.1	3	45–51	49	7
	All levels	6	45–63	54	13

Table 55 PAM–precision and accuracy data

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
Radish Roots (without Hydrolysis)	0.01	3	77–86	81	6
	0.1	3	100–102	101	1
	All levels	6	77–102	91	12
Radish Roots (with Hydrolysis)	0.01	3	78–83	81	3
	0.1	3	85–87	86	1
	All levels	6	78–87	83	4
Lettuce (without Hydrolysis)	0.01	3	85–102	94	9
	0.1	3	92–94	93	1
	All levels	6	85–102	94	6
Lettuce (with Hydrolysis)	0.01	3	82–102	92	11
	0.1	3	82–87	85	3
	All levels	6	82–102	89	9
Sorghum Forage (without Hydrolysis)	0.01	3	96–101	98	3
	0.1	3	97–99	98	1
	All levels	6	96–101	98	2
Sorghum Forage (with Hydrolysis)	0.01	3	87–94	91	4
	0.1	3	79–80	79	1
	All levels	6	79–94	85	8
Sorghum Stover (without Hydrolysis)	0.01	3	86–89	87	2
	0.1	3	82–87	85	3
	All levels	6	82–89	86	3
Sorghum Stover (with Hydrolysis)	0.01	3	76–77	77	1
	0.1	3	77–78	77	1
	All levels	6	76–78	77	1
Sorghum Grain (without Hydrolysis)	0.01	3	100–100	100	0
	0.1	3	100–103	102	2
	All levels	6	100–103	101	1
Sorghum Grain (with Hydrolysis)	0.01	3	84–88	86	2
	0.1	3	84–89	86	3
	All levels	6	84–89	86	2

Table 56 OH-PAM—precision and accuracy data

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
Radish Roots (without Hydrolysis)	0.01	3	94–101	97	4
	0.1	3	83–84	83	1
	All levels	6	83–101	90	9
Radish Roots (with Hydrolysis)	0.01	3	65–69	67	3
	0.1	3	60–62	61	2
	All levels	6	60–69	64	5
Lettuce (without Hydrolysis)	0.01	3	83–99	91	9
	0.1	3	88–89	88	1
	All levels	6	83–99	90	6
Lettuce (with Hydrolysis)	0.01	3	50–69	61	16
	0.1	3	59–61	60	2
	All levels	6	50–69	60	10
Sorghum Forage (without Hydrolysis)	0.01	3	89–93	91	2
	0.1	3	92–94	93	1
	All levels	6	89–94	92	2
Sorghum Forage (with Hydrolysis)	0.01	3	67–72	69	4
	0.1	3	61–63	62	2
	All levels	6	61–72	65	7
Sorghum Stover (without Hydrolysis)	0.01	3	91–93	92	1
	0.1	3	85–91	88	3
	All levels	6	85–93	90	3
Sorghum Stover (with Hydrolysis)	0.01	3	60–63	61	2
	0.1	3	59–61	60	2
	All levels	6	59–63	61	2
Sorghum Grain (without Hydrolysis)	0.01	3	84–88	86	2
	0.1	3	84–87	85	2
	All levels	6	84–88	86	2
Sorghum Grain (with Hydrolysis)	0.01	3	60–60	60	0
	0.1	3	59–60	59	1
	All levels	6	59–60	60	1

Table 57 OH-PCA—precision and accuracy data

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
Radish Roots (without Hydrolysis)	0.01	3	89–104	97	8
	0.1	3	132–145	138	5
	All levels	6	89–145	118	20
Radish Roots (with Hydrolysis)	0.01	3	70–78	73	6
	0.1	3	105–106	105	1
	All levels	6	70–106	89	20
Lettuce (without Hydrolysis)	0.01	3	70–91	82	13
	0.1	3	107–111	110	2
	All levels	6	70–111	96	18
Lettuce (with Hydrolysis)	0.01	3	94–104	98	5
	0.1	3	78–83	81	4
	All levels	6	78–104	90	11
Sorghum Forage (without Hydrolysis)	0.01	3	73–77	75	3
	0.1	3	111–116	114	2
	All levels	6	73–116	94	22
Sorghum Forage (with Hydrolysis)	0.01	3	73–101	84	18
	0.1	3	75–90	80	11
	All levels	6	73–101	82	13
Sorghum Stover (without Hydrolysis)	0.01	3	112–114	113	1
	0.1	3	88–93	90	3
	All levels	6	88–114	101	13
Sorghum Stover (with Hydrolysis)	0.01	3	70–80	75	7
	0.1	3	82–87	84	3

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
	All levels	6	70–87	80	8
Sorghum Grain (without Hydrolysis)	0.01	3	112–120	115	4
	0.1	3	96–98	97	1
	All levels	6	96–120	106	10
Sorghum Grain (with Hydrolysis)	0.01	3	112–116	114	2
	0.1	3	92–97	95	3
	All levels	6	92–116	105	10

Animal commodities

Animal tissues—Method 1841 W (Ref: 1841 W-1; R-10215, A-10042e)

Residues of tolfenpyrad and its metabolites PT-CA, OH-PT-CA and PCA were extracted twice from the sample with either methanol (milk) or a methanol /water mixture (muscle, liver, kidney and fat) by high speed homogenisation. The crude extract from each extraction was vacuum filtered, then combined. The combined filtrates were reduced to below the aqueous remainder and subjected to a liquid-liquid partition into ethyl acetate. The organic phases were combined and the muscle, kidney and fat extracts were evaporated dryness. The extract of muscle and kidney were reconstituted in methanol and subjected to HPLC-MS/MS analysis. Fat samples were reconstituted in hexane and subjected to SPE clean-up. For milk and liver samples, the extracts were split into two equivalent aliquots. The first was evaporated to dryness, reconstituted in methanol and subjected to HPLC-MS/MS analysis; the second was subjected to hydrolysis.

SPE Clean-up for fat only:

The fat sample was cleaned-up on Bond Elute SPE cartridge. The eluate containing the residues was split into two equivalent aliquots. The first was evaporated to dryness and reconstituted in methanol for direct HPLC-MS/MS analysis. The second was subjected to hydrolysis.

Hydrolysis (milk, liver and fat)

The sample extract was evaporated to dryness and reconstituted in an aqueous potassium hydroxide solution and subjected to hydrolysis for at least 15 hours at room temperature. The solution was adjusted to pH < 3, and the residues were partitioned into ethyl acetate four times. The combined organic layers were evaporated to dryness and reconstituted in methanol.

HPLC-MS/MS-analysis

Final sample extracts were analysed by high performance liquid chromatography with tandem mass specific detection (LC MS/MS) using specific mass transitions for tolfenpyrad (384 → 197; 384 → 154) and three transitions for PT-CA (414 → 117; 414 → 227; 414 → 145), OH-PT-CA (430 → 412; 430 → 394; 430 → 227) and PCA (189 → 117; 189 → 129; 189 → 145).

Linearity of detector response was demonstrated using five concentrations of external standard across the range of 2.0–120 ng/ml, with correlation coefficients of > 0.994.

The method allows the determination of tolfenpyrad and its metabolites PT-CA, OH-PT-CA and PCA. The LOQ for both compounds in all matrices is 0.01 mg/kg.

The method was also subjected to independent laboratory validation with muscle, liver fat and milk matrices (Class, T, Göcer, M 2010. Report no A-10042). The results concurred with those of initial validation.

A summary of the method validation and procedural recoveries for commodities included in this evaluation are summarized in Table 58.

Table 58 Summary of method validation and concurrent recovery data

Analyte	Crop	Fortification (mg/kg)	n	Range Recovery	Mean Recovery	% RSD	Reference
Method Validation							
Tolfenpyrad	Muscle	0.01–0.1	6	89–97	93	4	1841 W-1
PT-CA		0.01–0.1	6	82–92	87	5	
OH-PT-CA		0.01–0.1	6	77–92	85	8	
Tolfenpyrad	Muscle	0.01–0.1	10	62–98	83	16	P/B 1750 G
PT-CA		0.01–0.1	10	62–99	83	15	
OH-PT-CA		0.01–0.1	10	80–111	98	9	
Tolfenpyrad	Liver (without hydrolysis)	0.01–0.1	6	81–105	91	9	1841 W-1
PT-CA		0.01–0.1	6	79–92	86	5	
OH-PT-CA		0.01–0.4	9	75–123	95	19	
Tolfenpyrad	Liver (without hydrolysis)	0.01–0.1	10	70–92	83	8	P/B 1750 G
PT-CA		0.01–0.1	10	71–100	90	10	
OH-PT-CA		0.01–0.1	10	82–110	97	10	
Tolfenpyrad	Liver (with hydrolysis)	0.01–0.1	6	74–88	83	6	1841 W-1
PT-CA		0.01–10	9	62–88	75	13	
OH-PT-CA		0.01–0.4	9	53–95	75	22	
Tolfenpyrad	Liver (with hydrolysis)	0.01–0.1	10	75–95	83	7	P/B 1750 G
PT-CA		0.01–0.1	10	81–104	90	8	
OH-PT-CA		0.01–0.1	10	77–107	87	13	
Tolfenpyrad	Kidney	0.01–0.1	6	99–106	102	3	1841 W-1
PT-CA		0.01–3.0	9	91–112	100	8	
OH-PT-CA		0.01–0.1	6	85–105	97	9	
Tolfenpyrad	Kidney	0.01–0.1	10	83–93	88	4	P/B 1750 G
PT-CA		0.01–0.1	10	92–100	96	3	
OH-PT-CA		0.01–0.1	10	95–116	106	6	
Tolfenpyrad	Fat (without hydrolysis)	0.01–0.1	6	83–107	98	9	1841 W-1
PT-CA		0.01–0.1	6	75–89	83	6	
OH-PT-CA		0.01–0.1	6	71–96	84	11	
PCA		0.01–0.1	6	74–96	88	9	
Tolfenpyrad	Fat (without hydrolysis)	0.01–0.1	10	64–102	86	12	P/B 1750 G
PT-CA		0.01–0.1	10	91–102	98	4	
OH-PT-CA		0.01–0.1	10	86–99	94	5	
PCA		0.01–0.1	10	88–102	96	4	
Tolfenpyrad	Fat (with hydrolysis)	0.01–0.1	6	79–110	95	13	1841 W-1
PT-CA		0.01–0.1	6	57–73	66	10	
OH-PT-CA		0.01–0.1	6	60–72	67	6	
PCA		0.01–0.1	6	73–104	90	13	
Tolfenpyrad	Fat (with hydrolysis)	0.01–0.1	10	59–100	82	14	P/B 1750 G
PT-CA		0.01–0.1	10	74–97	87	8	
OH-PT-CA		0.01–0.1	10	63–81	74	7	
PCA		0.01–0.1	10	94–112	103	6	
Tolfenpyrad	Milk (without hydrolysis)	0.01–0.1	6	85–97	90	5	1841 W-1
PT-CA		0.01–0.1	6	79–98	90	9	
OH-PT-CA		0.01–0.1	6	74–96	85	14	
PCA		0.01–0.1	6	82–98	92	8	
Tolfenpyrad	Milk (without hydrolysis)	0.01–0.1	10	88–100	94	5	P/B 1750 G
PT-CA		0.01–0.1	10	89–102	95	4	
OH-PT-CA		0.01–0.1	10	88–96	91	3	
PCA		0.01–0.1	10	87–102	96	5	
Tolfenpyrad	Milk (with hydrolysis)	0.01–0.1	6	80–87	83	3	1841 W-1
PT-CA		0.01–1.0	12	73–96	83	9	
OH-PT-CA		0.01–0.1	6	75–112	90	18	
PCA		0.01–0.1	6	78–102	91	11	
Tolfenpyrad	Milk (with hydrolysis)	0.01–0.1	10	85–101	95	6	P/B 1750 G
PT-CA		0.01–0.1	10	86–100	92	6	
OH-PT-CA		0.01–0.1	10	77–92	84	6	
PCA		0.01–0.1	10	100–112	106	4	

Analyte	Crop	Fortification (mg/kg)	n	Range Recovery	Mean Recovery	% RSD	Reference
Procedural Recoveries							
Tolfenpyrad	Milk (without hydrolysis)	0.01–0.5	71	53–108	82	11	1841 W-1
PT-CA		0.01–0.5	72	50–116	96	10	
OH-PT-CA		0.01–0.5	70	56–128	101	12	
PCA		0.01–0.5	70	66–125	100	11	
Tolfenpyrad	Milk (with hydrolysis)	0.01–0.5	70	634–164	83	13	1841 W-1
PT-CA		0.01–0.5	70	68–131	91	14	
OH-PT-CA		0.01–0.5	70	64–145	95	21	
PCA		0.01–0.5	70	73–133	103	11	
Tolfenpyrad	Skimmed Milk (without hydrolysis)	0.01–0.5	6	87–106	95	8	1841 W-1
PT-CA		0.01–0.5	6	95–117	103	7	
OH-PT-CA		0.01–0.5	6	91–127	112	11	
PCA		0.01–0.5	6	98–118	109	6	
Tolfenpyrad	Skimmed Milk (with hydrolysis)	0.01–0.5	6	78–99	91	9	1841 W-1
PT-CA		0.01–0.5	6	70–109	95	14	
OH-PT-CA		0.01–0.5	6	86–116	103	10	
PCA		0.01–0.5	6	94–128	116	10	
Tolfenpyrad	Cream (without hydrolysis)	0.01–0.5	6	68–86	79	10	1841 W-1
PT-CA		0.01–0.5	6	100–109	103	3	
OH-PT-CA		0.01–0.5	6	100–122	112	7	
PCA		0.01–0.5	6	96–141	112	17	
Tolfenpyrad	Cream (with hydrolysis)	0.01–0.5	6	60–79	70	13	1841 W-1
PT-CA		0.01–0.5	6	73–105	89	12	
OH-PT-CA		0.01–0.5	6	71–90	82	10	
PCA		0.01–0.5	6	96–124	106	9	
Tolfenpyrad	Muscle	0.01–0.1	10	81–110	97	10	1841 W-1
PT-CA		0.01–0.1	10	70–113	95	14	
OH-PT-CA		0.01–0.1	10	70–118	99	14	
Tolfenpyrad	Liver (without hydrolysis)	0.01–0.1	4	76–101	89	13	1841 W-1
PT-CA		0.01–0.1	4	73–105	94	15	
OH-PT-CA		0.01–0.1	4	59–105	83	23	
Tolfenpyrad	Liver (with hydrolysis)	0.01–0.1	4	69–94	82	13	1841 W-1
PT-CA		0.01–0.1	4	60–90	79	16	
OH-PT-CA		0.01–0.1	4	60–86	71	15	
Tolfenpyrad	Kidney	0.01–0.1	6	81–102	93	9	1841 W-1
PT-CA		0.01–0.1	6	84–93	91	3	
OH-PT-CA		0.01–0.1	6	77–107	91	12	
Tolfenpyrad	Fat (without hydrolysis)	0.01–0.1	12	80–98	92	7	1841 W-1
PT-CA		0.01–0.1	12	92–114	101	8	
OH-PT-CA		0.01–0.1	12	88–138	106	13	
PCA		0.01–0.1	12	96–127	106	8	
Tolfenpyrad	Fat (with hydrolysis)	0.01–0.1	12	79–97	89	6	1841 W-1
PT-CA		0.01–0.1	12	72–90	80	6	
OH-PT-CA		0.01–0.1	12	67–87	80	6	
PCA		0.01–0.1	12	104–121	112	4	

Stability of pesticide residues in stored analytical samples

Plant commodities

The studies were conducted in a similar manner. Aliquots of pre-homogenised commodities (5 g) were spiked with test solutions and stored at about -20 ± 5 °C for various intervals ranging from 5 month to 18 months. With exception of the day zero interval, samples for frozen storage were fortified individually with either tolfenpyrad or OH-PT. The samples were analysed with Method 183-rev 2.

Study 1 (Reed, RL., Report no. R-10183)

Table 59 Summary of freezer storage stability data for tolfenpyrad in tomatoes, apples, head lettuce, grapes, oranges, almonds (nutmeat and hulls), potato flakes and cottonseed oil spiked at 0.1 mg/kg level

Matrix	Storage Interval months / days	Procedural Recovery (%)	Residue remained (%)
Tomato	0 / 0	84 (n=2)	–
	1 / 32	90 (n=2)	92 (n=2)
	4 / 111	76 (n=2)	78 (n=2)
	6 / 182	77 (n=2)	79 (n=2)
	12 / 364	78 (n=2)	78 (n=2)
	18 / 551	84 (n=2)	88 (n=2)
Apple	0 / 0	73 (n=2)	–
	1 / 29	94 (n=2)	93 (n=2)
	4 / 106	76 (n=2)	84 (n=2)
	6 / 183	79 (n=2)	87 (n=2)
	12 / 358	76 (n=2)	79 (n=2)
	18 / 549	83 (n=2)	82 (n=2)
Head Lettuce	0 / 0	90 (n=2)	–
	1 / 33	78 (n=2)	78 (n=2)
	4 / 110	78 (n=2)	81 (n=2)
	6 / 182	75 (n=2)	76 (n=2)
	12 / 363	82 (n=2)	78 (n=2)
	18 / 553	78 (n=2)	82 (n=2)
Grapes	0 / 0	90 (n=2)	–
	1 / 32	70 (n=2)	76 (n=2)
	4 / 111	115 (n=2)	90 (n=2)
	6 / 183	81 (n=2)	98 (n=2)
	12 / 364	76 (n=2)	78 (n=2)
	18 / 558	80 (n=2)	85 (n=2)
Orange	0 / 0	82 (n=2)	–
	1 / 33	88 (n=2)	88 (n=2)
	4 / 110	82 (n=2)	78 (n=2)
	6 / 182	77 (n=2)	80 (n=2)
	12 / 363	77 (n=2)	78 (n=2)
	18 / 553	76 (n=2)	76 (n=2)
Almond Nutmeat	0 / 0	78 (n=2)	–
	1 / 29	84 (n=2)	82 (n=2)
	4 / 105	91 (n=2)	89 (n=2)
	6 / 183	90 (n=2)	89 (n=2)
	12 / 358	82 (n=2)	80 (n=2)
	18 / 551	74 (n=2)	78 (n=1)
Almond Hulls	0 / 0	71 (n=2)	–
	1 / 31	79 (n=2)	72 (n=2)
	4 / 111	76 (n=2)	64 (n=2)
	6 / 182	76 (n=2)	76 (n=2)
	12 / 363	72 (n=2)	66 (n=2)
	18 / 553	76 (n=2)	76 (n=2)
Potato Flakes	0 / 0	80 (n=2)	–
	1 / 34	74 (n=2)	66 (n=2)
	4 / 111	77 (n=2)	68 (n=2)
	6 / 185	78 (n=2)	66 (n=2)
	12 / 367	77 (n=2)	68 (n=2)
	18 / 556	78 (n=2)	65 (n=2)
Cotton- seed Oil	0 / 0	98 (n=2)	–
	1 / 35	82 (n=2)	82 (n=2)
	3 / 99	82 (n=2)	84 (n=2)
	8 / 228	62 (n=2)	74 (n=2)
	12 / 370	84 (n=2)	97 (n=2)
	18 / 559	84 (n=2)	77 (n=2)

Table 60 Summary of freezer storage stability data for OH-PT in tomato, apple, head lettuce, grapes, orange, almond (nutmeat and hulls), potato flakes and cottonseed oil spiked at 0.1 mg/kg level

Matrix	Storage Interval months / days	Procedural Recovery (%)	Residue remained (%)
Tomato	0 / 0	93 (n=2)	–
	1 / 32	105 (n=2)	106 (n=2)
	4 / 111	92 (n=2)	100 (n=2)
	6 / 182	88 (n=2)	90 (n=2)
	12 / 364	98 (n=2)	96 (n=2)
	18 / 551	96 (n=2)	91 (n=2)
Apple	0 / 0	98 (n=2)	–
	1 / 29	100 (n=2)	103 (n=2)
	4 / 106	97 (n=2)	100 (n=2)
	6 / 183	88 (n=2)	94 (n=2)
	12 / 358	84 (n=2)	84 (n=2)
	18 / 549	88 (n=2)	90 (n=2)
Head Lettuce	0 / 0	92 (n=2)	–
	1 / 33	120 (n=2)	100 (n=2)
	4 / 110	110 (n=2)	98 (n=2)
	6 / 182	86 (n=2)	90 (n=2)
	12 / 363	93 (n=2)	88 (n=2)
	18 / 553	89 (n=2)	85 (n=2)
Grapes	0 / 0	83 (n=2)	–
	1 / 32	95 (n=2)	95 (n=2)
	4 / 111	120 (n=2)	120 (n=2)
	6 / 183	104 (n=2)	103 (n=2)
	12 / 364	85 (n=2)	94 (n=2)
	18 / 558	88 (n=2)	88 (n=2)
Orange	0 / 0	82 (n=2)	–
	1 / 33	100 (n=2)	103 (n=2)
	4 / 110	101 (n=2)	100 (n=2)
	6 / 182	87 (n=2)	84 (n=2)
	12 / 363	88 (n=2)	88 (n=2)
	18 / 553	89 (n=2)	84 (n=2)
Almond Nutmeat	0 / 0	90 (n=2)	–
	1 / 29	95 (n=2)	95 (n=2)
	4 / 105	94 (n=2)	96 (n=2)
	6 / 183	90 (n=2)	88 (n=2)
	12 / 358	86 (n=2)	90 (n=2)
	18 / 551	84 (n=2)	86 (n=2)
Almond Hulls	0 / 0	80 (n=2)	–
	1 / 31	98 (n=2)	98 (n=2)
	4 / 111	89 (n=2)	92 (n=2)
	6 / 182	100 (n=2)	106 (n=2)
	12 / 363	78 (n=2)	84 (n=2)
	18 / 553	78 (n=2)	82 (n=2)
Potato Flakes	0 / 0	88 (n=2)	–
	1 / 34	90 (n=2)	88 (n=2)
	4 / 111	99 (n=2)	82 (n=2)
	6 / 185	88 (n=2)	90 (n=2)
	12 / 367	89 (n=2)	87 (n=2)
	18 / 556	90 (n=2)	83 (n=2)
Cotton- seed Oil	0 / 0	106 (n=2)	–
	1 / 35	108 (n=2)	92 (n=2)
	3 / 99	102 (n=2)	94 (n=2)
	8 / 228	92 (n=2)	96 (n=2)
	12 / 370	84 (n=2)	87 (n=2)
	18 / 559	82 (n=2)	76 (n=2)

Study 2 (Greenland, RG 2009a, Report no. R-10178)

Table 61 Summary of freezer storage stability data for tolfenpyrad in almond nutmeat and hulls

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residue remained (%)
Almond Nutmeat	0 / 0	0.01	96 (n=3)	–
		5.0	94 (n=3)	–
	1.5 / 45	0.01	95 (n=1)	90 (n=1)
		5.0	81 (n=1)	88 (n=1)
	4 / 119	0.01	106 (n=1)	95 (n=1)
		5.0	82 (n=1)	96 (n=1)
Almond Hulls	0 / 0	0.01	91 (n=3)	–
		5.0	104 (n=3)	–
	1.5 / 45	0.01	93 (n=1)	96 (n=1)
		5.0	97 (n=1)	96 (n=1)
	4 / 119	0.01	103 (n=1)	91 (n=1)
		5.0	76 (n=1)	99 (n=1)

Table 62 Summary of freezer storage stability data for OH-PT in almond nutmeat and hulls

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residue remained (%)
Almond Nutmeat	0 / 0	0.01	94 (n=3)	–
		5.0	100 (n=3)	–
	1.5 / 45	0.01	85 (n=1)	95 (n=1)
		5.0	95 (n=1)	95 (n=1)
	4 / 119	0.01	96 (n=1)	104 (n=1)
		5.0	91 (n=1)	103 (n=1)
Almond Hulls	0 / 0	0.01	100 (n=3)	–
		5.0	103 (n=3)	–
	1.5 / 45	0.01	94 (n=1)	94 (n=1)
		5.0	106 (n=1)	92 (n=1)
	4 / 119	0.01	95 (n=1)	100 (n=1)
		5.0	97 (n=1)	102 (n=1)

Study 3 (Greenland, RG 2009.b, Report no. R-10175)

Table 63 Summary of freezer storage stability data for tolfenpyrad in peach and dried prune

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residues remained (%)
Peach	0 / 0	0.01	94 (n=3)	–
		5.3	106 (n=3)	–
	1.7 / 50	0.01	94 (n=1)	82 (n=1)
		4.9	99 (n=1)	99 (n=1)
	4 / 124	0.01	88 (n=1)	92 (n=1)
		4.7	86 (n=1)	93 (n=1)
Dried Prune	0 / 0	0.01	94 (n=3)	–
		4.9	98 (n=3)	–
	1 / 33	0.01	90 (n=1)	97 (n=1)
		4.7	109 (n=1)	94 (n=1)
	2 / 63	0.01	93 (n=1)	91 (n=1)
		4.8	102 (n=1)	96 (n=1)
	5 / 154	0.01	100 (n=1)	98 (n=1)
		4.7	100 (n=1)	94 (n=1)

Table 64 Summary of freezer storage stability data for OH-PT in peach and dried prune

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural Recovery (%)	Residue remained (%)
Peach	0 / 0	0.01	96 (n=3)	–
		4.9	99 (n=3)	–
	1.7 / 50	0.01	90 (n=1)	88 (n=1)
		4.6	92 (n=1)	93 (n=1)
	4 / 124	0.01	91 (n=1)	90 (n=1)
		4.9	97 (n=1)	98 (n=1)
Dried Prune	0 / 0	0.01	97 (n=3)	–
		4.8	98 (n=3)	–
	1 / 33	0.01	95 (n=1)	97 (n=1)
		4.7	117 (n=1)	93 (n=1)
	2 / 63	0.01	95 (n=1)	93 (n=1)
		4.8	103 (n=1)	96 (n=1)
	5 / 154	0.01	98 (n=1)	98 (n=1)
		4.7	89 (n=1)	94 (n=1)

Study 4 (Greenland, RG 2009c, Report no. R-10179)

Table 65 Summary of freezer storage stability data for tolfenpyrad and OH-TP in cucumbers

Storage Interval months / days	Fortification Level (mg/kg)	Tolfenpyrad		OH-PT	
		Procedural recovery (%)	Residue remained (%)	Procedural recovery (%)	Residue remained (%)
0 / 0	0.01	83 (n=3)	–	93 (n=3)	–
	10	93 (n=3)	–	98 (n=3)	–
2.8 / 86	0.01	84 (n=1)	87 (n=1)	94 (n=1)	90 (n=1)
	10	95 (n=1)	93 (n=1)	100 (n=1)	91 (n=1)
5.5 / 171	0.01	99 (n=1)	97 (n=1)	87 (n=1)	95 (n=1)
	10	99 (n=1)	94 (n=1)	95 (n=1)	90 (n=1)

Study 5 (Stewart, ER 2008a, Report no. R-10165)

Table 66 Summary of freezer storage stability data for tolfenpyrad and OH-TP in cauliflower

Storage Interval months / days	Fortification Level (mg/kg)	Tolfenpyrad		OH-PT	
		Procedural recovery (%)	Residue remained (%)	Procedural recovery (%)	Residue remained (%)
0 / 0	0.01	85 (n=3)	–	89 (n=3)	–
	5.4	109 (n=3)	–	89 (n=3)	–
3.0 / 95	0.01	73 (n=1)	75 (n=1)	95 (n=1)	101 (n=1)
	5	91 (n=1)	93 (n=1)	98 (n=1)	96 (n=1)
5.8 / 180	0.01	81 (n=1)	79 (n=1)	99 (n=1)	99 (n=1)
	5	95 (n=1)	91 (n=1)	94 (n=1)	91 (n=1)

Study 6 (Stewart, ER 2008b, Report no. R-10164)

Table 67 Summary of freezer storage stability data for tolfenpyrad and OH-TP in head lettuce

Storage Interval months / days	Fortification Level (mg/kg)	Tolfenpyrad		OH-PT	
		Procedural recovery (%)	Residue remained (%)	Procedural recovery (%)	Residue remained (%)
0 / 0	0.01	94 (n=3)	–	95 (n=3)	–
	5.0	91 (n=3)	–	98 (n=3)	–
3.0 / 96	0.01	91 (n=1)	82 (n=1)	97 (n=1)	98 (n=1)
	4.9	102 (n=1)	89 (n=1)	100 (n=1)	90 (n=1)
9.3 / 287	0.01	90 (n=1)	82 (n=1)	102 (n=1)	65 (n=1)
	5.0	102 (n=1)	86 (n=1)	101 (n=1)	56 (n=1)

Study 7 Yabusaki, T 2010a

The frozen storage stability of tolfenpyrad in tea was studied by analysing fortified samples after 71–360 days of storage at -20 °C.

Table 68 Summary of freezer storage stability data for tolfenpyrad in tea

Matrix	Storage Interval months / days	Fortification Level (mg/kg)	Procedural recovery (%)	Residue remained (%)
Tea	11.6 / 349	1.6	90 (n=4)	–
		2.0	–	93 (n=2)
	12 / 360	1.6	90 (n=4)	–
		2.0	–	94 (n=2)
Tea	2 / 71	1.0	100 (n=2)	–
		1.0	–	96 (n=2)
	2 / 71	1.0	99 (n=2)	–
		1.0	–	95 (n=2)

*Animal commodities**Study 8 (Arndt, T 2010, Report no. R-10215)*

The stability of residues in bovine tissues and milk was determined as part of the animal feeding study.

Fortification solutions containing tolfenpyrad, PT-CA, OH-PT-CA and PCA were added to aliquots of pre-homogenised commodities (10 g) at a fortification level of 0.10 mg/kg. After evaporation of the solvent, samples were stored frozen (< 0 °C) for intervals of 177 days for milk, 85 days for muscle and kidney, 111 days for liver and 99 days for fat. With exception of the day zero interval, samples for frozen storage were fortified individually with either tolfenpyrad or one of the metabolites. Residue analysis of stored samples was performed with *Method 1841 W*, as described under residue analytical methods.

Table 69 Summary of freezer storage stability data for tolfenpyrad in bovine tissue and milk

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residues remained (%)
Muscle	2.8 / 85	0.10	85 (n=2)	75 (n=3)
Liver (without hydrolysis)	3.6 / 111	0.10	62 (n=2)	58 (n=3)
Liver (with hydrolysis)	3.6 / 111	0.10	71 (n=2)	68 (n=3)
Kidney	2.8 / 85	0.10	86 (n=2)	73 (n=3)
Fat (without hydrolysis)	3.3 / 99	0.10	79 (n=2)	78 (n=3)
Fat (with hydrolysis)	3.3 / 99	0.10	75 (n=2)	71 (n=3)
Milk (without hydrolysis)	5.8 / 177	0.10	93 (n=2)	82 (n=3)
Milk (with hydrolysis)	5.8 / 177	0.10	78 (n=2)	74 (n=3)

Table 70 Summary of freezer storage stability data for PT-CA in bovine tissue and milk

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residues remained (%)
Muscle	2.8 / 85	0.10	89 (n=2)	78 (n=3)
Liver (without hydrolysis)	3.6 / 111	0.10	62 (n=2)	60 (n=3)
Liver (with hydrolysis)	3.6 / 111	0.10	56 (n=2)	54 (n=3)
Kidney	2.8 / 85	0.10	90 (n=2)	78 (n=3)
Fat (without hydrolysis)	3.3 / 99	0.10	94 (n=2)	98 (n=3)
Fat (with hydrolysis)	3.3 / 99	0.10	72 (n=2)	69 (n=3)
Milk (without hydrolysis)	5.8 / 177	0.10	102 (n=2)	95 (n=3)
Milk (with hydrolysis)	5.8 / 177	0.10	80 (n=2)	83 (n=3)

Table 71 Summary of freezer storage stability data for OH-PT-CA in bovine tissue and milk

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residues remained (%)
Muscle	2.8 / 85	0.10	93 (n=2)	83 (n=3)
Liver (without hydrolysis)	3.6 / 111	0.10	48 (n=2)	45 (n=3)
Liver (with hydrolysis)	3.6 / 111	0.10	41 (n=2)	39 (n=3)
Kidney	2.8 / 85	0.10	87 (n=2)	73 (n=3)
Fat (without hydrolysis)	3.3 / 99	0.10	95 (n=2)	98 (n=3)
Fat (with hydrolysis)	3.3 / 99	0.10	64 (n=2)	67 (n=3)
Milk (without hydrolysis)	5.8 / 177	0.10	117 (n=2)	112 (n=3)
Milk (with hydrolysis)	5.8 / 177	0.10	124 (n=2)	126 (n=3)

Table 72 Summary of freezer storage stability data for PCA in bovine tissue and milk

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residues remained (%)
Fat (without hydrolysis)	3.3 / 99	0.10	97 (n=2)	98 (n=3)
Fat (with hydrolysis)	3.3 / 99	0.10	101 (n=2)	101 (n=3)
Milk (without hydrolysis)	5.8 / 177	0.10	108 (n=2)	103 (n=3)
Milk (with hydrolysis)	5.8 / 177	0.10	100 (n=2)	108 (n=3)

USE PATTERN

The compound was only registered in Japan on teas. One foliar application of 15% EC formulation can be performed with 0.01–0.015 kg ai/ha using 2000–4000 L/ha water. The PHI is 14 days.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised field trials involving foliar applications of tolfenpyrad to the following crops.

Group	Crop	Country	Table
Citrus fruits	Orange, grapefruit, lemon	USA	73
Pome fruits	Pears	USA	74
Stone fruits	Cherry (sweet), peach, plum	USA	75
Fruiting vegetables–cucurbits	Cucumber, cantaloupe, summer squash	USA	76
Fruiting vegetables–other than cucurbits	Pepper (bell and chilli) tomato	USA	77
Root and tuber vegetables	Potato	USA	No residue
Tree nuts	Almond, pecan	USA	78
Oilseed	Cotton	USA	79
Processed food of plant origin	Tea	Japan	80
Animal feed	Almond hulls	USA	81
	Cotton gin trash	USA	82

The supervised trials were well documented with laboratory and field reports. Laboratory reports included method validation and provided information on procedural recoveries with spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analyses or duration of residue sample storage were also provided. No residues were detected in any of the control samples. The residues of OH-TP were looked for in all samples, but none of the samples contained it in detectable amounts, except cotton gin trash. These results are not included in the summary tables hereunder. In cotton gin trash, residues of OH-PT residues were in the range of 0.01–0.05 mg/kg. Residue data are recorded unadjusted for analytical recoveries.

Results from replicated field plots are presented as individual values. Results of repeated analyses are reported with the mean value. When residues were below the limit of quantification, they are reported as < LOQ (*e.g.* < 0.01 mg/kg).

Citrus fruits

Twenty-three residue trials were conducted on citrus fruit in the USA during 2007 and 2008 (Wyatt, DR 2008a, Report no. R-10173), 12 trials on oranges, six on grapefruit and five on lemons. In each trial, two treatments were applied by air blast sprayer (mist blower) at a rate of 0.3 kg ai/ha with an interval of 14 days. Two formulations of tolfenpyrad were used: 15% EC formulation, and a 15% SC formulation.

One untreated control and one or two treated plots were established at each test site. Five trials tested the 15EC formulation only (two orange and three grapefruit trials) and seven trials tested the 15% SC formulation only (four orange and three lemon trials). Eleven bridging trials (six orange, three grapefruit and two lemon) tested both formulations in a side-by-side comparison.

All crops were harvested at commercial maturity, 14 or 15 days after the second application. Each RAC sample was comprised of 24 fruit weighed a minimum of 2 kg. The citrus RAC samples were generally placed on dry ice or in freezer storage within approximately 3.0 hours after collection from the field.

Procedural mean recoveries at fortification levels in the range of 0.01 mg/kg to 1.0 mg/kg were in the range of 82% to 103%. Citrus samples were stored for 162 days prior to analysis.

Table 73 Summary of the tolfenpyrad residues in citrus treated two times with 0.3 kg ai/ha

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Oviedo, ^a Florida/2007 Trial: TCI-07- 184-01	Orange / Navel	EC	1) 0.306 2) 0.307	1) 1899 2) 1899	1) 0.016 2) 0.016	whole fruit	7 14 21 28	0.33 0.25 0.22 0.15
Oviedo, ^a Florida/2007 Trial: TCI-07- 184-02	Orange / Hamlin	EC	1) 0.299 2) 0.296	1) 842 2) 833	1) 0.036 2) 0.036	whole fruit	14	0.93 ^a
Mims, Florida/2007 Trial: TCI-07- 184-03	Orange / Hamlin	EC	1) 0.303 2) 0.307	1) 1889 2) 1918	1) 0.016 2) 0.016	whole fruit	14	0.62 ^a
Bithlo, Florida/2007 Trial: TCI-07- 184-04	Orange / Hamlin	EC	1) 0.295 2) 0.294	1) 842 2) 842	1) 0.036 2) 0.036	whole fruit	14	0.64 ^a
Holopaw, Florida/2007 Trial: TCI-07- 184-05	Orange / Mid Sweet	EC	1) 0.304 2) 0.304	1) 1890 2) 1890	1) 0.016 2) 0.016	whole fruit	14	0.43
Porterville, California/2008 Trial: TCI-07- 184-10	Orange / Valencia	EC	1) 0.299 2) 0.305	1) 851 2) 851	1) 0.036 2) 0.036	whole fruit	14	0.57 ^a
Porterville, California/2007 Trial: TCI-07- 184-11	Orange / Atwood Navel	EC	1) 0.300 2) 0.307	1) 1665 2) 1702	1) 0.018 2) 0.018	whole fruit	14	0.27
Richgrove, California/2007 Trial: TCI-07- 184-12	Orange / Atwood Navel	EC	1) 0.306 2) 0.305	1) 739 2) 945	1) 0.041 2) 0.032	whole fruit	14	0.33
Mims, Florida/2007 Trial: TCI-07- 184-03	Orange / Hamlin	SC	1) 0.297 2) 0.299	1) 1852 2) 1861	1) 0.016 2) 0.016	whole fruit	14	0.35
Bithlo, Florida/2007 Trial: TCI-07- 184-04	Orange / Hamlin	SC	1) 0.298 2) 0.298	1) 851 2) 851	1) 0.035 2) 0.035	whole fruit	14	0.58
Holopaw, Florida/2007 Trial: TCI-07- 184-05	Orange / Mid Sweet	SC	1) 0.305 2) 0.304	1) 1899 2) 1899	1) 0.016 2) 0.016	whole fruit	14	0.52 ^a
Clermont, Florida /2008 Trial: TCI-07- 184-06	Orange / Valencia	SC	1) 0.305 2) 0.301	1) 861 2) 851	1) 0.035 2) 0.035	whole fruit	14	0.21 ^a
Oviedo, Florida /2008 Trial: TCI-07- 184-07	Orange / Valencia	SC	1) 0.300 2) 0.299	1) 1777 2) 1768	1) 0.017 2) 0.017	whole fruit	14	0.47
			1) 1.50 2) 1.48	1) 1777 2) 1759	1) 0.084 2) 0.084	whole fruit	14	0.99
Winter Garden, Florida /2008 Trial: TCI-07-	Orange / Valencia	SC	1) 0.296 2) 0.297	1) 814 2) 814	1) 0.036 2) 0.036	whole fruit	14	0.39 ^a

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
184-08								
Alamo, Texas /2007 Trial: TCI-07- 184-09	Orange / N-33 Navel	SC	1) 0.300 2) 0.305	1) 2451 2) 2526	1) 0.012 2) 0.012	whole fruit	14	0.24 ^a
Porterville, California/2008 Trial: TCI-07- 184-10	Orange / Valencia	SC	1) 0.303 2) 0.303	1) 861 2) 842	1) 0.035 2) 0.036	whole fruit	14	0.54
Porterville, California/2007 Trial: TCI-07- 184-11	Orange / Atwood Navel	SC	1) 0.298 2) 0.303	1) 1665 2) 1683	1) 0.018 2) 0.018	whole fruit	14	0.32 ^a
Richgrove, California/2007 Trial: TCI-07- 184-12	Orange / Atwood Navel	SC	1) 0.305 2) 0.298	1) 730 2) 926	1) 0.042 2) 0.032	whole fruit	14	0.36 ^a
Oviedo, Florida/2007 Trial: TCI-07- 184-13	Grapefruit / Flame	EC	1) 0.306 2) 0.306	1) 1899 2) 1899	1) 0.016 2) 0.016	whole fruit	7 14 21 28	0.27 0.27 ^a 0.25 0.22
Mims, Florida/2007 Trial: TCI-07- 184-14	Grapefruit / Marsh-White	EC	1) 0.296 2) 0.294	1) 851 2) 842	1) 0.035 2) 0.035	whole fruit	14	0.35 ^a
Holopaw, Florida /2008 Trial: TCI-07- 184-15	Grapefruit / Marsh-White	EC	1) 0.305 2) 0.305	1) 1908 2) 1899	1) 0.016 2) 0.016	whole fruit	14	0.33 ^a
Alamo, Texas/2007 Trial: TCI-07- 184-16	Grapefruit / Rio Red	EC	1) 0.299 2) 0.305	1) 739 2) 748	1) 0.040 2) 0.041	whole fruit	14	0.13
Lindsay, California/2007 Trial: TCI-07- 184-17	Grapefruit / Mellogold	EC	1) 0.298 2) 0.298	1) 730 2) 851	1) 0.041 2) 0.035	whole fruit	14	0.10 ^a
Porterville, California/2007 Trial: TCI-07- 184-18	Grapefruit / Mellogold	EC	1) 0.304 2) 0.297	1) 1553 2) 1534	1) 0.020 2) 0.019	whole fruit	14	0.15 ^a
Mims, Florida/2007 Trial: TCI-07- 184-14	Grapefruit / Marsh-White	SC	1) 0.303 2) 0.303	1) 851 2) 842	1) 0.036 2) 0.036	whole fruit	14	0.29
Holopaw, Florida /2008 Trial: TCI-07- 184-15	Grapefruit / Marsh-White	SC	1) 0.305 2) 0.308	1) 1899 2) 1918	1) 0.016 2) 0.016	whole fruit	14	0.33
Alamo, Texas/2007 Trial: TCI-07- 184-16	Grapefruit / Rio Red	SC	1) 0.299 2) 0.307	1) 739 2) 758	1) 0.040 2) 0.041	whole fruit	14	0.14 ^a
Porterville, California/2007 Trial: TCI-07- 184-20	Lemon / Pryor	EC	1) 0.300 2) 0.297	1) 926 2) 917	1) 0.032 2) 0.032	whole fruit	7 14 21 28	0.44 0.43 0.33 0.27
TCI-07-184 Santa Paula, California/2008	Lemon / Lisbon	EC	1) 0.303 2) 0.300	1) 851 2) 861	1) 0.036 2) 0.035	whole fruit	14	0.42

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Trial: TCI-07-184-22								
Ft. Pierce, Florida/2008 Trial: TCI-07-184-19	Lemon / Bears	SC	1) 0.297 2) 0.294	1) 1787 2) 1759	1) 0.017 2) 0.017	whole fruit	14	0.57 ^a
Porterville, California/2007 Trial: TCI-07-184-20	Lemon / Pryor	SC	1) 0.299 2) 0.299	1) 926 2) 917	1) 0.032 2) 0.033	whole fruit	7 14 21 28	0.48 0.50 ^a 0.38 0.42
Richgrove, California /2007 Trial: TCI-07-184-21	Lemon / Lisbon	SC	1) 0.299 2) 0.299	1) 1665 2) 1702	1) 0.018 2) 0.018	whole fruit	14	0.36 ^a
Santa Paula, California/2008 Trial: TCI-07-184-22	Lemon / Lisbon	SC	1) 0.297 2) 0.303	1) 842 2) 870	1) 0.035 2) 0.035	whole fruit	14	0.50 ^a
Somis, California/2008 Trial: TCI-07-184-23	Lemon / Eureka	SC	1) 0.296 2) 0.299	1) 1543 2) 1581	1) 0.019 2) 0.019	whole fruit	14	0.61 ^a

^a Trials resulted in the highest residues from the side by side treatments carried out with EC or SC formulation on different varieties

Pome fruits

Pears

Six residue trials were performed on pears grown in the USA in 2008 (Carringer, SJ 2009a, Report no. R-10177). Two treatments were applied by air blast sprayer (mist blower) with an interval of 14 days. The first application was performed at about 300 g ai/ha and the second at about 150 g ai/ha ending up in a maximum seasonal application rate of about 0.448 kg ai/ha. Two formulations of tolfenpyrad were used: 15% EC and a 15% SC formulation.

One untreated control and two treated plots were established at each test site. All trials were performed as bridging trials testing both formulations in side-by-side comparisons.

All trials were harvested at commercial maturity, 14 days after the second application. One trial was conducted as a decline trial with samples taken 0, 14, 28 and 35 days after the second application.

A single control sample and duplicate treated RAC samples were harvested by hand at each location at normal crop maturity 14 days after the last application (DALA). Additionally, one trial collected duplicate treated decline samples 0, 14, 28 and 35 DALA. The pear samples were comprised of 24 fruit weighing at least 2 kg. Samples were collected from all quadrants of the trees and from at least four centre trees in the treated plots.

Pear samples were stored for 93 days prior to analysis. All samples were analysed for tolfenpyrad and its metabolite OH-PT. No quantifiable residues of OH-PT were present in any samples.

Table 74 Summary of tolfenpyrad residues in pears

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Alton, New York/2008 Trial: TCI-08-196-01	Pear / Clapps Favorite	EC	1) 0.301 2) 0.149	1) 561 2) 561	1) 0.054 2) 0.027	whole fruit	14	0.28 ^a
Poplar, California/2008 Trial: TCI-08-196-02	Pear / Olympic	EC	1) 0.297 2) 0.151	1) 1207 2) 1225	1) 0.025 2) 0.012	whole fruit	0 14 28 35	0.37 0.20 0.22 0.17
Lindsay, California/2008 Trial: TCI-08-196-03	Pear / Olympic	EC	1) 0.296 2) 0.149	1) 496 2) 514	1) 0.060 2) 0.029	whole fruit	14	0.04
Alton, New York/2008 Trial: TCI-08-196-01	Pear / Clapps Favorite	SC	1) 0.300 2) 0.150	1) 561 2) 561	1) 0.053 2) 0.027	whole fruit	14	0.19
Poplar, California/2008 Trial: TCI-08-196-02	Pear / Olympic	SC	1) 0.293 2) 0.151	1) 1188 2) 1216	1) 0.025 2) 0.012	whole fruit	0 14 28 35	0.38 0.21 ^a 0.15 0.13
Lindsay, California/2008 Trial: TCI-08-196-03	Pear / Olympic	SC	1) 0.300 2) 0.148	1) 505 2) 505	1) 0.059 2) 0.029	whole fruit	14	0.09 ^a
Royal City, Washington/2008 Trial: TCI-08-196-04	Pear / Barlett	SC	1) 0.295 2) 0.150	1) 186 1 2) 1861	1) 0.016 2) 0.008	whole fruit	14	0.15 ^a
Ephrata, Washington/2008 Trial: TCI-08-196-05	Pear / Concord	SC	1) 0.299 2) 0.152	1) 561 2) 561	1) 0.053 2) 0.027	whole fruit	14	0.37 ^a
Fruitland, Idaho/2008 Trial: TCI-08-196-06	Pear / Barlett	SC	1) 0.307 2) 0.154	1) 1450 2) 1422	1) 0.021 2) 0.011	whole fruit	14	0.32 ^a

Stone fruits

Twenty-one residue trials were conducted on stone fruit in the USA during 2008 (Greenland, RG, Report no. R-10175), six trials on sweet cherries, nine on peaches and six on plums. In each trial, two treatments were applied by air blast sprayer (mist blower) application at a rate of 0.31 kg ai/ha each with an interval of 10 days. Tolfenpyrad was used as a 15% SC formulation.

One untreated control and one treated plot were established at each test site. Two of the plum trials had an additional plot treated at an exaggerated rate (5×) to provide samples for processing.

All trials were harvested at commercial maturity, 14 days after the second application. Samples of minimum 2 kg were taken from 24 positions at random areas across the plots. Samples were taken to deep-freezer within 3.6 hours. One trial for peach was conducted as a decline trial with samples taken 6, 10, 14, 18 and 22 days after the second application.

All samples were analysed for tolfenpyrad and its metabolite OH-PT within 101 days after sampling. No OH-PT was detected in any of the samples.

Table 75 Summary of tolfenpyrad residues in stone fruits

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Ottawa, Michigan/2008 Trial: SARS-08- 13-MI	Sweet Cherry / Napoleon	SC	1) 0.307 2) 0.309	1) 901 2) 908	1) 0.034 2) 0.034	whole fruit	14	0.77
Oceana, Michigan/2008 Trial: SARS-08- 13-MI-2	Sweet Cherry / Gold	SC	1) 0.308 2) 0.308	1) 896 2) 829	1) 0.034 2) 0.033	whole fruit	14	0.80
Fresno, California/2008 Trial: SARS-08- 13-CA-1	Sweet Cherry / Brooks	SC	1) 0.306 2) 0.302	1) 708 2) 697	1) 0.043 2) 0.043	whole fruit	14	0.40
Madera, California/2008 Trial: SARS-08- 13-CA-2	Sweet Cherry / Tulare	SC	1) 0.307 2) 0.303	1) 709 2) 698	1) 0.043 2) 0.043	whole fruit	14	1.09
Grant, Washington/2008 Trial: SARS-08- 13-WA	Sweet Cherry / Bing	SC	1) 0.305 2) 0.305	1) 940 2) 938	1) 0.032 2) 0.032	whole fruit	14	0.57
Wasco, Oregon/2008 Trial: SARS-08- 13-OR	Sweet Cherry / Bing	SC	1) 0.307 2) 0.300	1) 1136 2) 1124	1) 0.027 2) 0.027	whole fruit	14	0.28
Wayne, New York/2008 Trial: SARS-08- 14-NY	Peach / Catherina	SC	1) 0.321 2) 0.316	1) 978 2) 961	1) 0.033 2) 0.033	whole fruit	14	0.39
Clarke, Georgia/2008 Trial: SARS-08- 14-GA-1	Peach / Contender	SC	1) 0.301 2) 0.301	1) 1316 2) 1312	1) 0.023 2) 0.023	whole fruit	14	0.44
Tifton Georgia/2008 Trial: SARS-08- 14-GA-2	Peach / Hawthorn	SC	1) 0.302 2) 0.300	1) 506 2) 502	1) 0.060 2) 0.060	whole fruit	14	0.37
Saluda, S-Carolina/2008 Trial: SARS-08- 14-SC	Peach / Monroe	SC	1) 0.302 2) 0.309	1) 1399 2) 1411	1) 0.022 2) 0.022	whole fruit	14	0.26
Ottawa, Michigan/2008 Trial: SARS-08- 14-MI	Peach / Red Haven	SC	1) 0.308 2) 0.304	1) 926 2) 913	1) 0.033 2) 0.033	whole fruit	14	0.42
Pontotoc, Oklahoma/2008 Trial: SARS-08- 14-OK	Peach / Contender	SC	1) 0.292 2) 0.304	1) 1401 2) 1377	1) 0.021 2) 0.022	whole fruit	14	0.63
Madera, California/2008 Trial: SARS-08- 14-CA-1	Peach / Angelus	SC	1) 0.244 2) 0.304	1) 703 2) 703	1) 0.035 2) 0.043	whole fruit	14	0.16
Fresno, California/2008 Trial: SARS-08- 14-CA-2	Peach / September Sun	SC	1) 0.302 2) 0.310	1) 1856 2) 1900	1) 0.016 2) 0.016	whole fruit	6 10 14 18 22	0.64 0.60 0.81 0.37 0.38
Madera, California/2008	Peach / June Crest	SC	1) 0.311 2) 0.308	1) 718 2) 709	1) 0.043 2) 0.043	whole fruit	14	0.28 ^a

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Trial: SARS-08-14-CA-3								
Jackson, Wisconsin/2008 Trial: SARS-08-15-WI	Plum / Mt Royal	SC	1) 0.317 2) 0.309	1) 484 2) 473	1) 0.065 2) 0.065	whole fruit	14	1.01
Fresno, California/2008 Trial: SARS-08-15-CA-1	Plum / Flavor Rich	SC	1) 0.308 2) 0.306	1) 712 2) 707	1) 0.043 2) 0.043	whole fruit	14	0.23
Glenn, California/2008 Trial: SARS-08-15-CA-2	Plum / French	SC	1) 0.308 2) 0.308	1) 937 2) 936	1) 0.033 2) 0.033	whole fruit	14	0.62
Fresno, California/2008 Trial: SARS-08-15-CA-3	Plum / French	SC	1) 0.300 2) 0.313	1) 1841 2) 1919	1) 0.016 2) 0.016	whole fruit	14	0.48
		SC	1) 1.512 2) 1.564	1) 1865 2) 1928	1) 0.081 2) 0.081	whole fruit	14	1.7
Fresno, California/2008 Trial: SARS-08-15-CA-4	Plum / French	SC	1) 0.307 2) 0.313	1) 1859 2) 1893	1) 0.017 2) 0.017	whole fruit	14	0.13
		SC	1) 1.526 2) 1.543	1) 1872 2) 1893	1) 0.082 2) 0.082	whole fruit	14	0.86
Polk, Oregon/2008 Trial: SARS-08-15-OR	Plum / Moyer	SC	1) 0.308 2) 0.307	1) 751 2) 776	1) 0.041 2) 0.040	whole fruit	14	0.22

^a Trials resulted in the highest residues from the side by side treatments carried out on different varieties

Fruiting vegetables, Cucurbits

Seventeen residue trials performed on cucurbits grown in the USA in 2008 (Greenland, RG, Report no. R-10179), six on cucumbers (including one decline trial), five on summer squash and six on melons (cantaloupe). In each trial, four treatments were performed by foliar application at a rate of 0.23 kg ai/ha each with an interval of seven days. Tolfenpyrad was applied as a 15% EC formulation.

One untreated control and one treated plot were established at each trial site. All trials were harvested at commercial maturity, one day after the last application. One trial on cucumber was conducted as a decline trial with samples taken 1, 4, 7, 10 and 13 days after the last application.

Samples of cucumber fruits, cantaloupe fruits and summer squash fruits (a minimum of 12 fruit per sample weighing at least 1.4 kg per sample) were taken from random areas across the plots. To reduce bulk, some large fruit were sectioned from top to bottom into two (2) or four (4) parts and ½ or ¼ of each fruit was randomly collected for the sample. Details of handling individual samples were not reported.

The untreated plot was sampled first, followed by the treated plot. Samples were placed in freezers (-20 °C ± 5 °C) within 2.3 hours after collection.

The samples were analysed within 131 days after collection.

No quantifiable residues of OH-PT were present at any PHI.

Table 76 Summary of tolfenpyrad residues in cucurbits

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Wayne, North Carolina/2008 Trial: SARS-08-10-NC	Cucumber / Ashley	EC	1) 0.240 2) 0.237 3) 0.231 4) 0.234	1) 167 2) 163 3) 168 4) 167	1) 0.143 2) 0.146 3) 0.137 4) 0.140	whole fruit	1	0.06
Tift, Georgia/2008 Trial: SARS-08-10-GA	Cucumber / Daytona	EC	1) 0.227 2) 0.229 3) 0.225 4) 0.236	1) 287 2) 276 3) 267 4) 271	1) 0.079 2) 0.083 3) 0.084 4) 0.087	whole fruit	1	0.10
Martin, Florida/2008 Trial: SARS-08-10-FL	Cucumber / Indy	EC	1) 0.230 2) 0.229 3) 0.230 4) 0.232	1) 403 2) 381 3) 349 4) 338	1) 0.057 2) 0.060 3) 0.066 4) 0.068	whole fruit	1	0.27
Shelby, Missouri/2008 Trial: SARS-08-10-MO	Cucumber / Straight Eight	EC	1) 0.230 2) 0.230 3) 0.233 4) 0.228	1) 186 2) 183 3) 185 4) 179	1) 0.123 2) 0.125 3) 0.126 4) 0.127	whole fruit	1 4 7 10 13	0.21 0.15 0.09 0.04 0.01
Walworth, Wisconsin/2008 Trial: SARS-08-10-WI	Cucumber / Spacemaster 80	EC	1) 0.230 2) 0.231 3) 0.229 4) 0.230	1) 174 2) 165 3) 164 4) 177	1) 0.132 2) 0.140 3) 0.139 4) 0.130	whole fruit	1	0.03
Wharton, Texas/2008 Trial: SARS-08-10-TX	Cucumber / Poinsett 76	EC	1) 0.234 2) 0.228 3) 0.228 4) 0.231	1) 186 2) 175 3) 174 4) 204	1) 0.125 2) 0.131 3) 0.131 4) 0.113	whole fruit	1	0.21
Tift, Georgia/2008 Trial: SARS-08-11-GA	Cantaloupe / Athena	EC	1) 0.224 2) 0.235 3) 0.231 4) 0.233	1) 275 2) 289 3) 287 4) 282	1) 0.082 2) 0.281 3) 0.081 4) 0.283	whole fruit	1	0.09
Shelby, Missouri/2008 Trial: SARS-08-11-MO	Cantaloupe / Hale's Best Jumbo	EC	1) 0.225 2) 0.228 3) 0.234 4) 0.235	1) 182 2) 182 3) 186 4) 185	1) 0.123 2) 0.125 3) 0.126 4) 0.127	whole fruit	1	0.24
Wharton, Texas/2008 Trial: SARS-08-11-TX	Cantaloupe / Hale's Best No. 36	EC	1) 0.227 2) 0.234 3) 0.231 4) 0.236	1) 187 2) 197 3) 194 4) 206	1) 0.121 2) 0.119 3) 0.119 4) 0.114	whole fruit	1	0.38
Fresno, California/2008 Trial: SARS-08-11-CA-1	Cantaloupe / Athena	EC	1) 0.228 2) 0.229 3) 0.229 4) 0.229	1) 280 2) 282 3) 282 4) 281	1) 0.081 2) 0.081 3) 0.081 4) 0.081	whole fruit	1	0.18
Fresno, California/2008 Trial: SARS-08-11-CA-2	Cantaloupe / Hale's Best Jumbo	EC	1) 0.229 2) 0.230 3) 0.230 4) 0.229	1) 186 2) 186 3) 186 4) 186	1) 0.123 2) 0.123 3) 0.123 4) 0.123	whole fruit	1	0.29
Madera, California/2008 Trial: SARS-08-11-CA-3	Cantaloupe / Hale's Best Jumbo	EC	1) 0.234 2) 0.233 3) 0.232 4) 0.235	1) 283 2) 281 3) 280 4) 284	1) 0.083 2) 0.083 3) 0.083 4) 0.083	whole fruit	1	0.34
Wayne, New York/2008 Trial: SARS-08-12-NY	Summer squash / Sunray	EC	1) 0.237 2) 0.230 3) 0.228 4) 0.232	1) 288 2) 279 3) 277 4) 281	1) 0.083 2) 0.082 3) 0.083 4) 0.083	whole fruit	1	0.05
Tifton Georgia/2008 Trial: SARS-08-12-GA	Summer squash / Lemon Drop L	EC	1) 0.227 2) 0.226 3) 0.233 4) 0.228	1) 284 2) 286 3) 280 4) 270	1) 0.080 2) 0.079 3) 0.083 4) 0.084	whole fruit	1	0.07
Martin, Florida/2008	Summer squash /	EC	1) 0.231 2) 0.228	1) 405 2) 380	1) 0.057 2) 0.060	whole fruit	1	0.08

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Trial: SARS-08-12-FL	Fortune		3) 0.227 4) 0.231	3) 345 4) 337	3) 0.066 4) 0.068			
Shelby, Missouri/2008 Trial: SARS-08-12-MO	Summer squash / Black Zucchini	EC	1) 0.235 2) 0.232 3) 0.232 4) 0.236	1) 191 2) 185 3) 185 4) 186	1) 0.123 2) 0.125 3) 0.126 4) 0.127	whole fruit	1	0.02
Fresno, California/2008 Trial: SARS-08-12-CA	Summer squash / Jackpot	EC	1) 0.228 2) 0.228 3) 0.229 4) 0.228	1) 281 2) 281 3) 281 4) 281	1) 0.081 2) 0.081 3) 0.081 4) 0.081	whole fruit	1	0.05

Fruiting vegetables, other than cucurbits

Twelve residue trials were performed on tomatoes and pepper grown in the USA in 2007 (Carringer, SJ Report no. R-10167), six trials on tomatoes and six trials on pepper. In each trial, two treatments were performed by foliar application at a rate of 0.23 kg ai/ha each with an interval of 14 days. Two formulations of tolfenpyrad were used: a 15% EC formulation, and a 15% SC formulation.

The pepper trials used the 15SC formulation only and the tomato trials were performed as bridging trials testing both formulations in side-by-side comparisons. One of the tomato trials had an additional plot treated at an exaggerated rate (5×) with the EC formulation to provide samples for processing.

All trials were harvested at commercial maturity, one day after the second application. One trial in each type of fruit was conducted as a decline trial with samples taken 0, 1, 7 and 14 days after the second application. Tomato and pepper samples were comprised of a minimum of 12 fruits weighing at least 2.2 kg. The samples were stored before analyses for a maximum of 184 days.

All samples were analysed for tolfenpyrad and its metabolite OH-PT.

No quantifiable residues of OH-PT were present in any samples.

Table 77 Summary of tolfenpyrad residues in tomatoes and peppers

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Germansville, Pennsylvania/2007 Trial: TCI-07-164-01	Tomato / Mountain Spring	EC	1) 0.231 2) 0.241	1) 290 2) 290	1) 0.080 2) 0.083	fruit	1	0.16 ^a
Seven Springs, North Carolina/2007 Trial: TCI-07-164-02	Tomato / Homestead	EC	1) 0.235 2) 0.234	1) 159 2) 159	1) 0.148 2) 0.147	fruit	1	0.09
Oviedo, Florida/2007 Trial: TCI-07-164-03	Tomato / Better Boy	EC	1) 0.233 2) 0.228	1) 290 2) 281	1) 0.080 2) 0.081	fruit	1	0.08 ^a
Quiney, Florida/2007 Trial: TCI-07-164-04	Tomato / Crista	EC	1) 0.228 2) 0.226	1) 187 2) 196	1) 0.122 2) 0.115	fruit	1	0.05
New Holland, Ohio/2007 Trial: TCI-07-164-05	Tomato / Hybrid 882 F1	EC	1) 0.229 2) 0.235	1) 150 2) 159	1) 0.153 2) 0.148	fruit	1	0.13
Paso Robles,	Tomato /	EC	1) 0.225	1) 561	1) 0.040	fruit	1	0.27

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
California/2007 Trial: TCI-07-164-06	Red Cherry		2) 0.235	2) 589	2) 0.040			
Hickman, California/2007 Trial: TCI-07-164-07	Tomato / Cannery Variety 179	EC	1) 0.232 2) 0.235	1) 234 2) 234	1) 0.099 2) 0.101	fruit	1	< 0.01
Lemoore, California/2007 Trial: TCI-07-164-08	Tomato / Orsetti 303	EC	1) 0.228 2) 0.236	1) 290 2) 299	1) 0.078 2) 0.079	fruit	1	0.19 ^a
		EC	1) 1.143 2) 1.154	1) 290 2) 290	1) 0.394 2) 0.398	fruit	1	0.14
Porterville, California/2007 Trial: TCI-07-164-09	Tomato / Roma	EC	1) 0.230 2) 0.236	1) 140 2) 140	1) 0.164 2) 0.169	fruit	0 1 7 14	0.11 0.07 0.10 0.09
Porterville, California/2007 Trial: TCI-07-164-10	Tomato / Quality 23	EC	1) 0.230 2) 0.230	1) 281 2) 281	1) 0.082 2) 0.082	fruit	1	0.09
San Ardo, California/2007 Trial: TCI-07-164-11	Tomato / Quality 2-3	EC	1) 0.231 2) 0.231	1) 94 2) 94	1) 0.247 2) 0.247	fruit	1	0.20
Huron, California/2007 Trial: TCI-07-164-12	Tomato / Orsetti 66509	EC	1) 0.233 2) 0.230	1) 281 2) 281	1) 0.083 2) 0.082	fruit	1	0.07
Germansville, Pennsylvania/2007 Trial: TCI-07-164-01	Tomato / Mountain Spring	SC	1) 0.241 2) 0.259	1) 290 2) 290	1) 0.083 2) 0.289	fruit	1	0.10
Seven Springs, North Carolina/2007 Trial: TCI-07-164-02	Tomato / Homestead	SC	1) 0.231 2) 0.234	1) 150 2) 159	1) 0.154 2) 0.147	fruit	1	0.17 ^a
Oviedo, Florida/2007 Trial: TCI-07-164-03	Tomato / Better Boy	SC	1) 0.224 2) 0.229	1) 281 2) 281	1) 0.080 2) 0.081	fruit	1	0.06
Quiney, Florida/2007 Trial: TCI-07-164-04	Tomato / Crista	SC	1) 0.231 2) 0.233	1) 187 2) 196	1) 0.123 2) 0.119	fruit	1	0.09 ^a
New Holland, Ohio/2007 Trial: TCI-07-164-05	Tomato / Hybrid 882 F1	SC	1) 0.236 2) 0.239	1) 159 2) 159	1) 0.149 2) 0.150	fruit	1	0.13 ^a
Paso Robles, California/2007 Trial: TCI-07-164-06	Tomato / Red Cherry	SC	1) 0.222 2) 0.232	1) 552 2) 580	1) 0.040 2) 0.040	fruit	1	0.51 ^a
Hickman, California/2007 Trial: TCI-07-164-07	Tomato / Cannery Variety 179	SC	1) 0.228 2) 0.231	1) 234 2) 234	1) 0.097 2) 0.099	fruit	1	0.23 ^a
Lemoore, California/2007 Trial: TCI-07-164-08	Tomato / Orsetti 303	SC	1) 0.234 2) 0.233	1) 390 2) 290	1) 0.081 2) .080	fruit	1	0.12
Porterville,	Tomato /	SC	1) 0.231	1) 140	1) 0.165	fruit	0	0.14

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
California/2007 Trial: TCI-07-164-09	Roma		2) 0.235	2) 140	2) 0.168		1 7 14	0.12 ^a 0.17 0.16
Porterville, California/2007 Trial: TCI-07-164-10	Tomato / Quality 23	SC	1) 0.230 2) 0.230	1) 281 2) 281	1) 0.082 2) 0.082	fruit	1	0.11 ^a
San Ardo, California/2007 Trial: TCI-07-164-11	Tomato / Quality 2-3	SC	1) 0.228 2) 0.241	1) 94 2) 103	1) 0.243 2) 0.234	fruit	1	0.24 ^a
Huron, California/2007 Trial: TCI-07-164-12	Tomato / Orsetti 66509	SC	1) 0.233 2) 0.230	1) 281 2) 281	1) 0.083 2) 0.082	fruit	1	0.11 ^a
Seven Springs, North Carolina/2007 Trial: TCI-07-164-13	Bell Pepper / Capistrano	SC	1) 0.231 2) 0.232	1) 168 2) 159	1) 0.137 2) 0.146	fruit	1	0.08
Quiney, Florida/2007 Trial: TCI-07-164-14	Bell Pepper / Aristotle	SC	1) 0.228 2) 0.230	1) 122 2) 122	1) 0.187 2) 0.189	fruit	1	0.07
Carlyle, Illinois/2007 Trial: TCI-07-164-15	Bell Pepper / Better Belle	SC	1) 0.233 2) 0.230	1) 94 2) 94	1) 0.249 2) 0.246	fruit	1	0.08
Uvalde, Texas/2007 Trial: TCI-07-164-16	Bell Pepper / Camelot	SC	1) 0.230 2) 0.226	1) 159 2) 178	1) 0.144 2) 0.127	fruit	1	0.22
Levelland, Texas/2007 Trial: TCI-07-164-17	Chili Pepper / Jalapeno M	SC	1) 0.231 2) 0.234	1) 140 2) 140	1) 0.165 2) 0.167	fruit	1	0.33
Porterville, California/2007 Trial: TCI-07-164-18	Bell Pepper / Encore	SC	1) 0.230 2) 0.230	1) 178 2) 178	1) 0.129 2) 0.129	fruit	0 1 7 14	0.07 0.05 0.07 0.05
San Ardo, California/2007 Trial: TCI-07-164-19	Bell Pepper / Choice	SC	1) 0.230 2) 0.230	1) 281 2) 281	1) 0.082 2) 0.082	fruit	1	0.13
Porterville, California/2007 Trial: TCI-07-164-20	Chili Pepper / Jalapeno 7042	SC	1) 0.231 2) 0.231	1) 178 2) 178	1) 0.130 2) 0.130	fruit	1	0.14
King City, California/2007 Trial: TCI-07-164-21	Chili Pepper / Valor	SC	1) 0.230 2) 0.231	1) 281 2) 281	1) 0.082 2) 0.082	fruit	1	0.32

*Root and tuber vegetables**Potatoes*

Sixteen residue trials conducted on potatoes in the USA in 2007 (Carringer, SJ 2008, Report no. R-10166). In each trial, two treatments were performed by foliar broadcast ground application at a rate of 230 g ai/ha with an interval of 27–29 days. Tolfenpyrad was used as a 15% EC formulation.

The harvest was at commercial maturity, 13–14 days after the second application. Two trials were conducted as decline trials with samples taken 7, 14, 21 and 28 days after the second application. One trial had an additional plot treated at an exaggerated rate (5×) with the EC formulation to provide samples for processing.

The samples were comprised of a minimum of 12 (if large) or 24 tubers. All samples were analysed for tolfenpyrad and its metabolite OH-PT.

The potato RAC samples were stored frozen (below freezing at the field sites, -17 ± 8 °C at the processing facility, and -20 ± 5 °C at the analytical laboratory) for a maximum of 179 days from collection to analysis.

In potatoes harvested 7 to 28 days after application, all residues of tolfenpyrad and OH-PT were below the LOQ (< 0.01 mg/kg).

Since the tolfenpyrad metabolites, PT-CA was detected more than 10% TRR in the metabolism study with tolfenpyrad in radishes (Quistad and Kovatchev, 2008), potatoes as root vegetables were selected for the confirmation of the residues of additional tolfenpyrad metabolites, OH-PAM, PT-CA, and PAM (Carringer, JS 2012, Report no. R-10255). The potato raw agricultural commodity and processing commodity samples generated in a previous study (Carringer, JS 2008) were analysed. The residues of relevant metabolites were below the limit of detection (< 0.01 mg/kg) in all treated samples.

Tree nuts

Ten residue trials were performed on tree nuts grown in the USA in 2008 (Greenland, RG 2009a, Report no. R-10178); five on almonds and five on pecans. Two treatments with a 15% SC formulation were performed at a rate of 300 g ai/ha by air blast sprayer with an interval of 10 days. Both applications were performed at about 300 g ai/ha.

All trials were harvested at commercial maturity, 13–14 days after the second application. One trial was conducted as a decline trial with samples taken 5, 9, 13, 17 and 21 days after the second application. Samples of almond nutmeat, almond hulls and pecan nutmeat weighing at least 2 kg were taken from random areas across the plots. Some of the samples were placed in a freezer more than 4 hours after collection because of the time it took to shell the nuts. The samples were stored at -20 °C $\pm$ 5 °C before and after homogenization in the freezers of the analytical facility. The samples were analysed within 60 days following their collection.

All samples were analysed for tolfenpyrad and its metabolite OH-PT. No quantifiable residues of OH-PT were present in any samples.

Table 78 Summary of tolfenpyrad residues in tree nuts

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Fresno, California/2008 Trial: SARS-08-01-CA-1	Almond / Nonpareil	SC	1) 0.305 2) 0.305	1) 706 2) 705	1) 0.043 2) 0.043	nutmeat	14	< 0.01
Madera, California/2008 Trial: SARS-08-01-	Almond / Nonpareil	SC	1) 0.308 2) 0.307	1) 1406 2) 1401	1) 0.022 2) 0.022	nutmeat	14	0.03

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
CA-2								
Fresno, California/2008 Trial: SARS-08-01-CA-3	Almond / Carmel	SC	1) 0.309 2) 0.308	1) 1874 2) 1877	1) 0.017 2) 0.016	nutmeat	5 9 13 17 21	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Glenn, California/2008 Trial: SARS-08-01-CA-4	Almond / Nonpareil	SC	1) 0.308 2) 0.307	1) 935 2) 933	1) 0.033 2) 0.033	nutmeat	14	< 0.01
Colusa, California/2008 Trial: SARS-08-01-CA-5	Almond / Nonpareil	SC	1) 0.302 2) 0.303	1) 923 2) 924	1) 0.033 2) 0.033	nutmeat	14	< 0.01
Screven, Georgia/2008 Trial: SARS-08-02-SC	Pecan / Desirable	SC	1) 0.309 2) 0.305	1) 977 2) 960	1) 0.032 2) 0.032	nutmeat	14	< 0.01
Tift, Georgia/2008 Trial: SARS-08-02-GA	Pecan / Sumner	SC	1) 0.306 2) 0.305	1) 1007 2) 988	1) 0.030 2) 0.031	nutmeat	14	< 0.01
Stoddard, Missouri/2008 Trial: SARS-08-02-AR	Pecan / Stuard	SC	1) 0.308 2) 0.306	1) 471 2) 469	1) 0.065 2) 0.065	nutmeat	14	< 0.01
Frio, Texas/2008 Trial: SARS-08-02-TX	Pecan / Wichita	SC	1) 0.310 2) 0.304	1) 701 2) 604	1) 0.044 2) 0.050	nutmeat	14	< 0.01
Stephens, Oklahoma/2008 Trial: SARS-08-02-OK	Pecan / Kiowa	SC	1) 0.309 2) 0.310	1) 1789 2) 1809	1) 0.017 2) 0.017	nutmeat	14	< 0.01

Cotton

Twelve residue trials were conducted on cotton in the USA in 2007 (Wyatt, DR 2008b, Report no. R-10159). In each trial, two treatments were performed by foliar application with 15% EC formulation at a rate of 0.23 kg ai/ha each with an interval of 14 days.

One trial had an additional plot treated at an exaggerated rate (5×) with the SC formulation to provide samples for processing.

All trials were harvested at commercial maturity, 13 or 14 days after the second application. One trial was conducted as a decline trial with samples taken 7, 14, 21 and 28 days after the second application.

All samples were analysed for tolfenpyrad and its metabolite OH-PT.

No quantifiable residues of OH-PT were present at a PHI of 13–14 days in undelinted seed.

In cotton gin trash, 13–14 days after second application, residues of tolfenpyrad were in the range of 1.17–5.90 mg/kg. Residues of OH-PT were in the range of 0.01–0.05 mg/kg.

Table 79 Summary of tolfenpyrad residues in cotton seed

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI days	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Chula, Georgia/2007 Trial: TCI-07- 165-01	Cotton / DP555 BG/RR	EC	1) 0.231 2) 0.232	1) 47 2) 47	1) 0.491 2) 0.494	undelinted seed	14	0.13
Newport, Arkansas/2007 Trial: TCI-07- 165-02	Cotton / DP143 B2RF	EC	1) 0.229 2) 0.231	1) 94 2) 94	1) 0.244 2) 0.246	undelinted seed	14	0.20
Cheneyville, Louisiana/2007 Trial: TCI-07- 165-03	Cotton / Phytogen 370 WR	EC	1) 0.232 2) 0.231	1) 140 2) 150	1) 0.166 2) 0.154	undelinted seed	14	0.43
West Memphis, Arkansas/2007 Trial: TCI-07- 165-04	Cotton / ST 4357 B2RF	EC	1) 0.230 2) 0.229	1) 47 2) 47	1) 0.489 2) 0.487	undelinted seed	14	0.07
Uvalde, Texas/2007 Trial: TCI-07- 165-05	Cotton / DPL 143	EC	1) 0.231 2) 0.223	1) 150 2) 150	1) 0.154 2) 0.149	undelinted seed	13 13	0.01
		EC	1) 1.18 2) 1.15	1) 150 2) 150	1) 0.787 2) 0.767	undelinted seed	13	1.1
Levelland, Texas/2007 Trial: TCI-07- 165-06	Cotton / Fibermex 9063 B2F	EC	1) 0.234 2) 0.228	1) 94 2) 94	1) 0.249 2) 0.243	undelinted seed	7 14 21 27	0.23. 0.18 0.19 0.18
Wolfforth, Texas/2007 Trial: TCI-07- 165-07	Cotton / Nex Gen 3550 RF	EC	1) 0.230 2) 0.229	1) 47 2) 47	1) 0.489 2) 0.487	undelinted seed	14	0.34
Claude, Texas/2007 Trial: TCI-07- 165-08	Cotton / Nex Gen 3550 RF	EC	1) 0.231 2) 0.230	1) 140 2) 140	1) 0.165 2) 0.164	undelinted seed	14	0.25
Hinton, Oklahoma/2007 Trial: TCI-07- 165-09	Cotton / FM 9063 B2F	EC	1) 0.228 2) 0.232	1) 47 2) 47	1) 0.485 2) 0.494	undelinted seed	14	0.24
Earlimart, California/2007 Trial: TCI-07- 165-10	Cotton / Roundup Ready	EC	1) 0.231 2) 0.240	1) 94 2) 103	1) 0.246 2) 0.233	undelinted seed	14	0.05
Hanford, California/2007 Trial: TCI-07- 165-11	Cotton / Phytogen 725 RR	EC	1) 0.230 2) 0.226	1) 94 2) 94	1) 0.245 2) 0.240	undelinted seed	14	0.29
Yuma, Arizona/2007 Trial: TCI-07- 165-12	Cotton / Delta Pine 445 BG/RR	EC	1) 0.230 2) 0.230	1) 140 2) 187	1) 0.164 2) 0.123	undelinted seed	13	0.14

Processed food of plant origin***Tea***

Four residue trials were conducted on green tea during 1997 in Japan (Yabusaki, T 2010a, R-10027 and R-10028). One foliar application of tolfenpyrad was made with 0.0015 kg/ha following the design

of reverse decline trials. The treated plots of each trial were harvested at a PHI of 7, 14, 21 and 30 days after treatment and the samples were analysed twice in two laboratories. The LOQ was 0.04 mg/kg.

Table 80 Summary of tolfenpyrad residues in tea

Report no. Location including Postal Code	Commodity Variety	Form.	Application rate per treatment		PHI (days)	Residues (mg/kg)		
			Water (L/ha)	kg ai/hL		R-10027 ^a	R-10028 ^b	Average
GAP in Japan			2000–4000	0.0015	14			
Nara Prefectural Agricultural Experiment Station Japan /1997	Tea / Yabukita	EC	1) 2000	1) 0.015	7	22.3 ^a	21.7 ^b	22.0
			1) 2000	1) 0.015	14	7.06	7.04	7.05
			1) 2000	1) 0.015	21	0.55	0.74	0.65
			1) 2000	1) 0.015	30	0.10	0.16	0.13
Kochi Prefectural Agricultural Technology Center, Japan /1997	Tea / Yabukita	EC	1) 3000	1) 0.015	7	16.6 ^a	18.0 ^b	17.3
			1) 3000	1) 0.015	14	4.24	4.34 ^b	4.29
			1) 3000	1) 0.015	21	0.79	0.78	0.79
			1) 3000	1) 0.015	30	0.12	0.18	0.15
Saitama Pref., Japan /2005	Tea / Hokumei	EC	1) 4000	1) 0.015	7	80.4 ^c	54.8 ^d	67.6
			1) 4000	1) 0.015	14	13.8	10.4	12.1
			1) 4000	1) 0.015	28	0.08	< 0.05	0.08
Kanagawa Agricultural Technology Center, Japan /2005	Tea / Yabukita	EC	1) 4000	1) 0.015	7	32.5 ^c	30.3 ^d	31.4
			1) 4000	1) 0.015	14	4.44	3.10	3.77
			1) 4000	1) 0.015	28	0.21	0.14	0.18

^a Average of duplicate analyses performed in 1998 (R-10027)

^b Average of duplicate analyses performed in 1997 (R-10028)

^c Average of duplicate analyses performed in 2005/8/1 (R-10097)

^d Average of duplicate analyses performed in 2005/7/19-25 (R-10098)

Animal feeds

Almond hulls

Table 81 Summary of tolfenpyrad residues in almond hull

Location including Postal Code	Commodity / Variety	Form	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Fresno, California/2008 Trial: SARS-08- 01-CA-1	Almond / Nonpareil	SC	1) 0.305 2) 0.305	1) 706 2) 705	1) 0.043 2) 0.043	hull	14	2.25
Madera, California/2008 Trial: SARS-08- 01-CA-2	Almond / Nonpareil	SC	1) 0.308 2) 0.307	1) 1406 2) 1401	1) 0.022 2) 0.022	hull	14	1.60
Fresno, California/2008 Trial: SARS-08- 01-CA-3	Almond / Carmel	SC	1) 0.309 2) 0.308	1) 1874 2) 1877	1) 0.017 2) 0.016	hull	5 9 13 17 21	2.88 1.6 3.42 2.92 2.46
Glenn, California/2008 Trial: SARS-08- 01-CA-4	Almond / Nonpareil	SC	1) 0.308 2) 0.307	1) 935 2) 933	1) 0.033 2) 0.033	hull	14	< 0.01

Location including Postal Code	Commodity / Variety	Form	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Colusa, California/2008 Trial: SARS-08-01-CA-5	Almond / Nonpareil	SC	1) 0.302 2) 0.303	1) 923 2) 924	1) 0.033 2) 0.033	hull	14	1.75

Cotton gin trash

Table 82 Summary of tolfenpyrad residues in cotton gin trash

Report no. Location including Postal Code	Commodity / Variety	Form	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Newport, Arkansas/2007 Trial: TCI-07-165-02	Cotton / DP143 B2RF	EC	1) 0.229 2) 0.231	1) 94 2) 94	1) 0.244 2) 0.246	gin trash	14	4.00/0.04/4.04
West Memphis, Arkansas/2007 Trial: TCI-07-165-04	Cotton / ST 4357 B2RF	EC	1) 0.230 2) 0.229	1) 47 2) 47	1) 0.489 2) 0.487	gin trash	14	1.17/0.01/1.18
Uvalde, Texas/2007 Trial: TCI-07-165-05	Cotton / DPL 143	EC	1) 0.231 2) 0.223	1) 150 2) 150	1) 0.154 2) 0.149	gin trash	13	3.90/0.04/3.94
Levelland, Texas/2007 Trial: TCI-07-165-06	Cotton / Fibermax 9063 B2F	EC	1) 0.234 2) 0.228	1) 94 2) 94	1) 0.249 2) 0.243	gin trash	7 14 21 27	7.47/0.05/7.52 3.55/0.03/3.58 3.32/0.03/3.36 3.22/0.04/3.26
Wolfforth, Texas/2007 Trial: TCI-07-165-07	Cotton / Nex Gen 3550 RF	EC	1) 0.230 2) 0.229	1) 47 2) 47	1) 0.489 2) 0.487	gin trash	14	5.90/0.04/5.94
Claude, Texas/2007 Trial: TCI-07-165-08	Cotton / Nex Gen 3550 RF	EC	1) 0.231 2) 0.230	1) 140 2) 140	1) 0.165 2) 0.164	gin trash	14	5.45/0.05/5.50

FATE OF RESIDUES IN STORAGE AND PROCESSING*In processing**Study 1 – Citrus (Wyatt, DR 2008a Report no. R-10173)*

One processing trial was conducted on oranges in 2008. The treated plot received two air-blast applications at an exaggerated rate of 1.5 kg ai/ha with an interval of 14 days. Samples were harvested at maturity 14 days after the last application.

The oranges were batch tub-washed for 5 minutes. The washed oranges were transferred to the modified Hobart Abrasive Peeler for scarifying. Approximately 2.20 kg of oranges per batch were

abraded for approximately 1 minute to scarify the flavedo for oil recovery. The scarified fruits were weighed and retained for juice processing.

The collected oil-water emulsion was transferred to the Sweco Sifter and screened using an (approximately) 180 µm screen to separate any flavedo fragments from the oil-water emulsion.

The scarified flavedo was set aside for later addition to the shredded peel. The first run oil-water emulsion was processed through the cream separator and IEC centrifuge to separate the oil. The free oil was removed. The residual emulsion was frozen overnight, thawed, centrifuged and the oil removed and added to the previously collected oil sample. The entire oil sample recovered was weighed and stored frozen until analysis.

An aliquot of the scarified oranges was weighed and transferred to the Hollymatic Juice Extractor to separate the juice from the peel. The juice and peel recovered were weighed and the Brix-degree taken on the fresh juice.

The collected juice was transferred to the pulper finisher and screened using an (approximately) 1.19 mm screen for removal of vesicular membranes, seeds, segment membranes and peel fragments from the juice. The collected rag and seeds were set aside for later addition to the shredded peel.

A representative aliquot of the fresh juice was sampled and stored frozen until analysis. The remaining juice was discarded.

The peel from the Hollymatic Juice Extractor was shredded using the Robot Coupe Food Processor. The shredded peel was combined with the scarified flavedo from the scarification process and rag and seeds from the juice finisher extraction process to generate wet peel.

Lime (approximately 95% CaO) was added to the wet peel and mixed on the Hobart mixer for 17 minutes. The limed peel was pressed using a Suntech Fruit press. The expressed liquid was weighed, checked for pH and Brix-degree and discarded.

The wet peel pulp was placed on the Laboratory Bin Air Dryer for removal of moisture to < 10%. The dried pulp was milled using the Suntech Fruit Press hammermill. Moisture of treated and untreated samples averaged between 3.1% and 3.5%.

A representative sample of the dried pulp was sampled and stored frozen until analysis. The remaining dried pulp was discarded.

The processed fractions were analysed with the method described under residue analysis.

Table 83 Summary of residues of tolfenpyrad and OH-PT in oranges and processed products

Compound	Total Treatment Rate (kg ai/ha)	PHI (days)	Sample	Residues (mg/kg) ^a	Processing Factor
Tolfenpyrad	2.98	14	RAC fruit	0.91	—
			juice	0.02	0.022
			dried pulp	8.03	8.8
			oil	74.4	82
OH-PT	2.98	14	RAC fruit	< 0.01	—
			juice	< 0.01	—
			dried pulp	0.02	—
			oil	0.08	—

^a mean of duplicate preparation

n.a. = Not applicable

Study 2 – Plums

Two processing trials were conducted on plums in the USA in 2008 (Greenland, RG 2009b, Report no. R-10175). The treated plots received two air-blast applications of about 1.5 kg ai/ha with an interval of 10 days. Samples were harvested at maturity 14 days after the last application.

Representative unwashed plum sample aliquots (treated and untreated) were used for processing. The plum samples were placed in model D-10 dehydrators (Homestead Harvest products). The dehydrators first were set to 57.2 °C for 10 hours and temperature was risen to 73.9 °C for additional 20 hours. The actual temperature range for the drying process was 22.8–49.4 °C. The loss of moisture was 55.4% for the untreated sample and 61.2% for the treated sample. Sample aliquots were taken and stored frozen until analysis. The samples were analysed with the method described under residue analysis.

Table 84 Summary of residues of tolfenpyrad and OH-PT in plums (fresh and dried)

Compound	Total Treatment Rate (kg ai/ha)	PHI (days)	Sample	Residues (mg/kg)	Processing Factor
Trial SARS-08-15-CA-3					
Tolfenpyrad	3.08	14	RAC fruit dried fruit	1.70 5.30 ^a	– 3.1
OH-PT	3.08	14	RAC fruit dried fruit	< 0.01 < 0.01	– n.a.
Trial SARS-08-15-CA-4					
Tolfenpyrad	3.07	14	RAC fruit dried fruit	0.86 2.35 ^a	– 2.7
OH-PT	3.07	14	RAC fruit dried fruit	< 0.01 < 0.01	– n.a.

^a Mean of duplicate preparation

n.a. = Not applicable

Study 3 – Potatoes

One trial was conducted at an exaggerated application rate to obtain RAC samples of potato tubers for processing (Carringer, SJ Report no. R-10166). The treated plot received two foliar broadcast applications, of about 1.05 kg ai/ha with an interval of 14 days. Samples were harvested at maturity 14 days after the last application.

Potato flake production

After washing, the potatoes were peeled (steam and scrub peeling). The potato peel was collected from the peeling and scrubbing process. Peeled potatoes were inspected and trimmed to remove peel, rot, green or other damages. The collected peel was hydraulically pressed and blended together with the collected cut trim waste. A sample aliquot was taken and stored frozen until analysis.

An aliquot of peeled potatoes was removed, cut into slabs using a LanElec slicer and spray-washed (tap water). The potato slabs were pre-cooked (steam) at approximately 70–77 °C for 21 minutes and cooled to less than 32 °C. An aliquot of the potato slabs was steam-cooked at 94–100 °C for 40–42 minutes, mashed and mixed with an emulsion of pre-weighed food additives. The sample was placed in a Drum Dryer for production of large flakes that were milled to uniform potato flakes by a hammermill. Moisture content of the flakes was ≤ 9%. Sample aliquots were taken and stored frozen until analysis.

Potato chip production

After washing and sugar analysis, potatoes were batch peeled using a restaurant-style Toledo Peeler. The collected peel was discarded. The peeled potatoes were inspected and trimmed as necessary to remove rot, green or otherwise damaged potato tissue. The peeled potatoes were cut into thin slices (1.6 mm) using a restaurant-style LanElec Slicer. Adhering free starch was removed with hot water and slices were drained over a screen to remove excess water. Chips were oil-fried at 163–191 °C for about 120 seconds, drained, salted and inspected. Sample aliquots were taken and stored frozen until analysis.

Flakes, chips and wet peel samples were analysed according to the analytical process for potatoes described under residue analysis. Neither the RAC nor the processed fractions contained residues of tolfenpyrad and OH-PT above LOQ of 0.01 mg/kg.

Study 4 – Tomatoes

One trial was conducted at an exaggerated application rate to obtain samples of tomato RAC fruits for processing (Carringer, SJ 2009b). The treated plot received two foliar broadcast applications, of about 1.15 kg as/ha with an interval of 14 days. Samples were harvested at maturity one day after the last application (DALA).

Juice production

After washing, tomato fruits were crushed and the crush was heated to a temperature of 91–100 °C in a hot break system. The hot crush was processed through a finisher equipped with a screen with 0.84 mm perforations that removed peel and seeds from the crush. The resulting juice was collected for further processing. The pomace was discarded.

Purée production

The juice was concentrated to puree using a vacuum evaporator. During concentration, the juice was recirculated through the evaporator until it was condensed to a natural tomato soluble solids (NTSS) content of 10%. A portion of puree was transferred to a steam jacketed kettle, heated while stirring to a minimum temperature of 88 °C and poured into cans. After heating the NTSS was 11–12%. The cans were sealed, inverted and water cooled. When cooled, the cans were dried and stored frozen until analysis.

Paste production

The remaining puree in the vacuum kettle evaporator was condensed to paste. The NTSS for the paste fraction was 27.5–30.0%. A portion of the paste was transferred into a small steam jacketed kettle and heated to 88–93 °C. The NTSS after heating was 31–45.5%. The paste was poured into cans that were sealed and inverted. After 5 minutes, the cans were water cooled, dried, and stored frozen until analysis. Puree and paste samples were analysed according to the analytical process for tomatoes described under residue analysis.

Table 85 Summary of residues of tolfenpyrad and OH-PT in tomato and tomato processed products

Compound	Total Treatment Rate (kg ai/ha)	PHI (days)	Sample	Residues (mg/kg) ^a	Processing Factor
Tolfenpyrad	2.31	1	RAC fruits	0.12	–
			puree	0.04	0.31
			paste	0.12	1.02
OH-PT	2.31	1	RAC fruits	< 0.01	–
			puree	< 0.01	n.a.
			paste	< 0.01	n.a.

^a Mean of duplicate preparation

n.a. = Not applicable

Study 5 – Cotton

One processing trial was conducted on cotton in 2007 (Wyatt, DR 2008b, Report no. R-10159). The treated plot received two applications with an interval of 14 days, the first at 1.18 kg ai/ha, the second at 1.15 kg ai/ha. Samples were harvested at maturity 13 days after the last application.

Delinting

Seed cotton was saw ginned (Continental Eagle 20 saw gin) to remove most of the lint from the seed. Remaining lint (11–15%) was mainly removed by saw delinted in a Carver delinter to produce

delinted cottonseed with approximately 3% lint remaining on the seed. Processed fractions obtained so far were delinted cottonseed, linters and linter motes.

Cotton seed hulls

A roller mill (AT Ferrell) cracked the delinted seed and most of the hull material was removed from the kernel by screening (10/64" and 12/64"). Aliquots of hull material were taken and stored frozen until analysis.

Cotton seed meal

The kernel fraction was heated in a Marion mixer to 79–90 °C for 15–30 minutes. Thereafter, kernels were flaked (AT Ferrell flaking roll) and fed into an extruder (Readco Manufacturing). By extruding, steam was injected directly on the product reaching a temperature of 77–113 °C (collets). Collets were dried in a tray oven (66–82 °C; 30–40 min.) and thereafter solvent extracted with hexane at 49–60 °C for 30 minutes. After draining of the solvent, extraction was repeated twice. After separating the extract the remaining hexane was removed from the cotton seed meal by heating to 99–104 °C in a paddle mixer. Aliquots of meal were taken and stored frozen until analysis.

Refined oil

Crude oil and hexane were separated by passing the sample through a laboratory vacuum evaporator. Remaining hexane was removed from the oil by heating to 91–96 °C. An aliquot of the crude oil was filtered and mixed with vigorously with sodium hydroxide solution (16° Baumé) for 15 minutes at 20–24 °C and for 12 minutes at 63–67 °C. After centrifugation, refined oil was decanted and vacuum filtered. Aliquots of refined oil were taken and stored frozen until analysis.

Undelinted cotton seed and the processed fractions cotton seed hulls and meal were analysed according to the analytical process described under residue analysis. Refined oil samples were extracted four times with methanol. Extracts were combined without filtration and further processed as mentioned in section 6.3.9/01.

Table 86 Summary of residues of tolfenpyrad and OH-PT in cotton and cotton processed products

Compound	Total Treatment Rate (kg ai/ha)	PHI (days)	Sample	Residues (mg/kg) ^a	Processing Factor
Tolfenpyrad	2.33	13	undelinted seed	1.04	–
			seed meal	< 0.01	n.a.
			seed hulls	0.03	0.03
			refined oil	0.05	0.05
OH-PT	2.33	13	undelinted seed	< 0.01	–
			seed meal	< 0.01	n.a.
			seed hulls	< 0.01	n.a.
			refined oil	< 0.01	n.a.

^a Mean of duplicate preparation

n.a. = Not applicable

Study 7 – Tea

Tea samples for processing were taken from the supervised field trials conducted for determining the magnitude of residues in tea (Haigo, S, Report no. R-10029). A sample of homogenised tea (6 g) was placed in a beaker and boiling water (360 mL) was added. The sample was infused for 5 minutes. The infusion was filtered by gravity.

An aliquot of the infusion (120 mL) was transferred into a separating funnel, diluted with saturated aqueous sodium chloride solution (15 mL) and partitioning into hexane (50 mL). After phase separation, the hexane phase was washed with ethanol (1.5 mL) which was subsequently added to the aqueous phase. Partitioning was repeated once, as described above, with hexane (25 mL). The

hexane layers were combined by filtration over sodium sulphate and evaporated to dryness by rotary evaporation.

The sample was re-dissolved in hexane (2 mL) and cleaned up over Sep-Pak Plus Silica. The sample was loaded to the column and washed with ethyl acetate/hexane (1:9; 10 mL). Tolfenpyrad was eluted with ethyl acetate/hexane (15:85; 10 mL). The sample solution was evaporated to dryness by gentle stream of air.

The sample was re-dissolved in hexane (1 mL). Determination of residues was performed by GC-NPD.

For tolfenpyrad procedural recoveries were in the range of 88–93%. Samples were stored for up to 97 days prior to analysis.

Table 87 Summary of residues of tolfenpyrad in tea and tea infusion

Trial	Total Treatment Rate (kg ai/ha)	PHI (days)	Residues (mg/kg) ^a		Processing Factor
			Tea	Infusion	
Saitama Prefectural Agricultural and Forest	0.30	7	21.7	0.20	0.009
		14	7.04	0.08	0.011
		21	0.74	0.01	0.014
		30	0.16	< 0.01	< 0.063
Kanagawa Agricultural Technology Center	0.45	7	18.0	0.20	0.011
		14	4.34	0.06	0.014
		21	0.78	0.01	0.013
		30	0.18	< 0.01	< 0.056

^a Mean of duplicate preparation

Study 8 – Tea

Two residue trials were conducted on tea in Japan during 2005 (Otsubo, S 2012, Report no. R-10099).

One broadcast foliar application of a “flowable” formulation (Hachi-Hachi) at a nominal rate of 0.60 kg as/ha was performed. Trials were set-up as reverse decline trials with sampling after PHIs of 7, 14 and 28 days after application. Processing to tea infusion was done for samples of both trials at each PHI.

Table 88 Summary of residues of tolfenpyrad in tea and tea infusion

Trial	Total Treatment Rate (kg as/ha)	PHI (days)	Residues (mg/kg) ^a		Processing Factor
			Tea	Infusion	
Saitama Prefectural Agricultural and Forest	0.60	7	54.8	2.21	0.040
		14	10.4	0.49	0.047
		28	< 0.05	< 0.01	–
Kanagawa Agricultural Technology Center	0.60	7	30.3	1.12	0.037
		14	3.10	0.14	0.045
		28	0.14	< 0.01	-

^a Mean of duplicate preparation

In summary the residues in RAC and processing factors are given in Table 89.

Table 89 Summary of processing factors

RAC	Processed product	Tolfenpyrad (mg/kg)	OH-PT (mg/kg)	Processing factor	
				Individual	Best estimate
Orange		0.91	< 0.01		
	Juice	0.02	< 0.01	0.022	
	Dried pulp	8.03	0.02	8.8	
	Oil	74.4	0.08	82	
Plum		1.7	< 0.01		
	Dried fruit	5.3	< 0.01	3.1	
Plum		0.86	< 0.01		2.93

RAC	Processed product	Tolfenpyrad (mg/kg)	OH-PT (mg/kg)	Processing factor	
				Individual	Best estimate
	Dried fruit	2.35	< 0.01	2.7	
Tomato		0.12	< 0.01		
	Puree	0.04	< 0.01	0.31	0.31
	Paste	0.12	< 0.01	1.0	1.0
Cotton seed ^a		1.04	< 0.01		
	Seed meal	< 0.01	< 0.01	< 0.01	
	Seed hulls	0.03	< 0.01	0.029	
	Refined oil	0.05	< 0.01	0.048	
Tea		21.7, 7.04, 0.74, 0.16			
	Infusion tea	0.20, 0.08, 0.01, < 0.01		0.009, 0.011, 0.014 < 0.125	
Tea		18.0 4.34 0.78 0.18			
	Infusion tea	0.20 0.06 0.01 < 0.01		0.011 0.014 0.013 < 0.056	0.012
Tea		54.8 10.4 < 0.05			
	Infusion tea	2.21 0.49 < 0.01		0.040 0.047 -	
Tea		30.3 3.10 0.14			
	Infusion tea	1.12 0.14 < 0.01		0.037 0.045 < 0.071	0.043

^a Undelinted

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

Cattle feeding studies

The magnitude of tolfenpyrad residues was determined in tissues and milk in a dairy cattle feeding study (Arndt, T, 2010, report no. R-10215). Tolfenpyrad was administered orally by gelatine capsules for 28 consecutive days to three groups of three cows at dose levels equivalent to 2.5, 7.5 and 25 ppm based on a weekly averaged feed consumption (dry weight). A single dose capsule was administered to each cow following the morning milking. The untreated control animals were dosed with empty placebo capsules.

Milk was collected twice daily (morning and evening) to produce daily milk composites every day for 28 days of treatment. Mean daily milk production levels observed during the acclimation period for the cows in the control, low, medium and high dose groups were consistent throughout the study period. Analysis was conducted on samples generated on dose days 1, 2, 3, 4, 5, 6, 7, 10, 13, 16, 19, 22, 25 and 28. Milk was also collected from four cows during the depuration phase for days 3, 7 and 14 after the final dose. An aliquot of the composite milk sample was mixed thoroughly and stored

frozen divided into three equivalent portions. From the control group (1), group 2 and group 4 extra pooled milk samples were separated into cream and skim milk on study days 13 and 28.

One control and three cows from each dose group were sacrificed within 24 hours after their last dose, while the depuration treated cows were sacrificed at days 3, 7 and 14 after termination of dosing. The second control cow was sacrificed at day +14.

Samples of muscle (loin and leg), liver (representative sampling from each lobe), kidney (representative sample from each), and perinephric, abdominal and subcutaneous fat were removed. After weighing, composite tissue samples from each animal were stored frozen in labelled storage bags.

The milk and fat analyses determined tolfenpyrad, The PT-CA, OH-PT-CA and PCA residues were determined with a non-hydrolysis and a hydrolysis method. The hydrolysis method was used to cleave conjugated metabolites and allow for the analysis of the free metabolites. The LOQ was 0.01 mg/kg for each analyte.

In muscles and kidneys tolfenpyrad, PT-CA and OH-PCA residues were determined using a nonhydrolysis method only with an LOQ of 0.01 mg/kg for each analyte. In liver tolfenpyrad, PT-CA and OH-PT-CA residues were determined using both a non-hydrolysis method and a hydrolysis method with LOQ of 0.01 mg/kg for each analyte.

The storage durations were longer than the longest storage period for the milk and tissue samples. The residues determined in various samples are summarized in Tables 90–95.

Table 90 Residues in milk from dairy cows determined without hydrolysis of extracts

Matrix	Day	Group 2 (2.5 mg/kg diet)				Group 3 (7.5 mg/kg diet)				Group 4 (25 mg/kg diet)			
		parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
Milk ^a	1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	4	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	5	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	6	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	7	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	10	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	13	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01
	16	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	19	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	22	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	25	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	28	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01
Cream ^b	13	< 0.01	< 0.01	< 0.01	< 0.01	not performed				0.03	0.02	< 0.01	< 0.01
	28	< 0.01	< 0.01	< 0.01	< 0.01					0.02	0.02	< 0.01	< 0.01
Skim Milk ^b	13	< 0.01	< 0.01	< 0.01	< 0.01	not performed				< 0.01	0.01	< 0.01	< 0.01
	28	< 0.01	< 0.01	< 0.01	< 0.01					< 0.01	0.01	< 0.01	< 0.01

^a Mean of multiple individual samples, two cows for group 1, three cows for groups 2 and 3, six cows for group 4

^b Mean of multiple individual samples, two cows for group 1, three cows for groups 2–4

Table 91 Residues in milk and tissues from dairy cows determined with hydrolysis of extracts

Matrix	Day	Group 2 (2.5 mg/kg diet)				Group 3 (7.5 mg/kg diet)				Group 4 (25 mg/kg diet)			
		parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
Milk ^a	1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.03	< 0.01	< 0.01

Matrix	Day	Group 2 (2.5 mg/kg diet)				Group 3 (7.5 mg/kg diet)				Group 4 (25 mg/kg diet)			
		parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
	3	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.03	< 0.01	< 0.01	< 0.01	0.08	< 0.01	< 0.01
	4	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	0.13	< 0.01	< 0.01
	5	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.08	< 0.01	< 0.01	< 0.01	0.22	< 0.01	< 0.01
	6	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.08	< 0.01	< 0.01	< 0.01	0.11	< 0.01	< 0.01
	7	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	0.16	< 0.01	< 0.01
	10	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.05	< 0.01	< 0.01	< 0.01	0.20	< 0.01	< 0.01
	13	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	0.18	< 0.01	< 0.01
	16	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.03	< 0.01	< 0.01	< 0.01	0.26	< 0.01	< 0.01
	19	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.05	< 0.01	< 0.01	< 0.01	0.18	< 0.01	< 0.01
	22	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.06	< 0.01	< 0.01	< 0.01	0.24	< 0.01	< 0.01
	25	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	0.27	< 0.01	< 0.01
	28	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	0.23	< 0.01	< 0.01
Cream ^b	13	< 0.01	0.02	< 0.01	< 0.01	not performed				0.02	0.40	< 0.01	< 0.01
	28	< 0.01	0.01	< 0.01	< 0.01					0.02	0.49	< 0.01	< 0.01
Skimmed Milk ^b	13	< 0.01	< 0.01	< 0.01	< 0.01					< 0.01	0.04	< 0.01	< 0.01
	28	< 0.01	< 0.01	< 0.01	< 0.01					< 0.01	0.05	< 0.01	< 0.01

^a Mean of multiple individual samples, two cows for group 1, three cows for groups 2 and 3, six cows for group 4

^b Mean of multiple individual samples, two cows for group 1, three cows for groups 2–4

Table 92 Residues in tissues from dairy cows determined without hydrolysis of extracts

Matrix	Day	Animal	Group 2 (2.5 mg/kg diet)				Group 3 (7.5 mg/kg diet)				Group 4 (25 mg/kg diet)			
			parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
Loin Muscle	28	1	< 0.01	< 0.01	< 0.01	n.a.	< 0.01	0.03	< 0.01	n.a.	< 0.01	0.04	< 0.01	n.a.
		2	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.09	< 0.01	n.a.
		3	< 0.01	< 0.01	< 0.01	n.a.	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.03	< 0.01	n.a.
		mean	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.02	< 0.01	n.a.	< 0.01	0.05	< 0.01	n.a.
Leg Muscle	28	1	< 0.01	< 0.01	< 0.01	n.a.	< 0.01	0.03	< 0.01	n.a.	< 0.01	0.06	< 0.01	n.a.
		2	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.02	< 0.01	n.a.	< 0.01	0.18	< 0.01	n.a.
		3	< 0.01	0.02	< 0.01	n.a.	< 0.01	0.02	< 0.01	n.a.	< 0.01	0.03	< 0.01	n.a.
		mean	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.02	< 0.01	n.a.	< 0.01	0.09	< 0.01	n.a.
Liver	28	1	< 0.01	0.59	0.01	n.a.	< 0.01	2.0	0.08	n.a.	< 0.01	2.9	0.22	n.a.
		2	< 0.01	0.55	0.02	n.a.	< 0.01	2.2	0.07	n.a.	< 0.01	6.0	0.23	n.a.
		3	< 0.01	0.91	0.05	n.a.	< 0.01	2.1	0.07	n.a.	< 0.01	5.4	0.35	n.a.
		mean	< 0.01	0.68	0.03	n.a.	< 0.01	2.1	0.07	n.a.	< 0.01	4.8	0.27	n.a.
Kidney	28	1	< 0.01	0.12	< 0.01	n.a.	< 0.01	0.68	< 0.01	n.a.	< 0.01	1.2	0.1	n.a.
		2	< 0.01	0.17	< 0.01	n.a.	< 0.01	0.44	0.02	n.a.	< 0.01	1.3	0.06	n.a.
		3	< 0.01	0.10	< 0.01	n.a.	< 0.01	0.35	0.02	n.a.	0.02	1.3	0.11	n.a.
		mean	< 0.01	0.13	< 0.01	n.a.	< 0.01	0.49	0.02	n.a.	0.01	1.3	0.09	n.a.
Subcutaneous Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.02	0.03	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.04	0.07	< 0.01	< 0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.08	0.03	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.05	0.04	< 0.01	< 0.01
Perinephric Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.01	< 0.01	< 0.01	0.04	0.03	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.02	< 0.01	< 0.01	0.06	0.06	< 0.01	< 0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.10	0.02	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.01	< 0.01	< 0.01	0.07	0.04	< 0.01	< 0.01
Abdominal Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	0.04	0.02	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	0.06	0.05	< 0.01	< 0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.10	0.02	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	0.07	0.03	< 0.01	< 0.01

Matrix	Day	Animal	Group 2 (2.5 mg/kg diet)				Group 3 (7.5 mg/kg diet)				Group 4 (25 mg/kg diet)			
			parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
Liver ^a	28	1	< 0.01	0.49	0.01	n.a.	< 0.01	1.8	0.07	n.a.	< 0.01	2.9	0.17	n.a.
		2	< 0.01	0.52	0.02	n.a.	< 0.01	2.2	0.07	n.a.	< 0.01	6.3	0.17	n.a.
		3	< 0.01	0.82	0.04	n.a.	< 0.01	2.0	0.06	n.a.	< 0.01	5.3	0.27	n.a.
		mean	< 0.01	0.61	0.03	n.a.	< 0.01	2.0	0.07	n.a.	< 0.01	4.8	0.20	n.a.
Subcutaneous Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.03	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.04	0.06	< 0.01	< 0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.07	0.02	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.04	0.04	< 0.01	< 0.01
Perinephric Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	0.04	0.02	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.02	< 0.01	< 0.01	0.06	0.05	0.01	0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.11	0.02	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	0.07	0.03	< 0.01	< 0.01
Abdominal Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.04	0.02	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.07	0.04	< 0.01	< 0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.09	0.02	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.07	0.03	< 0.01	< 0.01

n.a. = Not applicable

[illegible]

Table 95 Comparison of the concentration of major residues in cattle tissues

	7.5 ppm dose group				25 ppm dose group			
	No. hydr.	w.hydr..	No. hydr.	w. Hydr.	No. Hydr.	w. Hydr.	No. hydr.	w. hydr.
	Parent	Parent	PT-CA	PT-CA	Parent	Parent	PT-CA	PT-CA
Loin Muscle	< 0.01		0.02		< 0.01		0.05	
Leg Muscle	< 0.01		0.02		< 0.01		0.09	
Liver	< 0.01	< 0.01	2.1	2.0	< 0.01	< 0.01	4.8	4.8
Kidney	< 0.01		0.49		0.01		1.3	
Subcutaneous Fat	< 0.01	< 0.01	0.01	< 0.01	0.05	0.04	0.04	0.04
Perinephric Fat	0.02	0.01	0.01	0.01	0.07	0.07	0.04	0.03
Abdominal Fat	0.01	0.01	0.01	< 0.01	0.07	0.07	0.03	0.03

APPRAISAL

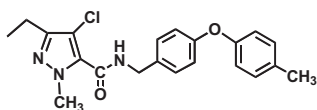
The toxicological and residue evaluation of tolfenpyrad was scheduled for the 2013 JMPR by the Forty-fourth Session of the CCPR.

Tolfenpyrad is a broad spectrum insecticide and a miticide, with contact activity against target pests on eggs, larvae, nymphs, and adults. It also has anti-feeding activity on larvae of lepidopteran insects. It belongs to the pyrazole class of insecticides. It has activity against several economically important insect pests of vegetables, fruits, nuts, vines and row crops.

The Meeting received information from the manufacturer on identity, the animal and plant metabolism, environmental fate analytical methods, storage stability, effect of processing, animal feeding studies, and results of supervised trials on almonds, cantaloupe,, cauliflower, cherries, cucumbers, cotton seed, grapes (table), grapefruits, lemons, oranges, peaches, pears, pecans, peppers, plums, potatoes, summer squash, tea and tomatoes.

Chemical name and structure

4-chloro-3-ethyl-1-methyl-*N*-[4-(*p*-tolylxy)benzyl]pyrazole-5-carboxamide



Chemical names and structures of metabolites referred to in the appraisal by codes:

Code Name	Chemical name	Structure	Matrices
PT-CA	4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		rat, plant, soil animal commodities
OH-PT-CA	4-[4-[[4-chloro-3-(1-hydroxyethyl)-1-methylpyrazol-5-yl]carbonylaminomethyl]phenoxy] benzoic acid		rat, plant, animal
CA-T-NH ₂	4-[4-(aminomethyl)phenoxy]benzoic acid		Photodecomposition, animal

Code Name	Chemical name	Structure	Matrices
OH-PAM	4-chloro-3-(1-hydroxyethyl)-1-methylpyrazole-5-carboxamide		rat, plant, soil, eggs
PCA	4-chloro-3-ethyl-1-methylpyrazole-5-carboxylic acid		Plant, soil, eggs
OH-PT	4-chloro-3-(1-hydroxyethyl)-1-methyl-N-[4-(p-tolyloxy)benzyl] pyrazole-5-carboxamide		rat, plant
CO-PT	3-acetyl-4-chloro-1-methyl-N-[4-(p-tolyloxy)benzyl] pyrazole-5-carboxamide		plant
PT-OH	4-chloro-3-ethyl-N-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		rat, plant, soil, photodecomposition
PT-CHO	4-chloro-3-ethyl-N-[4-[4-(formylphenoxy)benzyl]-1-methylpyrazole-5-carboxamide		rat, plant, soil, photodecomposition
PT-CA	4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		rat, plant, soil animal commodities
OH-PT-OH	4-chloro-3-(1-hydroxyethyl)-N-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		rat, plant, animal commodities
CO-PT-OH	3-acetyl-4-chloro-N-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		plant
CO-PT-CA	4-[4-[(3-acetyl-4-chloro-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		plant
CA-PT-OH	[4-chloro-5-[N-[4-(4-hydroxymethyl)phenoxy]benzyl]carbonyl]-1-methylpyrazol-3-yl]acetic acid		rat, plant
CA-PT-CA	4-[4-[3-(carboxymethyl)-4-chloro-1-methylpyrazol-5-yl]carbonylaminomethyl]phenoxy]benzoic acid		rat, plant
DM-PT	4-chloro-3-ethyl-N-[4-(p-tolyloxy)benzyl]pyrazole-5-carboxamide		plant
DM-PT-OH	4-chloro-3-ethyl-N-[4-[4-(hydroxymethyl)phenyl]benzyl] pyrazole-5-carboxami		plant

Code Name	Chemical name	Structure	Matrices
PAM	4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide		rat, plant, soil
OH-PAM	4-chloro-3-(1-hydroxyethyl)-1-methylpyrazole-5-carboxamide		rat, plant, soil, eggs
T-AM	[4-(<i>p</i> -toloxy)benzamide		plant
OH-T-AM	4-[4-(hydroxymethyl)phenoxy] benzamide		plant
CA-T-AM	4-(4-carbamoylphenoxy)benzoic acid		plant
T-CA	4-(<i>p</i> -toloxy)benzoic acid		rat, plant
OH-T-OH	<i>bis</i> [4-(hydroxymethyl)phenyl]ether		pant
OH-T-CA	4-[4-(hydroxymethyl)phenoxy] benzoic acid		rat, plant
CA-T-CA	4,4'-oxydibenzoic acid		rat, plant
T-CA-Glu	glucose conjugate of 4-(<i>p</i> -toloxy) benzoic acid		plant

Animal metabolism

The Meeting received reports of animal metabolism studies in lactating goats and laying hens. The studies were conducted with [^{14}C] tolfenpyrad labelled on the pyrazole and tolyl rings.

Metabolism in laboratory animals is summarized under toxicology.

Lactating goats

[Pyrazole- ^{14}C]-tolfenpyrad and [tolyl- ^{14}C]-tolfenpyrad were administered orally (12.3–12.5 mg/kg feed/day) to two lactating goats once daily for five consecutive days. Milk was collected twice daily and excreta were collected once daily. The total recovery of radiolabel was 76.1% and 96.3% of the administered dose (AD) for the pyrazole- and tolyl-labels, respectively. Most of the administered dose was recovered in the excreta (46.8–49.8%) and gastrointestinal tracts (19.2–32.6%) at sacrifice.

Administration of [tolyl- ^{14}C]-tolfenpyrad resulted in consistently higher residues in tissues than the administration of [pyrazole- ^{14}C]-tolfenpyrad. The total radioactive residues (TRR) expressed as tolfenpyrad mg equivalents/kg were in liver (25 mg/kg, 12%AD) and kidney (6.93 mg/kg, 0.7%AD) and substantially lower in the fat (0.36 mg/kg, 0.4%AD), milk (0.17 mg/kg, 19% AD) and muscle (0.14 mg/kg, 0.1–0.2%AD). No free metabolite unique to only one of the radiolabels was found.

The parent tolfenpyrad was present up to 4.1% TRR (< 0.01 mg/kg) in milk, 10% TRR (0.01 mg/kg) in muscle, 17.3%TRR (0.06 mg/kg) in fat, and was not detected in liver and kidney.

Following the administration of pyrazole- and tolyl- labelled tolfenpyrad, the predominant residues were PT-CA in free and its conjugated form. The free and conjugated PT-CA, respectively, amounted up to 7.6% and 48% of TRR (0.01–0.08 mg/kg) in milk, 68% TRR (0.09 mg/kg) (its conjugate was not detected (nd) in muscle from the tolyl label), 52% and 9.0% of TRR (13–1.74 mg/kg) in liver, 63% and 3.5% of TRR (4.33–0.21 mg/kg) in kidney and nd–34.1% of TRR(nd–0.09 mg/kg) in fat. PT-CA is rapidly conjugated in the liver. But in the gastrointestinal tract it is deconjugated.

OH-PT-CA was present in free form 17% TRR (0.03 mg/kg), in milk, 8.9%TRR (< 0.01 mg/kg,) in muscle, 27% TRR (6.69 mg/kg,) in liver, 19.3% TRR (1.34 mg/kg)in kidney, and in conjugated from 1.2%TRR (0.21 mg/kg) in liver and 0.3%TRR in kidney (0.02 mg/kg,). It was not detected in fat.

In addition, CA-T-NH₂ could be released by hydrolysis from milk (19.4%TRR) and fat (5.3%TRR).

In summary, tolfenpyrad is oxidized at the tolyl-methyl group to PT-CA. Further oxidation at the pyrazole ethyl group of PT-CA produces OH-PT-CA. Both PT-CA and OH-PT-CA occur as free metabolites in milk, liver, kidney, and muscle. PT-CA and its hydrolysis metabolites (PCA and CA-T-NH₂) are converted into nonpolar lipids in milk and fat. Saponification of the lipid conjugates releases PT-CA, PCA, and CA-T-NH₂.

Laying hens

[Pyrazole-¹⁴C]-tolfenpyrad and [tolyl-¹⁴C]-tolfenpyrad were administered orally (in gelatine capsules) to two separate groups of hens once daily for seven consecutive days. The administered daily dose was 12.6–13.5 mg/kg feed/day. Eggs were collected twice daily and excreta were collected once daily. Hens were sacrificed approximately 22–23 hours after the last dose administration. Liver, muscle, fat and gastrointestinal tracts with contents were collected for analysis.

The total recovery of radiolabel was 85.4% and 91.4% of the administered dose (AD) for the pyrazole- and tolyl-labels, respectively. Of the total dose 2.3–2.4% remained in the gastrointestinal tract one day after the last dose. The total identified residues were 66–78% in eggs, 85–89% in muscle, 84–96% in liver and 62–73% in fat. In tissues, the total radioactive residue (TRR) was highest in liver (up to 1.94 mg/kg; 0.8% AD) and lower in eggs (0.3% AD), fat (0.1% AD) and muscle (0.1% AD).

The parent tolfenpyrad was only present at 0.06 mg/kg concentration in fat (15% TRR) and < 0.01 mg/kg concentration in eggs (2.4%TRR), muscle (1.8% TR) and liver (0.2% TRR).

Following the administration of pyrazole- and tolyl-labelled tolfenpyrad, the predominant residues were PT-CA in free and its conjugated form. The free PT-CA amounted up to 40.5% TRR (0.07 mg/kg) in eggs, 85%TRR (0.1 mg/kg) in muscle and conjugated PT-CA, respectively, amounted up to 40.5–29% TRR (0.07–0.04 mg/kg) in eggs, 79% TRR (1.3 mg/kg) in liver, and 15% TRR ((0.07 mg/kg) in fat. The conjugated PT-CA was present in eggs, liver and fat at 29, 11.4, and 34.5% of TRR, respectively.

OH-PAM was present in free form at 12.6% TRR (0.02 mg/kg) in eggs, and 12.4% TRR (0.02 mg/kg) in muscle. It was not detected in liver and fat.

OH-PT-CA was detected at 2.7% TRR (< 0.01 mg/kg) in muscle, 5.2% TRR (0.09 mg/kg) in liver. It was not detected in eggs and fat.

In summary, the initial metabolite of tolfenpyrad is PT-CA occurring as a major residue in eggs, liver, kidney, muscle, and fat. Further oxidation at the pyrazole-ethyl group of PT-CA produces OH-PT-CA that occurs in liver and muscle. OH-PAM occurs as a free metabolite in eggs and muscle. Tolfenpyrad is a trace residue in eggs, liver, and muscle but was more abundant in fat. PT-CA and its hydrolysis product (PCA) are incorporated into non-polar lipid conjugates occurring in eggs and fat.

Plant metabolism

Cabbage

[Tolyl-¹⁴C]-tolfenpyrad was applied to individual cabbage plants in a spray chamber. One application was made at a rate corresponding to 750 g ai/ha. Samples were taken at day 0 (immediately after the spray dried) and at 7, 14 and 28 days.

Twenty eight days after application 99.7% of the TRR (8.39 mg tolfenpyrad equivalent/kg) was on the outer leaves, 78.7% in the organo-soluble fraction and 15.9% in the water-soluble fraction, and only 0.3% of the TRR (0.03 mg equiv./kg) was in the heads, distributed between the water soluble (0.2%) and organo soluble fraction (0.1%).

Tolfenpyrad was found in the outer leaves at levels of 12.6 mg/kg (89% of TRR) immediately after application decreasing to 4.6 mg/kg (55.0% of TRR) after 28 days. In samples taken 28 days after application, OH-PT, OH-T-CA, OH-T-OH, and CA-T-AM were present at 0.54 mg/kg (6.4% of TRR), 0.33 mg/kg (3.9% of TRR), 0.31 mg/kg (3.7% of TRR), and 0.20 mg/kg (2.4% of TRR), respectively. Other metabolites were present at lower proportions. In cabbage head without outer leaves neither the parent compound nor any of the identified metabolite were detected (< 0.01 mg/kg).

In a second cabbage study, [pyrazole-¹⁴C]-tolfenpyrad was applied once to individual cabbage in a spray chamber at a rate corresponding to 750 g ai/ha. Cabbage samples were collected at 28 days after application. At that time 97.2% of the AD (9.22 mg/kg) was distributed on the outer leaves and 2.8% (0.23 mg/kg) in the heads.

Tolfenpyrad was found in the outer leaves at levels of 4.7 mg/kg (49.8% of TRR). The identified metabolites, expressed as TRR, were 7.9% OH-PT (0.75 mg/kg), 3.4% OH-PT-OH and 2.9% OH-PT-CA. Other metabolites were detected at levels of ≤ 0.20 mg/kg (≤ 2.1% of AD). In the head, levels of metabolites did not exceed 0.1% of TRR.

Peach

[Tolyl-¹⁴C]-tolfenpyrad was applied to individual peach plants in a spray chamber. One branch and one fruit were treated on each plant. One application was made at a rate corresponding to 750 g ai/ha.

Immediately after application, 83.5% of the AD was distributed on the leaves with 11.8% on the stem and 4.7% on the fruit. There was no significant change in distribution 56 days after application; TRRs remained were 83.1%, 7.5% and 9.3%, respectively.

In the fruit, parent tolfenpyrad was found at 3.0 mg/kg (100% of AD) immediately after application decreasing to 0.79 mg/kg (77% of TRR) by day 56. The majority of residues (8.4% TRR) were in the peel while only 0.4% TRR in the pulp. The metabolites did not exceed 2.8% TRR throughout the study period, except the glucose conjugate of T-CA at 6.1% TRR.

In the second peach study [pyrazole-¹⁴C]-tolfenpyrad was applied to individual peach plants in a spray chamber. One branch and one fruit were treated on each plant. One application was made at a rate corresponding to 750 g ai/ha. Peach fruits were collected 53 days after application. At that time, 86.1% of the AD was distributed on the leaves, 7.3% on the stem and 6.6% (0.77 mg/kg) on the fruit concentrated mainly in the peel (11 mg/kg) with low concentration (0.12 mg/kg) in the pulp.

In the fruit, parent tolfenpyrad was found at levels of 0.53 mg/kg (65% of TRR) 53 days after application. The only identified metabolite, OH-PAM, was found in the pulp at 0.03 mg/kg (4.0% of TRR).

In the leaves, parent tolfenpyrad was found at levels of 21.1 mg/kg (32.7% of TRR) after 56 days. Free PT-CA was the main metabolite found at 10.0 mg/kg (15.5% of TRR) with a contribution of glucose-conjugated PT-CA at 0.94 mg/kg (1.5% of TRR) followed by other metabolites present at less than 10% TRR.

The studies indicated that the translocation of unchanged tolfenpyrad was very limited. The predominant part of the TRR was located in the peel (86.4–94.6%) of the fruit residue.

Radish

[Tolyl-U-¹⁴C]-tolfenpyrad or [pyrazole-¹⁴C]-tolfenpyrad were applied to radish located outdoors. Each plot received two applications, 14 days apart, at a nominal rate of 230 g ai/ha. Radish plants were sampled 1 day after the second application and separated into root and foliage samples.

Labelled tolfenpyrad distributed into the roots (0.44–0.59 mg/kg, 4.9–5.2% of AD) and the foliage (7.0–11 mg/kg, 94.8–95.1% of TRR).

The major residues in radish roots were tolfenpyrad (0.24 mg/kg, 54.0% of TRR), PT-CA (0.11 mg/kg, 21.5% of TRR). Other metabolites amounted to less than 10%TRR except conjugated OH-PAM and PAM which were the major metabolite found in radish roots at 32.2% and 26.7% TRR respectively.

The major residue in foliage was tolfenpyrad (9.31 mg/kg, 85.0% of TRR) with a much lesser amount of metabolites amounting to less than 4% of TRR.

In summary, the metabolic pathways of tolfenpyrad in three different crops were considered comparable. In each case, unchanged parent accounted for a very significant proportion of the residue. All three crops contain the identified metabolites OH-PT (not observed but assumed in radish as an intermediate to OH-PAM), OH-PAM, PAM and PT-CA.

Environmental fate in soil and water

The Meeting received information on photolysis on soil, aerobic degradation in soil, aqueous photolysis and confined and field rotational crop studies.

Soil photolysis

A photolysis study of [¹⁴C] tolfenpyrad was conducted in sandy loam soil exposed to artificial light (290 nm) for 13 days. In the light exposed samples, unextracted radiocarbon increased slowly reaching an average of 3.2% (pyrazole label) and 10.7% (tolyl label) of applied radioactivity (AR) by day 313. Only minimal radiocarbon was recovered (0.3%) in traps of organic volatiles for light exposed samples, and none in dark control samples. Photoproducts consisted mainly of PT-CHO, PAM and OH-PAM present at a maximum of 6.6%, 11.3% and 3.5% AD, respectively in both labels. Tolfenpyrad showed negligible degradation in dark control samples with an average of 90% still present as parent in both labels at the end of the study. The PT-CA was the major degradate (2.0% in pyrazole labelled material and 4.7% in tolyloxy labelled material). The calculated half-life of tolfenpyrad was 444 days from tolyl label and 624 days from pyrazole label. The results indicate that photolysis is a very minor route of the degradation of tolfenpyrad

Aerobic soil metabolism

An aerobic soil metabolism study was conducted on a California sandy loam soil using [¹⁴C] tolfenpyrad. The treated samples were incubated in the dark at 25 °C for periods up to 365 days. Tolfenpyrad degraded rapidly in soil under aerobic conditions and represented an average of 30.0% AR by day 21, declining to an average of 1.6% at the end of the incubation period. The primary degradates observed in the study were CO₂, PT-Cam PCA and soil bound residues. The soil bound residues were completely mineralised within one year. The calculated DT₅₀ and DT₉₀ values were maximum 14 and 78 days, respectively, indicating that tolfenpyrad is not persistent.

Confined rotational crop study

Tolfenpyrad radiolabelled in two positions (pyrazole- and tolyl-rings) was applied to test plots at a target application rate of 350 g ai/ha. Lettuce, radish and wheat were planted at intervals of 30, 120 and 365 days after single bare soil application. Samples were taken at appropriate harvest times and analysed for residues.

Metabolites at ≥ 0.01 mg/kg were OH-PAM (free and conjugated), OH-PCA (free and conjugated), and PAM (radish foliage and root only). A number of other metabolites were detected in combined extracts, but each was < 0.01 mg/kg or $< 10\%$ of TRR. Conjugates of OH-PAM and OH-PCA were liberated by acid hydrolysis.

Following pyrazole labelled tolfenpyrad application the detected metabolites in lettuce amounted up to 0.02 mg tolfenpyrad equivalent. The free and conjugated OH-PAM, OH-PCA and PAM were the major metabolites, each was less than 26% TRR. No other single metabolite represented more than 2.5% TRR (< 0.01 mg/kg).

In radish foliage the detected metabolites (at 0.02–0.03 mg tolfenpyrad equivalent/kg) were the OH-PAM conjugates (20%TRR) the OH-PCA conjugates (24% TRR) as well as free OH-PAM and PAM with lesser amounts of OH-PCA and PT-CA.

In radish roots, the only detected metabolites were the OH-PCA conjugates (27% TRR) as well as free OH-PAM (8.5%TRR) and PAM (24.5%TRR).

In wheat grain, none of the metabolites were detected (< 0.01 mg/kg).

In wheat forage the predominant metabolites were the OH-PAM conjugates (≤ 0.16 mg eq/kg, 29.7% TR at 30 days PBI) the OH-PCA conjugates (0.17 mg eq/kg) as well as free OH-PCA (0.09) with lesser amounts of OH-PAM, PAM and PCA. No other single metabolite represented more than 5.2% TRR (0.01 mg/kg).

In wheat hay and straw the maximum concentrations were for OH-PAM conjugates (0.4 mg eq/kg, 32%TR) and OH-PCA conjugates (0.17 mg eq/kg). With exception of OH-PAM conjugates in wheat hay, all identified metabolites show a decrease with increasing aging of the soil.

Following the treatment with tolyl- labelled compound no relevant concentration of any individual compounds were found in lettuce, radish, wheat forage, hay, straw and grain at any plant-back interval. Only trace amounts of PT-CA were found in radish (120-day) and wheat hay (30-day) samples. In summary, tolfenpyrad is a minor residue (< 0.01 mg/kg) in confined rotational crops (lettuce, radish, and wheat). Most radiolabelled residues derived from cleavage of the amide bond, resulting in pyrazole and diphenyl ether fragments.

Field rotational crop studies

Two field trials were carried on mustard greens as the primary crop treated at about maximum seasonal rate of 0.598 kg ai/ha. The primary crop was removed from the trials at normal harvest with a PHI of one day after last application. Rotational crops (radish, lettuce and sorghum) were planted at intervals of 14, 28–30 and 58–60 days after last application.

At normal harvest of the rotational crops, no residues of tolfenpyrad, OH-PAM, OH-PCA and PAM were found above the LOQ in radish roots, lettuce and sorghum forage, grain and stover. Residues of OH-PAM and OH-PCA at the LOQ (0.01 mg/kg) were found at rotational intervals of 14 and 30 days after last application only in radish tops from one trial site.

Methods of analysis

The HPLC methods for determining the parent compound and OH-PT metabolite residues in plant matrices are based on three repeated extractions with methanol, followed by various solid phase extraction clean-up(s). The cleaned samples either concentrated or diluted to known volume before determination with HPLC-MS/MS. The LOQ for both compounds in all matrices is 0.01 mg/kg, except tea (0.05 mg/kg). The specificity of the detection was assured with two mass transitions. Average recoveries were all within the acceptable range of 70–120%, with relative standard deviations (RSD) below 20%.

For the rotational crop study the method used was validated for the determination of tolfenpyrad, OH-PAM, PAM and OH-PCA. Recovery data were generated from three samples fortified at the LOQ and three samples fortified at $10 \times$ LOQ for each matrix. The mean percentage recoveries at 0.01 mg/kg and 0.1 mg/kg were generally between 70–110% with RSD $< 20\%$. There

were some deviations especially when the extracts were hydrolysed. The mean recoveries and RSD values were in some cases outside the nominal ranges, but the differences were not significant taking into account the limited number of tests.

The HPLC-MS/MS methods were developed for determination of tolfenpyrad and its metabolites PT-CA, OH-PT-CA and PCA in animal commodities with an LOQ of 0.01 mg/kg. The milk samples were extracted with methanol, the tissues with methanol/water (5/1). The extracts were partitioned into ethyl acetate after adding either citric acid (milk and fat) or sodium chloride (muscle, liver and kidney). After evaporation to dryness the extracts were taken up in methanol or hexane and partly subjected to SPE clean-up. The other part of the milk, liver and fat extracts was hydrolysed. The final extracts were analysed by HPLC/MS/MS. The specificity of the detection was assured by two mass transitions for tolfenpyrad and three transitions for the metabolites. Repeatability data was generated from three samples fortified at the LOQ and three samples fortified at $10 \times$ LOQ for each matrix. The mean percentage recoveries at each fortification level were within 70–110, except PT-CA in liver with hydrolysis (65% at 0.01 mg/kg), fat with hydrolysis (60% at 0.1 mg/kg) and OH-PT-CA in fat with hydrolysis (64% at 0.01 and 69% at 0.1 mg/kg). In spite of some deviations, the methods applied in the studies are considered suitable for the intended purpose.

Stability of residues in stored analytical samples

In plant matrices, freezer storage stability (at about -20 ± 5 °C) of tolfenpyrad and OH-PT has been demonstrated in tomatoes, apples, lettuce, grapes, oranges, almonds (nutmeat and hulls), cottonseed oil and potato flakes (18 months), peaches (4 months), prunes (dried) (5 months), cucumbers (5.5 months), cauliflower (6 months), and tea (12 months).

Freezer storage stability of tolfenpyrad, OH-PAM, OH-PCA and PAM has also been demonstrated in radish (roots) (112 days), lettuce (150 days) and sorghum forage (114 days), stover (87 days) and grain (109 days). This covers high acid, high water, high starch and high oil content crops.

When stored < 0 °C tolfenpyrad, PT-CA and OH-PT-CA were stable in bovine muscle (85 days), kidney (85 days), fat (99 days) and milk (177 days). The average OH-PT-CA residue remained in liver was 39% after 111 days storage, but the procedural recoveries (41%) were similar. PCA was stable in fat and milk.

Definition of the residue

In goat, the parent tolfenpyrad was not detected in liver, and kidney, but it was found at < 0.01 mg/kg in milk (2.9–4.1% of TRR) and muscle (10% TRR) and at 0.04–0.06 mg/kg in fat (13.6–17.3% TRR).

The major radioactive residue derived from the administration of pyrazole and tolyl labelled tolfenpyrad was PT-CA being present up to 0.03 mg/kg (16.9% TRR) in milk, 0.09 mg/kg (63.3% TRR) in muscle, 13.1 mg/kg (51.8% TRR) in liver, 4.33 mg/kg (62.6% TRR) in kidney, and 0.06 mg/kg (16.3% TRR) in fat.

The concentration and % proportion of TRR of OH-TP-PCA derived from administration of pyrazole- or tolyl-labelled tolfenpyrad was up to 0.03 mg/kg (16.9%) in milk, < 0.01 mg/kg (8.9%) in muscle, 6.8 mg/kg (26.9%) in liver, 1.3 mg/kg (19.3%) in kidney, and it was not detected in fat. The other metabolites identified were present at substantially lower concentrations.

Dairy cattle feeding study revealed that in milk, the only detected residue (> 0.01 mg/kg) is PT-CA which can be recovered after hydrolysis with maximum concentration of 0.27 mg/kg. In cream derived from 2.5 and 25 ppm dose groups the parent tolfenpyrad was present in about 0.01–0.02 mg/kg, respectively, and PT-CA were present at approximately 25 times higher concentration in conjugated form than in free form. In muscle, fat, liver and kidney the PT-CA is the major residue. Hydrolysis of samples revealed that only free PT-CA is present in the liver.

In the study with laying hens administered with labelled tolfenpyrad the parent tolfenpyrad was found at low concentrations < 0.01 mg/kg, (1.2–1.8% TRR) in eggs, muscle and liver, but it was present at 0.06 mg/kg (14–15%TRR) in fat.

The PT-CA occurs as a major residue up to 0.07 mg/kg (41%TRR) in eggs, 0.10 mg/kg (85%TRR) in muscle, 1.4 mg/kg (79%TRR) in liver, and 0.07 mg/kg 15% TRR) in fat. PT-CA is converted to OH-PT-CA, which was found up to 0.09 mg/kg (5.2% TRR) in liver and < 0.01 mg/kg (2.7%TRR) muscle.

Analytical methods are available for the simultaneous determination of tolfenpyrad, and free PT-CA, OH-PT-CA and PCA in one step and the conjugates can be released in a separate step after alkaline hydrolysis. However, the latter procedure could be carried out with sometimes low and varying recovery and it is not considered suitable for routine analyses.

Taking into account the relative proportions and concentration of the parent tolfenpyrad and its metabolites, and the availability suitable analytical method, the sum of tolfenpyrad and the free PT-CA are considered suitable marker compounds for enforcement purposes. For dietary risk assessment the free and the conjugated PT-CA, OH-PT-CA should be considered, because they have a toxic potency similar to PT-CA and OH-PT-CA.

PT-CA, the major residue component is present in higher concentration in muscle than in fat. OH-PT-CA was not present in fat. The Meeting concluded that the residue is not fat soluble.

The parent tolfenpyrad was present in outer leaves of cabbage at 4.71 mg/kg 28 days after treatment while the concentrations of all the identified metabolites were below 0.3 mg/kg

The concentrations of parent tolfenpyrad were 3.95 mg/kg (89.4%TRR) and 0.37 mg/kg (70% TRR) in peach fruits 14 and 28 days after treatment. In the same samples and sampling time T-AM, PT-OH, PT-CA were present at 0.12 and < 0.02 mg/kg, 0.06 and nd mg/kg, and 0.06 and nd mg/kg, respectively.

Radish leaves and roots on day 1 after the 2nd application contained 5.7 mg/kg and 0.24 mg/kg parent residue respectively, while any of the identified metabolites were present at less than 10% and 20% of the parent compound, respectively.

No residue is expected above 0.01 mg/kg in any rotational crops.

The Meeting noted that the parent tolfenpyrad is the major residue in plant commodities and it is a good marker for compliance with GAP.

The Meeting recommended the following residue definitions for tolfenpyrad:

Definition of the residue for compliance with the MRL and estimation of dietary intake for plant commodities: *tolfenpyrad*.

Definition of the residue for compliance with the MRL and estimation of dietary intake for animal commodities: *sum of tolfenpyrad, and free and conjugated PT-CA (4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylamino]methyl]phenoxy]benzoic acid and OH-PT-CA (4-[4-[(4-chloro-3-(1-hydroxyethyl)-1-methylpyrazol-5-yl]carbonylamino]methyl]phenoxy] benzoic acid) (released with alkaline hydrolysis) expressed as tolfenpyrad*.

The residue is not fat soluble.

Results of supervised trials on crops

The Meeting received supervised trials for a number of commodities from the USA for which there were no authorised uses. Trials were received from Japan where tolfenpyrad is authorised for use on tea. The residues obtained from supervised trials not supported by GAP are summarized in the JMPR Monograph but were not used for the estimation of STMR, HR and maximum residue levels.

Tea

Four residue trials were conducted on green tea in 1997–98 in Japan. One foliar application of tolfenpyrad was made with spray solutions of 0.0015 kg/hL following the design of reverse decline

trials. The treated plots of each trial were harvested at a PHI of 7, 14, 21 and 30 days after treatment and the samples were analysed twice at intervals of about 1 year.

The GAP in Japan permits one foliar application of 15% EC formulation in 1000 times dilution using 2000–4000 L/ha water. The PHI is 14 days.

The average residues obtained in replicate samples taken at 14 days were: 3.77, 4.29, 7.05 and 12.1 mg/kg.

The Meeting estimated a maximum residue level of 30 mg/kg, an STMR value of 5.65 mg/kg and 13.8 mg/kg of STMR and HR values for green tea, respectively

Fate of residues during processing

Following one application of tolfenpyrad at rates of 0.30 kg ai/ha or 0.45 kg ai/ha, mean residues of tolfenpyrad were substantially reduced in tea infusion to the levels of 0.20 mg/kg, 0.06–0.08 mg/kg, 0.01 mg/kg and < 0.01 mg/kg, respectively, at PHIs of 7, 14, 21 and 30 days.

In a second study tolfenpyrad was applied at a rate of 0.6 kg ai/ha. Tolfenpyrad residues were substantially reduced in tea infusion to the levels of 1.12–2.21 mg/kg, 0.14–0.49 mg/kg and < 0.01 mg/kg, respectively, at PHIs of 7, 14 and 28 days. The two sets of trials gave about four times different average processing factors, therefore the larger factor (0.043) is used for dietary intake assessment.

The Meeting estimated for green tea infusion an STMR value of 0.24 mg/kg.

Residues in animal commodities

Farm animal dietary burden

As there are no registered uses on animal feed, the animal burden cannot be calculated.

Farm animal feeding studies

In a dairy cattle feeding study, tolfenpyrad was administered orally by gelatine capsules for 28 consecutive days to 3 groups of 3 cows at dose levels equivalent to 2.5 (2×), 7.5 (6×) and 25 (20×) ppm in feed. Residues of tolfenpyrad and its metabolites PT-CA, OH-PT-CA or PCA were determined in milk and tissues. Neither the parent compound nor any of the metabolites were detected in any samples derived from control animals.

Residues in Milk

No quantifiable residues of tolfenpyrad, PT-CA, OH-PT-CA or PCA were detected in milk from cows treated with tolfenpyrad at the 2× and 6× dose levels, except PT-CA (0.02 mg/kg and 0.08 mg/kg, respectively) released by hydrolysis. In milk samples of the 6× dose group, no quantifiable free or conjugated residues were detected for tolfenpyrad, OH-PT-CA or PCA, whereas free or conjugated residues of PT-CA were present with maximums of 0.01 mg/kg and 0.27 mg/kg. In general the free metabolite corresponds to approximately 5–10% of the conjugated metabolite.

In milk samples of the 20× dose group, no free PCA and only trace levels of tolfenpyrad and OH-PT-CA averaging below LOQ were detected. Free PT-CA close to the LOQ was found after day 13. Conjugated PT-CA was found at significantly higher concentrations, reaching a plateau near 0.25 mg/kg by day 16. During two weeks of depuration no metabolites were detected in milk with the exception of a residue of 0.07 mg/kg PT-CA in the 31 days milk sample of the 20× dose group.

Residues in Cream and Skim Milk

In cream samples from the 2× dose group, only conjugated PT-CA residues were detected averaging 0.02 mg/kg and 0.01 mg/kg for days 13 and 28, respectively. No quantifiable residues were found in skimmed milk samples from the 2× dose group. In cream samples from the 20× dose group, comparable levels were found for free and conjugated tolfenpyrad corresponding to approximately

0.02 mg/kg for both 13 and 28 days. Conjugated PT-CA in cream was approximately 25 times higher than free PT-CA being present at a level of about 0.02 mg/kg. In skimmed milk only PT-CA was found in samples of the 20× dose group at levels of 0.01 mg/kg for free and 0.04–0.05 mg/kg for the conjugated form.

Residues in Muscle

Tolfenpyrad and OH-PT-CA residues were not present in quantifiable concentrations in the samples of every dose groups. The average PT-CA residues were present at 0.01 mg/kg, 0.02 mg/kg and 0.05–0.09 mg/kg in samples of dose groups of 2.5 ppm, 7.5 ppm and 25 ppm.

Residues in Liver

No parent tolfenpyrad residues were found in any treated liver sample. Residues of PT-CA were found in all dose levels in approximate proportion to the level of dosing. Free PT-CA residues after 28 days of dosing averaged for 0.65 mg/kg for the 2× dose level, 2.0 mg/kg for the 6× dose level, and 4.8 mg/kg for the 20× dose level. Conjugated residues of PT-CA were at a similar level, suggesting that only free PT-CA is present in the liver. After fourteen days of depuration, PT-CA residues (0.03 mg/kg) were reduced by a factor > 100 compared to the 28 days level (4.8 mg/kg). Also OH-PT-CA was found at a lesser extent than PT-CA. Residues of free OH-PT-CA averaged at 0.03 mg/kg, 0.07 mg/kg and 0.27 mg/kg for the 2×, 6× and 20× dose levels, respectively. Conjugated residues were less than or equal to residues of free OH-PT-CA, suggesting that only free metabolite is present in liver.

Residues in Kidney

No parent tolfenpyrad residues were found in kidney samples of the 2× and 6× dose groups. In the 20× dose group tolfenpyrad was present at the LOQ (0.01 mg/kg). Residues of PT-CA were found in all dose levels in approximate proportion to the level of dosing. PT-CA residues after 28 days of dosing were averaged for 0.13 mg/kg for the 2× dose level, 0.49 mg/kg for the 6× dose level, and 1.3 mg/kg for the 20× dose level. Residues of OH-PT-CA were less than the LOQ (< 0.01 mg/kg) for the 2× dose level and averaged at 0.02 mg/kg and 0.09 mg/kg for the 6× and 20× dose level, respectively. After fourteen days of depuration, residues of tolfenpyrad were below the LOD, and residues of PT-CA and OH-PT-CA were below the LOQ (< 0.01 mg/kg).

Residues in Fat

For the 2× dose level, no residues of tolfenpyrad, OH-PT-CA or PCA were found. Residues of free tolfenpyrad in the 6× and 20× dose levels averaged for 0.01 mg/kg and 0.065 mg/kg, respectively. Residues of free PT-CA in fat were below the LOQ (< 0.01 mg/kg) for the 2× dose level and averaged at 0.01 mg/kg and 0.04 mg/kg for the 6× dose level and the 20× dose level, respectively. Residues of OH-PT-CA and PCA were only detected in the 20× dose group samples at levels below the LOQ (< 0.01 mg/kg). Residues after sample hydrolysis were in a similar order indicating that no conjugated residues were present in fat. The depuration period showed a steady decline in residues with no determinable residues present by day 14 after last dosing.

Considering the residues in samples derived from the highest (20×) dose group, the free and conjugated PT-CA released with hydrolysis were the major residues in muscle (0.09 mg/kg), liver (6.9 mg/kg) kidney (1.8 mg/kg), and fat (0.04 mg/kg)

Parent tolfenpyrad was only present in milk cream and fat in the highest dose group.

PT-CA concentration rapidly decreased during depuration.

Animal commodity maximum residue levels

Without calculated animal burden no residue levels can be calculated for animal commodities.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

Definition of the residue for compliance with the MRL and estimation of dietary intake for plant commodities: *tolfenpyrad*.

Definition of the residue for compliance with the MRL and estimation of dietary intake for animal commodities: *sum of tolfenpyrad, and free and conjugated PT-CA (4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid and OH-PT-CA(4-[4-[[4-chloro-3-(1-hydroxyethyl)-1-methylpyrazol-5-yl]carbonylaminomethyl]phenoxy] benzoic acid) (released with alkaline hydrolysis) expressed as tolfenpyrad.*

The residue is not fat soluble.

Commodity		Recommended MRL, mg/kg	STMR or STMR-P (mg/kg)	HR or HR-P (mg/kg)
CCN	Name	New		
	Green tea	30	5.65	—
	Green tea infusion		0.24	—

DIETARY RISK ASSESSMENT

Long-term intake

The evaluation of tolfenpyrad resulted in recommendations for STMR-P value for green tea infusion which was used for the calculation. The results are shown in Annex 3 of the 2013 JMPR Report. The International Estimated Daily Intake for the 13 GEMS/Food diet based on estimated STMR value was up to 0–11% of maximum ADI of 0.006 mg/kg bw. The Meeting concluded that the long-term intake of residues of tolfenpyrad from green tea is unlikely to present a public health concern.

Short-term intake

The International Estimated Short-term Intake (IESTI) for tolfenpyrad was calculated for green tea infusion for which STMR-P value was estimated. The results are shown in Annex 4 of the 2013 JMPR Report. The IESTI was 50 to 100% of the ARfD (0.01 mg/kg bw) for the general population.

Meeting concluded that the short-term intake of residues of tolfenpyrad resulting from its use on green tea is unlikely to present a public health concern.

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R-10166	Carringer, SJ	2008	Magnitude of the residue of tolfenpyrad and its metabolite in or on potato raw agricultural and processed commodities following two foliar applications of NAI-2302 15EC The Carringers, Inc. report no. TCI-07-163 GLP,

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TRIAZAPHOS (143)

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EXPLANATION

Triazophos is an organophosphorus insecticide and acaricide and shows a broad-spectrum activity against a wide range of insect pests after soil or foliar treatment of crops. Triazophos was first evaluated by the JMPR in 1982 for toxicology and in 1983 for residues. Since then, triazophos has been evaluated several times. Triazophos has been evaluated within the periodic review programme by the 2002 JMPR for toxicological aspects and by the 2007 JMPR for residue aspects. The 2002 JMPR established an ADI of 0–0.001 mg/kg bw and ARfD of 0.001 mg/kg bw. The 2007 JMPR confirmed its previous residue definition: triazophos (for compliance with the MRL and for estimation of dietary intake). The 2007 JMPR evaluated the triazophos residues in food and withdrew its previous recommendations except for cotton seed, cotton seed oil and soya bean (immature seeds). The 2010 JMPR evaluated additional residue data on rice and soya bean (immature seeds).

The 2010 JMPR Meeting estimated a maximum residue level of 2 mg/kg in/on husked rice (brown rice), and a median residue of 0.421 mg/kg based on 15 trials conducted in China in 2008 and 2009. Triazophos was applied at the target rate of 3–4× 0.506 kg ai/ha (ME formulation) or 3–4× 0.45 kg ai/ha (EC formulation) with a 28 day PHI each. No recommendation of MRL was made because the short-term intake from residues in rice was 260 % of the ARfD for children and general population. There was no alternative GAP to be considered. The JMPR 2010 considered studies on the effect of processing (polishing, cooking, frying) desirable to obtain more realistic information on residue levels in food actually consumed. It was listed by the Forty-fourth Session of CCPR for the 2013 JMPR for reconsideration of MRL for rice.

China submitted processing data from rice, which were evaluated by the present Meeting.

RESIDUE ANALYSIS***Analytical methods***

The Meeting received additional information on the analytical method used in the processing study on rice.

In the analytical method used in the rice processing study, rice commodities of 20.0 g were immersed in 40 mL water for 30 min and extracted with 80 mL acetone by shaking for 30 min. The filtered solution was evaporated to 50 mL and extracted with ethyl acetate. The extract was evaporated at 40 °C to remove the ethyl acetate. Triazophos (parent) was determined with GC-FPD. The recoveries were within 70%–120% at 0.004–3.0 mg/kg for rice (paddy, husked, polished). Precision (RSD) was less than 20% at each level. The valid LOQ was 0.004mg/kg for each commodity [Lifen, 2011].

Stability of pesticide residues in stored analytical samples

No storage stability studies were submitted for rice or its processed commodities.

Storage stability studies were provided to the 2007 Meeting demonstrating the stability of residues in stored samples of cotton fibre, cotton seed, oranges, carrots and soil. No significant decrease of triazophos was observed in analytical samples of cotton fibre, cotton seed, oranges and carrots stored at ≤ -18 °C for up to 24 months. Therefore storage stability for rice commodities is covered up to 24 months.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

The Meeting received a processing study on rice.

Paddy rice plants were treated in the field in two locations in China in 2011 [Lifen, 2011]. In each location, two pre-harvest applications of 0.45 kg ai/ha with an interval of 10 days were conducted with an EC formulation. Rice plants were harvested at maturity at DAT 28 and 35. The rice plants were left to dry for 10 days in the field. Dried rice grains (10 kg) from each plot were processed into husked and polished rice in two locations in China (Hebei and Zhejiang).

Husked rice: Replicate 1 kg samples of dried rice grains were processed into husked rice (Longgu rice huller), resulting in 0.83 kg husked rice and 0.16–0.17 kg hulls.

Polished rice: A 3 kg sample of dried rice grains was processed into husked rice (Longgu rice huller). Then replicate 400 g samples of husked rice were processed into polished rice using a local-made rice polisher. Three polish times were used (50, 60 and 70 sec). Processing resulted in 330–335 g polished rice and 58–64 g rice bran (50 sec), 321–329 g polished rice and 64–71 g rice bran (60 seconds) and 306–307 g polished rice and 80–82 g rice bran (70 sec).

Polished rice 1 step: In reality, most of the rice grain is stored in China as rice grains (i.e. un-husked rice), then husked and milled together in one step before selling in the market. So a second processing experiment was conducted where replicate 10 kg dried rice grain samples were processed into polished rice in one step using a local-made rice polisher.

All samples (rice grains, husk, husked rice, polished rice, rice bran) were stored at -20 °C and were analysed within 30 days of storage. Samples were analysed using a GC-FPD method. Results are summarized in table 1. The average values for the rice grains (RAC) were 3.71 and 3.15 mg/kg in Hebei at 28 and 35 days PHI, respectively, and 4.14 and 4.86 mg/kg in Zhejiang at 28 and 35 days, respectively at 2× 0.45 kg ai/ha with an interval of 10 days.

Table 1 Residues of triazaphos after processing

Location, year, (variety)	Treatment	DAT	Processing location	processed products	residues, mg/kg	PF	reference
Zhanggeqian Village, Hebei, China, 2011, (Kenyu38)	2× 0.45 kg ai/ha; Interval 10 days	28	Hebei	rice grain	3.59	-	[Lifen, 2011]
				rice, husked	0.80	0.22	
				rice, polished, 50 sec	0.12	0.033	
				rice, polished, 60 sec	0.10	0.028	
				rice, polished, 70 sec	0.082	0.023	
				rice, polished, 1 step	0.15	0.042	
Zhanggeqian Village, Hebei, China, 2011, (Kenyu38)	2x 0.45 kg ai/ha; Interval 10 days	28	Hebei	rice grain	3.70	-	[Lifen, 2011]
				rice, husked	0.75	0.20	
				rice, polished, 50 sec	0.11	0.030	
				rice, polished, 60 sec	0.11	0.030	
				rice, polished, 70 sec	0.088	0.024	
				rice, polished, 1 step	0.15	0.041	
Zhanggeqian Village, Hebei, China, 2011, (Kenyu38)	2x 0.45 kg ai/ha; Interval 10 days	28	Hebei	rice grain	3.83	-	[Lifen, 2011]
				rice, husked	0.78	0.20	
				rice, polished, 50 sec	0.13	0.034	
				rice, polished, 60 sec	0.10	0.026	
				rice, polished, 70 sec	0.088	0.023	
				rice, polished, 1 step	0.14	0.037	
Zhanggeqian Village, Hebei,	2x 0.45 kg ai/ha;	35	Hebei	rice grain	3.08	-	[Lifen, 2011]
				rice, husked	0.73	0.24	

Location, year, (variety)	Treatment	DAT	Processing location	processed products	residues, mg/kg	PF	reference
China, 2011, (Kenyu38)	Interval 10 days			rice, polished, 50 sec rice, polished, 60 sec rice, polished, 70 sec rice, polished, 1 step	0.12 0.082 0.075 0.11	0.039 0.027 0.024 0.036	
Zhanggeqian Village, Hebei, China, 2011, (Kenyu38)	2x 0.45 kg ai/ha; Interval 10 days	35	Hebei	rice grain rice, husked rice, polished, 50 sec rice, polished, 60 sec rice, polished, 70 sec rice, polished, 1 step	3.11 0.71 0.10 0.080 0.074 0.12	- 0.23 0.032 0.026 0.024 0.039	[Lifen, 2011]
Zhanggeqian Village, Hebei, China, 2011, (Kenyu38)	2x 0.45 kg ai/ha; Interval 10 days	35	Hebei	rice grain rice, husked rice, polished, 50 sec rice, polished, 60 sec rice, polished, 70 sec rice, polished, 1 step	3.25 0.73 0.10 0.082 0.078 0.13	- 0.22 0.031 0.025 0.024 0.040	[Lifen, 2011]
Zhuji county, Zhejiang, China 2011 (Zheyu 1)	2x 0.45 kg ai/ha; Interval 10 days	28	Zhejiang	rice grain rice, husked rice, polished, 60 sec	4.74 1.43 0.37	- 0.30 0.078	[Lifen, 2011]
Zhuji county, Zhejiang, China 2011 (Zheyu 1)	2x 0.45 kg ai/ha; Interval 10 days	28	Zhejiang	rice grain rice, husked rice, polished, 60 sec	3.02 0.81 0.34	- 0.27 0.11	[Lifen, 2011]
Zhuji county, Zhejiang, China 2011 (Zheyu 1)	2x 0.45 kg ai/ha; Interval 10 days	28	Zhejiang	rice grain rice, husked rice, polished, 60 sec	5.27 1.61 0.43	- 0.31 0.19	[Lifen, 2011]
Zhuji county, Zhejiang, China 2011 (Zheyu 1)	2x 0.45 kg ai/ha; Interval 10 days	28	Zhejiang	rice grain rice, husked	4.41 1.38	- 0.31	[Lifen, 2011]
Zhuji county, Zhejiang, China 2011 (Zheyu 1)	2x 0.45 kg ai/ha; Interval 10 days	28	Zhejiang	rice grain rice, husked	2.95 0.78	- 0.26	[Lifen, 2011]
Zhuji county, Zhejiang, China 2011 (Zheyu 1)	2x 0.45 kg ai/ha; Interval 10 days	28	Zhejiang	rice grain rice, husked	4.43 1.23	- 0.28	[Lifen, 2011]
Zhuji county, Zhejiang, China 2011 (Zheyu 1)	2x 0.45 kg ai/ha; Interval 10 days	35	Zhejiang	rice grain rice, husked rice, polished, 60 sec	4.83 1.06 0.36	- 0.22 0.075	[Lifen, 2011]
Zhuji county, Zhejiang, China 2011 (Zheyu 1)	2x 0.45 kg ai/ha; Interval 10 days	35	Zhejiang	rice grain rice, husked rice, polished, 60 sec	4.76 0.98 0.38	- 0.21 0.080	[Lifen, 2011]
Zhuji county, Zhejiang, China	2x 0.45 kg ai/ha;	35	Zhejiang	rice grain rice, husked	4.98 0.96	- 0.19	[Lifen, 2011]

Location, year, (variety)	Treatment	DAT	Processing location	processed products	residues, mg/kg	PF	reference
2011 (Zheyu 1)	Interval 10 days			rice, polished, 60 sec	0.33	0.066	

Table 2 gives an overview of processing factors in rice grains into husked rice and polished rice. Since the maximum residue level recommendation was given for husked rice (brown rice), also the processing factors from husked rice to polished rice are indicated. Several processing studies were conducted on polished rice. The processing study in Zhejiang resulted in significantly higher processing factors for polished rice than in Hebei. Therefore only the processing data from Zhejiang were taken.

Table 2 Overview of processing factors for triazophos

processed products	individual processing factors	n	RSD	Mean or best estimate
rice grains–husked	0.19, 0.20, 0.20, 0.21, 0.22, 0.22, 0.22, 0.23, 0.24, 0.26, 0.27, 0.28, 0.30, 0.31, 0.31	15	17%	0.24 (mean)
rice grains–polished	0.037, 0.039, 0.039, 0.040, 0.041, 0.042 (Hebei) 0.066, 0.075, 0.080, 0.11, 0.19 (Zhejiang)	6 5	4.4% 49%	0.080 (median from Zhejiang)
rice grains–husked to polished	0.16, 0.17, 0.18, 0.18, 0.19, 0.20 (Hebei) 0.27, 0.34, 0.34, 0.39, 0.42 (Zhejiang)	6 5	7.9% 16%	0.35 (mean from Zhejiang)

APPRAISAL

Triazophos is an organophosphates insecticide and acaricide and shows broad-spectrum activity against a wide range of insect pests via soil or foliar treatment of crops. Triazophos was first evaluated by the JMPR in 1982 for toxicology and in 1983 for residues and has been evaluated several times since. Triazophos was evaluated within the periodic review programme by the 2002 JMPR for toxicology and by the 2007 JMPR for residues. The 2002 Meeting established an ADI of 0–0.001 mg/kg bw and an ARfD of 0.001 mg/kg bw. The 2007 JMPR confirmed its previous residue definition: *triazophos* (for compliance with the MRL and for estimation of dietary intake). The 2007 JMPR evaluated the triazophos residues in food and withdrew its previous recommendations except for cotton seed, cotton seed oil and soya bean (immature seeds). The 2010 JMPR evaluated additional residue data on rice and soya bean (immature seeds).

The 2010 JMPR Meeting estimated a maximum residue level of 2 mg/kg in/on husked rice (brown rice), and a median residue of 0.421 mg/kg based on 15 trials conducted in China in 2008 and 2009. Triazophos was applied at the target rate of either 3–4 × 0.506 kg ai/ha (ME formulation) or 3–4 × 0.45 kg ai/ha (EC formulation) both with PHIs of 28 days. No maximum residue level recommendation could be made because the estimated short-term intake from residues in rice was 260% of the ARfD for children and general population. There was no alternative GAP available. The 2010 JMPR considered that studies on the effect of processing (polishing, cooking, frying) to be desirable as they would enable a more realistic estimation of residue levels in food actually consumed. Triazophos was listed by the Forty-fourth Session of CCPR for the 2013 JMPR for reconsideration of residues in rice.

China submitted processing data for rice, which were evaluated by the present Meeting.

Methods of analysis

The Meeting received a description and validation data for an analytical method of triazophos on processed commodities of rice. The analytical method was based on extraction with acetone and

determination of triazaphos with GC-FPD. The Meeting considered the method valid in the range 0.003–3.0 mg/kg triazaphos in rice grains, husked rice, polished rice and rice bran.

Stability of residues in stored analytical samples

No storage stability data were received for rice or its processed commodities. Storage stability studies were provided to the 2007 Meeting which demonstrated stability of residues in stored samples of cotton fibre, cotton seed, oranges, carrots and soil for a period of up to 24 months. The Meeting agreed that these studies covered storage stability for rice commodities.

Results of supervised residue trials on crops

The 2010 JMPR Meeting estimated a maximum residue level of 2 mg/kg in/on husked rice (brown rice), and a median residue of 0.421 mg/kg based on 15 trials in/on paddy rice conducted in China in 2008 and 2009.

An additional two trials on paddy rice were submitted to the present Meeting. The trials were conducted in China with 2 applications at 0.45 kg ai/ha instead of 3 applications at 0.45 kg ai/ha (cGAP in China). Since the residues were higher compared to the JMPR 2010 data, the Meeting decided to include the mean value per location (3.7 and 4.9 mg/kg) from these trials with the JMPR 2010 data. This resulted in the following dataset: 0.059, 0.059, 0.060, 0.087, 0.13, 0.34, 0.35, 0.42, 0.51, 0.68, 0.76, 0.81, 0.89, 1.0, 1.2, 3.7, 4.9 mg/kg (n=17).

Based on the 17 trials conducted in China, the Meeting estimated a maximum residue level of 7 mg/kg in/on rice grain and a median residue of 0.51 mg/kg. As rice grains (i.e., rice with hulls) are not traded, the Meeting agreed that a maximum residue level recommendation for rice was not appropriate and decided to use the residue values for rice, to estimate maximum residue levels for husked rice and polished rice.

Fate of residues during processing

Information on the fate of triazaphos during processing was provided for rice. In the table below, relevant processing factors for this commodity are summarized based on the residue definition of *triazaphos*. Hydrolysis studies under cooking conditions or processing studies for cooking of rice were not submitted to the present or previous Meetings.

Using the $STMR_{RAC}$ obtained from triazaphos use, the Meeting estimated STMR-Ps for processed commodities as listed below. An HR-P is not required for processed rice commodities.

Commodity	Processing factors (triazaphos)	Max level = $Max_{RAC} \times PF$	$STMR-P = STMR_{RAC} \times PF$ mg/kg
rice grains – husked, dry	0.24 (n=15, mean)	$7 \times 0.24 = 1.68$	$0.51 \times 0.24 = 0.12$
rice grains – polished, dry	0.080 (n=6, median)	$7 \times 0.080 = 0.56$	$0.51 \times 0.080 = 0.041$

The Meeting confirmed its previous recommendation of 2 mg/kg in/on husked rice, and estimated an STMR-P of 0.12 mg/kg.

The Meeting estimated a maximum residue level of 0.6 mg/kg in polished rice and an STMR-P of 0.041 mg/kg.

Residues in animal commodities

The 2007 JMPR concluded that because of the lack of appropriate animal livestock metabolism study, a residue definition for animal products could not be determined and therefore the Meeting could not make use of the results of the feeding studies. Consequently, the residues in animal products derived from the use of triazaphos on rice and its processed commodities were not considered by the present Meeting.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for use in dietary risk assessment.

Definition of residue (for compliance with the MRL and for estimation of dietary intake): *triazophos*.

CCN	Commodity name	MRL mg/kg	STMR or STMR-P mg/kg	Notes
CM 0649	Rice, husked	2	0.12	A public health risk cannot be excluded
CM 1205	Rice, polished	0.6	0.041	-

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDI) of for triazophos was calculated from recommendations for STMRs for raw and processed commodities in combination with consumption data for corresponding food commodities by the 2007, 2010 and 2013 JMPR. The IEDI of in the 13 GEMS/Food cluster diets, based on the estimated STMRs were in the range 1–40% of the maximum ADI of 0.001 mg/kg bw. The 2013 Meeting concluded that the long-term intake of residues of triazophos from uses considered by the 2007, 2010 and 2013 Meeting is unlikely to present a public health concern. The results are shown in Annex 3 of the 2013 Report.

Short-term intake

The International Estimated Short Term Intake (IESTI) for triazophos was calculated for rice and its processed commodities for which maximum residue levels were estimated and for which consumption data were available. For those processed commodities, where no processing data were available, the STMR-P for polished rice was used for rice flour, rice beer and rice wine, while the STMR-P for husked rice was used on all other processed commodities. Since husked rice and polished rice are not consumed raw, but in cooked form and consumption data are available for the cooked form, a default dilution factor of 0.4 was used to compensate for the swelling during cooking. A default dilution factor of 0.04, 0.19 and 0.15 was used on rice milk, rice beer, and rice wine respectively. The results are shown in Annex 4 of the 2013 Report.

The IESTI for rice and its processed commodities and based on the 2012 consumption data and an ARfD of 0.001 mg/kg bw represents 0–130% of the ARfD for cooked husked rice consumption of children of 1–6 years in Japan, and 0–100% of the ARfD for all other processed rice commodities by children or general population.

The Meeting concluded that the short-term intake of residues of triazophos resulting from its uses that have been considered by JMPR might present a public health concern. There was no alternative GAP to be considered and refinement of the dietary risk assessment by using processing factors for husked rice still showed a potential public health concern. Processing studies from rice (husked and polished) are desirable for further refinement of the exposure.

The 2002 Meeting established an ARfD of 0.001 mg/kg bw on the basis of the NOAEL of 0.0125 mg/kg bw per day in the 3-week study in humans and a safety factor of 10. Hence, further refinement is unlikely in the toxicological assessment.

REFERENCES

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-

GLP. Published/Unpublished			
-	W. Lifen	2011	Processing study of triazophos on rice Hebei Institute for the Control of Agrochemicals (Hebei ICA), China and Zhejiang University, China, no report number. Non-GLP, Unpublished. English translation of relevant parts of a Chinese report Original Chinese report available during the 2013 Meeting

TRIFLUMIZOLE (270)

Draft prepared by Dr Michael Doherty, U.S. Environmental Protection Agency, Washington, DC USA

EXPLANATION

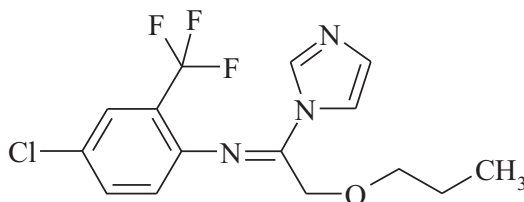
Triflumizole is a broad-spectrum foliar fungicide that controls a variety of fungal diseases in fruits and vegetables. It acts as a protectant and as an eradicant by preventing disease symptoms after infection has occurred. The anti-sporulant activity of triflumizole reduces spores after lesions become visible. Triflumizole belongs to the demethylation inhibitor (DMI) group of fungicides classified as Group 3 by the Fungicide Resistance Action Committee (FRAC). Triflumizole has protective and curative actions, and acts as an inhibitor of chitin biosynthesis. The product is mixed with water and applied as a foliar spray using ground equipment equipped for conventional spraying on crops.

Triflumizole was scheduled by the Forty-fourth Session of the CCPR for evaluation as a new compound by the 2013 JMPR. The Meeting received information on identity, animal and plant metabolism, environmental fates in soil, rotational crops, analytical methods, storage stability, use patterns, supervised trials, dairy cattle feeding studies, and fates of residues in processing.

IDENTITY

Common name	Triflumizole
IUPAC	(E)-4-chloro- α,α,α -trifluoro-N-(1-imidazol-1-yl-2-propoxyethylidene)-o-toluidine
CAS	[N(E)]-4-chloro-N-[1-(1H-imidazol-1-yl)-2-propoxyethylidene]-2-(trifluoromethyl)benzenamine (formerly 1-[(1E)-1-[[4-chloro-2-(trifluoromethyl)phenyl]imino]-2-propoxyethyl]-1H-imidazole)
CAS Registry No	68694-11-1 (formerly 99387-89-0)
CIPAC No	730
Synonyms	NF-114, A815

Structural formula:



Molecular formula	$C_{15}H_{15}ClF_3N_3O$
Molecular weight	347.5 g/mol

PHYSICAL AND CHEMICAL PROPERTIES***Pure active ingredient***

Property	Result	Reference
Vapour pressure	$(5.2 \pm 0.4) \times 10^{-2}$ Pa at 20 °C	Rijsbergen, 2002
Henry's Law Constant	1.71 Pa m ³ mol ⁻¹ at 20 °C	Pierce, 1994
Solubility in water (g/L)	12.5 at 20 °C	IPCS Website www.inchem.org (9/2013)

Property	Result		Reference
Solubility in organic solvents at 25 °C (g/L)	n-Octanol	605	Saito, 1990
	Acetonitrile	1187	
	Ethyl acetate	1486	
	Dichloromethane	3016	
Solubility in organic solvents at 20 °C (g/L)	n-Hexane	17.6	Soeda, Nomura, 1988
	Methanol	496	
	Xylene	639	
	Acetone	1440	
	Chloroform	2220	
Partition coefficient (Log P _{ow})	5.06 (water at 20 °C)		Higashida, Tanaka, 1998 Nomura, Nakashima, 1987
	5.10 (buffer pH 7 at 20 °C)		
	5.12 (buffer pH 8 at 20 °C)		
Hydrolysis rate at 25 °C	pH buffer	DT ₅₀ (days)	Soeda, Shiotani, 1987a
	5	8.9	
	7	64.6	
	9	3.9	
Photolysis	DT ₅₀ =2.55 days at pH 7 at 25 °C		Soeda, Shiotani, 1987b
	DT ₅₀ =16.97 days in distilled water at 25 °C		Knight, 2002
	DT ₅₀ =8.04 days in natural water at 25 °C		
Dissociation constant	pKa=3.7 at 25 °C		Soeda, Shiotani, 1988

Formulations

Triflumizole is available in the following formulations:

- Suspension concentrate (SC) nominally containing 480 g/L active ingredient;
- Water soluble concentrate (WS) nominally containing 500 g/kg active ingredient;
- Emulsifiable concentrate (EC) nominally containing 150 g/L active ingredient.

The common trade names are Procure[®] 480SC, Procure[®] 50WS, Terraguard[®] SC, and Rocket[®] EC.

METABOLISM AND ENVIRONMENTAL FATE

The metabolism of triflumizole was investigated in animals, plants, and environmental systems using test material universally labelled with ¹⁴C in the phenyl ring (Figure 1). The major metabolites/degradation products from these studies are shown in the table below.

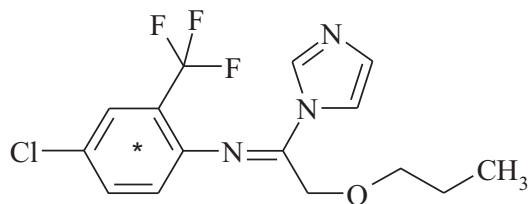
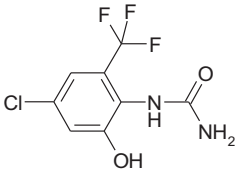
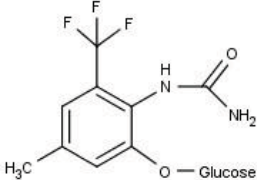


Figure 1 Test material for the studies using radiolabelled triflumizole

Chemicals identified as major components in the metabolic and degradation pathways of triflumizole

Identifier	Chemical Name	Chemical Structure	Test System
Triflumizole	(E)-4-chloro- α,α,α -trifluoro-N-(1-imidazol-1-yl-2-propoxyethylidene)-o-toluidine		Primary Crops
FM-6-1	N'-[4-chloro-2-(trifluoromethyl) phenyl]-2-propoxyethanimidamide		Primary Crops, Soil
FA-1-1	4-chloro-2-(trifluoromethyl)aniline		Egg and Milk
FM-8-1 (Free and sulphate conjugate)	N'-[4-chloro-2-(trifluoromethyl) phenyl]-2-hydroxyethanimidamide		Milk
FA-1-glucuronide	6-[4-chloro-2-(trifluoromethyl) phenoxyethyl]-3,4,5-trihydroxyoxane-2-carboxylic acid		Milk
FA-1-5 (Free and sulphate conjugate)	2-amino-5-chloro-3-(trifluoromethyl)phenol		Milk

Identifier	Chemical Name	Chemical Structure	Test System
FD-2-1	N-[4-chloro-2-(trifluoromethyl) phenyl]-2-hydroxyacetamide		Milk
FD-7-1	{[4-chloro-2-(trifluoromethyl) phenyl]carbamoyl} formic acid		Milk, Soil
FD-9-1 (IV)	[4-chloro-2-(trifluoromethyl) phenyl]urea		Rotational Radish Top Wheat Grain Wheat Hay Wheat Straw
FM-5-1	N-(1-{[4-chloro-2-(trifluoromethyl) phenyl]imino}-3-propoxypropyl)formamide		Egg
XIV	(2Z)-4-hydroxyhex-2-enedioic acid		Rotational Lettuce Radish Top
XXV	1-[4-chloro-2-hydroxy-6-(trifluoromethyl)phenyl]-3-hydroxyurea		Rotational Radish Root
XXVIII	3-(2-aminoprop-2-enoyl)-1-[4-chloro-2-(trifluoromethyl) phenyl]urea		Rotational Wheat Grain
XXIII	Glucose conjugate of FM-8-1		Rotational Lettuce

Identifier	Chemical Name	Chemical Structure	Test System
V	[4-chloro-2-hydroxy-6-(trifluoromethyl)phenyl]urea		Rotational Wheat Straw
XXVI	Glucose conjugate of V		Rotational Wheat Forage

Animal metabolism

The meeting received studies investigating the metabolism of triflumizole in rats, lactating goats and laying hens.

Rats

The metabolism of [^{14}C]triflumizole by rats was evaluated by the WHO Core Assessment Group.

Lactating Goats

The metabolism of [^{14}C]triflumizole by lactating goats was investigated by Knipe and Harned (1985), with a continuation by Knipe (1986). A single goat was orally dosed for 5 consecutive days with [^{14}C]triflumizole labelled in the phenyl ring. Dosing was twice daily by gelatin capsule at 500 $\mu\text{Ci}/\text{dose}$, amounting to 14.3 mg/kg/day (280 ppm in feed). Milk, urine, and faeces were collected twice daily for 6 days, and tissue samples (muscle, fat, kidney and liver) were obtained at sacrifice, which was 6 days after the first dose.

Total radioactive residue (TRR) was determined by direct liquid scintillation counting (LSC) of urine and milk, and by combustion/LSC of faeces, blood, and tissues. Characterization of the metabolite profiles of the various matrices was accomplished by solvent extraction, HPLC fraction collection, enzymatic digestion, thin-layer chromatography, and comparison with known standards.

Levels of radiolabel material reached a plateau in milk within approximately 24 hours. Radioactivity in urine and faeces showed an initial rapid increase for the first 36–48 hours after dosing, followed by a gradual increase for the remainder of the study (Table1).

Radioactivity in tissues was generally low (Table 2). Liver contained the highest concentration of residue at approximately 11 mg/kg (0.4% of the cumulative dose). The stomach contents accounted for 8.63 ± 1.01 mg/kg triflumizole-equivalents; radioactivity in the small and large intestines was not determined. Of the radioactivity in the liver tissue, slightly more than half occurred as bound residue. Digestion with protease released approximately 70% of the bound radioactivity.

Characterization of the radioactivity showed that glucuronide- and sulphate-conjugated forms of metabolites FA-1-1 and FA-1-5 occur in urine, milk, liver and kidney; parent compound was not observed. Additional work, using an analytical system with higher resolution, was performed with milk and liver extracts. Those analyses (Table 3) showed major milk metabolites to be FA-1-5-sulphate, FA-1-5-glucuronide, and FM-8-1-sulphate. Minor residues in the milk extract were FD-6-1, FD-2-1, FD-7-1, and FM-6-1. Liver extracts were shown to contain primarily FA-1-5-sulphate and species yielding FA-1-1 after proteolytic digestion. Insufficient data were provided to derive quantitative residue levels for metabolites in milk.

Table 1 Cumulative radiocarbon residues in excreta and milk from a goat orally administered [^{14}C]triflumizole

Hours after First Dosing	% of Cumulative Dose ^{a, b}		
	Urine	Faeces	Milk
4	6.7	< LOD	< LOD
8	11.3	< LOD	< LOD
12	24.4	0.3	0.07
24	36.0	5.3	0.15
36	33.8	8.0	0.15
48	43.0	11.4	0.15
60	41.8	13.4	0.15
72	49.7	16.5	0.16
84	48.4	16.7	0.16
96	53.7	17.7	0.18
108	53.1	17.9	0.16
120	56.0	19.9	0.18

^a Cumulative dose is total administered dose up to indicated time point.

^b Based upon 10 equal doses of 500 μCi

Table 2 Radiocarbon residues in tissues of a goat orally administered [^{14}C]triflumizole

Tissue	% TAR	Triflumizole Equivalents (mg/kg $\pm$ Std. Dev.)
Kidney	0.01	3.36 $\pm$ 0.13
Liver	0.40	11.26 $\pm$ 0.59
Muscle	0.18	0.30 $\pm$ 0.20
Fat	0.06	0.66 $\pm$ 0.05

Table 3 Identification of radioactivity in goat liver and milk following administration of [^{14}C]triflumizole

Metabolite	Matrix	% TRR	Triflumizole Equivalents (mg/kg ^a)
FA-1-1	Liver (chloroform fraction)	24.4	2.75
FA-1-1	Liver (dried pellet)	54.8	6.17
FA-1-5-Sulphate	Liver (acetone fraction)	12.4	1.40
	Milk	29.1	—
FA-1-5-Glucuronide	Milk	11.8	—
FD-2-1	Milk	10.4	—
FD-6-1	Milk	5.5	—
FD-7-1	Milk	3.2	—
FM-6-1	Milk	5.2	—
FM-8-1-Sulphate	Milk	12.6	—

^a Based on a total concentration of triflumizole-equivalent residue in liver of 11.26 mg/kg. Total triflumizole-equivalent residue in milk was not provided.

The proposed metabolic pathway of triflumizole in livestock is shown in Figure 2

Laying hens

The metabolism of [^{14}C]triflumizole by laying hens was investigated by Knipe and Lengen (1986) using triflumizole universally labelled in the phenyl ring. Five hens were dosed, orally, for five consecutive days. Three birds were dosed with 39 ppm in feed and two were dosed with 53 ppm in feed. Eggs and excreta were collected once daily during the dosing period. The birds were killed on the 6th day after the initial dosing and liver, kidneys, fat and muscle were collected for analysis.

Total radioactivity in excreta and tissues was determined by combustion and LSC; radioactivity in egg was determined by LSC directly and was on a whole-egg basis for the three low-

dose birds and separately for egg white and egg yolk for the two high-dose birds. Metabolic profiles of the collected matrices were investigated using solvent extraction, and, for skin-with-fat and liver samples, base or enzymatic digestion. Extracted residues were subjected to HPLC, TLC, and MS analysis, with comparison against known standards.

Analysis of total radioactivity indicates that the majority of the administered dose was excreted (Table 4 4) and that levels did not plateau in eggs within the dosing period (Table 5 5). By the fifth day of dosing, levels of radioactivity in the egg yolk were greater than those in the whites. That pattern may have been evident as early as Day 3 of dosing; however, insufficient samples were collected to make a firm conclusion. In tissues, total radioactivity was approximately an order of magnitude greater in liver and kidney than in fat or muscle (Table 6).

Table 4 Recovery of administered radioactivity in the excreta of chickens administered [^{14}C]triflumizole for 5 days

Chicken # ^a	μCi Excreted						% TAR
	Day 1	Day 2	Day 3	Day 4	Day 5	Total	
6 (control)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
1	18.81	18.63	21.19	23.35	22.08	104.16	93.0
2	18.90	21.99	16.59	23.18	18.06	98.72	88.1
3	18.35	18.80	13.95	20.38	19.92	91.40	81.6
7	34.69	27.75	27.05	27.95	28.02	145.46	83.4
8	24.26	19.09	30.20	31.08	35.79	140.42	80.5

^a The dose administered to Chickens 1, 2, and 3 was 112 μCi (22.4 $\mu\text{Ci}/\text{day}$ for 5 days), while the dose administered to Chickens 7 and 8 was 174.5 μCi (34.90 $\mu\text{Ci}/\text{day}$ for 5 days).

Table 5 Radiocarbon residues in the eggs of chickens administered [^{14}C]triflumizole for 5 days

Chicken # ^a	Triflumizole equivalents (mg/kg)				
	Day 1	Day 2	Day 3	Day 4	Day 5
1	NS ^b	0.028	NS	NS	0.215
2 ^c	0.003	0.053	0.135	0.148	0.242 / 0.303
3	0.024	NS	NS	0.270	0.431
7 ^c Yolk	0.006	0.197	1.080	NS	2.312 / 1.706
White	0.009	0.111	0.072		0.401 / 0.408
8 ^c Yolk	0.002	0.095	NS	0.224 ^d	0.899 / 1.187
White	0.011	0.081			0.133 / 0.074

^a Chickens 1, 2, and 3 received 39 mg/kg/day while chickens 7 and 8 received 53 mg/kg/day.

^b No egg sample obtained.

^c Chickens 2, 7 and 8 each gave two eggs per day.

^d This egg was broken when received, so the analysis was performed on the whole egg.

Table 6 Tissue radiocarbon residues in chickens administered [^{14}C]triflumizole for 5 days

Chicken # ^b	Triflumizole Equivalents (mg/kg ^a)				
	Liver	Kidney	Fat	Muscle (leg)	Muscle (breast)
1	1.107	0.677	0.067	0.047	0.049
2	0.989	0.537	0.050	0.017	0.026
3	1.232	0.600	0.058	0.026	0.029
7	— ^c	1.115	0.358	0.066	0.087
8	— ^c	0.781	0.312	0.073	0.054

^a Values obtained for control tissues have been subtracted to obtain the tissues values given.

^b Chickens 1, 2 and 3 received 39 mg/kg/day, while Chickens 7 and 8 received 53 mg/kg/day.

^c The livers of these birds were used for metabolite identification and were not analysed for total radioactivity.

HPLC analysis of chicken excreta resulted in three peaks with higher levels of radioactivity at retention time fractions of 8–9 minutes, 24–26 minutes, and 27.5–29 minutes. The first peak was identified as FM-8-1-sulphate based on co-chromatography with an authenticated standard. The second peak was identified as FD-7-1 based on co-chromatography, stability to β -glucuronidase and sulfatase hydrolysis, and cleavage to FA-1-1 after overnight incubation with HCl at 37 °C. The third peak was resistant to both β -glucuronidase and sulfatase and was not further investigated. Based on retention time, the third peak may have been FM-6-1.

Analysis of egg yolk and egg white from a high-dose chicken (Chicken #7, Day 5) by HPLC and protease treatments resulted in identification of a number of metabolites (Table 7). The primary components were triflumizole, FD-6-1/FD-4-1 (white), and FA-1-1 (yolk).

Livers from Chickens 7 and 8 (composited) and from Chicken 2 were processed through either a Bligh-Dyer extraction protocol or exhaustive pentane extractions, respectively. For both extraction schemes, the majority of radioactivity in liver was associated with bound residues in the dried pellet (Table 8). HPLC analysis and proteolytic digestion indicate that chicken liver contained a single metabolite: Metabolite FA-1-1 or a metabolite converted to FA-1-1 during proteolytic digestion.

Table 7 Distribution of radioactivity in chicken egg (Chicken #7, day 5)

Total	Egg white (0.401 mg/kg) ^a		Egg yolk (2.312 mg/kg) ^a	
	mg/kg	% TRR	mg/kg	% TRR
Extractables	0.335	83.6 ^b	1.209	52.3 ^b
Triflumizole	0.054	13.4 ^c	0.085	3.7 ^c
FD-6-1/FD-4-1 ^d	0.050	12.6 ^c	0.069	3.0 ^c
FM-5-1	0.016	4.1 ^c	—	—
FA-1-1	0.009 + (0.132) ^e	2.2 ^d + (33.05) ^e	(0.0511) ^e	(22.1) ^e
FA-1-5	0.008	1.9 ^c	—	—
FD-2-1	—	—	0.067	2.9 ^c
FD-1-1/FM-2-1/FM-3-1 ^d	0.008	1.9 ^c	—	—
Polar A	—	—	0.072	3.1 ^c
Polar B	—	—	0.064	2.8 ^c
Not identified ^f	0.058	14.4 ^c	0.210	9.1 ^c
Other	—	—	0.132	5.7 ^g
Losses	—	—	0.183	7.9 ^h
Unextractable	0.069	17.2	0.921	39.8

^a Data from Table 55.

^b Extractable prior to concentration and resultant losses of ¹⁴C (attributable to FA-1-1).

^c Percent of total after correction made for loss of ¹⁴C after extract concentration

^d Poor HPLC resolution of the standards did not allow further assignment of peaks in the egg samples.

^e Evaporative losses of ¹⁴C from the extract are most likely FA-1-1; based on that compound's known volatility and the HPLC analysis of the extract of acidic digestion of egg yolk. These residues were characterized by protease digestion (see text) and by acidic Bleidner digestion.

^f Radioactivity not clearly distinguishable as a definite peak or too low to assign a definite peak identity.

^g Other-5.7% of yolk was extractable with acetone but could not be separated from the sample matrix for HPLC analysis.

^h Losses - Additional loss of material balance presumed to be volatiles as FA-1-1

Table 8 Distribution of radioactivity in chicken liver extracts

Fraction	% TRR
Bligh-Dyer Extraction (Chickens 7 and 8)	
Chloroform	15.4
Methanol/water	6.8
Acetone	7.8
Dried Pellet	70.0
Extensive Pentane Extractions (Chicken 2)	

Fraction	% TRR
Pentane	13.7
Acetonitrile	12.9
Dried Pellet	73.4

Summary of animal metabolism

The metabolism of ^{14}C labelled triflumizole has been studied in lactating goats and laying hens. In both studies, the majority (> 80%) of the administered triflumizole was excreted. Livers and kidneys of both species had the highest amount of the retained material. In livers, the predominant residue was FA-1-1. Triflumizole was observed as a major residue, at approximately 13% of the total residue, in egg white only.

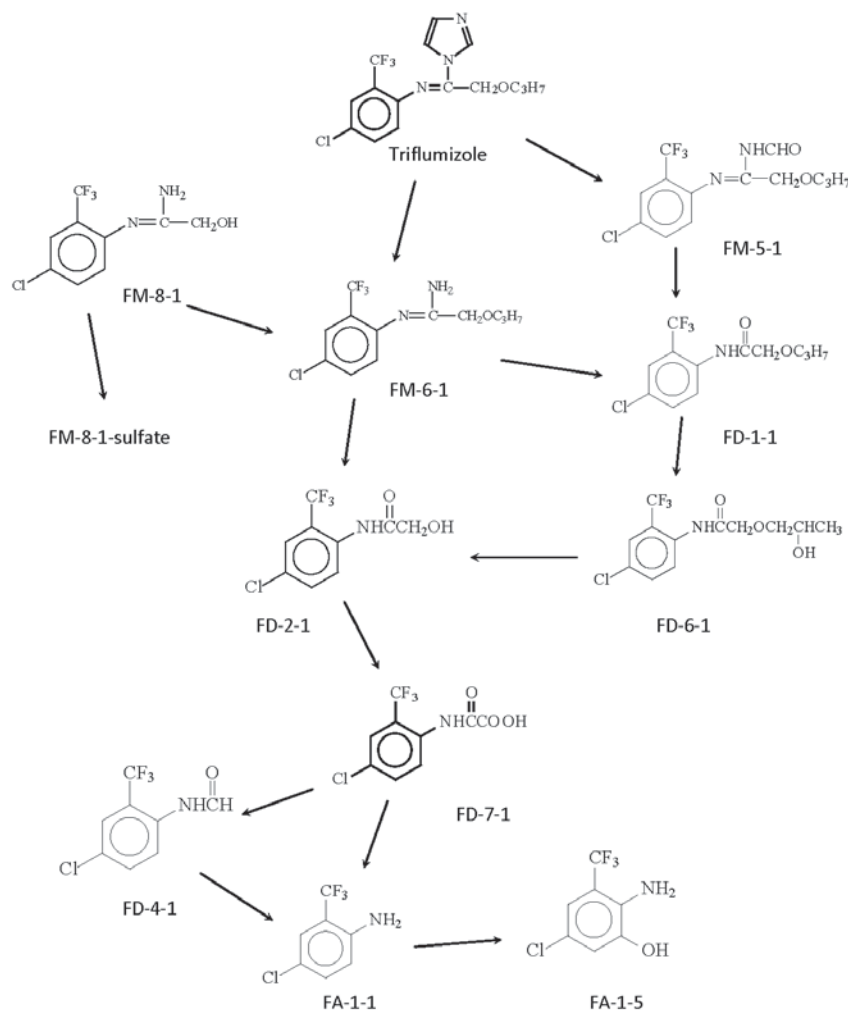


Figure 2 Proposed metabolic pathways of triflumizole in livestock

Plant metabolism

Plant metabolism studies were performed on cucumbers, apples, pears and grapes. Treatment was with triflumizole ^{14}C - universally labelled in the phenyl ring. Metabolites were identified using solvent partitioning and thin-layer chromatography with authentic standards.

Apples

The metabolism of triflumizole in apple trees grown in a greenhouse was investigated (Soeda and Hashimoto, 1987b). Triflumizole, uniformly labelled with ^{14}C in the phenyl ring, was applied as uniformly as possible to four leaves of a branch cluster containing 16–18 leaves. The application rate was approximately 0.127 mg triflumizole/4-leaf cluster. Branches were harvested and separated into treated leaves and upper and lower untreated leaves at 0, 1, 3, 7, 14, 21, 31, 60, and 90 DAT.

Treated leaves were surface washed with chloroform and then extracted three times with methanol:water (7:3, v/v) and the resulting extract was partitioned three times against chloroform. Radioactivity in the washes and extracts was determined by LSC. Radioactivity in the extracted fibrous material was determined by combustion followed by LSC. For samples other than treated leaves, the plant parts were each homogenized in a blender in the presence of dry ice and the radioactivity determined by combustion/LSC. Thin-layer chromatography was used to further analyse leaf washes as well as aqueous and chloroform extracts. Prior to TLC, the aqueous extracts were concentrated *in vacuo* to remove methanol and the residues transferred to 1-butanol. For TLC, the locations of radioactive compounds were determined by autoradiography and identification of residues was by comparison to authentic standards. Quantification of residues was made by collecting the silica gel from the TLC plates and counting by LSC. In the case of the metabolite FA-1-1, which is extremely volatile, TLC scraping and LSC was done immediately after two-dimensional co-chromatography with authentic standards, using UV light to locate the residue for scraping.

Radiocarbon residues in chloroform washes, extracts, and plant material are summarized below (Table 9). The data show that most of the radiocarbon residues were removed in the chloroform wash through the early stages of sampling and that there was very little translocation of radioactivity from treated to untreated leaves. The data also show a rapid decline in radiocarbon residues, with an initial half-life of approximately 4 days.

Table 9 Distribution of radiocarbon residues in apple leaves treated with [^{14}C] triflumizole

Plant Part or Fraction	0 DAT	1 DAT	3 DAT	7 DAT	14 DAT	21 DAT	31 DAT	60 DAT	90 DAT
% TAR →	98.6	80.6	60.8	34.1	17.3	18.1	19.2	15.5	9.0
Radiocarbon Residue (% TRR)									
Treated Leaves									
CHCl ₃ Wash	100.0	94.4	88.0	69.5	45.3	38.8	38.9	25.2	10.6
MeOH:H ₂ O									
CHCl ₃	— ^a	4.1	8.6	19.8	26.0	24.2	22.0	19.9	17.7
Aq. MeOH	—	0.9	2.0	6.5	14.9	19.3	24.2	28.7	39.3
PES	—	0.4	1.0	3.0	9.4	9.2	10.3	15.0	19.8
Subtotal	100.0	99.8	99.6	98.8	95.5	91.5	95.3	88.7	87.3
Untreated Leaves									
Upper Leaves	—	0.1	0.3	0.8	3.1	4.3	3.4	7.7	7.7
Lower Leaves	—	0.1	0.1	0.6	1.2	4.4	1.3	3.8	4.4
Subtotal	—	0.2	0.4	1.4	4.3	8.7	4.7	11.5	12.1
Total	100.0	100.0	99.9	100.2	99.8	100.2	100.1	100.2	99.4
Triflumizole equivalents (mg eq/kg)									
Treated Leaves	51.65	45.42	35.24	22.21	9.87	7.64	7.33	4.58	3.03
Upper Untreated Leaves	—	0.04	0.05	0.06	0.07	0.06	0.04	0.04	0.05
Lower Untreated Leaves	—	0.02	0.03	0.10	0.08	0.24	0.07	0.18	0.13

^a Not determined.

The TLC analysis shows that the only major (> 10% TRR) identified compounds that appear consistently in the residue data are triflumizole and FM-6-1. As overall residues of radiocarbon decline with increasing time after treatment, FD-2-1 and unidentified metabolites ("Others" in Table 10) become more prominent in the residue profile in terms of %TRR.

Residues of treatment-related compounds in apple fruits were not reported in the study.

Table 10 Identification and distribution of radiocarbon residues in apple leaves treated with [¹⁴C] triflumizole. Concentration is only shown if > 0.01 mg eq/kg

Plant Part or Fraction	0 DAT	1 DAT	3 DAT	7 DAT	14 DAT	21 DAT	31 DAT	60 DAT	90 DAT
% TAR→	98.57	80.44	60.53	33.68	16.52	16.57	18.3	13.75	7.86
Radiocarbon Residue (% TRR) [mg eq/kg]									
Chloroform Wash									
Triflumizole	92.8 [0.116]	40.9 [0.042]	21.4 [0.016]	9.5	3.9	3.0	1.5	< 0.01	< 0.01
FM-5-1	0.7	7.4	5.7	2.5	1.9	1.1	1.0	1.2	0.8
FM-6-1	1.4	22.9 [0.023]	29.0 [0.022]	17.9	7.3	6.0	3.6	1.7	0.6
FM-8-1	0.2	1.4	2.5	4.2	3.2	3.0	4.0	2.5	0.9
FD-1-1	1.0	2.4	2.5	2.4	1.6	1.4	1.6	1.2	0.5
FA-1-1	0.2	1.0	0.9	0.4	0.4	0.3	0.4	0.3	0.1
Others	3.9	18.6 [0.019]	26.4 [0.020]	33.5 [0.014]	29.2	27.6	28.6	21.5	9.2
Subtotal	100.0	94.6	88.4	70.4	47.4	42.4	40.8	28.4	12.1
Chloroform Extract									
Triflumizole	— ^a	1.3	2.0	0.9	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
FM-5-1	—	0.2	0.4	0.4	0.7	0.8	0.6	0.5	0.8
FM-6-1	—	1.0	2.3	9.4	7.7	5.1	1.4	0.7	0.5
FM-8-1	—	0.1	0.3	1.3	4.2	4.8	4.1	3.7	1.4
FD-1-1	—	0.2	0.3	0.4	0.4	0.4	0.6	0.6	0.4
FD-2-1	—	0.1	0.1	0.7	0.6	0.5	1.2	1.5	1.5
FD-6-1	—	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
FA-1-1	—	0.1	0.3	0.4	0.7	0.5	1.0	0.7	0.6
Others	—	1.1	2.8	6.5	12.9	14.2	13.4	14.8	15.0
Subtotal	—	4.1	8.6	20.1	27.2	26.4	23.1	22.4	20.2
Aqueous Methanol Extract									
FM-8-1	—	—	—	0.4	0.7	1.0	0.9	1.2	0.9
FD-7-1	—	—	—	1.0	2.3	3.1	3.6	4.4	4.8
M-1 (FD-6-1) ^b	—	—	—	< 0.01	0.4	0.5	0.8	0.9	1.3
M-2	—	—	—	0.2	0.5	0.7	0.6	0.7	1.3
M-3 (FD-2-1, FD-6-1)	—	—	—	0.9	1.9	2.6	2.2	2.4	4.2
M-4 (FA-1-1)	—	—	—	< 0.01	< 0.01	< 0.01	1.2	2.2	2.9
M-5	—	—	—	< 0.01	< 0.01	0.6	1.1	1.5	2.2
M-6	—	—	—	< 0.01	< 0.01	0.8	1.5	2.0	2.8
M-7	—	—	—	0.7	1.8	2.5	2.9	3.6	3.9
M-8 (FD-2-1)	—	—	—	0.6	1.6	2.7	3.1	3.6	6.9
M-9 (FD-2-1)	—	—	—	0.2	0.7	1.1	1.2	< 0.01	< 0.01
Others	—	—	—	2.5	5.6	5.4	6.4	10.0	13.9
Subtotal	—	0.9	2.0	6.5	15.6	21.1	25.4	32.4	45.0
PES	—	0.4	1.0	3.3	9.9	10.1	10.8	16.9	22.6
Sum of Chloroform Wash, Chloroform Extract, and Aqueous Methanol									
Triflumizole	92.8 [0.116]	42.2 [0.043]	23.4 [0.018]	10.4	3.9	3.0	1.5	< 0.01	< 0.01
FM-5-1	0.7	7.6	6.1	2.9	2.6	2.0	1.6	1.7	1.5
FM-6-1	1.4	23.9 [0.024]	31.3 [0.024]	27.3 [0.012]	15.0	11.0	4.9	2.4	1.2
FM-8-1	0.2	1.5	2.9	5.9	8.1	8.8	9.0	7.3	3.2
FD-1-1	1.0	2.6	2.9	2.9	2.0	1.8	2.2	1.7	0.9
FD-2-1 ^c	—	0.1	0.1	2.3	4.8	7.0	7.7	7.5	12.6
FD-6-1 ^c	—	—	—	—	0.4	0.5	2.2	2.0	2.8
FD-7-1	—	—	—	1.0	2.3	3.1	3.6	4.4	4.8
FA-1-1 ^c	0.2	1.1	1.2	0.7	1.0	0.9	2.0	2.0	2.2
Others ^d	3.9	20.6 [0.021]	31.1 [0.024]	43.5 [0.019]	50.0 [0.010]	51.9 [0.011]	54.5 [0.013]	54.0	48.2
PES	—	0.4	1.0	3.0	9.9	10.1	10.8	16.9	22.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

^a Not determined.^b Compound in parenthesis is an aglycone of the conjugate.

^c Includes conjugate.

^d Includes M-2, M-5, M-6, and M-7.

Pears

The metabolism of triflumizole in pear trees grown in a greenhouse was investigated (Soeda and Hashimoto, 1987a). Treatments were with triflumizole, uniformly labelled with ^{14}C in the phenyl ring, applied either as uniformly as possible to four leaves of a branch cluster containing 8–12 leaves or to the surface of a pear fruit. The leaf application rate was approximately 1 mg triflumizole/4-leaf cluster and the fruit application rate was approximately 0.166 mg triflumizole/fruit. Branches from leaf-treated trees were harvested at 0, 1, 3, 7, 14, 21, 31, 60, and 90 DAT and were divided into treated leaves, untreated leaves and fruit. Treated fruits were harvested 0, 1, 3, 7, and 14 DAT. After harvest, the treated leaves and fruits were surface washed with chloroform. The fruits were then peeled and sectioned into flesh and core. The leaves and fruit peel were separately homogenized and extracted with methanol:water (7:3, v/v). The methanol extract was diluted and partitioned with chloroform. Radioactivity in the extracts was determined directly by LSC. Radioactivity in fibrous residue (PES) was determined by combustion/LSC. The chloroform surface washes, the chloroform partition phases, and the water partition phases were concentrated. The water phases of leaf extracts were extracted with 1-butanol and the solvent was evaporated. All remainders were subjected to quantitative and qualitative 1-D TLC analysis using co-chromatography with known standards. The location of radioactivity on the TLC plates was determined by autoradiography and the activity in ^{14}C spots was determined by LSC of the scrapings derived from the TLC plates. The nature of the aglycones in the combined water phases of all leaf samples from 7 DAT onwards was investigated by means of column chromatography and subsequent treatment of the water-soluble metabolites with β -glucosidase, cellulase, acid- or alkali pectinase. The reaction products were also subjected to 1-D TLC. In the case of the metabolite FA-1-1, which is extremely volatile, TLC scraping and LSC was done immediately after two-dimensional co-chromatography with authentic standards, using UV light to locate the residue for scraping.

Radiocarbon residues in chloroform washes, extracts, and plant material from pear leaves are summarized below (Table 11). The data show that most of the radiocarbon residues were removed in the chloroform wash through the early stages of sampling and that there was very little translocation of radioactivity from treated to untreated leaves. The data also show a rapid decline in radiocarbon residues, with an initial half-life of approximately 4 days.

Table 11 Distribution of radiocarbon residues in leaves and fruit from pear trees leaf-treated with [^{14}C] triflumizole

Plant Part or Fraction	0 DAT	1 DAT	3 DAT	7 DAT	14 DAT	21 DAT	31 DAT	60 DAT	90 DAT
% TAR →	103.04	96.74	77.00	50.20	15.09	25.50	21.97	19.10	16.73
Radiocarbon Residue (% TRR)									
Treated Leaves									
CHCl ₃ Wash	100.0	95.0	92.8	82.1	48.2	54.7	43.7	24.0	13.6
MeOH:H ₂ O									
CHCl ₃	- ^a	3.5	4.2	9.7	20.7	16.9	17.8	18.3	15.7
Aq. MeOH	-	0.9	1.8	5.5	13.6	15.9	23.0	34.9	40.8
PES	-	0.5	0.9	2.4	10.8	9.2	12.2	20.2	25.6
Subtotal	100.0	99.9	99.8	99.8	93.4	96.7	96.8	97.4	95.7
Untreated Leaves	-	0.1	0.2	0.2	6.5	3.1	3.0	2.3	3.2
Fruit	-	< 0.01	< 0.01	0.0	0.1	0.2	0.3	0.4	1.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Triflumizole equivalents (mg eq/kg)									
Treated Leaves	73.27	77.66	53.03	36.74	8.79	14.46	10.11	8.83	8.31
Untreated Leaves	- [*]	0.03	0.06	0.08	0.24	0.13	0.06	0.03	0.17
Fruit	-	0.001	0.002	0.006	0.007	0.006	0.006	0.002	0.002

^a - Not determined

The TLC analysis shows that the only major (> 10% TRR) identified metabolite that appears consistently in the residue data is FM-6-1. With the overall decline in radiocarbon residues with increasing time after treatment, unidentified residues (Others) and bound residues (PES) become more prominent in the residue profile in terms of %TRR (Table 12).

Table 12 Identification and distribution of radiocarbon residues in pear leaves treated with [^{14}C] triflumizole

Plant Part or Fraction	0 DAT	1 DAT	3 DAT	7 DAT	14 DAT	21 DAT	31 DAT	60 DAT	90 DAT
% TAR →	103.0	96.7	77.1	51.3	24.0	31.8	31.2	35.5	38.5
Radiocarbon Residue (% TRR)									
Chloroform Wash									
Triflumizole	92.3	51.5	24.1	12.4	4.5	3.4	2.6	0.5	< 0.01
FM-5-1	0.6	4.8	4.5	1.7	1.1	0.9	1.4	0.6	0.4
FM-6-1	1.3	18.4	32.2	29.7	6.6	8.7	6.3	1.3	0.6
FM-8-1	0.2	1.0	2.2	3.4	0.8	2.7	2.6	1.0	0.4
FD-1-1	0.7	1.4	2.4	1.8	2.9	1.9	1.5	1.1	0.5
FA-1-1	0.2	0.7	0.9	0.4	0.2	0.3	0.4	0.1	0.1
Others	4.7	17.1	26.5	31.0	14.1	25.9	16.0	8.2	4.0
Subtotal	100.0	95.0	92.7	80.4	30.3	43.8	30.8	12.9	5.9
Chloroform Extract									
Triflumizole	— ^a	1.1	0.8	0.8	0.3	< 0.01	< 0.01	< 0.01	< 0.02
FM-5-1	—	0.2	0.2	0.3	0.4	0.4	0.2	0.2	0.1
FM-6-1	—	0.3	0.4	1.8	3.0	3.0	1.0	0.4	0.2
FM-8-1	—	0.2	0.3	0.9	1.2	2.0	0.7	0.6	0.4
FD-1-1	—	0.2	0.2	0.2	0.3	0.2	0.3	0.4	0.3
FD-2-1	—	0.1	0.1	0.2	0.5	0.3	0.5	0.4	0.3
FD-6-1	—	0.1	0.1	0.2	0.3	0.2	0.3	< 0.01	< 0.01
FA-1-1	—	0.1	0.1	0.2	0.4	0.3	0.2	0.2	0.1
Others	—	1.3	2.0	4.9	6.6	7.3	9.4	7.7	5.5
Subtotal	—	3.5	4.2	9.5	13.0	13.6	12.5	9.9	6.8
Aqueous Methanol Extract									
FM-8-1	—	—	—	0.2	0.1	0.2	0.2	0.3	0.2
FD-7-1	—	—	—	0.6	0.9	1.5	1.9	2.1	2.0
M-1 (FD-6-1) ^b	—	—	—	0.1	0.3	0.4	0.5	0.5	0.5
M-2	—	—	—	0.2	0.4	0.4	0.5	0.5	0.6
M-3 (FD-2-1)	—	—	—	0.6	1.2	1.4	1.9	1.7	2.1
M-4 (FA-1-1, FD-6-1)	—	—	—	0.2	0.6	0.7	1.3	1.7	1.4
M-5	—	—	—	0.1	0.2	0.4	0.7	0.9	0.7
M-6	—	—	—	0.1	0.3	0.6	0.9	1.2	0.9
M-7	—	—	—	0.5	0.7	1.3	1.5	1.7	1.6
M-8 (FD-2-1)	—	—	—	0.3	0.6	1.0	1.3	1.6	2.4
M-9 (FD-2-1)	—	—	—	0.4	0.5	0.8	1.2	1.1	1.2
Others	—	—	—	2.0	2.6	4.1	4.3	5.3	4.1
Subtotal	—	0.9	1.8	5.4	8.5	12.8	16.2	18.8	17.7
PES	—	0.5	1.2	4.7	48.1	29.9	40.5	58.4	69.5
Sum of Chloroform Wash, Chloroform Extract, and Aqueous Methanol. [mg eq/kg] if > 0.01									
Triflumizole	92.3 [0.954]	52.6 [0.509]	24.9 [0.192]	13.2 [0.066]	4.8	3.4	2.6	0.5	< 0.01
FM-5-1	0.6	5 [0.048]	4.7 [0.036]	2 [0.01]	1.5	1.3	1.5	0.8	0.5
FM-6-1	1.3 [0.013]	18.7 [0.181]	32.6 [0.251]	31.5 [0.158]	9.6 [0.014]	11.6 [0.03]	7.3 [0.016]	1.7	0.8
FM-8-1	0.2	1.2 [0.012]	2.5 [0.019]	4.5 [0.023]	2.2	4.9 [0.012]	3.4	2	0.9
FD-1-1	0.7	1.6 [0.015]	2.6 [0.02]	2 [0.01]	3.2	2.1	1.8	1.5	0.8
FD-2-1 ^c	—	0.1	0.1	1.4	2.6	3.1	4.4	4.3	5.5
FD-6-1 ^c	—	0.1	0.1	0.4	0.8	0.8	1.2	1	0.9
FD-7-1	—	—	—	0.6	0.9	1.5	1.9	2.1	2
FA-1-1 ^c	0.2	0.8	0.9	0.7	0.9	1	1.3	1.1	0.8

Plant Part or Fraction	0 DAT	1 DAT	3 DAT	7 DAT	14 DAT	21 DAT	31 DAT	60 DAT	90 DAT
% TAR →	103.0	96.7	77.1	51.3	24.0	31.8	31.2	35.5	38.5
Others	4.7 [0.049]	19.3 [0.187]	30.3 [0.233]	39 [0.196]	25.3 [0.038]	40.4 [0.103]	34.1 [0.075]	26.5 [0.051]	18.4 [0.031]
PES	—	0.5	1.2	4.7 [0.024]	48.1 [0.073]	29.9 [0.076]	40.5 [0.089]	58.4 [0.112]	69.5 [0.116]
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

^a Not determined.

^b Aglycone formed by enzymatic hydrolysis.

^c Includes conjugate.

Radiocarbon residues in chloroform washes, extracts, and plant material from pear fruit are summarized below (Table). The data show that through the two-week sampling period, nearly all of the radiocarbon residues were associated with the peel of the fruit and that most of that radioactivity was removed in the chloroform wash from fruit at the first three sampling intervals. The data also show a rapid decline in radiocarbon residues, with an initial half-life of between 1 and 3 days, and a slower rate of decline between 3 and 14 DAT.

Table 13 Distribution of radiocarbon residues in fruit from pear trees treated with [¹⁴C] Triflumizole

Plant Part or Fraction	0 DAT	1 DAT	3 DAT	7 DAT	14 DAT
% TAR →	100.4	68.6	57.7	55.0	41.7
Radiocarbon Residue (% of Applied)					
Peel					
CHCl ₃ Wash	100.0	63.3	47.6	39.0	23.2
MeOH:H ₂ O					
CHCl ₃	— ^a	22.1	28.7	27.1	27.8
Aq. MeOH	—	1.5	2.5	4.8	7.6
Acetone	—	4.5	7.0	7.5	12.4
NaOH					
CHCl ₃	—	6.3	9.6	14.1	19.1
H ₂ O	—	0.4	0.5	1.0	1.4
PES	—	1.4	2.1	2.9	4.3
Subtotal	100.0	99.4	97.9	96.5	95.8
Flesh	—	0.4	1.9	3.1	3.8
Core	—	0.2	0.2	0.3	0.4
Total	100.0	100.0	100.0	99.9	100.0
Triflumizole equivalents (mg eq/kg)					
Peel	9.61	6.52	4.79	3.05	2.11
Flesh	—	0.005	0.013	0.017	0.013
Core	—	0.013	0.008	0.015	0.010
Total	1.19	0.62	0.53	0.42	0.27

^a Not determined

The metabolic profile in pear fruits is summarized in Table 214. Major residues in pear fruit were triflumizole (through 3 DAT), FM-6-1, and FD-1-1 (3 DAT only). Residues of FM-6-1 and FA-1-1 were greater in fruit than in leaves. Individual unknown metabolites (Others) were < 5% TRR.

Table 2 Identification and distribution of radiocarbon residues in pear fruits treated with [¹⁴C] triflumizole

Plant Part and Compound	0 DAT		1 DAT		3 DAT		7 DAT		14 DAT	
% TAR →	100.35		68.59		57.68		54.97		41.69	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Peel										
Triflumizole	93.56	1.11	25.67	0.16	13.89	0.07	7.86	0.03	1.80	<0.01
FM-5-1	1.16	0.01	7.77	0.05	4.51	0.02	2.95	0.01	2.30	0.01

Plant Part and Compound	0 DAT		1 DAT		3 DAT		7 DAT		14 DAT	
% TAR →	100.35		68.59		57.68		54.97		41.69	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
FM-6-1	< 0.01	< 0.01	25.92	0.16	30.03	0.16	32.36	0.14	32.05	0.09
FM-8-1	< 0.01	< 0.01	0.63	< 0.01	1.23	0.01	1.64	0.01	1.94	0.01
FD-1-1	1.33	0.02	9.30	0.06	10.51	0.06	7.53	0.03	7.32	0.02
FA-1-1	0.39	0.01	4.51	0.03	4.26	0.02	4.98	0.02	5.13	0.01
Others	3.56	0.04	24.22	0.15	31.47	0.17	36.40	0.15	40.99	0.11
PES	— ^a	—	1.36	0.01	2.08	0.01	2.86	0.01	4.32	0.01
Flesh	—	—	0.42	< 0.01	1.87	0.01	3.13	0.02	3.79	0.01
Core	—	—	0.2	< 0.01	0.15	< 0.01	0.29	< 0.01	0.36	< 0.01

^a Not determined

Grapes

The metabolism of triflumizole in grape vines grown in a greenhouse was investigated (Soeda and Hashimoto, 1987c). Treatments were with triflumizole, uniformly labelled with ¹⁴C in the phenyl ring, applied either to a branch of approximately 10 leaves and blossoms at the berry crossing time (67 days prior to harvesting mature fruit) or to a bunch of young fruits 35 days before harvesting mature fruit. For both treatments, the rate was equivalent to 280 g ai/ha. Branches were harvested 0, 3, 7, 14, 31, and 67 DAT and were divided into treated leaves and fruit. In the second experiment, treated fruits were harvested 0, 3, 7, 14, and 35 DAT. Samples were surface washed with dichloromethane (DCM) and then extracted with methanol:water (8:2, v/v). The methanol extract was partitioned against DCM. Radioactivity in the washes and extracts was determined by LSC directly and in PES by combustion/LSC. The concentrated DCM wash, DCM partition phase, and the water partition phase were subjected to 1D-TLC analysis using co-chromatography of known standards. The activity in ¹⁴C-spots was determined by LSC of the scrapings derived from the TLC plates.

Most of the radioactivity in leaves was recovered from the surface wash. Residues decreased from 99% of the applied dose (AD) to 15% TAR at 67 DAT (Table). Radioactivity was translocated to fruits at less than 2% TAR. The parent compound was found to be the major residue (decreasing from 98% TRR at 0 DAT to 7.5% TRR at 67 DAT). The only other major residue was FM-6-1 (11.1% TRR at 67 DAT). Post-extraction residues in leaves gradually increased from 3.1% TRR (1.73 mg eq/kg) to 26.02% TRR (1.79 mg eq/kg) over the course of the study. Minor metabolites and those remaining at the origin increased to 39% TRR at 67 DAT (

Table).

Table 15 Residues in grape leaf and fruit after application of [¹⁴C] triflumizole to leaves, expressed as % TAR and mg eq/kg (triflumizole-equivalents)

Plant Part or Fraction	0 DAT		3 DAT		7 DAT		14 DAT		31 DAT		67 DAT	
	% TAR	mg eq/kg	% TAR	mg eq/kg	% TAR	mg eq/kg	% TAR	mg eq/kg	% TAR	mg eq/kg	% TAR	mg eq/kg
Fruit	0.96	0.64	1.72	1.00	1.97	0.82	1.28	0.47	0.43	0.26	0.24	0.11
Leaves												
Surface wash	99.0	65.6	85.9	50.17	75.6	31.21	34.7	12.73	17.3	10.43	4.8	2.21
MeOH extract												
CHCl ₃ phase	n.a.	n.a.	5.8	3.39	7.6	3.13	3.4	1.248	3.7	2.23	2.9	1.33
Water phase	n.a.	n.a.	0.9	0.53	2.7	1.11	2.3	0.844	3.4	2.05	3.8	1.75
PES			3.0	1.75	4.3	1.77	4.1	1.505	4.1	2.47	3.9	1.79
Total	99.0	65.6	95.6	55.9	90.1	37.2	44.4	16.3	28.5	17.2	15.0	6.9

Table 16 Residues in grape leaf after application of [^{14}C] triflumizole to leaves, expressed as % TRR ^a and mg eq/kg (triflumizole-equivalents)

	0 DAT		3 DAT		7 DAT		14 DAT		31 DAT		67 DAT	
Compound or fraction ^b	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Triflumizole	98	64.3	87.4	48.8	80.0	29.7	70.8	11.5	50.9	8.8	7.5	0.51
FM-5-1	0.16	0.11	0.65	0.36	0.68	0.25	0.68	0.11	0.91	0.16	< 0.01	< 0.01
FM-6-1	0.12	0.08	2.13	1.19	3.08	1.15	3.98	0.65	7.09	1.22	11.07	0.76
FM-8-1	0.14	0.09	0.44	0.25	0.81	0.30	1.19	0.19	2.35	0.40	4.87	0.33
FD-1-1	0.18	0.11	0.97	0.54	1.67	0.62	1.28	0.21	0.98	0.17	2.47	0.17
FD-2-1	—	—	0.29	0.16	0.49	0.18	0.99	0.16	1.83	0.31	5.14	0.35
FD-6-1	—	—	0.07	0.04	0.07	0.03	0.11	0.02	0.32	0.05	1.73	0.12
FD-7-1	—	—	0.06	0.03	0.13	0.05	0.29	0.05	0.53	0.09	1.20	0.08
FA-1-1	0.15	0.10	0.28	0.16	0.36	0.13	0.34	0.06	0.21	0.04	0.73	0.05
Other	1.25	0.82	4.58	2.56	7.92	2.95	11.21	1.82	20.61	3.54	39.3	2.70
PES	—	—	1.73	4.79	1.78	9.12	1.48	14.29	2.46	26.02	1.79	—
Total	100	—	100	—	100	—	100	—	100	—	100	—

^a Expressed as percentage of total radioactivity at sampling time^b From surface wash and methanol extracts; Other includes minor components and TLC-origin activity.

After fruit application, most of the radioactivity was recovered from the surface wash, and decreased to approximately 7.5% TAR at 35 DAT (Table 17 317). Triflumizole decreased from 95.45% TRR (7.44 mg eq/kg) to 31% TRR (0.31 mg eq/kg) at 35 DAT, and the metabolite FM-6-1 increased to 7.6% TRR (0.07 mg eq/kg) at 35 DAT. Post-extraction solids increased to 17.1% TRR at 35 DAT. The results are summarized in Table 18.

Table 17 3Residues in grape fruits after application of [^{14}C] triflumizole to fruits, expressed as % TAR ^a and mg eq/kg

	0 DAT		3 DAT		7 DAT		14 DAT		35 DAT	
%TAR →	100		49.7		24.6		22.7		24.8	
Fraction	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Surface wash	100	7.79	88.24	5.44	68.1	1.46	44.4	0.68	30.3	0.298
MeOH extract										
CHCl ₃ phase	—	—	7.8	0.488	16.1	0.348	22.2	0.341	22.5	3.73
Water phase	—	—	1.7	0.106	6.9	0.148	15.6	2.379	30.0	4.99
PES	—	—	2.2	0.002	8.9	0.152	17.8	0.295	17.1	2.83

^a Expressed as percentage of total radioactivity as appliedTable 18 Residues in grape fruits after application of [^{14}C] triflumizole to fruits, expressed as % TRR ^a and mg eq/kg

	0 DAT		3 DAT		7 DAT		14 DAT		35 DAT	
Compound or fraction ^b	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Triflumizole	95.45	7.44	86.89	5.37	69.77	1.49	49.38	0.76	31.17	0.31
FM-5-1	0.25	0.02	0.66	0.04	1.10	0.02	1.01	0.02	< 0.01	< 0.01
FM-6-1	1.43	0.11	1.29	0.08	1.75	0.04	2.56	0.04	7.59	0.07
FM-8-1	< 0.01	< 0.01	0.71	0.04	1.87	0.04	3.88	0.06	3.64	0.04
FD-1-1	0.31	0.02	2.96	0.18	4.03	0.09	4.89	0.08	3.67	0.04
FD-2-1	—	—	0.77	0.05	3.05	0.07	6.83	0.11	7.63	0.07
FD-6-1	—	—	0.20	0.01	0.57	0.01	0.66	0.01	1.69	0.02
FD-7-1	—	—	0.16	0.01	0.49	0.01	0.75	0.01	2.30	0.02
FA-1-1	0.01	< 0.01	0.62	0.04	1.10	0.02	0.97	0.01	0.65	0.01
Other	2.55	0.20	3.46	0.21	7.4	0.16	11.27	0.17	24.58	0.24
PES	—	—	2.19	0.14	8.87	0.19	17.80	0.27	17.08	0.16

^a Expressed as percentage of total radioactivity at sampling time^b From surface wash and methanol extracts; Other includes minor components and TLC-origin activity.

Cucumbers

The metabolism of triflumizole in cucumbers was studied under greenhouse conditions by Soeda (1983). Three types of treatment were made: Foliar treatment to investigate metabolism, fruit treatment to investigate metabolism, and foliar treatment to investigate translocation.

In the foliar metabolism study, radio-labelled triflumizole was applied to leaves (0.13 mg/plant) of multiple plants at the 2nd-to-3rd leaf stage. At sampling times of 1, 3, 7, 14, 21, and 45 (one plant) days after treatment (DAT), two whole plant was harvested, the roots were washed with water, and the plants were sectioned into root, lower part (below the treated leaf), treated leaf, upper part (above the treated leaf), and fruit. Treated leaves were surface washed with chloroform and then the leaf was homogenized with methanol (80%). The methanol extract was adjusted to 50% with distilled water and then partitioned against chloroform. Chloroform leaf wash and extract were assayed, separately, by 1-D and 2-D TLC for residue identification. The aqueous extract was assayed for radioactivity by LSC, and the extracted treated leaf and the remaining plant parts (post-extraction solids, PES) were assayed for radioactivity by combustion followed by LSC. Levels of total radioactivity in the various washes, extracts, and tissues demonstrate that the majority of the applied material is recovered in the surface wash of treated leaves and that very little is distributed throughout the plant (Table19). Residue in the leaves decreased with increasing DAT. The decrease was most significant for triflumizole, with no concomitant increase seen in any of the identified metabolites (Table). Residue levels (mg eq/kg) were not provided in the study.

Table19 Distribution of radiocarbon residues in treated cucumber plants

	1 DAT		3 DAT		7 DAT		14 DAT		21 DAT		45 DAT	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Plant parts and fractions	87.0% TAR	0.113	81.6% TAR	0.106	62.4% TAR	0.081	44.2% TAR	0.057	28.4% TAR	0.037	13.8% TAR	0.018
Treated Leaf												
Chloroform wash	87.4	0.099	84.2	0.089	81.7	0.066	73.8	0.042	54.9	0.020	29.7	0.005
80% MeOH extract												
Chloroform fraction	7.2	0.008	8.8	0.009	9.3	0.008	13.1	0.008	16.9	0.006	13.8	0.002
Aqueous fraction	5.3	0.006	6.5	0.007	8.5	0.007	9.7	0.006	19.7	0.007	33.3	0.006
PES	0.1	< 0.001	0.4	< 0.001	0.3	< 0.001	2.7	0.002	7	0.003	14.5	0.003
Subtotal	100	0.113	99.9	0.106	100.6	0.082	99.3	0.057	98.6	0.036	91.3	0.016
Upper parts	0.01	< 0.001	0.01	< 0.001	0.08	< 0.001	0.52	< 0.001	0.74	< 0.001	4.6	0.001
Lower parts	0.01	< 0.001	0.07	0.000	0.11	< 0.001	0.16	< 0.001	0.49	< 0.001	0.43	< 0.001
Root	— ^a	< 0.001	—	< 0.001	—	< 0.001	0.02	< 0.001	0.28	< 0.001	1.7	< 0.001
Fruit	— ^b	< 0.001	—	< 0.001	—	< 0.001	—	< 0.001	—	< 0.001	1.9	< 0.001

^a Less than 0.01.

^b Fruit were not present.

Table 20 Distribution and identification of radiocarbon residues in cucumber leaves

Fraction	Analyte	1 DAT		3 DAT		7 DAT		14 DAT		21 DAT		45 DAT	
		% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
		82.3% TAR	0.107	75.9% TAR	0.099	56.8% TAR	0.074	38.4% TAR	0.050	20.4% TAR	0.027	6.0% TAR	0.008
Surface wash	Triflumizole	79.5	0.085	73.4	0.072	52.3	0.039	28.9	0.014	15.7	0.004	5	—
	FM-5-1	1.7	0.002	2.2	0.002	3	0.002	4.2	0.002	2	0.001	3.3	—

Fraction	Analyte	1 DAT		3 DAT		7 DAT		14 DAT		21 DAT		45 DAT	
		% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
	FM-6-1	5	0.005	7.2	0.007	11.6	0.009	13.8	0.007	13.2	0.004	5	—
	FM-8-1	— ^a	—	—	—	3.3	0.002	3.1	0.002	5.4	0.001	6.7	0.001
	FD-1-1	1.6	0.002	2.9	0.003	4.4	0.003	2.9	0.001	2.9	0.001	3.3	—
	FA-1-1	0.4	—	0.7	0.001	0.5	—	1.3	0.001	0.5	—	—	—
	Others ^b	4.3	0.005	4.1	0.004	14.6	0.011	30.7	0.015	36.8	0.010	45	0.004
	Subtotal	92.3	0.099	90.5	0.089	89.8	0.066	84.9	0.042	76.5	0.020	68.3	0.005
Flesh extract	Triflumizole	1.8	0.002	3.8	0.004	1.4	0.001	2.1	0.001	1.5	0.000	1.7	—
	FM-5-1	0.2	—	0.3	—	0.2	—	0.3	—	—	—	—	—
	FM-6-1	1.8	0.002	1.3	0.001	1.9	0.001	2.9	0.001	2	0.001	1.7	—
	FM-8-1	0.4	—	1.2	0.001	1.1	0.001	1.8	0.001	5.9	0.002	1.7	—
	FD-1-1	0.2	—	0.3	—	0.5	—	0.5	—	0.5	0.000	1.7	—
	FA-1-1	—	—	0.1	—	0.4	—	0.3	—	0.5	—	—	—
	Others	3.2	0.003	2.5	0.002	4.8	0.004	7.3	0.004	13.2	0.004	25	0.002
	Subtotal	7.7	0.008	9.5	0.009	10.2	0.008	15.1	0.008	23.5	0.006	31.7	0.002
Total (Surface & flesh)	Triflumizole	81.3	0.087	77.2	0.076	53.7	0.040	31	0.015	17.2	0.005	6.7	0.001
	FM-5-1	1.9	0.002	2.5	0.002	3.2	0.002	4.4	0.002	2	0.001	3.3	—
	FM-6-1	6.8	0.007	8.6	0.008	13.6	0.010	16.7	0.008	15.2	0.004	6.7	0.001
	FM-8-1	0.4	—	1.2	0.001	4.4	0.003	4.9	0.002	11.3	0.003	8.3	0.001
	FD-1-1	1.8	0.002	3.2	0.003	4.9	0.004	3.4	0.002	3.4	0.001	5	—
	FA-1-1	0.4	—	0.8	0.001	0.9	0.001	1.6	0.001	1	—	—	—
	Others	7.4	0.008	6.6	0.007	19.4	0.014	33.1	0.017	50	0.013	70	0.005
	Total	100	0.107	100	0.099	100	0.074	100	0.050	100	0.027	100	0.008

^a Less than 0.1^b Sum of minors and origin materials.

In the fruit metabolism study, radio-labelled triflumizole (0.041 mg/plant) was applied as small droplets to a small fruit. Two fruits were harvested at each sampling time of 1, 3, 7, and 14 DAT. Total radioactive residues and residue identification and characterization was by the same methods used for treated leaves. The behaviour of total residues (Table) and the distribution of residues (Table 22) is similar to that observed for leaves.

Table 21 Distribution of radiocarbon residues in treated cucumber fruit

	Fraction	1 DAT		3 DAT		7 DAT		14 DAT	
		% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Plant part	Fraction	100.4% TAR	0.041	96.0% TAR	0.039	94.2% TAR	0.038	83.4% TAR	0.034
Surface	Chloroform wash	71	0.029	54.1	0.021	41.8	0.016	20.9	0.007
Peel	80% MeOH								
	Chloroform extract	21.9	0.009	23	0.009	23	0.009	18.7	0.006
	Aqueous residue	1.8	0.001	3.1	0.001	8.8	0.003	21.7	0.007
	PES	3.2	0.001	5.6	0.002	9.1	0.003	16.4	0.006
	Subtotal	26.9	0.011	31.8	0.013	41	0.016	56.8	0.019
Flesh	80% MeOH								
	Chloroform extract	1.7	0.001	10.2	0.004	12.4	0.005	14.5	0.005
	Aqueous residue	0	0.000	2	0.001	3.1	0.001	5.3	0.002
	PES	0.4	0.000	2	0.001	1.7	0.001	2.5	0.001
	Subtotal	2.1	0.001	14.2	0.006	17.2	0.007	22.3	0.008
Peel + Flesh	80% MeOH								
	Chloroform extract	23.6	0.010	33.2	0.013	35.5	0.013	33.2	0.011

		1 DAT		3 DAT		7 DAT		14 DAT	
		% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
	Aqueous residue	1.8	0.001	5.1	0.002	11.9	0.005	27	0.009
	PES	3.6	0.001	19.8	0.008	26.3	0.010	38.7	0.013
	Subtotal	29	0.012	45.9	0.018	58.2	0.022	67.1	0.023
Weight of fruit, g		39		75		160		280	

Table 22 Distribution and Identification of Radiocarbon Residues in Treated Cucumber Fruit

Fraction	Analyte	Radiocarbon Residue (% TRR) ^a			
		1 DAT 95.0% TAR	3 DAT 83.8% TAR	7 DAT 72.8% TAR	14 DAT 45.1% TAR
Surface Wash	Triflumizole	69.1 (0.027 mg eq/kg)	57.2 (0.020 mg eq/kg)	46.0 (0.014 mg eq/kg)	24.4 (< 0.01 mg eq/kg)
	FM-5-1	0.8	0.5	0.7	1.1
	FM-6-1	1.7	1.0	1.8	2.7
	FM-8-1	0.3	0.4	0.4	0.9
	FD-1-1	0.3	0.5	0.7	1.1
	FA-1-1	— ^b	—	0.1	0.7
	Others ^c	2.8	2.5	4.4	7.5
Fruit [Peel/Flesh]	Triflumizole	15.9 [15.4/0.5]	17.8 [14.0/3.8]	15.8 [13.9/1.9]	17.5 [15.7/1.8]
	FM-5-1	0.5 [0.5/—]	0.8 [0.6/0.2]	1.1 [1.0/0.1]	1.1 [0.7/0.4]
	FM-6-1	2.9 [2.3/0.6]	9.4 [4.1/4.8]	15.4 [5.1/10.3]	24.2 [7.1/17.1]
	FM-8-1	0.2 [0.2/—]	0.8 [0.5/0.4]	1.1 [0.7/0.4]	2.7 [1.1/1.6]
	FD-1-1	1.3 [1.2/0.1]	2.5 [2.0/0.5]	2.5 [2.2/0.3]	1.6 [1.3/0.2]
	FA-1-1	0.6 [0.5/0.1]	0.8 [0.5/0.4]	1.4 [1.2/0.1]	1.6 [0.9/0.7]
	Others	3.5 [3.1/0.4]	5.8 [4.2/1.7]	8.7 [5.8/2.9]	12.9 [7.8/5.1]
Total	Triflumizole	84.9	74.9	61.8	41.9
	FM-5-1	1.4	1.3	1.8	2.2
	FM-6-1	4.6	10.4	17.2	27.1
	FM-8-1	0.5	1.2	1.5	3.5
	FD-1-1	1.6	3.0	3.2	2.7
	FA-1-1	0.6	0.8	1.5	2.2
	Others	6.3	8.4	13.0	23.1
	Total	100.0	100.0	100.0	100.0

^a Except for triflumizole in surface wash, all other residues are < 0.01 mg eq/kg.

^b Less than 0.1%.

^c Sum of minors and origin materials.

To investigate translocation, an application of radio-labelled triflumizole (0.16 mg/plant) was made to the surface of a leaf which had a young fruit growing at the base of its petiole. Fruits were harvested 3, 7, and 14 DAT, weighed, and total radioactive residue determined by combustion/LSC. The results (Table) show that very little radioactivity was translocated from the treated leaf to the adjacent fruit.

Table 23 Translocation of Triflumizole Residues from a Treated Leaf to an Adjacent Fruit

Measurement	3 DAT	7 DAT	14 DAT
Fruit weight (g)	5.2	74.5	234
Radiocarbon residue (% of applied)	0.02	0.05	0.07
Radiocarbon residue (mg eq/kg triflumizole equivalents)	0.01	0.01	0.01

Summary of plant metabolism

The metabolism of triflumizole was studied in apples (leaves only), pears, cucumbers and grapes. The metabolic profile observed in these studies was similar across all four crops (

). The most abundant residue was parent triflumizole. Generally triflumizole decreased rather rapidly (half-life on the order of 3 days), with the exception of grapes where metabolism was considerably

slower. Loss of triflumizole was accompanied by an increase in the FM-6-1 metabolite, which was the only metabolite to consistently occur at $\geq 10\%$ TRR.

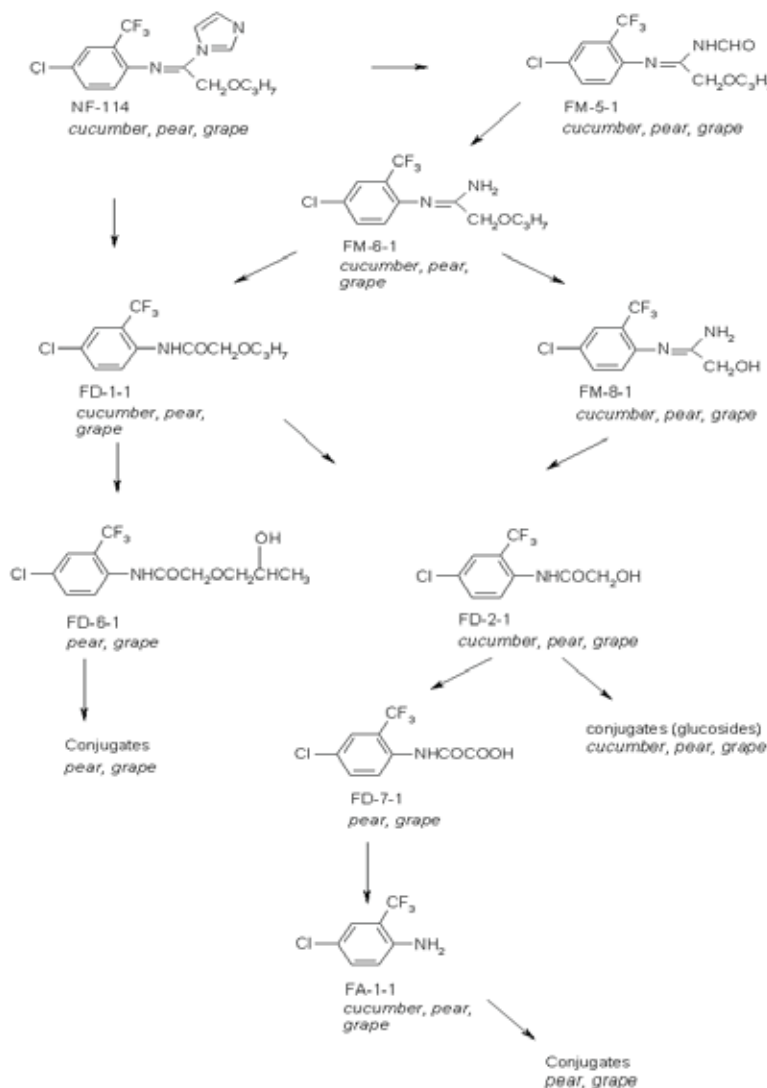


Figure 3 Proposed metabolic pathways of triflumizole in plants

ENVIRONMENTAL FATE

The Meeting received information on aqueous and soil-surface photolysis, soil dissipation, aerobic soil metabolism, and confined and field rotational crop studies.

Environmental fate in soil

The fate and behaviour of triflumizole in soil were investigated using [^{14}C] triflumizole labelled in the phenyl ring.

*Aerobic degradation**Study 1*

The metabolism and degradation rate (DT₅₀ and DT₉₀) of triflumizole was investigated in a sandy loam soil (Harned, 1985; Doc. No. 84253). Soil was added to incubation flasks and adjusted to 75% 1/3-bar moisture. Radio-labelled triflumizole was added to achieve a concentration of 0.60 mg eq/kg (approximately 0.56 kg/ha in the top 7.6 cm of soil). The flasks were capped with trapping towers and incubated, in darkness at 25 °C. Samples for extractable, bound, and volatile ¹⁴C were collected at 0, 0.33, 1, 2, 3, 4, 8, 12, 24, and 42 days after treatment.

Table 24 Soil characteristics

Parameters	Soil
pH	5.6
Organic matter (%)	7.34
Cation exchange capacity (meq/100 g soil)	43.5
Soil type (USDA)	Sandy loam
Clay (%)	6.4
Silt (%)	26.0
Sand (%)	67.6

Total extractable residues were determined by acetone extraction and LSC. Extracts were examined by HPLC, using known standards, to identify individual components. Quantification of extracted components was by fraction collection and LSC. Bound residues were determined by combustion/LSC. Total volatile organics were determined by combustion/LSC of the foam plugs in the trapping towers and ¹⁴CO₂ was determined by ascarite traps in the trapping towers. The results are summarized below (Table). The residue profile of the extracted radiocarbon is summarized in Table . The profile shows and increasing proportion of bound residues with increased incubation time and also indicates that the majority of the volatile radioactivity is not in the form of CO₂.

Table 25 Distribution of radiocarbon following aerobic incubation of soil treated with [¹⁴C] triflumizole

Fraction	Radiocarbon Residues (% TAR)									
	0 DAT	0.33 DAT	1 DAT	2 DAT	3 DAT	4 DAT	8 DAT	12 DAT	24 DAT	42 DAT
Extractable ^a	101.1	107.9	93.7	94.7	100.0	96.3	90.5	84.8	70.7	52.6
Bound	1.8	2.8	4.3	4.6	5.8	5.8	7.5	9.5	12.5	19.3
Volatile ^b	—	0.3	0.3	0.8	1.1	1.5	3.1	3.5	3.9	7.9
CO ₂	—	—	—	0.0	—	—	—	—	0.1	0.8
Total Recovery	102.9	111.0	98.3	100.1	106.9	103.6	101.1	97.8	87.2	80.6

^a Acetone extract

^b Trapped in polyurethane plug

Table 26 Profile of extractable radiocarbon residues from soil treated with [¹⁴C] triflumizole

Compound	Extractable Radiocarbon Residues (% TAR)									
	0 DAT	0.33 DAT	1 DAT	2 DAT	3 DAT	4 DAT	8 DAT	12 DAT	24 DAT	42 DAT
Triflumizole	88.1	95.0	78.6	82.5	84.1	83.1	73.7	63.1	40.4	26.0
FA-1-1	1.3	1.2	2.4	4.1	6.3	7.4	9.4	13.1	21.4	22.2
FM-6-1	2.8	0.0	0.0	0.0	1.4	0.0	0.0	0.0	0.0	0.0
FM-5-1	0.0	0.7	0.0	0.7	0.7	0.2	0.6	0.4	0.0	0.0
FD-1-1	2.7	2.9	1.9	2.4	1.5	1.8	2.2	2.3	2.1	1.1
Polar	0.8	4.0	2.7	0.2	1.1	1.0	0.9	0.2	1.6	1.7

Study 2

In a second study (Shiotani, 1982), the residue profile from two Japanese soils (Odawara or Oiso) was investigated. In this study, soils treated with [¹⁴C] triflumizole were incubated indoors at 15 °C or

25 °C for 1 hr, 7, 14, 21, 28, 42, 56, 70, 84, and 98 days after treatment. Extractable, bound, volatile residues and $^{14}\text{CO}_2$ were examined. In the case of extractable residues, methanol:water (8:2, v/v) extracts were partitioned against dichloromethane and cleaned-up on silica gel columns. Residue identification was by HPLC. In a separate part of the study, the Odawara and Oiso soils were treated and incubated outdoors during the day and inside at night and during rainy days. The soils were sampled at intervals of 1, 3, 7, 14, and 28 days after treatment and extracted in the same manner as those incubated indoors (polyurethane plugs and CO_2 traps were not used with the outdoor-incubated soils).

Residue profiles by soil, incubation temperature, and time are summarized in Table –32.

Table 27 Recovery of radioactivity and proportion of radioactive components in the CH_2Cl_2 fraction of the extracts for Odawara soil, incubated at 15 °C (expressed as % TAR)

Time (d)	Me-OH-H ₂ O extract	CH_2Cl_2 fraction	H ₂ O fraction	Soil residue	Polyurethane foam	Trapped $^{14}\text{CO}_2$	Total	Triflumizole	FM5-1	FM6-1	FD1-1	FA-1-1	Others
0	94.7	94.7	0	5.3	—	—	100.0	88.0	0.3	1.5	0.8	n.d. ^a	1.5
7	88.9	87.9	1.0	11.2	2.3	n.d.	102.4	70.8	1.2	3.6	3.2	2.4	4.8
14	82.0	80.8	1.2	14.5	4.1	n.d.	100.6	60.8	1.7	4.2	4.0	4.9	3.5
21	73.1	71.9	1.2	18.1	8.5	0.1	99.8	52.3	1.2	2.5	3.1	8.2	3.2
28	67.0	64.7	2.3	22.3	12.0	0.2	101.5	45.3	1.1	3.2	2.7	7.7	3.5
42	54.1	51.1	3.0	24.4	19.2	0.3	98.0	35.8	1.3	2.6	2.8	4.3	3.1
56	43.2	40.0	3.2	28.1	27.4	0.5	99.2	27.0	1.1	2.4	2.2	3.9	2.6
70	35.5	32.3	3.2	28.1	27.4	0.5	97.9	22.5	0.9	1.7	1.8	2.3	1.9
84	27.5	24.5	3.0	30.3	31.3	0.8	96.4	14.9	0.9	1.4	1.6	2.4	2.2
98	23.3	20.3	3.0	33.0	37.6	1.0	94.9	9.9	0.8	1.3	1.6	2.4	3.1

^a Not detected

Table 28 Recovery of radioactivity and proportion of radioactive components in the CH_2Cl_2 fraction of the extracts for Odawara soil, incubated at 25 °C (expressed as % TAR)

Time (d)	Me-OH-H ₂ O extract	CH_2Cl_2 fraction	H ₂ O fraction	Soil residue	Polyurethane foam	Trapped $^{14}\text{CO}_2$	Total	Triflumizole	FM5-1	FM6-1	FD1-1	FA-1-1	Others
0	94.7	94.7	0	5.3	—	—	100.0	88.0	0.3	1.5	0.8	n.d. ^a	1.5
7	76.4	75.4	1.0	16.2	9.2	0.1	101.9	60.7	1.0	2.8	2.4	4.3	2.9
14	60.7	59.4	1.3	27.0	14.3	0.4	102.4	38.2	1.2	3.5	2.9	9.1	2.9
21	46.3	44.1	2.2	31.5	21.3	0.8	99.9	28.6	0.9	2.7	2.3	5.9	2.4
28	34.0	31.3	2.7	34.3	26.4	1.2	95.9	19.0	0.9	2.0	1.8	4.6	1.9
42	23.4	21.0	2.4	38.4	32.1	1.6	95.5	12.7	0.4	1.5	1.1	2.9	1.4
56	13.1	11.8	1.3	40.1	39.0	2.3	94.5	6.3	0.3	0.6	0.6	2.1	1.2
70	8.8	7.5	1.3	42.2	40.6	2.7	94.3	n.a. ^b	n.a.	n.a.	n.a.	n.a.	n.a.
84	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
98	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

^a Not detected

^b Not analysed

Table 29 Recovery of radioactivity and proportion of radioactive components in the CH_2Cl_2 fraction of the extracts for Oiso soil, incubated at 15 °C (expressed as % TAR)

Time (d)	Me-OH-H ₂ O extract	CH_2Cl_2 fraction	H ₂ O fraction	Soil residue	Polyurethane foam	Trapped $^{14}\text{CO}_2$	Total	Triflumizole	FM5-1	FM6-1	FD1-1	FA-1-1	Others
0	91.2	91.2	0	8.8	—	—	100.0	80.1	0.2	2.9	1.5	n.d. ^a	2.1
7	87.3	86.9	0.4	13.0	1.2	n.d.	101.5	58.9	1.2	3.0	3.6	14.1	3.1
14	81.6	81.1	0.5	18.2	2.0	0.1	101.9	41.6	2.1	4.8	4.4	20.6	3.7

Time (d)	Me-OH-H ₂ O extract	CH ₂ Cl ₂ fraction	H ₂ O fraction	Soil residue	Polyurethane foam	Trapped ¹⁴ CO ₂	Total	Triflumizole	FM5-1	FM6-1	FD1-1	FA-1-1	Others
21	75.3	74.8	0.5	22.1	3.5	0.2	101.1	38.5	1.7	4.3	4.9	19.8	2.9
28	69.1	68.6	0.5	25.3	7.1	0.4	101.9	34.8	2.3	3.8	5.7	16.7	2.7
42	58.3	56.9	1.4	30.7	10.3	0.7	100.0	28.0	2.1	3.5	5.2	12.6	3.1
56	48.1	46.4	1.7	35.5	12.1	1.3	97.0	22.3	1.7	2.9	4.2	10.5	2.8
70	40.7	38.7	2.0	37.6	13.3	1.8	93.4	18.9	1.5	2.2	3.5	8.0	2.5
84	34.4	32.4	2.0	37.8	14.4	2.3	88.9	14.2	1.4	2.1	3.5	7.0	2.5
98	26.9	24.7	2.2	39.0	17.5	2.5	85.9	9.8	1.2	2.0	3.0	5.3	2.1

^a Not detected

Table 30 Recovery of radioactivity and proportion of radioactive components in the CH₂Cl₂ fraction of the extracts for Oiso soil, incubated at 25 °C (expressed as % TAR)

Time (d)	Me-OH-H ₂ O extract	CH ₂ Cl ₂ fraction	H ₂ O fraction	Soil residue	Polyurethane foam	Trapped ¹⁴ CO ₂	Total	Triflumizole	FM5-1	FM6-1	FD1-1	FA-1-1	Others
0	91.2	91.2	0	8.8	—	—	100.0	80.1	0.2	2.9	1.5	n.d. ^a	2.1
7	77.6	77.0	0.6	20.1	2.1	0.2	100.0	43.2	2.1	6.0	4.8	17.2	2.5
14	69.9	69.2	0.7	26.3	4.0	0.7	100.9	29.2	1.8	5.3	4.1	23.4	2.8
21	57.5	56.8	0.7	30.0	9.2	1.2	97.9	22.1	1.6	3.9	3.8	20.5	2.9
28	48.5	47.8	0.7	34.6	11.9	2.3	97.3	18.1	1.4	2.7	3.2	17.4	2.7
42	34.0	32.4	1.6	45.7	14.2	3.6	97.5	8.3	1.0	1.8	2.6	15.0	2.0
56	24.6	23.2	1.4	46.5	20.3	5.1	96.5	8.0	0.8	1.0	2.1	8.5	1.9
70	16.3	14.9	1.4	48.6	28.0	5.7	98.6	n.a. ^b	n.a.	n.a.	n.a.	n.a.	n.a.
84	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
98	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

^a Not detected

^b Not analysed

Table 31 Recovery of radioactivity and proportions of radioactive components in the CH₂Cl₂ fraction of the extracts for Odawara soil, from the outdoor experiment (expressed as % a.r.)

Time (d)	Me-OH-H ₂ O extract	CH ₂ Cl ₂ fraction	H ₂ O fraction	Soil residue	Total	Triflumizole	FM5-1	FM6-1	FD1-1	FA-1-1	Others
1	66.6	63.3	3.3	17.8	84.4	50.4	2.3	4.3	4.1	0.6	2.4
3	53.8	50.8	3.0	21.9	75.7	34.5	3.2	5.1	2.5	1.8	4.3
7	36.8	35.9	0.9	23.0	59.8	19.9	3.5	5.9	1.3	2.6	2.4
14	29.2	27.8	1.4	23.4	52.6	14.3	3.5	5.9	1.0	2.0	0.5
28	20.1	18.4	1.7	23.6	43.7	12.7	0.5	3.5	0.8	0.8	0.7

Table 32 Recovery of radioactivity and proportions of radioactive components in the CH₂Cl₂ fraction of the extracts for Oiso soil, from the outdoor experiment (expressed as % a.r.)

Time (d)	Me-OH-H ₂ O extract	CH ₂ Cl ₂ fraction	H ₂ O fraction	Soil residue	Total	Triflumizole	FM5-1	FM6-1	FD1-1	FA-1-1	Others
1	73.0	71.4	1.6	16.3	89.3	59.6	2.7	1.3	5.3	0.9	3.3
3	64.2	62.2	2.0	21.0	85.2	46.1	2.8	2.0	4.6	2.1	2.7
7	51.3	50.2	1.1	21.0	72.3	36.6	3.3	3.1	3.2	3.7	2.2
14	47.2	44.7	2.5	24.0	71.2	30.4	4.7	4.0	2.6	3.9	0.7
28	41.4	40.5	0.9	24.4	65.8	28.7	2.5	3.9	2.0	2.5	0.8

Table 33 4DT₅₀ values and DT₉₀ values for [¹⁴C] triflumizole and FA-1-1 applied in two soils, incubated indoor at 15 and 25 °C respectively

Soil	Odawara				Oiso			
	15°C		25°C		15°C		25°C	
Substance →	Triflumizole	FA-1-1	Triflumizole	FA-1-1	Triflumizole	FA-1-1	Triflumizole	FA-1-1
DT ₅₀ (days)	33 (22) ^a	9.3 (6.2)	13 (19)	7.8 (12)	27 (18)	12 (8)	11 (16)	13 (19)
DT ₉₀ (days)	110 (74)	31 (21)	43 (64)	26 (39)	91 (61)	40 (27)	37 (55)	26 (39)
r ²	0.996		0.996		0.95		0.97	

^a Recalculation to 20 °C are given in parentheses

Table 34 DT₅₀ values and DT₉₀ values for [¹⁴C] triflumizole applied in two outdoor soils

Soil	Odawara	Oiso
DT ₅₀ (days)	7.1	22
DT ₉₀ (days)	23	74
r ²	0.85	0.75

Dissipation times for 50% and 90% loss for parent triflumizole and the FA-1-1 metabolite are summarized in Table 33 4 and Table and the proposed metabolic pathway for triflumizole in soil is shown in

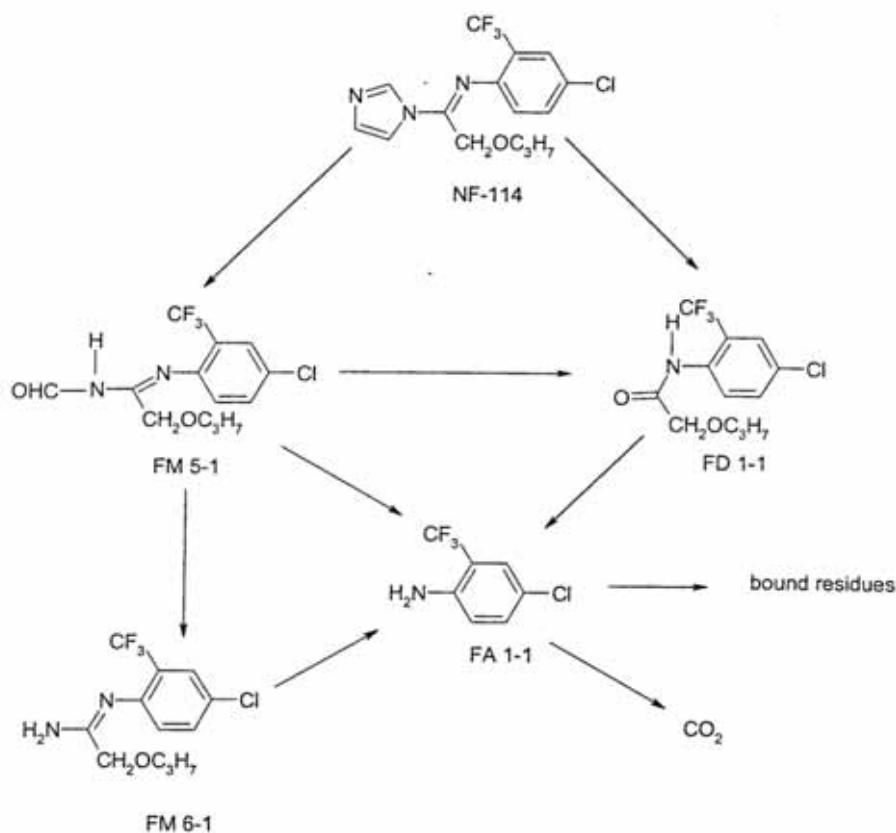


Figure 4 Proposed metabolic pathway of triflumizole in soil

Residues in rotational crops*Confined rotational crop studies*

The metabolic profile of triflumizole in rotational lettuce, radish (roots and tops), and wheat (forage, hay, straw, and grain) was investigated (Yu *et al.*, 2001). The study consisted of two untreated control plots, six plots treated at 1× GAP, and two plots treated at 10× GAP with [¹⁴C] triflumizole. The rotational crops were planted into the 1× treated plots at plant-back intervals (PBIs) of 30, 120, and 365 days after treatment. The 10× plots had a single PBI of 30 days.

For each PBI, samples were harvested and homogenized in the presence of dry ice. In the case of radish samples, the roots were washed to remove soil particles prior to homogenization. Homogenized samples were extracted with methanol:water and assayed by LSC to determine extractable residues. Post-extraction solids were dried for several days and then assayed by combustion/LSC to determine non-extractable radioactivity. Metabolite characterization and identification was done using the 10× matrices (30-day PBI) except for wheat forage, for which the 1× 30-day PBI samples were used. Metabolite characterization and identification was accomplished via HPLC (multiple systems) with known standards. Structural information for unknown metabolites was evaluated using mass spectrometry techniques including ESI/LC/MS, ESI/MS/CID/MS (CID chemical ionization positive ion/negative ion modes), and TOF/LC/MS. Enzymatic hydrolysis with β-glucosidase was used to elucidate structures where MS analysis indicated the presence of glucoside conjugates (lettuce and wheat hay samples). Finally, PES samples were subjected to fractionation and derivatization procedures to determine the distribution of non-extractable residues in natural components such as starch, cellulose, and lignin.

Table 35 Total radiocarbon residues in rotational crop matrices

Crop	Total Radiocarbon Residues as Triflumizole-Equivalents (mg eq/kg)		
	30 DAT	120 DAT	365 DAT
Lettuce	0.0824	0.0861	0.0206
Radish Root	0.2336	0.1882	0.0320
Radish Top	0.1944	0.1449	0.0960
Wheat Forage	0.4420	0.3729	0.1263
Wheat Hay	0.9958	0.5834	0.3208
Wheat Straw	1.6495	0.6095	0.4784
Wheat Grain	0.1051	0.0554	0.0672

Forty-nine metabolites were identified, five of which were > 10% TRR and > 0.01 mg eq/kg in at least one matrix (Table). Five of the remaining forty-four metabolites were identified as having a hydroxide (or O-conjugate) appended at the Number 6 position of the aniline ring.

Table 36 Major metabolites identified in the confined rotational crop study at a 30-day plant-back interval. See Figure 5 for chemical structures.

Metabolite Identification	Molecular Weight	Crop Commodity	% TRR	Triflumizole Equivalents (mg eq/kg)
XIV (2Z)-4-hydroxyhex-2-enedioic acid	160	Radish Tops	12.54	0.2464
		Wheat Grain	61.35	0.3999
		Wheat Hay	14.87	0.8757
		Wheat Straw	11.06	1.1877
FD-9-1 [4-chloro-2-(trifluoromethyl) phenyl]urea	238	Lettuce	34.87	0.425
		Radish Tops	30.62	0.6016
		Wheat Straw	11.7	1.2564
XXVI 1-[4-chloro-2-hydroxy-6-	270	Radish Roots	11.36	0.1087

Across the two site locations, residues of triflumizole in treated cucumbers ranged from 0.12 to 0.20 mg eq/kg. Residues in rotational crops are summarized in Table ; residues in samples from untreated plots were < 0.01 mg eq/kg for all matrices.

Table 37 Triflumizole-equivalent residues in rotational lettuce, turnip, and wheat

Crop Matrix	California			Texas		
	PBI (days)	Sample 1	Sample 2	PBI (days)	Sample 1	Sample 2
Lettuce	30	< 0.01	< 0.01	30	< 0.01	< 0.01
	59	< 0.01	< 0.01	60	< 0.01	< 0.01
	94	0.013	0.012	91	< 0.01	< 0.01
	120	< 0.01	< 0.01	177	< 0.01	< 0.01
Turnip Tops	30	0.02	0.02	30	< 0.01	< 0.01
	59	< 0.01	< 0.01	60	< 0.01	< 0.01
	94	< 0.01	< 0.01	91	< 0.01	< 0.01
	120	< 0.01	< 0.01	177	< 0.01	< 0.01
Turnip Roots	30	< 0.01	< 0.01	30	< 0.01	< 0.01
	59	< 0.01	< 0.01	60	< 0.01	< 0.01
	94	< 0.01	0.01	91	< 0.01	< 0.01
	120	< 0.01	< 0.01	177	< 0.01	< 0.01
Wheat Forage	30	0.02	0.03	30	0.01	0.01
	59	0.05	0.06	60	0.01	< 0.01
	103	0.03	0.03	91	< 0.01	< 0.01
	120	0.04	0.04	177	< 0.01	< 0.01
Wheat Hay	30	0.02	0.02	30	< 0.01	< 0.01
	59	0.02	0.02	60	< 0.01	< 0.01
	103	0.01	0.01	91	< 0.01	< 0.01
	120	0.03	0.03	177	< 0.01	< 0.01
Wheat Grain	30	< 0.01	< 0.01	30	< 0.01	< 0.01
	59	< 0.01	< 0.01	60	< 0.01	< 0.01
	103	< 0.01	< 0.01	91	< 0.01	< 0.01
	120	< 0.01	< 0.01	177	< 0.01	< 0.01
Wheat Straw	30	0.02	0.02	30	< 0.01	0.011
	59	0.02	0.02	60	< 0.01	0.011
	103	0.02	0.02	91	< 0.01	0.011
	120	0.02	0.04	177	< 0.01	< 0.01

In the second study (Puhl, 2005), triflumizole (as Procure[®] 50 WS) was applied to squash at approximately 30 days prior to harvest followed by four subsequent applications at 7 ± 1 day intervals. Trials were in Yuma, Arizona and Uvalde, Texas. Applications were each 0.28 kg ai/ha for a total rate of 1.4 kg ai/ha. At approximately 30, 60, 90, 180, and 270 days after the last application, cabbage, cotton, onion, tomato, and wheat were planted into treated and untreated plots. Samples were analysed by a common-moiety method that converts triflumizole and its aniline-containing metabolites to FA-1-1, as described in the residue methods section below. Results are expressed as triflumizole-equivalents. The limit of quantitation (LOQ) was 0.01 mg eq/kg. Average procedural recoveries of triflumizole and FA-1-1 ranged from 79 to 95%, with a maximum standard deviation of 13%.

In the rotational crops, quantifiable residues were found only in wheat forage, wheat straw, wheat hay, and onion; residues in wheat grain, cabbage, tomato, and cottonseed were < 0.01 mg eq/kg in all samples (Table).

Table 38 Triflumizole-equivalent residues in rotational cabbage, cotton, onion, tomato, and wheat

Crop Matrix	PBI (days)	Arizona		Texas	
		Sample 1	Sample 2	Sample 1	Sample 2
Cabbage	30	< 0.01	< 0.01	< 0.01	< 0.01
	60	< 0.01	< 0.01	< 0.01	< 0.01
	90	< 0.01	< 0.01	< 0.01	< 0.01
	180	< 0.01	< 0.01	< 0.01	< 0.01
	270	< 0.01	< 0.01	< 0.01	< 0.01
Cottonseed	30	< 0.01	< 0.01	< 0.01	< 0.01
	60	< 0.01	< 0.01	< 0.01	< 0.01
	90	< 0.01	< 0.01	< 0.01	< 0.01
	180	< 0.01	< 0.01	< 0.01	< 0.01
	270	< 0.01	< 0.01	< 0.01	< 0.01
Onion	30	0.01	0.01	< 0.01	< 0.01
	60	< 0.01	< 0.01	< 0.01	< 0.01
	90	< 0.01	< 0.01	< 0.01	< 0.01
	180	< 0.01	< 0.01	< 0.01	< 0.01
	270	< 0.01	< 0.01	< 0.01	< 0.01
Tomato	30	< 0.01	< 0.01	< 0.01	< 0.01
	60	< 0.01	< 0.01	< 0.01	< 0.01
	90	< 0.01	< 0.01	< 0.01	< 0.01
	180	< 0.01	< 0.01	< 0.01	< 0.01
	270	< 0.01	< 0.01	< 0.01	< 0.01
Wheat Forage	30	0.02	< 0.01	< 0.01	0.013
	60	0.14	0.20	0.01	< 0.01
	90	0.19	0.12	0.01	0.011
	180	< 0.01	< 0.01	< 0.01	< 0.01
	270	0.077	0.089	< 0.01	< 0.01
Wheat Grain	30	< 0.01	< 0.01	< 0.01	< 0.01
	60	< 0.01	< 0.01	< 0.01	< 0.01
	90	< 0.01	< 0.01	< 0.01	< 0.01
	180	< 0.01	< 0.01	< 0.01	< 0.01
	270	< 0.01	< 0.01	< 0.01	< 0.01
Wheat Hay	30	0.14	0.08	0.02	0.01
	60	0.11	0.07	0.02	0.01
	90	0.09	0.07	0.02	0.02
	180	< 0.01	< 0.01	< 0.01	< 0.01
	270	0.04	0.04	< 0.01	< 0.01
Wheat Straw	30	0.05	0.09	< 0.01	< 0.01
	60	0.08	0.09	< 0.01	< 0.01
	90	0.14	0.09	< 0.01	0.134
	180	< 0.01	0.01	< 0.01	< 0.01
	270	0.06	0.05	< 0.01	< 0.01

RESIDUE ANALYSIS

Analytical methods

The Meeting received analytical methods and validation data for analysis of triflumizole in plant and animal commodities. These methods fall into two classes. The first are common-moiety methods which analysed for residues of triflumizole and its aniline-containing metabolites, FM-6-1, FM-5-1, FD-1-1, FD-2-1, FM-8-1, and FA-1-1 by converting each of the metabolites to FA-1-1. The second

class are residue specific methods which were developed to analyse, separately, triflumizole and FM-6-1 in crops or FA-1-5 (free and sulphate-conjugated) in animal matrices. For both classes, alterations have been made as necessary to resolve analytical issues and to permit use of different separation/detection strategies. Limits of quantitation and detection are reported as being 0.01 to 0.02 mg eq/kg, with no consistent distinction between the two. Descriptions are provided below.

Common-moiety methods

The analytical method described by Ball (1986a) is the basis for the common moiety methods for crop commodities. In this method, extraction of residues begins by macerating the sample in distilled water for 5 minutes. Concentrated glacial acetic acid and sodium acetate are added to the homogenate and the mixture is then refluxed at boiling for 90 minutes. A sodium hydroxide solution (20%) is added to the flask, which is then fitted with a distillation head and heated until a volume of 100 mL is distilled into hexane. The distillate is shaken against 0.1 N HCl. The organic phase is collected, concentrated, and an aliquot taken for analysis. Separation/quantification strategies that have been used with this extraction method include GC-MSD, GC-FTD, GC-NPD, HPLC-UV (254 nm), and HPLC-Amperometric detector. Residues are analysed as FA-1-1 and expressed in terms of triflumizole.

A common-moiety method was also developed for animal commodities (Perkins and Polakoff, 1986). This method uses 20% NaOH and a Bleidner extractor to digest/distil/extract residues into hexane. The hexane is passed over anhydrous sodium sulphate and concentrated prior to analysis. As with the common-moiety method for crops, the terminal residue is the FA-1-1 metabolite. Parameters are described for GC-NPD analysis.

Residue-specific methods

A method for the analysis of triflumizole and FM-6-1 is described by Gomyo *et al.* (1990). In this method, residues are extracted from crop matrices with methanol by shaking for 30 min. The extract is then filtered and partitioned against dichloromethane. Residues in the organic phase are cleaned up by column chromatography, concentrated to dryness, and then reconstituted in dichloromethane for HPLC determination or acetone for GC determination.

Corley (2012) describes a method for the analysis of triflumizole and FM-6-1 in hops by HPLC-MS/MS. In that study, residues were extracted with acetonitrile, the extract cleaned up by polymeric and NH₂ solid-phase extraction, and the extract analysed by HPLC-MS/MS. Transitions for triflumizole were m/z 346.1 $\Rightarrow$ 73 (quant.) and 346.1 $\Rightarrow$ 278 (conf.). Transitions for FM-6-1 were m/z 295.1 $\Rightarrow$ 215 (quant.) and 295.1 $\Rightarrow$ 73 (conf.).

Analysis of FA-1-5 (free and sulphate-conjugate) in animal matrices is described in Perkins and Polakoff (1986). In this method, residues are extracted from milk and liver with 0.2 N HCl (boiling, 1 hr). Following extraction, the residues are cleaned up by solid-phase extraction (C-18) and analysed by HPLC with amperometric detection.

Table 39 Summary of method validation recovery results for triflumizole and metabolites in crop and livestock matrices

Matrix	Method Type	Separation/Quantification	Residue	Fortification (mg./kg)	Recovery (%)	Reference
Apple	Common	HPLC-UV	Triflumizole	0.05	75.4, 75.6	Ball, 1986a
				0.1	85, 74.4, 81.5	
				1	75.8, 78.3	
			FM-5-1	0.1	76	
			FM-6-1	0.1	97	
			FM-8-1	0.1	103	
			FD-1-1	0.1	94	
			FD-2-1	0.1	91	
			FA-1-1	0.1	79	
Apple	Common	HPLC-UV	Triflumizole	0.05	86, 83, 80, 72, 71	Gomyo, Morishima, Ono, 1990

Matrix	Method Type	Separation/Quantification	Residue	Fortification (mg./kg)	Recovery (%)	Reference
				0.2	77, 70, 69	
	Common	GC-FTD	Triflumizole	0.05	91, 81	
				0.2	94, 84, 80	
			FM-5-1	0.2	81	
			FM-6-1	0.2	78	
			FM-8-1	0.2	91	
			FD-1-1	0.2	84	
			FD-2-1	0.2	87	
			FA-1-1	0.2	77	
			FD-7-1	0.2	91	
			FM-2-1	0.2	73	
	Specific	HPLC-UV	Triflumizole	0.05	93, 90	
				0.2	92, 90	
			FM-6-1	0.05	90, 86	
				0.2	86, 85	
	Specific	GC-FTD	Triflumizole	0.2	95, 85	
			FM-6-1	0.2	92, 86	
Cucumber	Specific	GC-FTD	Triflumizole	0.2	90, 84	
			FM-6-1	0.2	90, 88	
Cucumber	Common	HPLC-UV	Triflumizole	0.05	91, 91, 86, 81, 80	
				0.2	97, 97	
			FM-5-1	0.05	74	
			FM-6-1	0.05	76	
			FM-8-1	0.05	85	
			FD-1-1	0.05	79	
			FD-2-1	0.05	85	
			FA-1-1	0.05	75	
	Specific	HPLC-UV	Triflumizole	0.05	80, 78	
				0.2	83, 80	
			FM-6-1	0.05	78, 78	
				0.2	95, 85	
Grape	Common	HPLC-UV	Triflumizole	0.05	100, 70	Ball, 1986a
				0.1	74, 74, 108, 69.8	
				0.5	87.4, 77.4	
			FM-5-1	0.05	82, 82	
				0.1	71, 61	
			FM-6-1	0.05	64, 94	
				0.1	82, 91	
			FM-8-1	0.05	104, 142	
				0.1	92, 98	
			FD-1-1	0.05	70, 94	
				0.1	57, 65	
			FD-2-1	0.05	86, 144	
				0.1	87, 78	
			FA-1-1	0.05	94, 126	
				0.1	86, 79	
Grape	Specific	HPLC-UV	Triflumizole	0.2	91, 81	Gomyo, Morishima, Ono, 1990
			FM-6-1	0.5	87, 87	
		GC-FTD	Triflumizole	0.2	87	
			FM-6-1	0.5	80	
	Specific	HPLC-UV	Triflumizole	0.2	91, 87	
			FM-6-1	0.2	87, 80	
		GC-FTD	Triflumizole	0.2	82, 75	
			FM-6-1	0.2	90, 87	
Green Pepper	Specific	HPLC-UV	Triflumizole	0.2	84, 73	
			FM-6-1	0.2	84, 81	
Hops	Specific	LC-MS/MS	Triflumizole	0.05	98, 98, 97	Corley, 2012
				1	99, 94, 91	

Matrix	Method Type	Separation/Quantification	Residue	Fortification (mg./kg)	Recovery (%)	Reference
				50	102, 103, 101	
			FM-6-1	0.05	97, 105, 98	
				1	106, 97, 94	
				50	102, 97, 99	
Lettuce	Common	GC-MSD	Triflumizole	0.01	75, 78, 82, 72, 75, 80	Gaydosh, 2000a
				0.5	71, 70, 75, 70, 71, 70	
			FM-5-1	0.01	92, 89, 91	
				0.5	73, 73, 76	
			FM-6-1	0.01	84, 80, 87	
				0.5	87, 82, 88	
			FM-8-1	0.01	94, 93, 97	
				0.5	77, 82, 83	
			FD-1-1	0.01	99, 98, 105	
				0.5	84, 83, 85	
			FD-2-1	0.01	84, 80, 85	
				0.5	86, 86, 94	
			FA-1-1	0.01	92, 86, 91, 82, 89, 88	
				0.5	78, 77, 79, 78, 79, 75	
			FD-9-1	0.01	73, 77, 73	
				0.5	74, 74, 71	
Pear	Common	HPLC-UV	Triflumizole	0.1	60	Ball, 1986a
			FM-5-1	0.1	58	
			FM-6-1	0.1	65	
			FM-8-1	0.1	117	
			FD-1-1	0.1	72	
			FD-2-1	0.1	91	
			FA-1-1	0.1	86	
Pear	Common	HPLC-UV	Triflumizole	0.2	81, 73	Gomyo, Morishima, Ono, 1990
			FM-6-1		80, 76	
	Common	GC-FTD	Triflumizole	0.05	90, 87	
				0.2	89, 86	
			FM-6-1	0.2	82	
			FM-8-1	0.2	89	
Peas	Specific	HPLC-UV	Triflumizole	0.2	87,84	
			FM-6-1	0.2	101,98	
Strawberry	Common	HPLC-UV	Triflumizole	0.2	86, 83	
	Specific	HPLC-UV	Triflumizole	0.2	91,87	
			FM-6-1	0.2	81,77	
		GC-FTD	Triflumizole	0.2	79, 77	
			FM-6-1	0.2	74, 72	
Tomato	Common	HPLC-UV	Triflumizole	0.1	83, 80	
	Specific	HPLC-UV	Triflumizole	0.2	81,81	
			FM-6-1		88, 87	
Turnip Root	Common	GC-MSD	Triflumizole	0.01	73, 73, 76, 84, 85, 90	Gaydosh, 2000a
				0.5	74, 70, 82, 78, 74, 78	
			FM-5-1	0.01	86, 90, 95	
				0.5	85, 81, 82	
			FM-6-1	0.01	89, 79, 80	
				0.5	83, 81, 82	
			FM-8-1	0.01	83, 80, 91	
				0.5	78, 78, 80	
			FD-1-1	0.01	91, 88, 92	
				0.5	90, 86, 83	
			FD-2-1	0.01	102, 95, 99	
				0.5	90, 80, 84	
			FA-1-1	0.01	86, 79, 91, 95, 87, 97	
				0.5	79, 77, 78, 78, 78, 85	

Matrix	Method Type	Separation/Quantification	Residue	Fortification (mg./kg)	Recovery (%)	Reference
			FD-9-1	0.01	79, 80, 79	
				0.5	75, 74, 74	
Watermelon	Common	HPLC-UV	Triflumizole	0.2	75, 75	Gomyo, Morishima, Ono, 1990
Wheat Forage	Common	GC-MSD	Triflumizole	0.01	100, 96, 98, 78, 63, 78	Gaydosh, 2000a
				0.5	81, 84, 82, 84, 77, 75	
			FM-5-1	0.01	90, 83, 90	
				0.5	73, 71, 72	
			FM-6-1	0.01	78, 85, 88	
				0.5	78, 75, 75	
			FM-8-1	0.01	82, 81, 87	
				0.5	73, 72, 76	
			FD-1-1	0.01	81, 88, 67	
				0.5	77, 77, 79	
			FD-2-1	0.01	77, 76, 93	
				0.5	80, 80, 83	
			FA-1-1	0.01	76, 65, 63, 81, 77, 75	
				0.5	72, 72, 71, 73, 76, 77	
			FD-9-1	0.01	74, 79, 86	
				0.5	74, 67, 70	
Wheat Grain	Common	GC-MSD	Triflumizole	0.01	91, 89, 82, 91, 79	
				0.5	80, 76, 74, 70, 81	
			FM-5-1	0.01	89, 85, 94	
				0.5	71, 74, 80	
			FM-6-1	0.01	84, 81, 91	
				0.5	75, 78, 76	
			FM-8-1	0.01	87, 94, 94	
				0.5	75, 75, 76	
			FD-1-1	0.01	90, 96, 91	
				0.5	76, 74, 78	
			FD-2-1	0.01	104, 80, 106	
				0.5	87, 88, 90	
			FA-1-1	0.01	78, 78, 75, 79, 76, 70	
				0.5	78, 79, 80, 76, 79, 74	
			FD-9-1	0.01	69, 64, 85	
				0.5	68, 72, 70	
Wheat Straw	Common	GC-MSD	Triflumizole	0.01	80, 72, 71, 78, 80, 69	
				0.5	74, 76, 74, 68, 75, 69	
			FM-5-1	0.01	94, 87, 88	
				0.5	78, 77, 78	
			FM-6-1	0.01	80, 68, 72	
				0.5	73, 73, 74	
			FM-8-1	0.01	83, 88, 80	
				0.5	78, 78, 78	
			FD-1-1	0.01	87, 81, 82	
				0.5	80, 77	
			FD-2-1	0.01	82, 77, 77	
				0.5	80, 81, 81	
			FA-1-1	0.01	72, 68, 59, 71, 60, 62, 65, 62, 61	
				0.5	68, 74, 71, 75, 72, 75, 64, 68, 71	
			FD-9-1	0.01	74, 68, 81	
				0.5	69, 70, 67	
Egg	Common	HPLC-Amperometric	Triflumizole	100	84 (avg.)	Parkins & Polakoff, 1986
			FM-6-1	100	84 (avg.)	
			FD-1-1	100	33 (avg.)	

Matrix	Method Type	Separation/Quantification	Residue	Fortification (mg./kg)	Recovery (%)	Reference
			FA-1-1	25	86 (avg.)	
				50	82 (avg.)	
Fat	Common	HPLC-Amperometric	FA-1-1	25	76 (avg.)	
				50	80 (avg.)	
				20		
				25	104 (avg.)	
				50	90 (avg.)	
Kidney	Common	HPLC-Amperometric	FA-1-1	25	87 (avg.)	
				50	83 (avg.)	
				20	85 (avg.)	
				25	88 (avg.)	
				50	82 (avg.)	
Liver	Common	HPLC-Amperometric	FA-1-1	25	80 (avg.)	
				50	90 (avg.)	
				100	86 (avg.)	
			Triflumizole	100	90 (avg.)	
			FM-8-1	100	88 (avg.)	
			FM-8-1-S	100	90 (avg.)	
			FA-1-1	20	82 (avg.)	
				80	85 (avg.)	
				50	92 (avg.)	
				100	75 (avg.)	
			FA-1-5	18	69 (avg.)	
	Specific	HPLC-Amperometric	FA-1-5-S	0.01	89.1, 76.6, 74.7, 66.2, 85.3, 74.4, 82.5, 116.3, 77.3, 68.1, 75.1, 105.4	Batorewicz & Bakker, 1990
				0.1	108.6, 122.9, 104.7, 103.5, 87.9, 98.1, 95.0, 58.7, 100.2, 69.0, 81.8, 96.3	
				0.05	70.2, 63.3, 52.2	Noon, 1993
				0.2	71.6, 64.7, 40.0	
Milk	Common	GC-NPD	Triflumizole	0.2 (2 hr reflux)	61, 88	Eckert, 1989
				0.2 (4 hr reflux)	50, 80	
				0.2 (6 hr reflux)	40, 80	
	Common	HPLC-Amperometric	FA-1-1	10	89 (avg.)	Parkins & Polakoff, 1986
				20	84 (avg.)	
			FA-1-5	50	109 (avg.)	
			FA-1-1	20	88 (avg.)	
				50	92 (avg.)	
			FA-1-5	49	80 (avg.)	
			Triflumizole	100	92 (avg.)	
			FD-2-1	100	87 (avg.)	
			FM-8-1	100	78 (avg.)	
	Specific	HPLC-Amperometric	FA-1-5-S	0.01	59.1, 110.0, 64.7, 68.8, 68.5, 76.0, 63.7, 77.9, 90.2, 68.7, 77.9, 71.7	Batorewicz & Bakker, 1990
				0.1	127.2, 101.2, 111.6, 109.9, 87.0, 98.6, 109.6, 99.6, 91.6, 67.2, 96.8, 95.1	
				0.025	75.4, 81.9, 79.6	Noon, 1993
				0.1	78.3, 80.2, 81.4	
Muscle	Common	GC-NPD	Triflumizole	0.2 (2 hr reflux)	86, 79	Eckert, 1989

Matrix	Method Type	Separation/Quantification	Residue	Fortification (mg./kg)	Recovery (%)	Reference
				0.2 (4 hr reflux)	99	
				0.2 (6 hr reflux)	102	
				0.2 (4 hr reflux)	104, 87, 87, 70, 94, 80	
	Common	HPLC-Amperometric	FA-1-1	25	100 (avg.)	Parkins & Polakoff, 1986
				50	72 (avg.)	
				20	94 (avg.)	
				25	96 (avg.)	
				50	94 (avg.)	

Stability of pesticide residues in stored analytical samples

The Meeting received data on the stability of residues of triflumizole and its metabolites in crops (apples, grapes, strawberries, cucumbers, cherries, muskmelons, squash, lettuce, and wheat forage) and livestock. In many cases, the storage stability data were submitted as an integral part of the field trial study rather than as a separate storage stability study volume. The storage stability data are summarized in Table . Compounds, as listed in Table 40 were added to control samples and placed into frozen storage for the time indicated. For all matrices except cherries and strawberries, the fortification was to homogenized sample matrix. The state of the cherry and strawberry storage stability matrices was not described in the study report. Samples were stored frozen (-20 °C).

Table 40 Summary of storage stability data for triflumizole and metabolites in crop and livestock matrices

Matrix	Method	Compound	Storage Time	Amount Fortified (mg eq/kg)	Concurrent Recovery (%)	Residue Remaining (%)	Reference
Apple	Common—HPLC	Triflumizole	0 Day	2	n.s.	81.5	Ball, 1988
			38 Months		n.s.	59	
		FM-6-1	0 Day		n.s.	76.5	
			38 Months		n.s.	52	
	Specific—GC	Triflumizole	0 Day	0.5	82	85	Ball, 1989
			1 Month		78	78.5	
			2 Months		86	79.5	
			3 Months		91	78	
			6 Months		98	77	
			12 Months		91	60	
		FM-6-1	0 Day		81	82	
			1 Month		—	—	
			2 Months		94	82	
			3 Months		94	81.5	
			6 Months		108	99.5	
			12 Months		112	71	
		FD-2-1	0 Day		77	86	
			1 Month		—	—	
			2 Months		84	85.5	
			3 Months		95	84.5	
			6 Months		82	87	
			12 Months		112	73	
		FA-1-1	0 Day		77	80.5	
			1 Month		—	—	
			2 Months		86	77.5	
			3 Months		89	82.5	
			6 Months		74	64.5	
			12 Months		106	60.5	
Cherries	Common—GC	Triflumizole	0 Day	0.2	75.5	75.5	Gaydosh, 1997
			30 Days		69.5	75.7	

Matrix	Method	Compound	Storage Time	Amount Fortified (mg eq/kg)	Concurrent Recovery (%)	Residue Remaining (%)	Reference
			60 Days		73	62	
			120 Days		84.5	85.7	
			354 Days		86	88	
Cucumber	Common—GC	Triflumizole	832 Days	0.2	74	51	Homa, 2012
		FM-6-1			94	72	
		FA-1-1			79	30.7 ^a	
		Triflumizole	0 Day	0.5	84.9	85.4	Maselli, 1999
			1 Month		106.7	89.8	
			3 Months		107.3	96.4	
			6 Months		74	72.9	
			8 Months ^b		61.6	61	
	Common—HPLC	Triflumizole	0 Day	2	n.s.	76	Ball, 1988
			38 Months		n.s.	52	
		FM-6-1	0 Day		n.s.	70.5	
			38 Months		n.s.	48	
Grape	Specific—GC	Triflumizole	0 Day	2	75	80.5	Ball, 1989
			1 Month		77	78	
			2 Months		88	88	
			3 Months		93	86	
			6 Months		86	78	
			12 Months		78	76.5	
		FM-6-1	0 Day	2	70	71	
			1 Month		—	—	
			2 Months		83	79	
			3 Months		82	81	
			6 Months		108	86.5	
			12 Months		78	70	
		FD-2-1	0 Day	2	85	81	
			1 Month		—	—	
			2 Months		88	86	
			3 Months		92	80	
			6 Months		90	79	
			12 Months		91	81	
		FA-1-1	0 Days	2	78	86	
			1 Month		—	—	
			2 Months		86	88	
			3 Months		90	84	
			6 Months		82	70.5	
			12 Months		80	83	
Lettuce	Common—GC	FD-1-1	0 Month	5	79	79	Marin, 2011
			2 Months		111	90	
			4 Months		70	68	
		FM-6-1	0 Month		83	83	
			2 Months		98	93	
			4 Months		84	63	
Cabbage	Common—GC	Triflumizole	0 Day	5	—	—	Barney, 2007d
			238 Days		90	40	
		FM-6-1	0	5	—	—	
			238		92	26	
		FA-1-1	0	5	—	—	
			240		92	58	
Mustard Greens	Common—GC	Triflumizole	0 Day	5	—	—	Barney, 2006
			287 Days		77	54	
		FM-6-1	0 Day	5	—	—	
			287 Days		85	46	
		FA-1-1	0 Day	5	—	—	
			288 Days		83	37	
Swiss Chard	Common—GC	Triflumizole	0 Day	5	—	—	Barney, 2007g

Matrix	Method	Compound	Storage Time	Amount Fortified (mg eq/kg)	Concurrent Recovery (%)	Residue Remaining (%)	Reference
			218 Days		73	71	
		FM-6-1	0 Day	5	—	—	
			225 Days		71	54	
Muskmelon	Common—GC	Triflumizole	0 Day	0.5	82.9	80.6	Gaydosh, Maselli, Puhl, 1999
			29 Days		117.2	115.1	
			97 Days		75.5	82.1	
			181 Days		53.2	67.2	
			299 Days		53.7	56.2	
Tomato	Common—GC	Triflumizole	0 Days	0.5–10	—	—	Barney, 2012
			552 Days		85	68	
		FM-6-1	0 Days	0.5–10	—	—	
			552 Days		85	80	
		FA-1-1	0 Days	0.5–10	—	—	
			552 Days		91	75	
Summer Squash	Common—GC	Triflumizole	0 Day	0.5	91.8	112.1	Gaydosh, 1999
			32 Days		98.3	100.1	
			89 Days		93.9	100.1	
			179 Days		49.7	61.1	
			280 Days		45.5	50.9	
Strawberry	Common—GC	Triflumizole	0 Day	0.5	78	86	Gaydosh, 2001
			42 Days		92.5	83	
			184 Days		78.5	70	
			310 Days		85	63	
	Common—HPLC	Triflumizole	0 Day	2	n.s.	75	Ball, 1988
			38 Months		n.s.	56	
		FM-6-1	0 Day		n.s.	71.5	
			38 Months		n.s.	53	
Papaya	Common—GC	Triflumizole	0 Day	5	—	—	Barney, 2007f
			18 Months		78	74	
Hazelnut	Common—GC	Triflumizole	0 Day	0.5	—	—	
			97 Days		68	70	Thompson, 2002
		FA-1-1	0	0.5	—	—	
			97 Days		67	66	
Wheat Forage	Common—GC	FD-1-1	0 Month	5	93	93	Marin, 2011
			2 Months		117	80	
			4 Months		82	78	
		FM-6-1	0 Month		94	94	
			2 Months		93	92	
			4 Months		60	59	
Fat	Common—GC	FA-1-1	0 Days	0.1	88	88	Eckert, 1990
			14 Days		73	96	
			30 Days		96	98	
			90 Days		87	82	
			6 Months		86	88	
		Triflumizole	0 Days	0.1	80	80	
			14 Days		80	86	
			30 Days		88	101	
			90 Days		85	94	
			6 Months		90		
Kidney	Common—GC	FA-1-1	0 Days	0.1	81	81	
			14 Days		82	82	
			30 Days		87	103	
			90 Days		89	78	
			6 Months		88		

Matrix	Method	Compound	Storage Time	Amount Fortified (mg eq/kg)	Concurrent Recovery (%)	Residue Remaining (%)	Reference
		Triflumizole	0 Days	0.1	97	97	
			14 Days		94	104	
			30 Days		84	88	
			90 Days		94	76	
			6 Months		90	92	
Liver	Common—GC	FA-1-1	0 Days	0.1	97	97	
			14 Days		85	80	
			30 Days		86	78	
			90 Days		92	62	
			6 Months		92	90	
		Triflumizole	0 Days	0.1	102	102	
			14 Days		88	73	
			30 Days		86	74	
			90 Days		110	65	
			6 Months		88	97	
	Specific—HPLC	FA-1-5-S ^b	0 Day	0.1	68.6	86.6	Batorewicz, 1990, 1991
			102 Days		n.s.	89.2	
			15 Months		n.s.	113	
Milk	Common—GC	FA-1-1	0 Days	0.1	84	84	Eckert, 1990
			14 Days		99	101	
			30 Days		92	88	
			90 Days		85		
			6 Months		84	87	
		Triflumizole	0 Days	0.1	80	80	
			14 Days		83	84	
			30 Days		85	88	
			90 Days		84	89	
			6 Months		96	88	
	Specific—HPLC	FA-1-5-S ^b	0 Day	0.1	73.7	73.7	Batorewicz, 1990, 1991
			87 Days		n.s.	100	
			15 Months		n.s.	96.1	
Muscle	Common—GC	FA-1-1	0 Days	0.1	94	94	Eckert, 1990
			14 Days		102	102	
			30 Days		97	107	
			90 Days		98	88	
			6 Months		77	83	
		Triflumizole	0 Days	0.1	100	100	
			14 Days		89	97	
			30 Days		90	94	
			90 Days		96	80	
			6 Months		86	83	

n.s.=Not Specified.

^a FA-1-1 was subject to evaporative loss in the hen metabolism study. That phenomenon may account for the low recovery from cucumber considering the long storage time involved.

^b The 0 Day samples were quantitated using external standards. FA-1-5-S was shown to be not stable in the acid used to digest the samples, leading to inaccurate quantitation. Recovery at other time points in this study were quantitated based on procedural standards only (i.e., no correction for 0-day recovery).

USE PATTERN

Labels for triflumizole were provided for registrations in the USA and the Netherlands. Triflumizole is a broad-spectrum foliar fungicide that controls a variety of fungal diseases in fruits and vegetables. It acts as a protectant and as an eradicant by preventing disease symptoms after infection has occurred. Triflumizole's anti-sporulant activity reduces spores after lesions become visible. Triflumizole belongs to the demethylation inhibitor (DMI) group of fungicides classified as Group 3

by the Fungicide Resistance Action Committee (FRAC). Triflumizole displays protective and curative action, and acts as an inhibitor of chitin biosynthesis. The product is mixed with water and applied as a foliar spray using ground equipment equipped for conventional spraying on crops as listed in Table .

Table 41 Use pattern summary for triflumizole

Crop	Country	Application							Max/ season kg ai/ ha	PHI days	Remarks
		use	form ^a	no. ^b	max. kg ai/ hL	min water L/ha	kg ai/ ha	RTI days			
Apple Pear	USA	F	480SC	(4–8)	0.6	94	0.28–0.56	7–14	2.24	14	–
			50WS		n.s.	n.s.					
Brassica: Head/Stem & Leafy Greens Leafy Greens	USA	F	480SC	(2–3)	0.3 (ground) 1.5 (aerial)	94 (ground) 19 (aerial)	0.21–0.28	14	0.63	1	–
										0	
Cherry	USA	F	480SC	(6–12)	n.s. (ground) 0.6 (aerial)	n.s. (ground) 94 (aerial)	0.28–0.56	7–14	3.36	1	Apply early popcorn, full bloom, and petal fall
			50WS	(6–9)	n.s.	n.s.	0.35–0.56				
Cucurbits	USA	G	SC	(5–10)	0.03	935	0.14–0.28	7–14	1.4	0	–
		F, G	480SC 50WS		n.s.	n.s.					
Tomato	USA	G	SC	(5–10)	0.03	935	0.14–0.28	7–14	1.4	0	–
Grape Strawberry	USA	F	480SC	(4–8)	0.06	468	0.14–0.28	7–14	1.12	7	Apply pre- bloom
			50WS		(50WS, grape; others: n.s.)	(50WS, grape; others: n.s.)				1	
Hazelnut	USA	F	480SC	(4–6)	0.02	935	0.14–0.21	10– 14	0.84	18	Apply at bud-break
			50WS	(5–8)	(ground) 0.15 (aerial)	(ground) 140 (aerial)			1.12		
Hops	USA	F	480SC	(3)	0.09 (ground) 0.45 (aerial)	468 (ground) 94 (aerial)	0.42	14	1.4	7	Do not graze livestock in treated areas or harvest for silage or hay
Papaya (and other tropicals)	USA	F	480SC	(2–3)	0.05 (ground) 1.87 (aerial)	701 (ground) 19 (aerial)	0.28–0.35	14	0.84	0	–
Cucumber Courgette (Summer Squash)	Nether- lands	G	EC	1–6	0.015	500	0.075– 0.225	7	1.35	1	Treat during harvesting period or 4 wks after planting
Tomato	Nether- lands	G	EC	1–5	0.015	500	0.075– 0.225	7	1.125	1	Treat during harvesting period or 4 wks after planting

^a SC=Terraguard® SC, 480 SC=Procure® 480 SC, 50WS=Procure® 50WS, EC=rocket®

^b Numbers in parentheses are implied based on the maximum seasonal rate divided by the per-application rate.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on triflumizole supervised field trials for the following crops.

Crop Group	Commodity	Table
Pome fruits	Apple	Table 42
	Pear	Table 43
Stone fruits	Cherry	Table 44
Berries and other small fruits	Grape	Table 45
	Strawberry	Table 46
Assorted tropical and sub-tropical fruits - inedible peel	Papaya	Table 47
Brassica (cole or cabbage) vegetables, Head cabbages,	Broccoli	Table 48
Flowerhead brassicas	Cabbage	Table 49
Fruiting vegetables, Cucurbits	Cucumber	Table 50
	Muskmelon	Table 51
	Squash	Table 52
Fruiting Vegetables, other than Cucurbits	Tomato	Table 53
Leafy Vegetables	Lettuce (Head and Leaf)	Table 54
	Mustard Green	Table 55
	Swiss Chard	Table 56
	Turnip Green	Table 57
Tree Nuts	Filberts	Table 58
Dried Herbs	Hops	Table 59

For all crops, triflumizole was applied as a foliar spray. Each field trial site consisted of an untreated control plot and at least one treated plot; at some locations, a second plot was treated at an exaggerated rate.

Parameters of the supervised residue trials were generally well reported in the detailed field reports and study volumes, including application equipment, environmental conditions, dates of application and harvest. The study volumes also include post-harvest treatment of the samples, shipping dates and conditions, method validation data from the analytical laboratories, and sufficient details regarding the analytical method. Information on varieties was not always available.

The supervised residue trials and results are summarized below. Residue data are corrected for concurrent recovery. Residues in samples from control plots were < LOQ and are not shown. Formulations in the tables below are as reported in the study volume and may not correspond to the submitted labels (e.g., “Procure W” or “Procure WP” reported vs. “Procure WS” label submitted. Residues in bold typeface are the highest residues considered appropriate for assessment where replicate residues have been identified. Labels from the USA do not specify the number of applications that may be made per growing season.

In the tables that follow, the GAP number of applications from USA labels are expressed in parenthesis to denote that they are implied based on the application rates and the maximum allowed seasonal rate. Also, residues in bold are the highest residue in a given data set appropriate for estimating short-term dietary intake and underlined residues are those for consideration in MRL and STMR estimations.

*Pome fruits**Apples*

A total of 18 supervised trials on apples were conducted in the USA from 1984 to 1987. Trials were conducted in Washington (four), Michigan (two), Ohio (three), Vermont (four), California (three), Pennsylvania (one), and New York (one) and are reported in Ball 1986c and Ball 1988b.

Trials reported by Ball 1986c consisted of four foliar applications of the triflumizole 50W formulation containing 500 g ai/kg (nominal), except for one trial each in Yakima, Washington; Wapato, Washington; and Lodi, California, which each consisted of two sets of four foliar applications at two different application rates. Trials reported by Ball 1988b consisted of four to six foliar applications of the triflumizole 50W formulation containing 498 to 523 g ai/kg, except for the trial located in Smith Flat, California, which consisted of one foliar application. All applications were made at a rate of approximately 0.56 kg ai/ha per application or 1.12 kg ai/ha per application. Applications were made on a 4-day to 109-day schedule until apples were ready to be harvested. The apples were harvested 7 and 14 days after the last treatment (PHI=7, 14 days), except for the trials located in Bennington, Vermont, and Smith Flat, California, which were residue decline trials with PHIs of 0, 7–9, 13–14, 20–21, and 28–29 days. One to three samples of apples were collected from the treated plots and untreated plots. Samples were stored for less than 2 years (Ball 1986c) or less than 10 months (Ball 1988b) before analysis.

The method for analysis was a common moiety method with gas chromatography. The LOQ was not determined, and the LOD was 0.02 mg eq/kg. Average recovery of all fortifications was $96.4 \pm 19.5\%$ for Ball 1986c (n=8) and $81.4 \pm 12.9\%$ for Ball 1988b (n=10). All control samples had residues below the limit of quantitation of the method, with two exceptions (in Wooster, Ohio, one control sample had residues of 0.04 mg eq/kg, and in Zillah, Washington, one control sample had residues of 0.03 mg eq/kg), and these are not considered significant. Apples treated with the triflumizole 50W formulation had detectable residues.

A total of two supervised trials on apples were conducted in Japan from 1982 to 1983. Trials were conducted in Aomori (one) and Nagano (one). Trials were reported by Gomyo 1992. None of the trials were conducted at the critical GAP.

The trial located in Aomori received eight foliar applications of the triflumizole WP formulation containing 300 g ai/kg, and the trial located in Nagano had three treated plots that received eight foliar applications of the triflumizole WP formulation containing 300 g ai/kg. Application volume was 6000 L/ha. Applications were made on a 9-day to 34-day schedule until apples were ready to be harvested. The apples were harvested 1, 7, and 21 days after the last treatment.

Apple samples were collected from treated plots and untreated plots. Specimens were stored frozen until analysis (approximately 1–3 months after harvest) by The Institute of Environmental Toxicology, Ibaraki, Japan. Samples were analysed for triflumizole and FM-6-1, and reported as the sum of both.

The method for analysis was high performance liquid chromatography. The LOQ was 0.008 mg eq/kg. Average recovery at 0.4 mg eq/kg was $86.4 \pm 1.00\%$ (n=4). All control samples had residues at or below the limit of quantitation of the method, and these are not considered significant. Apples treated with the triflumizole WP formulation had detectable residues.

Table 42 Summary of triflumizole residues in apple trials

Trial ID/Country/Year	Storage Time (months)	Form	Application		No. of Appl.	DAT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)					
USA GAP			0.56	n.s.	(4–8)	14	—	—	Label
UR1302/ USA, Yakima, WA/1985	13	W	0.56	n.a.	4	7	0.2	0.2	UR1302 Ball, 1986c

Trial ID/Country/Year	Storage Time (months)	Form	Application		No. of Appl.	DAT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)					
									^a
			1.12	n.a.	4	7	0.1	0.1	^a
UR1302/ USA, East Lansing, MI/1986	1	W	0.56	n.a.	4	14	0.26	0.26	
UR1302/ USA, Wooster, OH/1986 (Red Delicious)	1	W	0.56	n.a.	4	14	0.1	0.1	
UR1302/ USA, Wooster, OH/1986 (Rome)	1	W	0.56	n.a.	4	14	0.1	0.1	
UR1302/ USA, Wooster, OH/1986 (Golden Delicious)	1	W	0.56	n.a.	4	14	0.3	0.3	
UR1302/ USA, Bennington, VT/1986 (McIntosh)	1	W	0.56	n.a.	4	14	< 0.02	< 0.02	
UR1302/ USA, Bennington, VT/1986 (McIntosh)	1	W	0.56	n.a.	4	14	< 0.02	< 0.02	
UR1302/ USA, Wapato, WA/1984 (Jonathan)	24	W	0.56	n.a.	4	14	< 0.02	< 0.02	^a
			1.12	n.a.	4	14	0.16	0.16	^a
UR1302/ USA, Wapato, WA/1984 (Golden Delicious)	24	W	0.56	n.a.	4	14	0.24	0.24	^a
UR1302/ USA, Lodi, CA/1984	24	W	0.56	n.a.	4	14	0.18	0.18	^a
			1.12	n.a.	4	14	0.34	0.34	^a
UR1306/ USA, Zillah, WA/1987	8	WP	0.56	0.12	4	14	0.20, 0.38	0.29	UR1306 Ball, 1988b ^a
			0.56	0.015	4	14	0.29, 0.27	0.28	^a
UR1306/ USA, Linden, CA/1987	8	WP	0.56	0.023	4	14	< 0.02	< 0.02	^a
			0.56	0.12	4	14	0.06	0.06	^a
			0.56	0.12	6	14	0.15	0.15	^a
UR1306/ USA, Bennington, VT/1987	8	WP	0.56	0.05	4	14	0.09	0.09	^a
			0.56	0.12	4	14	0.06	0.06	^a
			0.56	0.05	6	14	0.09	0.09	^a
			0.56	0.12	6	14	0.14	0.14	^a
UR1306/ USA, Bennington, VT/1987	8	WP	0.56	0.05	4	0	0.29	0.29	^a
						7	0.16	0.16	^a
						13	0.17	0.17	^a
						20	0.06	0.06	^a
						29	0.12	0.12	^a
			0.56	0.05	4	0	0.27	0.27	^a
						9	0.12	0.12	^a
						14	0.17	0.17	^a
						21	0.04	0.04	^a
						28	0.02	0.02	^a
UR1306/ USA, Upper Black Eddy, PA/1987	9	WP	0.56	0.12	4	14	0.19	0.19	^a
			0.56	0.015	4	14	0.07	0.07	^a
			0.56	0.12	6	14	0.15	0.15	^a

Trial ID/Country/Year	Storage Time (months)	Form	Application		No. of Appl.	DAT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)					
			0.56	0.015	6	14	0.11	0.11	^a
UR1306/ USA, East Lansing, MI/1987	9	WP	0.56	0.12	4	14	0.12	0.12	^a
			0.56	0.015	4	14	0.15	0.15	^a
			0.56	0.12	6	14	< 0.02	< 0.02	^a
			0.56	0.015	6	14	0.14	0.14	^a
UR1306/ USA, Clifton Springs, NY/1987	9	WP	0.56	0.015	4	14	0.14	0.14	^a
			0.56	0.12	4	14	< 0.02	< 0.02	^a
			0.56	0.015	6	14	0.12	0.12	^a
			0.56	0.12	6	14	< 0.02	< 0.02	^a
UR1306/ USA, Smith Flat, CA/1987	9	WP	0.56	0.015	1	0	0.08	0.08	^a
						7	0.05	0.05	^a
						14	< 0.02	< 0.02	^a
						21	< 0.02	< 0.02	^a
						28	< 0.02	< 0.02	^a
RD-9235 Japan, Aomori/ 1982	3	WP	0.9	0.015	8	1	0.09	0.09	RD-9235 Gomyo, 1992
						7	0.03	0.03	
						21	0.02	0.026	
RD-9235 Japan, Nagano/ 1983	1	WP	0.9	0.015	8	1	0.24	0.24	
						7	0.03	0.03	
						21	0.01	0.01	

^a The residue value(s) are not supported by the available storage stability data.

Pears

A total of seven supervised trials on pears were conducted in the USA from 1985 to 1987. Trials were conducted in Washington (two), California (two), Vermont (one), Oregon (one), and New York (one). Trials were reported in Ball 1986d and Ball 1988d.

Trials reported by Ball 1986d consisted of four foliar applications of the triflumizole 50W formulation containing 500 g ai/kg, except for one trial located in Ryde, California, which consisted of three sets of four foliar applications. Trials reported by Ball 1988d consisted of four to six foliar applications of the triflumizole 50W formulation containing 500 to 514 g ai/kg. All applications were made at a rate of approximately 0.56 kg ai/ha per application or 1.12 kg ai/ha per application. Applications were made on a 7-day to 100-day schedule until pears were ready to be harvested. The pears were harvested 14 days after the last treatment (PHI=14), except for the trial located in Ryde, California, which had a PHI of 15 days.

One to two samples of pears were collected from each of the treated and untreated plots and shipped, frozen, to the analytical laboratories. At each laboratory, samples were processed in a Hobart food processor and stored frozen until analysis. Samples were stored for less than 14 months (Ball 1986b) or less than 7 months (Ball 1988d) before analysis.

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/ECD. The LOQ was not determined, and the LOD was 0.02 mg eq/kg. Average recovery of all fortifications was $78.4 \pm 21.1\%$ for Ball 1986d (n=7) and $79.2 \pm 13.6\%$ for Ball 1988d (n=10). All control samples had residues below the limit of quantitation of the method. Pears treated with the triflumizole 50W formulation had detectable residues.

A total of two supervised trials on pears were conducted in Japan in 1985. Trials were conducted in Niigata (one) and Hiroshima (one). Trials were reported in Gomyo 1992.

The trials each had two plots that received eight foliar applications of the triflumizole WP formulation containing 300 g ai/kg. Application volume was 5000 L/ha, resulting in a rate of 0.75 kg ai/ha. Applications were made on a 4-day to 10-day schedule until pears were ready to be harvested. The pears were harvested 1, 7, and 21 days after the last treatment (PHI=1, 7, and 21). None of the trials were conducted at the critical GAP.

Pear samples were collected from treated plots and untreated plots. Specimens were stored frozen (approximately 1–2 months) until analysis by The Institute of Environmental Toxicology, Ibaraki, Japan. Samples were analysed for triflumizole and FM-6-1, and reported as the sum of both.

The method for analysis was high performance liquid chromatography. The LOQ was 0.02 mg eq/kg. Average recovery at 0.5 mg eq/kg was 87.3% (n=2). All control samples had residues at or below the limit of quantitation of the method, and these are not considered significant. Pears treated with the triflumizole WP formulation had detectable residues.

Table 43 Summary of triflumizole residue data in pears

Trial ID/Country/Year	Storage Time (months)	Form.	Use Pattern		No. of Appl.	D A T	Residue (mg eq/kg) ^a	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)					
USA GAP			0.56	n.s.	(4–8)	14	–	–	Label
UR1303/ USA, Wapato, WA/1985	14	W	0.56	0.015	4	14	0.29	0.29	UR1303 Ball, 1986d ^a
UR1303/ USA, Ryde, CA/1985	14	W	0.56	0.015	4	15	0.19	0.23	^a
			0.56	0.015	4	15	0.27		^a
			1.12	0.03	4	15	0.72	0.72	^a
UR1303/ USA, Bennington, VT/1986	1	W	0.56	0.015	4	14	0.26, 0.30	0.28	
UR1307/ USA, Hood River, OR/1987	9	WP	0.56	0.12	4	14	0.13, 0.14	0.14	UR1307 Ball, 1988d ^a
				0.015	4	14	0.17, 0.11	0.14	^a
				0.12	6	14	0.21, 0.15	0.18	^a
UR1307/ USA, Clifton Springs, NY/1987	8	WP	0.56	0.015	4	14	0.34	0.34	^a
			0.56	0.12	4	14	0.43	0.43	^a
UR1307/ USA, Zillah,, WA/1987	13	WP	0.56	0.015	4	14	0.36	0.36	^a
UR1307/ USA, Linden, CA/1987	9	WP	0.56	0.023	4	14	0.12	0.12	^a
					6	14	0.15	0.15	^a
RD-9235 Japan, Niigata/ 1985	32	WP	0.75	0.075	8	1	0.31	0.31	RD-9235 Gomyo, 1992 ^a
						7	0.22	0.22	^a
						21	0.11	0.11	^a
RD-9235 Japan, Hiroshima/ 1985	32	WP	0.75	0.075	8	1	0.32	0.32	^a
						7	0.23	0.23	^a
						21	0.14	0.14	^a

^a The residue value(s) are not supported by the available storage stability data.

Cherries

A total of eight supervised trials on cherries were conducted in the USA in 1995. Trials were conducted in California (one), Michigan (three), New York (two), Washington (one), and Utah (one). Trials were reported in Gaydosh 1997 and Maselli 1997.

Each trial site, with the exception of California, contained two treated plots. One plot received six airblast applications of the triflumizole 50WS formulation containing 522.5 g ai/kg in 750 litres of water, and the second plot received six airblast applications of the triflumizole 50WS formulation containing 500 g ai/kg in 2340 litres of water. The treated plot in California received six airblast applications of the triflumizole 50WS formulation containing 522.5 g ai/kg in 2340 litres of water. All applications were made at a rate of approximately 0.52 to 0.57 kg ai/ha per application on a 1-day to 34-day schedule until cherries were ready to be harvested. The cherries were harvested 1, 3, and 7 days after the last treatment (PHI=1, 3, and 7).

Two samples of cherries each were collected from two treated plots (one treated plot in California) and one untreated plot. Specimens were stored frozen and shipped frozen to Morse Laboratories, Sacramento, California. Samples were de-stemmed, pitted, and ground in the presence of dry ice in a Hobart food grinder. Samples were stored frozen until analysis (< 12 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/ECD. The LOQ was 0.05 mg eq/kg, and the LOD was not reported. Average recovery of all fortifications was $76.5 \pm 5.59\%$ (n=11) for Gaydosh 1997 and $76.9 \pm 7.77\%$ (n=24) for Maselli 1997. All control samples had residues below the limit of quantitation of the method. Cherries treated with the triflumizole 50WS formulation had detectable residues.

Table 44 Summary of triflumizole residue data in cherries

Trial ID/Country/Year	For m.	Use Pattern		No. of Appl.	D AT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)					
USA GAP		0.56	n.s.	(6–12)	1	–	–	Label
RP-95012/ USA, Ripon, CA/1995	WS	0.52–0.57	0.024	6	1	1.0, 1.3	1.14	RP-95012 Gaydosh, 1997
					3	0.98	0.98	
					7	0.74, 0.54	0.64	
RP-95012/ USA, Conklin, MI/1995	WS	0.56	0.076–0.079	6	1	0.70, 0.68	0.69	
					3	0.65, 0.79	0.72	
					7	0.38, 0.57	0.47	
			0.023–0.024	6	1	0.88, 1.0	0.96	
					3	1.0, 0.64	0.84	
					7	0.45, 0.78	0.61	
RP-95012/ USA, Lyons, NY/1995	WS	0.56	0.072–0.074	6	1	0.91, 0.77	0.84	
					3	0.37, 0.56	0.47	
					7	0.35, 0.43	0.39	
			0.023–0.024	6	1	1.5, 0.91	1.19	
					3	0.61, 0.68	0.64	
					7	0.48, 0.45	0.47	
RP-95012/ USA, Zillah, WA/1995	WS	0.56	0.075	6	1	0.50, 0.62	0.56	
					3	0.28, 0.44	0.36	
					7	0.4, 0.32	0.36	
			0.024	6	1	0.50, 0.68	0.59	
					3	0.40, 0.51	0.46	
					7	0.49, 0.21	0.35	
RP-95013/ USA, Conklin, MI/1995	WS	0.56	0.075–0.079	6	1	1.1, 1.1	1.08	RP-95013 Maselli, 1997
					3	0.67, 0.99	0.83	

Trial ID/Country/Year	Form.	Use Pattern		No. of Appl.	D AT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)					
					7	0.79, 0.67	0.73	
			0.023–0.024	6	1	1.0, 1.1	1.03	
					3	0.73, 0.81	0.77	
					7	0.99, 0.59	0.79	
RP-95013/ USA, Hart, MI/1995	WS	0.56	0.075–0.078	6	1	1.2, 1.2	1.19	
					3	0.52, 0.58	0.55	
					7	0.47, 0.7	0.58	
			0.023–0.024	6	1	1.5, 1.5	1.50	
					3	0.77, 0.74	0.75	
					7	0.52, 0.53	0.53	
RP-95013/ USA, Lyons, NY/1995	WS	0.55–0.57	0.075	6	1	0.32, 0.76	0.54	
					3	0.84, 0.83	0.84	
					7	0.3, 0.34	0.32	
		0.56–0.57	0.024	6	1	0.78, 0.66	0.72	
					3	1.0, 1.4	1.21	
					7	0.44, 0.41	0.42	
RP-95013/ USA, Perry, UT/1995	WS	0.56	0.075	6	1	0.82, 1.1	0.96	
					3	0.54, 0.63	0.59	
					7	0.33, 0.92	0.63	
			0.024	6	1	1.4, 1.1	1.26	
					3	0.90, 0.86	0.88	
					7	0.57, 0.78	0.68	

Berries and other small fruits

Grapes

A total of 18 supervised trials on grapes were conducted in the USA from 1985 to 1987. Trials were conducted in Washington (three), California (six), New York (eight), and Ohio (one). Trials were reported in Ball 1986b and Ball 1988c.

Trials reported by Ball 1986b received four foliar applications of the triflumizole 50W formulation containing 500 g ai/kg, except for the trials located in Portland, New York, which received three foliar applications. Trials reported by Ball 1988c received four foliar applications of the triflumizole 50W formulation containing 500 g ai/kg (nominal), with the exception of one site in Selma, California, which received one foliar application. All applications were made at a rate of approximately 0.28 kg ai/ha per application or 0.56 kg ai/ha per application. Applications were made on a 14-day to 78-day schedule until grapes were ready to be harvested. The grapes were harvested 7 days after the last treatment (PHI=7), except for the 44852 trial, which has PHIs of 0, 3, 7, 14, and 21 days.

Samples of grapes were collected from treated plots and untreated plots. Specimens were stored frozen and shipped frozen to the analytical laboratories. Samples were processed in a Hobart grinder and stored frozen until analysis (< 9 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by HPLC/UV or GC/NPD. The LOD was 0.02 mg eq/kg. Average recovery of all fortifications was $80.0 \pm 14.1\%$ (n=11) for Ball 1986b and $95.8 \pm 16.0\%$ (n=13) for Ball 1988c. Three control samples had residues at or below the limit of detection (in Madera, California, one control sample had residues of 0.03 mg eq/kg, and in Selma, California, two control samples had residues of 0.03 mg eq/kg each), and these are not considered significant. Grapes treated with the triflumizole 50W formulation had detectable residues.

Table 45 Summary of triflumizole residue data in grapes

Trial ID/ Country/Year	Form	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
USA GAP		0.28	n.s.	4–8	7	—	—	Label
UR1304/ USA, Grandview, WA/1985	W	0.28	0.060	4	7	0.09	0.09	UR1304 Ball, 1986b
UR1304/ USA, Manteca, CA/1985	W	0.28	n.a.	4	7	0.10	0.10	
		0.56	n.a.	4	7	0.20	0.20	
UR1304/ USA, Madera, CA/1985	W	0.28	n.a.	4	7	0.18	0.18	
UR1304/ USA, Selma, CA/1985 Thompson Seedless	W	0.28	n.a.	4	7	0.15	0.15	
UR1304/ USA, Selma, CA/1985 Thompson Seedless	W	0.28	n.a.	4	7	0.15	0.15	
UR1304/ USA, Naples, NY/1985	W	0.28	n.a.	4	7	0.94	0.94	
UR1304/ USA, Portland, NY/1985	W	0.28	n.a.	3	7	0.09	0.09	
UR1304/ USA, Portland, NY/1985	W	0.28	n.a.	3	7	0.09	0.09	
UR1304/ USA, Geneva, NY/1986 Rosette	W	0.28	n.a.	4	7	1.2	1.2	
UR1304/ USA, Geneva, NY/1986 Rosette	W	0.28	n.a.	4	7	1.4	1.4	
UR1308/ USA, Phelps, NY/1987 Aurora	W	0.28	0.060	4	7	0.89	0.89	UR1308 Ball, 1988c
UR1308/ USA, Phelps, NY/1987 Catawba	W	0.28	0.060	4	7	2.02	2.02	
UR1308/ USA, Dundee, NY/1987	W	0.28	0.015	4	7	0.50	0.50	

Trial ID/ Country/Year	Form	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
UR1308/ USA, Grandview, WA/1987 White Reisling	W	0.28	0.015	4	7	0.15, 0.16	0.16	
UR1308/ USA, Grandview, WA/1987 Chardonnay	W	0.28	0.015	4	7	0.21	0.21	
UR1308/ USA, Wooster, OH/1987	W	0.56	0.200	4	7	0.84	0.84	
UR1308/ USA, Selma, CA/1987 Thompson Seedless	W	0.28	0.030	1	0	0.38	0.38	
					3	0.16	0.16	
					7	0.05	0.05	
					14	0.06	0.06	
					21	< 0.02	< 0.02	
UR1308/ USA, Selma, CA/1987 Thompson Seedless	W	0.28	0.060	4	7	0.21	0.21	
			0.015	4	7	0.31	0.31	

Strawberries

A total of eight supervised trials on strawberries were conducted in the USA in 1999. Trials were conducted in Pennsylvania (one), Georgia (one), Florida (one), Indiana (one), California (three), and Oregon (one). Trials were reported in Gaydosch 2001.

At each trial, plots received three foliar applications of the triflumizole 50WS formulation containing 500 g ai/kg. All applications were made at a rate of approximately 0.41 to 0.43 kg ai/ha per application. Applications were made on a 10-day to 14-day schedule until strawberries were ready to be harvested. The strawberries were harvested 1 and 3 days after the last treatment (PHI=1 and 3 days).

Two samples of strawberries were collected from one treated plot and one sample was collected from one untreated plot. Specimens were stored frozen and shipped frozen to Morse Laboratories, Inc., Sacramento, California. Samples were processed with dry ice in a Hobart grinder and stored frozen until analysis (< 9 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/MSD. The LOQ was 0.02 mg eq/kg, and the LOD was not reported. Average recovery of all fortifications was $80.5 \pm 5.0\%$ (n=12) for strawberries. All control samples had residues at or below the limit of quantitation of the method. Strawberries treated with the triflumizole 50WS formulation had detectable residues.

Table 46 Summary of triflumizole residue data in strawberries

Trial ID/Country/Year	Storage Time (days)	Form.	Use Pattern		No. of Appl.	DAT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)					
USA GAP			0.28	n.s.	(4–8)	1	–	–	Label
RP-99005/ USA, New Tripoli, PA/1999	232	WS	0.42	0.09	3	1	0.68, 0.71	0.70	RP-99005 Gaydosh, 2001 ^a
						3	0.40, 0.22	0.31	^a
RP-99005/ USA, Cochran, GA/1999	232	WS	0.41–0.43	0.088–0.091	3	1	0.95, 0.82	0.89	^a
						3	0.83, 0.48	0.66	^a
RP-99005/ USA, Eustis, FL/1999	253	WS	0.42	0.09	3	1	0.97, 0.75	0.86	^a
						3	0.44, 0.30	0.37	^a
RP-99005/ USA, Noblesville, IN/1999	195	WS	0.42–0.43	0.090–0.091	3	1	0.48, 0.45	0.47	^a
						3	0.24, 0.22	0.23	^a
RP-99005/ USA, Salinas, CA/1999	235	WS	0.42	0.089–0.094	3	1	1.2, 0.88	1.0	^a
						3	0.65, 0.22	0.44	^a
RP-99005/ USA, Watsonville, CA/1999	246	WS	0.42	0.088–0.091	3	1	1.6, 2.0	1.8	^a
						3	0.86, 1.2	1.0	^a
RP-99005/ USA, Oceanside, CA/1999	253	WS	0.41–0.43	0.089–0.091	3	1	0.53, 0.89	0.71	^a
						3	0.57, 0.22	0.41	^a
RP-99005/ USA, Mt. Angel, OR/1999	230	WS	0.42	0.09	3	1	0.40, 0.41	0.41	^a
						3	0.30, 0.17	0.24	^a

^a The residue value(s) are not supported by the available storage stability data.

Assorted Tropical and Sub-Tropical Fruits-Inedible Peel

Papaya

A total of four supervised trials on papaya were conducted in the USA from 2005 to 2006. Trials were conducted in Hawaii (three), and Florida (one). Trials were reported by Barney 2007f.

At each trial, plots received five foliar applications of the triflumizole 480SC formulation containing 453 g ai/L. All applications were made at a rate of approximately 0.41 to 0.44 kg ai/ha per application. Applications were made on a 12-day to 14-day schedule until papaya was ready to be harvested. The papaya was harvested 0 days after the last treatment (PHI=0).

Two samples of papaya were collected from one treated plot and one untreated plot. Specimens were stored frozen and shipped frozen to IR-4 Western Region Satellite Laboratory, Honolulu, Hawaii. Samples of whole fruit were processed with dry ice in a Hobart food cutter and stored frozen until analysis (< 19 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/MSD. The LOQ was 0.033 mg eq/kg, and the LOD was 0.011 mg eq/kg. Method validation results for triflumizole averaged $82 \pm 7\%$ at 0.050 mg eq/kg, $76 \pm 6\%$ at 1.0 mg eq/kg and $81 \pm 4\%$ at 10 mg eq/kg. Method validation results for FM-6-1 averaged $81 \pm 4\%$ at 0.050 mg eq/kg, $72 \pm 5\%$ at 1.0 mg eq/kg and $73 \pm 4\%$ at 10 mg eq/kg. Method validation results for FA-1-1 averaged $85 \pm 4\%$ at 0.050 mg eq/kg, $79 \pm 3\%$ at 1.0 mg eq/kg and $75 \pm 1\%$ at 10 mg eq/kg. All control

samples had residues at or below the limit of quantitation of the method. Papaya treated with the triflumizole 480SC formulation had detectable residues.

Table 47 Summary of triflumizole residues in papaya

Trial ID/ Country/Year	Storage Time (days)	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
USA GAP			0.35	n.s.	2–3	0	–	–	Label
09332/ USA, Pahoa, HI/2005	461	SC	0.41–0.43	0.050	5	0	0.85, 0.92	0.89	09332 Barney, 2007f
09332/ USA, Keaau, HI/2005	423	SC	0.42–0.43	0.041	5	0	0.53, 0.53	0.53	
09332/ USA, Waimanalo, HI/2005– 2006	351	SC	0.41–0.44	0.034	5	0	0.91, 0.85	0.88	
09332/ USA, Homestead, FL/2005	561	SC	0.43	0.024	5	0	0.20, 0.24	0.22	

Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead brassicas

Broccoli

A total of 10 supervised trials on broccoli were conducted in the USA from 2003 to 2007. Trials were conducted in Texas (two), Maryland (one), California (five), New Mexico (one), and Oregon (one). Trials were reported in Gaydosh 2004a and Barney 2007c.

The trial reported in Gaydosh 2004a received five foliar applications of the triflumizole 50WS formulation containing 501 g ai/kg. Trials reported in Barney 2007c received four to six foliar applications of the triflumizole 480SC formulation containing 430 g ai/l. All applications were made at a rate of approximately 0.27 to 0.57 kg ai/ha per application. Applications were made on a 6-day to 8-day schedule until broccoli was ready to be harvested. The broccoli was harvested 0 days after the last treatment (PHI=0), except for the AWD-03907 trial, which had PHIs of 1, 3, and 7 days, and the 06-CA11 trial, which had PHIs of 0, 1, 4, 7, and 11 days.

Samples of broccoli were collected from treated plots and untreated plots. Specimens were stored frozen and shipped frozen to Morse Laboratories, Sacramento, California, where they were processed with dry ice in a Hobart food grinder and stored frozen until analysis (approximately 9 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/MSD. The LOQ was 0.05 mg eq/kg (Gaydosh 2004a) or 0.032 mg eq/kg (Barney 2007c), and the LOD was not determined (Gaydosh 2004a) or 0.011 mg eq/kg (Barney 2007c). Average recovery of all triflumizole fortifications was $74 \pm 4\%$ (Gaydosh 2004a) and $81 \pm 10\%$, $82 \pm 3\%$, and $84 \pm 4\%$, for the three validation levels. All control samples had residues at or below the limit of quantitation of the method. Broccoli treated with the triflumizole 50WS formulation and the triflumizole 480SC formulation had detectable residues.

Table 48 Summary of triflumizole residue data in broccoli

Trial ID/ Country/Year	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
USA GAP		0.28	n.s.	2–3	1	—	—	Label
RP-03006/ USA, Uvalde, TX/2003	WS	0.53–0.57	0.204–0.245	5	1	0.32, 0.86, 0.93	0.70	RP-03006 Gaydosh, 2004a
					3	0.50, 0.81, 0.28	0.53	
					7	0.17, 0.20, 0.20	0.19	
09319/ USA, Salisbury, MD/2006	SC	0.27–0.28	0.214–0.218	5	0	4.0, 3.8	3.9	09319 Barney, 2007c ^a
09319/ USA, Salinas, CA/2006 Everest	SC	0.29–0.30	0.077–0.094	4	0	0.89, 1.8	1.4	^a
09319/ USA, Salinas, CA/2006 Greenbelt	SC	0.28–0.29	0.053–0.073	4	0	0.35, 1.2	0.80	^a
09319/ USA, Parlier, CA/2006	SC	0.28–0.29	0.099–0.101	4	0	0.82, 0.41	0.62	^a
09319/ USA, Las Cruces, NM/2006	SC	0.28–0.30	0.099	4	0	0.28, 0.61	0.45	^a
09319/ USA, Aurora, OR/2006	SC	0.28–0.30	0.199–0.200	5	0	0.43, 0.54	0.49	^a
09319/ USA, Holtville, CA/2007	SC	0.28	0.115–0.119	4	0	0.78, 0.89	0.83	^a
					1	0.74, 0.43	0.59	^a
					4	0.10, 0.29	0.19	^a
					7	0.46, 0.37	0.41	^a
					11	0.11, 0.26	0.18	^a
09319/ USA, Davis, CA/2006	SC	0.28–0.31	0.100–0.120	4	0	0.65, 0.53	0.59	^a
09319/ USA, Weslaco, TX/2006–2007	SC	0.28–0.29	0.159–0.160	6	0	1.1, 0.85	0.97	^a

^a The residue value(s) are not supported by the available storage stability data.

Cabbages, Head

A total of nine supervised trials on cabbage were conducted in the USA from 2006 to 2007. Trials were conducted in Maryland (one), New Jersey (one), New York (one), Wisconsin (one), Florida (one), Texas (one), Tennessee (one), Colorado (one) and California (one). Trials were reported in Barney 2007d.

At each trial, plots received four foliar applications of the triflumizole 480SC formulation containing 430 g ai/kg, except for the Tennessee trial, which received five foliar applications. All applications were made at a rate of approximately 0.27 to 0.30 kg ai/ha per application. Applications

were made on a 6-day to 8-day schedule until cabbage was ready to be harvested. The cabbage was harvested 0 days after the last treatment (PHI=0).

Two samples of cabbage (with wrapper leaves) each were collected from one treated plot and one untreated plot. Specimens were stored frozen and shipped frozen to Morse Laboratories, Sacramento, California, where they were processed with dry ice in a Hobart food grinder and stored frozen until analysis (< 9 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/MSD. The LOQ was 0.030 mg eq/kg, and the LOD was 0.010 mg eq/kg. Average recovery of all fortifications was $83 \pm 7\%$ (n=16) for cabbage. All control samples had residues at or below the limit of quantitation of the method. Cabbage treated with the triflumizole 480SC formulation had detectable residues.

Table 49 Summary of triflumizole residue data in cabbage

Trial ID/ Country/Year	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
USA GAP		0.28	n.s.	2–3	1	–	–	Label
09143/ USA, Salisbury, MD/2006	SC	0.28–0.29	0.084	4	0	0.61, 0.26	0.43	09143 Barney, 2007d ^a
09143/ USA, Bridgeton, NJ/2006	SC	0.27–0.29	0.069–0.074	4	0	0.57, 1.0	0.79	^a
09143/ USA, Freeville, NY/2006	SC	0.28	0.099	4	0	0.41, 0.55	0.48	^a
09143/ USA, Arlington, WI/2006	SC	0.28–0.30	0.086–0.090	4	0	0.47, 0.18	0.33	^a
09143/ USA, Citra, FL/2006	SC	0.29	0.086	4	0	1.2, 1.0	1.10	^a
09143/ USA, Weslaco, TX/2007	SC	0.28	0.077–0.079	4	0	0.42, 0.19	0.31	^a
09143/ USA, Crossville, TN/2006	SC	0.29–0.30	0.085–0.088	5	0	0.17, 0.19	0.18	^a
09143/ USA, Brighton, CO/2006	SC	0.28–0.30	0.149–0.150	4	0	0.75, 0.36	0.55	^a
09143/ USA, Salinas, CA/2006	SC	0.27–0.28	0.051–0.083	4	0	0.63, 0.60	0.62	^a

^a The residue value(s) are not supported by the available storage stability data.

Fruiting vegetables, Cucurbits

The Meeting received supervised residue trials on cucurbit vegetables. Trials with cucumbers were conducted in both indoor and outdoor environments.

Cucumbers (Outdoor)

A total of six supervised trials on cucumbers were conducted in the USA in 1997. Trials were conducted in North Carolina (one), South Carolina (one), Florida (one), Indiana (two), and Texas (one). Trials were reported in Maselli 1999.

At each trial, plots received five foliar applications of the triflumizole 50WS formulation containing 500 g ai/kg. All applications were made at a rate of approximately 0.26 to 0.30 kg ai/ha per application. Applications were made on a 7-day to 11-day schedule until cucumbers were ready to be harvested. The cucumbers were harvested 0 day after the last treatment (PHI=0).

Two samples of cucumbers were collected from one treated plot and one sample was collected from one untreated plot. Specimens were stored frozen and shipped frozen to PTRL West, Inc., Richmond, California. Samples were processed with dry ice in either a Hobart or WestBend food processor and were stored frozen until analysis (< 30 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/NPD. The LOQ was 0.05 mg eq/kg, and the LOD was not determined. Average recovery of all fortifications was $82.0 \pm 9.8\%$ (n=18) for cucumbers. All control samples had residues below the limit of quantitation of the method. Cucumbers treated with the triflumizole 50WS formulation had detectable residues.

Cucumbers (Indoor)

A total of four supervised trials on cucumbers were conducted in USA from 2009 to 2010. Trials were conducted in Texas (one), Florida (one), Colorado (one), and Maryland (one). Trials were reported in Homa 2012.

At each trial, plots received five foliar applications of the triflumizole 480SC formulation containing 431 g ai/L. All applications were made at a rate of approximately 0.26 to 0.30 kg ai/ha per application. Applications were made on a 6- to 8-day schedule until cucumbers were ready to be harvested. The cucumbers were harvested 0 day after the last treatment (PHI=0), except for the trial in Colorado which had PHIs of 0, 3, 7, 12, and 15 days.

Two samples of cucumbers were collected from one treated plot and one untreated plot. Specimens were stored frozen and shipped frozen to the Western Region Laboratory at the University of California, Davis (UCD), Davis, California. Samples were processed with dry ice in a Hobart food chopper and were stored frozen until analysis (< 15 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/MSD in selective ion monitoring (SIM) mode. Average recovery of all fortifications was $76 \pm 8\%$ (n=9) for cucumbers. All control samples had residues below the limit of quantitation of the method. Cucumbers treated with the triflumizole 480SC formulation had detectable residues.

A total of four supervised trials on cucumbers were conducted in Japan from 1982 to 1990. Trials were conducted in Ibaragi (one), Osaka (two), and Chiba (one). Trials were reported in Gomyo 1993.

Two plots received five foliar applications of the triflumizole 15EC formulation containing 150 g ai/L, and two plots received five foliar applications of the triflumizole 30WP formulation containing 300 g ai/kg. All applications were made at a rate of approximately 0.06 to 0.30 kg ai/ha per application. Applications were made on a 6-day to 9-day schedule until cucumbers were ready to be harvested. The cucumbers were harvested 1, 3, and 7 days after the last treatment (PHI=1, 3, and 7 days).

One sample of cucumber was collected from one treated plot and one untreated plot. Specimens were stored frozen until analysis by Environmental Toxicology Laboratory of Nippon Soda Co., Odawara, Japan. Storage time was less than 30 months.

The method for analysis was high performance liquid chromatography with UV detection and results are reported as combined residues of triflumizole and FM-6-1. The LOQ was 0.02 mg eq/kg. All control samples had residues at or below the limit of quantitation of the method. Cucumbers treated with the triflumizole 15EC formulation and the triflumizole 30WP formulation had detectable residues.

A total of eight supervised trials on cucumbers were conducted in the Netherlands in 1993. Trials were conducted in Harmelen (one), Vleuten (one), Houten (one), Maarssen (one), Zevenhuizen (one), Moerkapelle (one), Bleiswijk (one), and Bergschenhoek (one). Trials were reported in Geuijen 1994.

For each trial, plots received three to four foliar applications of the triflumizole 15EC formulation containing 150 g ai/L. All applications were made at a rate of approximately 0.228 to 0.533 kg ai/ha per application. Applications were made on a 7-day schedule until cucumbers were ready to be harvested. The cucumbers were harvested 3 days after the last treatment (PHI=3), except for the trials located in Vleuten and Zevenhuizen, which had PHIs of 0, 1, 3, and 7 days.

One sample each of cucumber was collected from two treated plots and one untreated plot. Specimens were received by the analysis department, TNO Nutrition Research Institute, AJ Zeist, Netherlands, on the day they were harvested. Samples were homogenized using a Stephan cutter. Processed samples were stored refrigerated until analysis.

The method for analysis was high performance liquid chromatography with UV detection. The LOQ was approximately 0.1 mg eq/kg, and the LOD was 0.02 mg eq/kg. A total of 7 control samples had residues at or above the limit of quantitation of the method, and these are not considered significant. Cucumbers treated with the triflumizole 15EC formulation had detectable residues.

Table 50 Summary of triflumizole residue data in cucumbers

			Use Pattern						
Trial ID/Country/Year	Storage Time (months)	Form	Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
USA (Outdoor)									
USA GAP			0.28	n.s.	(5-10)	0	—	—	Label
RP-97006/ USA, Knightdale, NC/1997	6	WS	0.28–0.29	0.098–0.103	5	0	0.18, 0.17	0.18	RP-97006 Maselli, 1999
RP-97006/ USA, Elko, SC/1997	7	WS	0.28–0.29	0.069–0.149	5	0	0.12, 0.21	0.17	^a
RP-97006/ USA, Duette, FL/1997	8	WS	0.28	0.097–0.099	5	0	0.13, 0.11	0.12	^a
RP-97006/ USA, Noblesville, IN/1997 Marketmore 76	4	WS	0.28	0.099–0.145	5	0	0.18, 0.15	0.17	
RP-97006/ USA, Noblesville, IN/1997 Wisconsin SMR 58	5	WS	0.28–0.29	0.101–0.147	5	0	0.13, 0.12	0.13	
RP-97006/ USA, Donna, TX/1997	6	WS	0.26–0.30	0.101–0.126	5	0	0.11, 0.14	0.13	
USA (Indoor)									
09300/ USA,	1	SC	0.28	0.027	5	0	0.11, < 0.10 ^b	0.11	09300

Trial ID/Country/Year	Storage Time (months)	Form	Use Pattern		No. of Appl.	DAT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)					
Weslaco, TX/2009									Homa, 2012
09300/ USA, Citra, FL/2010	14	SC	0.28–0.29	0.03	5	0	0.27, 0.25	0.26	^a
09300/ USA, Fort Collins, CO/2009	2	SC	0.27–0.30	0.030–0.033	5	0	0.10, < 0.10 ^b	0.1	
						3	< 0.10 ^b , 0.11	0.11	
						7	< 0.10 ^b , < 0.10 ^b	< 0.10	
						12	< 0.10 ^b , < 0.10 ^b	< 0.10	
						15	< 0.10 ^b , < 0.10 ^b	< 0.10	
09300/ USA, Salisbury, MD/2009	4	SC	0.26	0.022	5	0	0.17, 0.25	0.21	
Japan									
RD-9331/ Japan, Ibaragi/1990	3	EC	0.0600–0.1875	0.0075	5	1	< 0.02	< 0.02	RD-9331 Gomyo, 1993
						3	< 0.02	< 0.02	
						7	< 0.02	< 0.02	
RD-9331/ Japan, Osaka/1990	2	EC	0.25	0.01	5	1	0.04	0.04	
						3	< 0.02	< 0.02	
						7	< 0.02	< 0.02	
RD-9331/ Japan, Chiba/1982	2	WP	0.3	0.01	5	1	0.1	0.1	
						3	0.09	0.09	
						7	0.04	0.04	
RD-9331/ Japan, Osaka/1983	1	WP	0.2	0.01	5	1	0.28	0.28	
						3	0.25	0.25	
						7	0.1	0.1	
Netherlands									
Netherlands GAP			0.225	0.015	1–6	1	–	–	Label
F-93-30-NL-00/02/ Netherlands, Harmelen/ 1993	> 9 months ^c	EC	0.228–0.244	0.015	3	3	< 0.04	< 0.04	F-93-30 Geuijen, 1994
			0.231–0.250	0.015	3	3	< 0.04	< 0.04	
F-93-30-NL-00/02/ Netherlands, Vleuten/1993	> 9 months	EC	0.234–0.264	0.015	3	0	< 0.05	< 0.05	
						1	< 0.05	< 0.05	
						3	< 0.04	< 0.04	
						7	< 0.02	< 0.02	
			0.246–0.267	0.015	3	0	< 0.06	< 0.06	
						1	< 0.05	< 0.05	
						3	< 0.04	< 0.04	
						7	< 0.02	< 0.02	
F-93-30-NL-00/02/ Netherlands,	> 9 months	EC	0.243–0.268	0.015	3	3	< 0.04	< 0.04	

Trial ID/Country/Year	Storage Time (months)	Form	Use Pattern		No. of Appl	DAT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)					
Houten/1993									
			0.242–0.269	0.015	3	3	< 0.04	< 0.04	
F-93-30-NL-00/02/ Netherlands, Maarssen/ 1993	> 9 months	EC	0.244–0.268	0.022	3	3	< 0.04	< 0.04	
			0.241–0.270	0.021–0.022	3	3	< 0.04	< 0.04	
F-93-30-NL-00/02/ Netherlands, Zevenhuizen/ 1993	> 9 months	EC	0.498–0.509	0.025	4	0	0.17	0.17	
						1	0.17	0.17	
						3	0.11	0.11	
						7	0.07	0.07	
			0.497–0.505	0.025–0.026	4	0	0.16	0.16	
						1	0.18	0.18	
						3	0.10	0.10	
						7	0.06	0.06	
F-93-30-NL-00/02/ Netherlands, Moerkapelle/ 1993	> 9 months	EC	0.483–0.491	0.025	4	3	0.11	0.11	
			0.500–0.509	0.025–0.026	4	3	0.09	0.09	
F-93-30-NL-00/02/ Netherlands, Bleiswijk/ 1993	> 9 months	EC	0.484–0.500	0.025	4	3	0.14	0.14	
			0.495–0.505	0.025	4	3	0.13	0.13	
F-93-30-NL-00/02/ Netherlands, Bergschenhoek/ 1993	> 9 months	EC	0.492–0.497	0.025	4	3	0.23	0.23	
			0.503–0.533	0.025	4	3	0.18	0.18	

^a The residue value(s) are not supported by the available storage stability data.

^b 0.10 mg eq/kg was used to calculate the average residue.

^c Based on harvest and communication dates specified in the study report.

Muskmelons

A total of six supervised trials on muskmelons were conducted in the USA in 1997. Trials were conducted in North Carolina (one), Indiana (one), Texas (one) and California (three). Trials were reported by Gaydos, Maselli, and Puhl 1999.

At each trial, plots received five foliar applications of the triflumizole 50WS formulation containing 500 g ai/kg (nominal). All applications were made at a rate of approximately 0.26 to 0.32 kg ai/ha per application. Applications were made on a 7-day to 10-day schedule until muskmelons were ready to be harvested. The muskmelons were harvested 0 day after the last treatment (PHI=0).

Two samples of muskmelons were collected from each treated plot and one sample was collected from each untreated plot. Specimens were stored frozen and shipped frozen to PTRL West, Inc., Richmond, California. Whole melon samples were sectioned and composited to obtain a representative sample for the field. Samples (pulp + peel) were processed with dry ice in a Hobart cutter/mixer and were stored frozen until analysis (< approximately 7 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/NPD. The LOQ was 0.05 mg eq/kg. Average recovery of all fortifications was $93.5 \pm 19.0\%$ (n=6) for muskmelons. All control samples had residues below the limit of quantitation of the method. Muskmelons treated with the triflumizole 50WS formulation had detectable residues.

Table 51 Summary of triflumizole residue data in muskmelons

Trial ID/Country/Year	Storage Time (days)	Form.	Use Pattern		No. of Appl.	DAT	Residue mg eq/kg	Average Residue mg eq/kg	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)					
USA GAP			0.28	n.s.	(5–10)	0	–	–	Label
RP-97005/ USA, Knightdale, NC/1997	174	WS	0.27–0.28	0.094–0.101	5	0	0.15, 0.13	0.14	RP-97005 Gaydosch, Maselli, Puhl, 1999 ^a
RP-97005/ USA, Noblesville, IN/1997	160	WS	0.28–0.29	0.102–0.146	5	0	0.40, 0.35	0.38	^a
RP-97005/ USA, Donna, TX/1997	203	WS	0.26–0.32	0.107–0.122	5	0	0.15, 0.15	0.15	^a
RP-97005/ USA, Winters, CA/1997	214	WS	0.28–0.30	0.054–0.104	5	0	0.07, 0.08	0.07	^a
RP-97005/ USA, Manteca, CA/1997	158	WS	0.28	0.098–0.100	5	0	0.27, 0.24	0.25	^a
RP-97005/ USA, Fresno, CA/1997	153	WS	0.28	0.040–0.060	5	0	0.17, 0.25	0.21	^a

^a The residue value(s) are not supported by the available storage stability data.

Squash, Summer

A total of five supervised trials on summer squash were conducted in the USA in 1997. Trials were conducted in Pennsylvania (one), South Carolina (one), Florida (one), Indiana (one), and California (one). Trials were reported in Gaydosch 1999.

At each trial, plots received five foliar applications of the triflumizole 50WS formulation containing 522 g ai/kg. All applications were made at a rate of approximately 0.28 to 0.29 kg ai/ha per application. Applications were made on a 7-day to 10-day schedule until squash was ready to be harvested. The squash was harvested 0 days after the last treatment (PHI=0).

Two samples of squash were collected from one treated plot and one sample was collected from one untreated plot. Specimens were stored frozen and shipped frozen to PTRL West, Inc., Richmond, California. Samples were processed with dry ice in a Hobart or WestBend food processor and stored frozen until analysis (< 9 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/NPD. The LOQ was 0.05 mg eq/kg. Average verification recoveries for triflumizole in two verification sets were $79.0 \pm 8.0\%$ (n=6) and $77.2 \pm 3.7\%$ (n=6), while verification recoveries for FM-6-1 averaged $74.3 \pm 11.6\%$ (n=6) and $81.1 \pm 8.2\%$ (n=6). All control samples had residues at or below the limit of quantitation of the method. Squash treated with the triflumizole 50WS formulation had detectable residues.

Table 52 Summary of triflumizole residue data in summer squash

Trial ID/Country/Year	Storage Time (days)	Form.	Use Pattern		No. of Appl.	DAT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)					
USA GAP			0.28	n.s.	(5–10)	0	–	–	Label
RP-97007/ USA, Hamburg, PA/1997	186	WS	0.28–0.29	0.065–0.143	5	0	0.12, 0.15	0.14	RP-97007 Gaydosh, 1999 ^a
RP-97007/ USA, Elko, SC/1997	234	WS	0.28–0.29	0.070–0.151	5	0	0.14, 0.14	0.14	^a
RP-97007/ USA, Duette, FL/1997	254	WS	0.28	0.097–0.099	5	0	0.13, 0.11	0.12	^a
RP-97007/ USA, Noblesville, IN/1997	196	WS	0.28–0.29	0.102–0.145	5	0	0.19, 0.19	0.19	^a
RP-97007/ USA, Lathrop, CA/1997	188	WS	0.28	0.099–0.100	5	0	0.31, 0.39	0.35	^a

*Fruiting vegetables, Other than Cucurbits**Tomatoes*

A total of four supervised trials on tomato were conducted in USA in 2010. Trials were conducted in greenhouses in California (1), Maryland (1), Texas (1), and Wisconsin (1). Trials were reported by Barney 2012.

At each trial, plots received four or five foliar applications of the triflumizole 480SC formulation containing 431 g ai/L. All applications were made at a rate of approximately 0.26 to 0.29 kg ai/ha per application. Applications were made on a 6-day to 14-day schedule until tomatoes were ready to be harvested. The tomatoes were harvested 0 day after the last treatment (PHI=0), except for the trial located in California, which had PHIs of 0, 1, 4, 8, 10, and 15 days.

Two samples of tomatoes were collected from one treated plot and one untreated plot. Specimens were stored frozen and shipped frozen to USDA-ARS laboratory, Beltsville, MD. After reassignment of the analytical laboratory, samples were shipped frozen to IR-4 Western Region Laboratory, Davis, CA. Samples were processed with dry ice in a Hobart or Robot Coupe food chopper and stored frozen until analysis (< 19 months).

The analytical method assayed triflumizole and its aniline-containing metabolites. Total triflumizole residues are quantified using a gas chromatograph equipped with a mass selective detector (MSD) in selective ion monitoring (SIM) mode. The LOQ was 0.50 mg eq/kg. Average recovery of all fortifications was $85.3 \pm 9.6\%$ for tomatoes (n=13). All control samples had residues below the limit of quantitation of the method. Tomatoes treated with the triflumizole 480SC formulation had detectable residues.

A total of four supervised trials on tomatoes were conducted in the Netherlands in 1995 and 1996. Trials were conducted in greenhouses in Haps (one), Siebengewald (one), and Wellerlooi (two). Trials were reported by van de Ruit 1997.

At each trial, plots received three foliar applications of the triflumizole EC formulation containing 158 g ai/L. All applications were made at a rate of approximately 0.310 to 0.322 kg ai/ha per application. Applications were made on a 7-day schedule until tomatoes were ready to be harvested. The tomatoes were harvested 3 days after the last treatment (PHI=3), except for the trial located in Haps which was a decline trial with PHIs of 0, 1, 3, and 7 days.

One sample of tomato was collected from one treated plot and one untreated plot, except for the trial located in Haps (PHI=0) and the trial located in Siebengewald, in which duplicate samples were collected. Specimens were stored frozen and shipped frozen to BCO Analytical Services B.V.,

Bergschot, Breda, Netherlands. Samples were homogenized in a blender and stored frozen until analysis (< 19 months).

The analytical method assayed residues of triflumizole and FM-6-1, with quantitation by HPLC/UV. The results are reported as combined residues. The LOQ was 0.01 mg eq/kg. Average recovery of all fortifications was $93.3 \pm 5.6\%$ (n=6) for tomatoes. All control samples had residues below the limit of quantitation of the method. Tomatoes treated with the triflumizole EC formulation had detectable residues.

A total of four supervised trials on tomatoes were conducted in Belgium in 1995 and 1996. Trials were conducted in greenhouses in Onze-Lieve-Vrouw-Waver (one), St. Katelijne-Waver (two), and Duffel (one). Trials were reported in van de Ruit 1997.

At each trial, plots received three foliar applications of the triflumizole EC formulation containing 158 g ai/L. All applications were made at a rate of approximately 0.308 to 0.319 kg ai/ha per application. Applications were made on a 7-day schedule until tomatoes were ready to be harvested. The tomatoes were harvested 3 days after the last treatment (PHI=3), except for the trial located in Onze-Lieve-Vrouw-Waver which was a decline trial with PHIs of 0, 1, 3, and 7 days.

One sample of tomato was collected from one treated plot and one untreated plot, except for the trial located in Duffel in which three samples were collected from the treated plot and two samples were collected from the untreated plot. Specimens were stored frozen and shipped frozen to BCO Analytical Services B.V., Bergschot, Breda, Netherlands. Samples were homogenized in a blender and stored frozen until analysis (< 19 months).

The analytical method assayed residues of triflumizole and FM-6-1, with quantitation by HPLC/UV. Results are reported as combined residues. The LOQ was 0.01 mg eq/kg. Average recovery of all fortifications was $93.3 \pm 5.6\%$ (n=6) for tomatoes. All control samples had residues below the limit of quantitation of the method. Tomatoes treated with the triflumizole EC formulation had detectable residues.

Table 53 Summary of triflumizole residue data in tomatoes

		Use Pattern						
Trial ID/ Country/Year	Form.	Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT	Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
USA (Greenhouse; Residue by common-moiety)								
USA GAP		0.28	n.s.	5–10	0	–	–	Label
09299/ USA, Parlier, CA/2010	SC	0.28–0.29	0.059–0.060	4	0	< 0.50 ^a , < 0.50 ^a	< 0.50	09299 Barney, 2012
					1	< 0.50 ^a , < 0.50 ^a	< 0.50	
					4	< 0.50 ^a , < 0.50 ^a	< 0.50	
					8	< 0.50 ^a , < 0.50 ^a	< 0.50	
					10	< 0.50 ^a , < 0.50 ^a	< 0.50	
					15	< 0.50 ^a , < 0.50 ^a	< 0.50	
09299/ USA, Salisbury, MD/2010	SC	0.26	0.023	4	0	< 0.50 ^a , < 0.50 ^a	< 0.50	
09299/ USA, Weslaco, TX/2010	SC	0.29	0.034–0.035	5	0	< 0.50 ^a , 0.67	0.59	

Trial ID/ Country/Year	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
09299/ USA, Arlington, WI/2010	SC	0.28–0.29	0.039–0.044	4	0	0.63 , 0.88	0.76	
Netherlands (Greenhouse; Residue=triflumizole + FM-6-1)								
Netherlands GAP		0.225	0.015	1-5	1	–	–	Label
3096040731/ Netherlands, Haps, Brabant/1996	EC	0.311–0.322	0.016	3	0	0.63	0.63	3096040731 van de Ruit, 1997
					1	0.94	0.94	
					3	0.78	0.78	
					7	0.51	0.51	
3096040731/ Netherlands, Siebengewald, Limburg /1996	EC	0.313–0.322	0.016	3	3	0.20	0.20	
3096040731/ Netherlands, Wellerlooi, Limburg /1996	EC	0.314–0.316	0.016	3	3	0.48	0.48	
3096040731/ Netherlands, Wellerlooi, Limburg /1996	EC	0.310–0.316	0.016	3	3	0.48	0.48	
Belgium (Greenhouse; Residue=triflumizole + FM-6-1)								
3096040731/ Belgium, Onze-Lieve- Vrouw-Waver, Antwerpen /1996	EC	0.310–0.314	0.016	3	0	0.26	0.26	3096040731 van de Ruit, 1997
					1	0.20	0.20	
					3	0.18	0.18	
					7	0.27	0.27	
3096040731/ Belgium, St. Katelijne- Waver, Antwerpen /1996	EC	0.308–0.316	0.016	3	3	0.21	0.21	
3096040731/ Belgium, Duffel, Antwerpen /1996	EC	0.314–0.318	0.016	3	3	0.36, 0.38, 0.30	0.35	
3096040731/ Belgium, St. Katelijne- Waver, Antwerpen /1996	EC	0.314–0.319	0.016	3	3	0.14	0.14	

^a 0.50 mg eq/kg was used to calculate the average residue.

Leafy vegetables (Including brassica leafy vegetables)

The critical GAP in the USA is 2–3 applications at 0.28 kg ai/ha at a 14-day interval. The maximum seasonal use rate is 0.63 kg ai/ha. The PHIs are 0 days for leafy vegetables and 1 day for Brassica leafy vegetables.

Lettuce

A total of 17 supervised trials on head and leaf lettuce were conducted in USA from 2003 to 2006. Trials were conducted in Texas (one), Maryland (one), New Jersey (two), California (eight), New Mexico (two), Georgia (two), and Colorado (one). Once New Jersey trial and the Colorado trial were conducted in a greenhouse. Trials were reported by Gaydosh 2004b and Barney 2007e.

The trial reported by Gaydosh 2004b received five foliar applications of the triflumizole 50WS formulation containing 501 g ai/kg. Trials reported by Barney 2007e received four foliar applications of triflumizole 480SC formulation containing 453 g ai/kg. All applications were made at a rate of approximately 0.27 to 0.59 kg ai/ha per application. Applications were made on a 6-day to 9-day schedule until lettuce was ready to be harvested. The lettuce was harvested 0 days after the last treatment (PHI=0), except for the AWD-03906 trial, which was a decline trial with PHIs of 1, 3, and 7 days, and the 05-NM05 and 05-CA27 trials, which was a decline trial with PHIs of 0, 2–3, 7–8, and 14 days.

Two to three samples of lettuce each were collected from one treated plot and one untreated plot. Specimens were stored frozen and shipped frozen to Morse Laboratories, Inc., Sacramento, California, or to Cornell Analytical Laboratories, Geneva, New York. Samples were processed with dry ice in a Hobart grinder or Hobart FP 30011 stored frozen until analysis (< approximately 2 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/MSD. The LOQ was 0.05 mg eq/kg. Average recovery of all fortifications was $74 \pm 4\%$ (n=12) for Gaydosh 2004b and $90 \pm 19\%$ (n=8) for Barney 2007e. All control samples had residues below the limit of quantitation of the method. Lettuce treated with the triflumizole 50WS formulation and the triflumizole 480SC formulation had detectable residues.

Table 54 Summary of triflumizole residue data in lettuce

Trial ID/ Country/Year	Lettuce Type	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
USA GAP	–		0.28	n.s.	2–3	0	–	–	Label
RP-03005/ USA, Uvalde, TX/2003	n.s.	WS	0.55–0.59	0.201–0.250	5	1	4.8, 5.8, 6.3	5.6	RP-03005 Gaydosh, 2004b
						3	3.6, 2.4, 2.6	2.9	
						7	0.34, 0.32, 0.39	0.35	
08993/ USA, Salisbury, MD/2005	Head	SC	0.28–0.29	0.086	4	0	3.0, 2.0	2.5	08993 Barney, 2007e
08993/ USA, Bridgeton, NJ/2005	Head	SC	0.28–0.31	0.087	4	0	2.1, 3.7	2.9	
08993/ USA, Salinas, CA/2005	Head	SC	0.28	0.050–0.086	4	0	1.2, 1.4	1.3	
08993/ USA, Salinas, CA/2005	Head	SC	0.27–0.29	0.050–0.079	4	0	1.2, 0.68	0.94	

Trial ID/ Country/Year	Lettuce Type	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
			Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
08993/ USA, Holtville, CA/2006	Head	SC	0.28–0.29	0.111–0.117	4	0	6.9, 8.3	7.6	
08993/ USA, Five Points, CA/2006	Head	SC	0.28–0.29	0.100	4	0	1.0, 0.99	1.0	
08993/ USA, near Mesilla, NM/2005	Head	SC	0.28	0.056	4	0	4.6, 4.5	4.6	
						3	0.40, 1.1	0.75	
						7	0.78, 0.42	0.60	
						14	0.08, 0.11	0.09	
08993/ USA, Tifton, GA/2005	Leaf	SC	0.28	0.094	4	0	11, 10	11	
08993/ USA, Tifton, GA/2005	Leaf	SC	0.28	0.094	4	0	17, 16	17	
08993/ USA, Salinas, CA/2005	Leaf	SC	0.28–0.29	0.051–0.073	4	0	1.2, 1.4	1.3	
08993/ USA, Salinas, CA/2005	Leaf	SC	0.27–0.29	0.069–0.085	4	0	18, 24	21	
08993/ USA, Holtville, CA/2005– 2006	Leaf	SC	0.28–0.29	0.109–0.117	4	0	18, 17	18	
						2	13, 16	15	
						8	7.0, 9.1	8.1	
						14	4.4, 2.8	3.6	
08993/ USA, Parlier, CA/2005	Leaf	SC	0.28	0.099–0.100	4	0	3.2, 4.8	4.0	
08993/ USA, near Mesilla, NM/2005	Leaf	SC	0.28–0.29	0.201–0.202	4	0	6.3, 4.6	5.5	
08993/ USA, Bridgeton, NJ/2005	Leaf (Green- house)	SC	0.27–0.30	0.058	4	0	9.6, 9.3	9.5	
08993/ USA, Fort Collins, CO/2005	Leaf (Green- house)	SC	0.28–0.29	0.149–0.150	4	0	17, 12	15	

Mustard greens

A total of ten supervised trials on mustard greens were conducted in the USA from 2004 to 2005. Trials were conducted in New Jersey (one), Maryland (one), Wisconsin (one), Georgia (one), Texas (one), Florida (one), North Carolina (one), Tennessee (one), and California (two). Trials were reported by Barney 2006.

At each trial, plots received four foliar applications of the triflumizole 50WS formulation containing 500 g ai/kg. All applications were made at a rate of approximately 0.27 to 0.29 kg ai/ha per application. Applications were made on a 6- to 10-day schedule until mustard greens were ready to be harvested. The mustard greens were harvested 1 day after the last treatment (PHI=1), except for the New Jersey trial, which was a decline trial with PHIs of 0, 1, 4, and 6 days.

Two samples of mustard greens were collected from one treated plot and one untreated plot. Specimens were stored frozen and shipped to Morse Laboratories, Inc., Sacramento, California. Samples were processed with dry ice in a Hobart food grinder and stored frozen until analysis (< 7 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/MSD. The LOQ was 0.05 mg eq/kg. Average recovery of all fortifications was $84.6 \pm 6.4\%$ (n=9) for mustard greens. All control samples had residues below the limit of quantitation of the method. Mustard greens treated with the triflumizole 50WS formulation had detectable residues.

Table 55 Summary of triflumizole residue data in mustard greens

Trial ID/ Country/Year	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
USA GAP		0.28	n.s.	2–3	0	–	–	Label
08865/ USA, Bridgeton, NJ/2004	WS	0.27–0.28	0.144–0.145	4	0	6.9, 4.5	5.7	08865 Barney, 2006 ^a
					1	0.99, 1.4	1.2	^a
					4	1.2, 0.64	0.91	^a
					6	0.59, 0.56	0.57	^a
08865/ USA, Salisbury, MD/2004	WS	0.27–0.28	0.134–0.136	4	1	8.0, 13	11	^a
08865/ USA, Arlington, WI/2004	WS	0.28–0.29	0.108–0.111	4	1	3.7, 3.8	3.8	^a
08865/ USA, Tifton, GA/2004	WS	0.28–0.29	0.062–0.093	4	1	12, 6.3	8.9	^a
08865/ USA, Weslaco, TX/2004	WS	0.28	0.066–0.099	4	1	2.7, 3.5	3.1	^a
08865/ USA, Citra, FL/2004	WS	0.28–0.29	0.086	4	1	13, 18	15	^a
08865/ USA, Clinton, NC/2004	WS	0.28–0.29	0.096–0.097	4	1	2.3, 4.1	3.2	^a
08865/ USA, Jackson, TN/2004	WS	0.28	0.107–0.109	4	1	13, 11	12	^a
08865/ USA, Salinas, CA/2004	WS	0.28–0.29	0.064–0.070	4	1	4.9, 4.3	4.6	^a

Trial ID/ Country/Year	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
08865/ USA, Holtville, CA/2004–2005	WS	0.27–0.28	0.109–0.114	4	1	4.1, 6.7	5.4	^a

Swiss chard

A total of three supervised trials on Swiss chard were conducted in the USA in 2005. Trials were conducted in Maryland (one), Texas (one), and Oregon (one). Trials were reported by Barney 2007g.

At each trial, plots received four foliar applications of the triflumizole 480SC formulation containing 453 g ai/L. All applications were made at a rate of approximately 0.28 to 0.29 kg ai/ha per application. Applications were made on a 6-day to 8-day schedule until Swiss chard was ready to be harvested. The Swiss chard was harvested 0 day after the last treatment (PHI=0).

Two samples of Swiss chard each were collected from one treated plot and one untreated plot. Specimens were stored frozen and shipped frozen to Cornell Analytical Laboratories, Geneva, New York. Samples were processed with dry ice in a Hobart chopper and stored frozen until analysis (< 7 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/MSD. The LOQ was 0.066 mg eq/kg, and the LOD was 0.022 mg eq/kg. Average recovery of all fortifications was $93 \pm 16\%$ (n=19) for Swiss chard. All control samples had residues at or below the limit of quantitation of the method. Swiss chard treated with the triflumizole 480SC formulation had detectable residues.

Table 56 Summary of triflumizole residue data in Swiss chard

Trial ID/ Country/Year	Form.	Use Pattern				Residue (mg eq/kg)	MRL GAP Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
USA GAP		0.28	n.s.	2–3	0	—	—	Label
08867/USA, Salisbury, MD/2005	SC	0.28	0.126	4	0	7.7, 9.2	8.5	08867 Barney, 2007g ^a
08867/USA, Weslaco, TX/2005	SC	0.28	0.093	4	0	2.2, 3.1	2.7	^a
08867/USA, Aurora, OR/2005	SC	0.28–0.29	0.165–0.166	4	0	5.4, 5.3	5.4	^a

Turnip greens

One supervised trial on turnip greens was conducted in the USA in 2003. The trial was conducted in Texas and was reported by Gaydosh 2004c.

The treated plot received five foliar applications of the triflumizole 50WS formulation containing 501 g ai/kg. All applications were made at a rate of approximately 0.27 to 0.30 kg ai/ha per application. Applications were made on a 7-day schedule until turnip greens were ready to be harvested. The turnip greens were harvested 1, 3, and 7 days after the last treatment.

Specimens were stored frozen and shipped frozen to Morse Laboratories, Inc., Sacramento, California. Samples were processed with dry ice in a Hobart food grinder and stored frozen until analysis (< 4 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/MSD. The LOQ was 0.05 mg eq/kg, and the LOD was not determined. Average recovery of all fortifications was $91 \pm 12\%$ ($n=5$). All control samples had residues at or below the limit of quantitation of the method. Turnip greens treated with the triflumizole 50WS formulation had detectable residues.

Table 57 Summary of triflumizole residue data in turnip greens

Trial ID/Country/Year	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
USA GAP		0.28	n.s.	(5–10)	0	–	–	Label
RP-03004/USA, Uvalde, TX/2003	WS	0.27–0.30	0.100–0.127	5	Top			RP-03004
					1	4.3, 8.9, 8.1	7.1	Gaydosh, 2004c
					3	3.6, 2.9, 2.4	3.0	
					7	0.88, 0.78, 0.50	0.72	
					Root			
					1	0.15, 0.10, 0.15	0.13	
					3	0.13, 0.12, 0.11	0.12	
					7	0.098, 0.17, 0.08	0.12	

Tree nuts

Hazelnuts

A total of three supervised trials on hazelnuts (filberts) were conducted in the USA in 2001. Trials were conducted in Oregon. Trials were reported by Thompson 2002.

At each trial, plots received six foliar applications of the triflumizole 50WS formulation containing 500 g ai/kg. All applications were made at a rate of approximately 0.80 to 0.87 kg ai/ha per application. Applications were made on a 13-day to 111-day schedule until hazelnuts were ready to be harvested. The hazelnuts were harvested approximately 18 days after the last treatment.

Two samples of hazelnuts each were collected from one treated plot and one untreated plot. Specimens were stored frozen and shipped frozen to Morse Laboratories, Inc., Sacramento, California. Nutmeat samples were processed with dry ice in a Hobart food grinder and stored frozen until analysis (< 4 months).

The analytical method assayed triflumizole and its aniline-containing metabolites, with quantitation by GC/MSD. The LOQ was 0.05 mg eq/kg for triflumizole and for FA-1-1, and the estimated LOD was 0.01 mg eq/kg for triflumizole and 0.02 mg eq/kg for FA-1-1. Average recovery of all fortifications was $91 \pm 8\%$ ($n=9$) for triflumizole and $88 \pm 9\%$ ($n=9$) for FA-1-1. All control samples had residues below the limit of quantitation of the method. Hazelnuts treated with the triflumizole 50WS formulation had no detectable residues above the LOQ.

Table 58 Summary of triflumizole residue data in hazelnuts

Trial ID/Country/Year ^a	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
USA GAP		0.21	n.s.	(4–6)	18	–	–	Label
07996/USA, Aurora, OR/2001	WS	0.86–0.87	0.050–0.073	6	18	< 0.05, < 0.05	< 0.05	07996 Thompson, 2002
07996/USA, Aurora, OR/2001	WS	0.80–0.87	0.051–0.072	6	18	< 0.05, < 0.05	< 0.05	

Trial ID/ Country/Year ^a	Form.	Use Pattern				Residue (mg eq/kg)	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)	No. of Appl.	DAT			
07996/USA, Aurora, OR/2001	WS	0.84–0.86	0.051–0.073	6	19	< 0.05, < 0.05	< 0.05	

^a Trials were conducted in the same orchard complex. One trial was on young, vigorous trees with large nuts, the second was on older, less vigorous trees with smaller nuts, and the third was in a different orchard block with different soil type and trees of an intermediate age.

Dried Herbs

Hops

A total of eight supervised trials on hops were conducted in the USA from 2002 to 2011, from three separate residue studies (#10798/RP-02011, 2006-008, and #10798). Trials were conducted in Idaho, Oregon, and Washington. Trials were reported by Corley 2012, Barney 2007b, and Barney 2007a.

Trials reported in Corley 2012 received three foliar applications of the triflumizole 480SC formulation containing 424.7 g ai/L. Trials reported by Barney 2007b received four foliar applications of the triflumizole 50WS formulation containing 503 g ai/kg. One of two trials reported by Barney 2007a received four foliar applications of the triflumizole 50WS formulation containing 509 g ai/kg, and the second trial received four foliar applications of the triflumizole 480SC formulation containing 430 g ai/L. All applications were made at a rate of approximately 0.42 to 0.58 kg ai/ha per application. Applications were made on a 10-day to 14-day schedule until hops were ready to be harvested. The hops were harvested 7 and 13–14 days after the last treatment (PHI=7, 13–14), except for the OR40 and WA 36 trials, which only had PHIs of 7, and the ID18 and WA35 trials, which was a decline trial with PHIs of 0, 3, 7–8, 14, and 21 days.

Samples of hops were collected from one treated plot and one untreated plot, except for the trial reported in Barney 2007a, which had two treated plots. Specimens were dried in a hop kiln (time not specified; ≤ 3 –6 days based on transport dates) stored frozen and shipped frozen to IR-4 Western Region Laboratory, Davis, California, or Morse Laboratories, Inc., Sacramento, California. Samples were processed with a Geno/Grinder or with dry ice in a Rietz disintegrator. Samples were stored frozen from harvest until analysis (< 5 months Corley or < 27 months Barney).

For sample analysis, residue data from Corley 2012 were obtained using two separate analytical procedures, with one measuring triflumizole and FM-6-1 separately by LC-MS/MS, while the second method determined the total triflumizole equivalents by GC-MS (i.e., triflumizole and aniline-containing metabolites that were converted to FA-1-1, and expressed as triflumizole equivalents). The method used (Barney 2007a and Barney 2007b) also determined the total triflumizole by GC-MS. The LOQs were 0.050 mg eq/kg (Corley 2012), 0.01 mg eq/kg (Barney 2007b), or 0.02 mg eq/kg (Barney 2007a). Average recovery of all fortifications was $90.0 \pm 18.1\%$ ($n=37$) for Corley 2012 or $97.6 \pm 5.1\%$ ($n=18$) for Corley 2012, $81.5 \pm 13.0\%$ ($n=6$) for Barney 2007b and $79.2 \pm 6.4\%$ ($n=6$) for Barney 2007a. All control samples had residues at or below the limit of quantitation of the method. Hops treated with the 480SC formulation and the 50WS formulation had detectable residues.

Table 59 Summary of triflumizole residue data in dry hops

Trial ID/Country/Year	Form.	Use Pattern		No. of Appl.	DAT	Residue (mg eq/kg) A	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)					
USA GAP		0.42	n.s.	3	7	—		Label
10798/USA, Parma, ID/2011 (New Port)	SC	0.42– 0.43	0.075	3	0	10, 13	12	10798 Corley, 2012 Common/moiety

Trial ID/Country/Year	Form.	Use Pattern		No. of Appl.	DAT	Residue (mg eq/kg) A	Average Residue (mg eq/kg)	Reference, remarks
		Rate (kg ai/ha)	Rate (kg ai/hL)					
					3	10, 11	11	Common/moiety
					8	7, 6	6.5	Common/moiety
					14	8, 6	7	Common/moiety
					21	6.4, 5.3	5.9	Common/moiety
					0	6.5	6.5	Triflumizole + FM-6-1
					3	3.8	3.8	Triflumizole + FM-6-1
					8	1.7	1.7	Triflumizole + FM-6-1
					14	1.2	1.2	Triflumizole + FM-6-1
					21	0.9	0.9	Triflumizole + FM-6-1
10798/USA, Hubbard, OR/2011 (Nugget)	SC	0.43–0.44	0.082	3	7	12, 8.1	10.1	Common/moiety
					7	3.5	3.5	Triflumizole + FM-6-1
10798/USA, Prosser, WA/2011 (Nugget)	SC	0.43–0.45	0.027–0.028	3	0	18, 20	19	Common/moiety
					3	12, 13	13	Common/moiety
					7	12, 9.9	11	Common/moiety
					14	8.9, 8.3	8.6	Common/moiety
					21	6.6, 7	6.8	Common/moiety
					0	9.3	9.3	Triflumizole + FM-6-1
					3	4.4	4.4	Triflumizole + FM-6-1
					7	2.9	2.9	Triflumizole + FM-6-1
					14	1.5	1.5	Triflumizole + FM-6-1
					21	1.3	1.3	Triflumizole + FM-6-1
10798/USA, Prosser, WA/2011 (Willamette)	SC	0.42–0.44	0.024	3	7	7.6, 7.9	7.8	Common/moiety
					7	1.4	1.4	Triflumizole + FM-6-1
08967/USA, Zillah, WA/2002	WS	0.54–0.58	0.12	4	7	8.8, 6.4, 8.5	7.9	08967 Barney, 2007b
					14	7.1, 3.6, 7.4	6.0	
08967/USA, Woodburn, OR/2002	WS	0.56–0.57	0.12	4	6	16, 4.6	11	
					13	7.5, 6.4	7.0	
2006–2008/USA, Greenleaf, ID/2006 (Zeus)	WS	0.56–0.57	0.06	4	7	17, 26, 24	22	2006–2008 Barney, 2007a
					14	22, 21, 23	21	
2006–2008/USA, Greenleaf, ID/2006 (Zeus)	SC	0.56–0.57	0.06	4	7	17, 15, 14	15	
					14	14, 13, 12	13	

FATE OF RESIDUES IN STORAGE AND PROCESSING

In Processing

The Meeting received data depicting the effects of processing on residue levels in apple and grape processed commodities. For apples, processing factors have been calculated for juice, sauce, and wet and dry pomace. For grapes, processing factors have been calculated for juice, raisins (and related commodities), stems, and wet and dry pomace.

Apples

A processing study on apples was conducted from samples taken in three field trials located in commercial apple growing areas of the United States (Ball 1986c). In those trials, the treated plots each received four applications of triflumizole 50W at a rate of 0.56 kg ai/ha (0.5 lb ai/acre), which represents 1–2× the recommended label rate, or 1.12 kg ai/ha (1.0 lb ai/acre), which represents 2–4× the recommended label rate. Samples were collected 14 days after the last treatment. One sample was taken at each treated plot for processing into juice, sauce, wet pomace, and dry pomace. Processed commodities were produced by grinding and pressing, using a procedure that simulated commercial practice. Processed samples and a retained whole apple sample were shipped frozen to the laboratory, where the samples remained frozen until being assayed for total triflumizole via GC analysis.

The method was validated prior to analysis with a limit of quantitation of 0.02 mg eq/kg in all matrices. The performance of the method was also demonstrated during analysis of the samples by analysing fortified control matrices concurrently with experimental samples. The recoveries were 62% for whole unwashed apples, 125% for apple juice, 85% for apple sauce, 106% for wet pomace, and 96% for dry pomace. The overall mean concurrent recovery for all matrices was $95 \pm 25\%$ (n=5).

The results of the processing study are summarized in Table . Results indicate that residues did not concentrate in apple juice, sauce, or wet pomace, but was concentrated in dry apple pomace during processing.

Table 60 Processing factors for residues of triflumizole in apple processed fractions

Processed Fraction	Residues (mg eq/kg)		Processing Factors	Reference
	Apple (RAC)	Fraction		
Juice	< 0.02	0.04	Not determined	Ball 1986c (UR1302)
	0.16	0.04	0.25	
	0.24	0.05	0.21	
	0.18	0.04	0.22	
	0.34	0.08	0.24	
	Average		0.23	
Sauce	< 0.02	0.02	Not determined	
	0.16	0.02	0.13	
	0.24	0.02	0.08	
	0.18	0.05	0.28	
	0.34	0.31	0.91	
	Average		0.35	
Pomace, wet	< 0.02	0.18	Not determined	
	0.16	0.16	1.0	
	0.24	0.20	0.83	
	0.18	0.17	0.94	
	0.34	0.28	0.82	
	Average		0.90	
Pomace, dry	< 0.02	0.45	Not determined	
	0.16	0.50	3.13	
	0.24	0.62	2.58	
	0.18	0.10	0.56	
	0.34	0.13	0.38	
	Average		1.67	

Grapes

A processing study on grapes was conducted from samples taken in nine field trials located in commercial grape growing areas of the United States (Ball 1986b and Ball 1988c). Each field trial site consisted of control and treated plots. The treated plots each received four applications of triflumizole 50W at a rate of 0.28 kg ai/ha (0.25 lb ai/acre), which represents 1–2× the recommended label rate, except for the trials located in Portland, New York which received three applications.

Samples were collected 7 days after the last treatment. One sample was taken at each treated plot for processing into wet pomace, dry pomace, raisins (washed and unwashed), stems, and juice. Two samples were taken at the plot treated with triflumizole 50W at a rate of 0.56 kg ai/ha for processing into raisin waste. Samples were processed by grinding and pressing, using a procedure that simulated commercial practice. Processed samples and a retained whole grape sample were shipped frozen to the laboratory, where the samples remained frozen until analysis.

Combined residues of triflumizole and its aniline-containing metabolites were analysed in the different grape matrices using a validated analytical method with residue determinations made by HPLC (Ball 1986b) or GC (Ball 1988c). The method was validated prior to sample analysis. The performance of the method was also demonstrated during analysis of the samples by analysing fortified control matrices concurrently with experimental samples. The overall mean recoveries were 80–84% for whole grapes, 92–101% for wet pomace, 78–98.2% for dry pomace, 94% for raisins, 64% for stems, and 116% for juice. The overall mean concurrent recovery for all matrices was $88 \pm 14\%$ (n=11).

The results of the processing study are summarized in Table . Results indicate that residues in raisins (washed and unwashed), grape juice and raisin waste are reduced, but those in wet and dry grape pomace and grape stems were concentrated during processing.

Table 61 Processing factors for residues of triflumizole in grape processed fractions

Processed Fraction	Residues (mg eq/kg)		Processing Factors	Reference
	Grape (RAC)	Fraction		
Pomace, wet	0.09	0.07	0.78	Ball 1986b (UR1304)
	0.10	0.13	1.30	
	0.15	0.12	0.80	
	0.94	6.20	6.60	
	0.09	0.60	6.67	
	0.09	0.88	9.78	
	Average		4.32	
Pomace, dry	0.09	0.20	2.22	
	0.10	0.63	6.30	
	0.15	0.12	0.80	
	0.94	7.83	8.33	
	0.09	0.69	7.67	
	0.09	1.12	12.44	
	Average		6.29	
Raisins	0.18	0.03	0.17	
	0.15	0.04	0.27	
	Average		0.22	
Stems	0.18	0.68	3.78	
	0.15	0.38	2.53	
	Average		3.16	
Juice	0.94	0.24	0.26	
	0.09	0.03	0.33	
	0.09	0.06	0.67	
	Average		0.42	
Unwashed raisins	0.21	0.11	0.52	Ball 1988c (UR1308)
	0.31	0.07	0.23	
	Average		0.37	
Washed raisins	0.21	0.05	0.24	
	0.31	< 0.02	>0.06	
	Average		0.15	
Raisin Waste	0.21	< 0.02	>0.10	
	0.31	0.17, 0.22 (Avg.=0.20)	0.65	
	Average		0.37	

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

The Meeting received a lactating dairy cow feeding study (Parkins, 1988). The only crop with potential impact to the poultry dietary burden is cabbage; this crop represents 5% of the poultry diet in the EU only, which is of minimal impact. Therefore, a poultry feeding study has not been submitted.

Lactating dairy cows

Six dairy cows were dosed, for 28 consecutive days, orally via gelatin capsules containing technical triflumizole. The cows were randomly divided into two groups of three, each group receiving one of the following feeding levels: 10 ppm (low dose) and 50 ppm (high dose) of triflumizole in the diet. An additional two cows served as control animals. Samples of milk were taken each morning and evening. At the end of the experiment, the animals were sacrificed and samples of muscle, fat, entire liver and both kidneys were taken for analysis.

Samples from the low-dose group and the high-dose group were analysed for residues containing the 2-amino-3-trifluoro-methyl-4-chloroaniline (FA-1-1) moiety using gas chromatography with a nitrogen-phosphorus detector (GC-NPD). The limit of determination was 0.01 mg eq/kg. The total residues in milk and cattle tissues were reported as triflumizole (MW: 346) equivalents by converting the analysed FA-1-1 (MW: 195) level using a molecular weight conversion factor of 1.77. The reported LOQ in terms of triflumizole is 0.02 mg eq/kg.

For the high-dose group, the metabolite 2-amino-3-trifluoro-methyl-5-chlorophenol (FA-1-5) was also analysed using HPLC with electrochemical detection. Recoveries from milk fortified with either 0.01 mg eq/kg or 0.05 mg eq/kg FA-1-1 averaged 86.3% and 86.8%, respectively; for FA-1-5, concurrent recoveries in milk were 98%, 95% and 97% for spiked levels of 0.1, 0.2, and 0.3 mg eq/kg, respectively. For tissues, the average recoveries of FA-1-1 were 86% for fat, 93% for kidney, 73% for liver, and 85% for muscle. In the fortified samples with FA-1-5, the concurrent recovery in kidney and liver averaged 70%.

During the 28-day feeding period, residues analysed as FA-1-1 in milk samples from the low-dose group were < 0.01 mg eq/L. Residues analysed as FA-1-1 in milk from the high-dose group ranged from 0.01 mg eq/L to 0.06 mg eq/L. On average, residues were fairly consistent in milk after Day 2 of dosing (Table). Residues of FA-1-5 in milk (high-dose group) were < 0.01 mg/L.

Table 62 Total residues in milk (high-dose group)

Time (days)	Triflumizole-Equivalent Residues (mg/L) ^a	FA-1-5
0	< 0.02, < 0.02, < 0.02 [< 0.02]	< 0.01
2	0.04, 0.04, 0.04 [0.04]	< 0.01
4	0.04, 0.04, 0.02 [0.03]	< 0.01
6	0.05, 0.05, 0.04 [0.05]	< 0.01
8	0.04, 0.04, 0.05 [0.04]	< 0.01
10	0.04, 0.04, 0.05 [0.04]	< 0.01
14	0.04, 0.04, 0.02 [0.03]	< 0.01
16	0.04, 0.04, 0.02 [0.03]	< 0.01
18	0.05, 0.04, 0.05 [0.05]	< 0.01
20	0.05, 0.05, 0.07 [0.06]	< 0.01
22	0.04, 0.04, 0.02 [0.03]	< 0.01
26	0.04, 0.05, 0.04 [0.04]	< 0.01
28	0.04, 0.04, 0.11 [0.06]	< 0.01

^a Bracketed values are mean

In tissues, average residues (as triflumizole-equivalents) in the low-dose group were < 0.02 mg eq/kg in muscle, 0.06 mg eq/kg in fat, 0.31 mg eq/kg in kidney, and 0.48 mg eq/kg in liver. In the high-dose group, average tissue residues were 0.09 mg eq/kg in muscle, 0.33 mg eq/kg in fat,

1.55 mg eq/kg in kidney, and 4.25 mg eq/kg in liver (Table 63). No residues of FA-1-5 were found in kidney or liver (LOD=0.03 mg eq/kg).

Table 63 Summary of feeding study results with triflumizole in dairy cattle

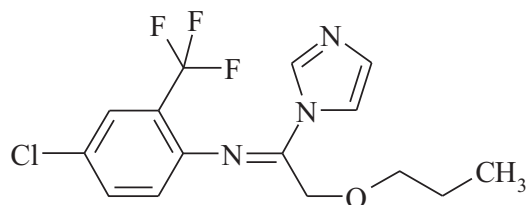
Matrix	Feeding Level (mg eq/kg feed)		
	0	10	50
	Triflumizole-Equivalent Residue (mg eq/kg) ^a		
Fat	< 0.02, < 0.02, < 0.02 [< 0.02 ± 0.00] {-}	0.02, 0.04, 0.12 [0.06 ± 0.05] {0.00560}	0.27, 0.25, 0.48 [0.33 ± 0.13] {0.00661}
Kidney	< 0.02, < 0.02, < 0.02 [< 0.02 ± 0.00] {-}	0.25, 0.21, 0.46 [0.31 ± 0.13] {0.03068}	1.7, 1.3, 1.6 [1.6 ± 0.20] {0.03103}
Liver	< 0.02, < 0.02, < 0.02 [< 0.02 ± 0.00] {-}	0.50, 0.46, 0.50 [0.48 ± 0.02] {0.04838}	3.9, 4.6, 4.2 [4.2 ± 0.35] {0.08496}
Muscle	< 0.02, < 0.02, < 0.02 [< 0.02 ± 0.00] {-}	< 0.02, < 0.02, < 0.02 [< 0.02 ± 0.00] {< 0.002}	0.09, 0.09, 0.11 [0.09 ± 0.01] {0.00189}
Milk	< 0.02-< 0.02 [< 0.02 ± 0.00] {-}	< 0.02-< 0.02 [< 0.02 ± 0.00] {< 0.002}	0.02-0.11 [0.04 ± 0.02] {0.00082}

^a Values in brackets are mean ± std. dev.; values in braces are average matrix:feed ratios. For milk, the range of residues from Day 2 to Day 28 is shown.

APPRAISAL

Residue and analytical aspects of triflumizole were considered for the first time by the present Meeting. The residue evaluation was scheduled for the 2013 JMPR by the Forty-fourth Session of the CCPR.

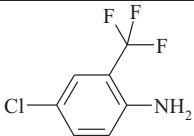
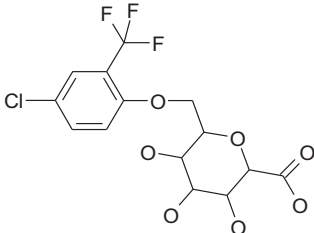
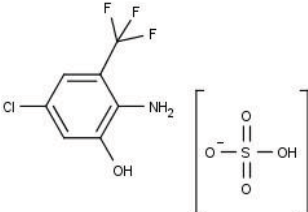
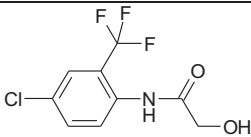
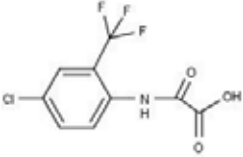
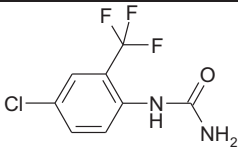
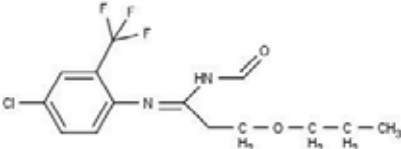
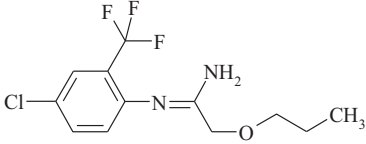
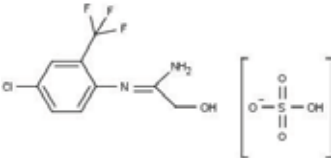
Triflumizole is a broad-spectrum foliar fungicide that controls a variety of fungal diseases in fruits and vegetables. It acts as a protectant and as an eradicant by preventing disease symptoms after infection has occurred. Triflumizole has anti-sporulant activity which reduces spores after lesions become visible. Triflumizole belongs to the demethylation inhibitor (DMI) group of fungicides classified as Group 3 by the Fungicide Resistance Action Committee (FRAC). Triflumizole has protective and curative action, and acts as an inhibitor of chitin biosynthesis. The product is mixed with water and applied as a foliar spray using ground equipment equipped for conventional spraying on crops. The Meeting received information on identity, animal and plant metabolism, environmental fates in soil, rotational crops, analytical methods, storage stability, use patterns, supervised trials, dairy cattle feeding studies, and fates of residues in processing.

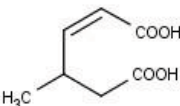
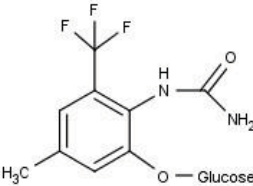


(E)-4-chloro- α,α,α -trifluoro-N-(1-imidazol-1-yl-2-propoxyethylidene)-o-toluidine

In this appraisal, the following abbreviated names were used for metabolites.

Identifier	Chemical Structure

Identifier	Chemical Structure
FA-1-1	
FA-1-glucuronide	
FA-1-5 (Free and sulphate conjugate)	
FD-2-1	
FD-7-1	
FD-9-1	
FM-5-1	
FM-6-1	
FM-8-1 (Free and sulphate conjugate)	

Identifier	Chemical Structure
XIV	
XXVI	

Animal metabolism

The Meeting received animal metabolism studies with triflumizole in rats, lactating goat and laying hens. The metabolism and distribution of triflumizole in animals were investigated using triflumizole universally labelled in the phenyl ring.

In the metabolism studies, rats were dosed at 10 mg/kg bw per day (single and multiple dose studies) or at 300 mg/kg bw per day (single dose study). Metabolite identification in tissues was not provided. The metabolite profile indicates that triflumizole is extensively metabolized in rats: less than 2% of the radiolabel recovered from urine or faeces was identified as parent compound. A few differences in metabolite pattern were observed between males and females after repeated low and single high doses, but not after a single low dose. The major urinary metabolites are the sulphate conjugates of N-(4-chloro-2-trifluoromethylphenyl)-2-hydroxy-acetamidine (FM-8-1) and 2-amino-5-chloro-3-trifluoromethylphenol (FA-1-5). In faeces, N-(4-chloro-2-trifluoromethylphenyl)-2-hydroxy-acetamide (FD-2-1) is a major metabolite. Differences between dose regimens exist with respect to other major metabolites. 2-(4-Chloro-2- trifluoromethylphenylimino)- 2-imidazol- 1-yl-ethanol (FM-2-1) is the major metabolite after a single oral low dose, 4-Chloro-2-trifluoromethylphenylamine (FA-1-1) is a major metabolite after single and repeated low dosing, whereas N-(4-chloro-2-trifluoromethylphenyl)-2-propoxy-acetamide (FD-1-1) is the major metabolite after a single high dose. The presence of the metabolite N-(4-chloro-2-trifluoromethylphenyl)- 2-propoxy-acetamidine (FM-6-1) was confirmed in rat faeces and urine.

Lactating goat was dosed with [^{14}C]triflumizole at a dose equivalent to approximately 280 ppm in the diet twice daily for 5 consecutive days. Gelatine capsules containing [^{14}C]triflumizole were administered orally via a balling gun. The majority of the dose was rapidly excreted in urine (56% of the TAR) and faeces (19.9% TAR).

Total radioactive residues (TRR) in the milk accounted for 0.18% TAR. Tissues contained approximately 0.65% TAR. Total material balance was 76.7% TAR, with an additional 5–12% TAR estimated to be in the bladder, digestive tract and carcass; $^{14}\text{CO}_2$ was not monitored.

Levels of radiolabel material reached a plateau in milk within approximately 24 hours and account for approximately 0.16% TAR. TRR was highest in liver and kidney (11.3 and 3.4 mg eq/kg, respectively) and approximately an order of magnitude lower in muscle (0.3 mg eq/kg) and fat (0.66 mg eq/kg). The residue in liver accounted for 0.4% TAR.

Triflumizole was not detected in any matrix. Major residues in liver were FA-1-1 (79.2% TRR, of which 54.8% TRR was bound) and FA-1-5-sulphate (12.4% TRR). In milk, major residues were FA-1-5-sulphate (29.1% TRR), FA-1-5-glucuronide (11.8% TRR), FD-2-1 (10.4% TRR), and FM-8-1-sulphate (12.6% TRR). No other individual compounds accounted for more than 10% of the TRR. The study noted that residues in other matrices were not identified due to low radioactivity; however, it is unclear why further characterization/identification was not done in muscle and liver given the level of residues in those tissues (0.3 and 0.66 mg eq/kg, respectively).

Laying hens were orally dosed with [^{14}C]triflumizole at a dose equivalent to 39 (3 hens) or 53 (2 hens) ppm in the diet twice daily for 5 consecutive days. The majority of the dose was rapidly eliminated in the excreta. Average radioactive residues in the excreta and cage wash accounted for 85.3% of the total administered dose.

Total ^{14}C residues in eggs did not plateau during the dosing period. Egg yolk and white were assayed separately for the eggs from hens treated at 53 ppm. Initially, TRR levels were greater in egg white than in the yolk; however, by Day 3 of dosing residues in yolk were much greater than in the egg white. On Day 5, residues in whole eggs from hens treated at 39 ppm ranged from 0.215 to 0.431 mg eq/kg. Residues ranged from 0.899 to 2.312 mg eq/kg in egg yolk and from 0.074 to 0.408 mg eq/kg in egg white. Residues in tissues from hens treated at the lower rate were consistently lower than those from hens treated at the higher rate. At the lower rate, residue ranges (mg eq/kg) were 0.989–1.232 in liver, 0.537–0.677 in kidney, 0.050–0.067 in fat, 0.017–0.047 in leg muscle, and 0.026–0.049 in breast muscle. At the higher rate, residues (mg eq/kg) were 0.781 and 1.115 in kidney, 0.312 and 0.358 in fat, 0.066 and 0.073 in leg muscle, and 0.054 and 0.087 in breast muscle; liver samples were used for metabolite identification and were not assayed for total radioactivity.

Major residues identified in egg white/yolk consisted of triflumizole (13.4/3.7% TRR), FD-6-1 or FD-4-1 (12.6/3.0% TRR), and FA-1-1 (35.3/22.1% TRR). Volatility of FA-1-1 resulted in some evaporative losses of that analyte. Unextracted residues accounted for 17.2 and 39.8% TRR in egg white and yolk, respectively. All other identified or characterized residues were less than approximately 4% TRR. Analysis of the liver samples indicated that the only metabolite was FA-1-1 or a compound convertible to FA-1-1 during proteolytic digestion.

In animal metabolism studies, triflumizole was metabolized to several compounds. The majority of the dosed radioactivity was excreted and radioactive residues in tissues were generally low. Triflumizole was identified as a residue in egg whites only. Metabolite FA-1-1 was the most prominent component in liver and egg. Sulphur- and glucuronide-conjugated FA-1-5 was the most prominent residue in milk.

Plant metabolism

The Meeting received plant metabolism studies performed on apple, pear, grape, and cucumber with triflumizole universally labelled in the phenyl ring.

In the apple metabolism study, trees were grown in a greenhouse and treated by spotting clusters of leaves with the test substance (approximately 0.127 mg/4-leaf cluster). Branches were harvested at 0, 1, 3, 7, 14, 21, 31, 60, and 90 DAT; fruits were not harvested.

Over the 90-day time span, the overall residue decreased from 51.65 mg eq/kg to 3.03 mg eq/kg, with an initial half-life of approximately 4 days, and was associated primarily with the treated leaves. Radioactive residue in the surface wash of treated leaves accounted for the majority of the residue until 14-DAT sampling. By the 14-DAT sampling, over half of the radioactivity in treated leaves was accounted for as extracted residues or associated with the post-extraction solids (PES). Radioactivity in untreated leaves above the treatment location remained relatively constant throughout the study, ranging from 0.04–0.07 mg eq/kg. Residues in untreated leaves below the treatment location showed a small increase in levels with time, with a maximum of 0.24 mg eq/kg at the 21-DAT sampling. In treated leaves, the only major (> 10% TRR) identified compounds that appeared consistently in the residue profile were triflumizole (0.02–0.12 mg eq/kg) and FM-6-1 (1.2–31% TRR, 0.01–0.02 mg eq/kg); FD-2-1 accounted for 12.6% TRR (< 0.01 mg eq/kg) at the 90-DAT sampling. As overall residues of radiocarbon declined with increasing time after treatment FD-2-1, unidentified metabolites and the contribution from PES became more prominent in the residue profile in terms of %TRR.

In the pear metabolism study, pear trees grown in a greenhouse were treated with test substance by spotting leaves (approximately 1 mg/4-leaf cluster) or the surface of pear fruits (approximately 0.166 mg/fruit) with radiolabelled test substance. Branches from leaf-treated trees

were harvested at 0, 1, 3, 7, 14, 21, 31, 60, and 90 DAT and were divided into treated leaves, untreated leaves, and fruit. Treated fruits were harvested 0, 1, 3, 7, and 14 DAT.

Data from the leaf-treatment samples showed very little movement of radioactivity away from the treated leaves. Radioactivity reached maxima of 0.98% TAR in untreated leaves and 0.18% TAR in untreated fruit. In treated leaves, the majority of the radioactivity was associated with the surface wash through the 31-DAT sampling, at which point extractable residues and PES-associated residues, combined, constitute more than half of the TRR (56% TRR, 5.6 mg eq/kg). As with the apple study, the data show a rapid decline in radiocarbon residues, with an initial half-life of approximately 4 days.

For treated fruit, the vast majority (> 95%) of the radioactive residue was confined to the peel, with very little movement into the flesh or core of the pear. For peel, residues in surface wash were the majority at the 0- and 1-DAT sampling times, after which extractable residues became the most prominent. The data also show a rapid decline in radiocarbon residues, with an initial half-life of between 1 and 3 days, and a slower rate of decline between 3 and 14 DAT.

In leaves, triflumizole and FM-6-1 were the only residues > 10% TRR. After 3 days and for the remainder of the study, FM-6-1 occurred at levels greater than triflumizole, peaking at 0.25 mg eq/kg at 3 DAT. In fruit, major residues were triflumizole (maximum = 93.56% TRR, 1.11 mg eq/kg, 0 DAT), FM-6-1 (maximum = 30.0% TRR, 0.14 mg eq/kg, 7 DAT) and FD-1-1 (10.51% TRR, 0.06 mg eq/kg, 3 DAT).

In the grape metabolism study, grape vines were grown in a greenhouse. Treatments were with triflumizole, uniformly labelled with ^{14}C in the phenyl ring, applied either to a branch of approximately 10 leaves and blossoms approximately 67 days prior to harvesting mature fruit, or to a bunch of young fruits 35 days before harvesting mature fruit. For both treatments, the rate was equivalent to 0.280 kg ai/ha. Treated branches were harvested 0, 3, 7, 14, 31, and 67 DAT and were divided into treated leaves and fruit; treated fruits were harvested 0, 3, 7, 14, and 35 DAT.

Following treatment of leaves, the % TAR decreased from 99% TAR to 15% TAR at 67 DAT. Most of the radioactivity in leaves was recovered from the surface wash, with < 2% TAR being translocated to fruits. Triflumizole was the major residue out to 31 DAT (51% TRR, 8.8 mg eq/kg). The only other major residue was FM-6-1 (11.1% TRR, 0.76 mg eq/kg at 67 DAT). Post-extraction residues in leaves gradually increased from 3.1% TRR (1.73 mg eq/kg) to 26.02% TRR (1.79 mg eq/kg) over the course of the study. Minor metabolites and those remaining at the origin increased to 39% TRR at 67 DAT, with no individual component exceeding 8% TRR.

In treated fruit over the 35-day period of the study, overall radioactivity decreased from 100% TAR (7.79 mg eq/kg) to 24.8% TAR (1.93 mg eq/kg). The majority of the radioactivity in treated fruit was recovered from the surface wash for the 0-, 3-, and 7-DAT samples; at the 14- and 35-DAT sampling points. More of the total residue was associated with extracted and bound residues. At all of the sampling times, the only major residue was triflumizole. FM-6-1 reached a maximum of 7.59% TRR (0.07 mg eq/kg) at 35 DAT, at which point triflumizole constituted 31% TRR (0.31 mg eq/kg).

The cucumber study was conducted under greenhouse conditions. Three types of treatment were made: Foliar treatment to investigate metabolism (0.13 mg/plant), fruit treatment to investigate metabolism (0.041 mg/plant), and foliar treatment to investigate translocation (0.16 mg/plant). In the case of the foliar treatment for metabolism, whole plants were harvested 1, 3, 7, 14, 21, and 45 days after treatment (DAT). For the fruit metabolism and translocation investigations, fruits were harvested 1 (metabolism only), 3, 7, and 14 DAT.

Results from all three lines of investigation demonstrated that the majority of the radioactivity (65–76% of applied) remained on the surface of the harvested material and that there was very little movement of radioactivity within the cucumber plants. Triflumizole accounted for most of the radioactivity through 14 DAT; at 21 DAT and 45 DAT, FM-6-1 residues were approximately equal to those of triflumizole and at 45 DAT, residues of F-8-1 were greater than either triflumizole or FM-6-1 on a % TRR basis. No metabolite exceeded 10% of the TRR except for FM-6-1 approximately 12% TRR, < 0.01 mg eq/kg) at the 7- and 14-DAT sampling times in the cucumber fruit study. In those samples, FM-6-1 was associated with the peel and flesh of the fruit and not the surface wash.

The metabolic profile observed in these studies was similar across all four crops. Over the time course of the studies, triflumizole and FM-6-1 account for the majority of the radioactivity. Generally triflumizole decreased rather rapidly (half-life on the order of 3 days), with the exception of grapes where metabolism was slower (half-life approximately 14 days). Loss of triflumizole was accompanied by an increase in the FM-6-1 metabolite, which was the only metabolite to consistently occur at $\geq 10\%$ TRR.

Environmental fate in soil

The Meeting received information on soil-surface photolysis, soil dissipation, aerobic soil metabolism, and confined and field rotational crop studies.

Under aerobic conditions in soil, the imidazole ring of triflumizole is opened to yield FM-5-1, FD-1-1, and FM-6-1. The resulting amide or amine moiety is then hydrolysed to form the FA-1-1 metabolite, which then becomes associated with bound residues or is oxidized to CO₂. The DT₅₀ was 16–22 days at 20 °C with indoor studies and 7.1–22 days with outdoor studies.

In the soil photolysis study, triflumizole degraded significantly. On average after 11 days of exposure, triflumizole had declined to 30.0% of the AD. This was accompanied by formation of FM-6-1, which reached a maximum of 21.8% TAR after 7 days of exposure to simulated sunlight and then dissipated to 15.6% TAR at Day 11. The metabolites FD-1-1 (3.6% TAR at Day 11), FM-8-1 (1.8% TAR, Day 11), FD-7-1 (8.6% TAR, Day 11), and CO₂ (3.5% TAR, Day 11) were also observed. Bound residues increased over the time course of the study and averaged 18.7% TAR by the end of the 11-day period.

The results of both the aerobic soil and soil photolysis study indicate that triflumizole is not likely to be persistent in the environment.

In the confined rotational crop study, radiolabelled triflumizole was applied to bare soil at approximately 1.4 kg ai/ha (1× GAP; 6 plots) or approximately 12.7 kg ai/ha (10× GAP; 2 plots) and rotational crops of lettuce, radish, and wheat were planted into each. Plant-back intervals (PBIs) were 30, 120, and 365 days for the 1× plots and 30 days for the 10× plots. Radish was sampled for roots and tops, and wheat was sampled for forage, grain, hay, and straw. The 1X plots were used to determine % TRR only and the 10× plots were used to make metabolite identifications (except for 1× samples for wheat forage).

Quantifiable levels of TRR occurred for all crop matrices at all PBIs. Highest values were for wheat straw, starting at 1.65 mg eq/kg at the 30-day PBI and declining to 0.478 mg eq/kg at the 365-day PBI. The lowest values were for lettuce (0.086 to 0.021 mg eq/kg at the 120- and 365-day PBI, respectively). For each crop matrix, the TRR declined when going from shorter to longer PBIs with the exception of lettuce which had a maximum at the 120-day PBI (0.086 mg eq/kg) and wheat grain for which the 365-day PBI TRR (0.067 mg eq/kg) was greater than the 120-day PBI TRR (0.055 mg eq/kg).

Triflumizole underwent extensive metabolism in the confined rotational crop study. Forty-nine metabolites were identified, four of which were $> 10\%$ TRR and > 0.01 mg eq/kg in at least one matrix. No triflumizole was identified in any crop and no single metabolite was consistently the predominant residue. Two of the major metabolites were identified as glucose conjugates of FM-6-1 and FM-8-1, which constituted 22.9% TRR in lettuce and 16.1% TRR in wheat forage, respectively. The other major metabolites in the confined rotational crop study (XIV and XXVI) were not significant residues in either the crop or livestock metabolism profiles.

Field rotational crop studies were conducted with lettuce, turnip, cabbage, cotton, onion, tomato and wheat. Triflumizole was applied to squash at approximately 30 days prior to harvest or to cucumbers at the vining stage. In both studies, the initial application was followed by four subsequent applications at 7 ± 1 day intervals. All applications were 0.28 kg ai/ha for a total rate of 1.4 kg ai/ha. For all commodities except wheat fodder, forage, and hay, residues of triflumizole, analysed by the common-moiety method, were < 0.01 mg/kg, or in a few cases slightly above 0.01 mg/kg, at plant-back intervals (PBIs) of 30, 60, 90, 120, 180, and 270 days (not all crops were sampled at all

intervals). In wheat animal forage, hay, and straw, quantifiable residues persisted throughout all of the plant-back intervals with no particular trend related to PBI. Residue ranges were < 0.01–0.20 mg/kg in wheat forage, < 0.01–0.144 mg/kg in wheat hay, and < 0.01–0.134 mg/kg in wheat straw.

The field rotational crop study indicates that residues are generally not expected (< 0.01 mg/kg) in food crops planted in rotation following treatment to the previous crop. When residues do occur, they are not expected to be much above 0.01 mg/kg. In contrast, readily quantifiable residues in forage/fodder, hay, and straw commodities from cereal grains are expected when such crops are planted in rotation following a treated.

Methods of analysis

The Meeting received description and validation data for analytical methods for residues of total triflumizole (all residues convertible to the FA-1-1 metabolite, expressed as triflumizole) as well as methods for specific residues (e.g., triflumizole, FM-6-1, FA-1-5). Recovery data were provided for raw and processed agricultural commodities as well as animal commodities.

Methods that analyse total triflumizole in crops involve an initial extraction with water. Hydrolysis is accomplished by refluxing in concentrated acetic acid and sodium acetate followed by distillation in the presence of sodium hydroxide into hexane. Residues are cleaned up by column chromatography, and analysed by GC-NPD, GC-MSD, or HPLC-UV.

Methods for the analysis of specific residues in crops use solvent extraction (methanol or acetonitrile), clean-up by solid-phase partitioning and liquid/liquid partitioning, and analysis by GC-NPD, GC-MSD, HPLC-UV, or LC-MS/MS.

Recoveries for the common-moiety method averaged 80.8% and recoveries for the specific-residue method averaged 86.5%. Recoveries for both methods were generally within the range of 70–120%. Limits of quantitation are reported as being of 0.01 mg/kg for most matrices, 0.02 mg/kg for hops, and 0.05 mg/kg for nutmeats.

Data describing multi-residue method testing for residues of triflumizole were not provided.

In animals, the common-moiety method uses 20% NaOH and a Bleidner extractor to digest/distil/extract residues into hexane. The terminal residue is the FA-1-1 metabolite and analysis is by GC-NPD. Recoveries for this method ranged from 78 to 92%.

In the procedure for determining residues containing FA-1-5, the sample was extracted using an acidic digestion followed by clean up and concentration using solid phase extraction (SPE) on reversed phase C18 columns. Final separation and quantification was conducted by HPLC on a C18 column and electrochemical detection. Recoveries for this method averaged 85%.

All of the submitted methods are adequate for the analysis of triflumizole residues.

Stability of residues in stored analytical samples

The Meeting received data on the stability of residues of triflumizole and its metabolites in crops (apple, grape, strawberry, cucumber, cherry, muskmelon, squash, lettuce, and wheat forage) and livestock. The test compound was added to homogenized test matrix. Samples were placed into frozen storage and analysed by the common-moiety or analyte-specific method(s) used in the supervised residue trial.

For the following commodities, stability of residues during storage was demonstrated for at least 3 months in hazelnut, 4 months in wheat forage, 6 months in animal commodities, 12 months in cherries and grapes, and 18 months in papaya.

For the following commodities, stability of residues during storage was demonstrated for no longer than 2 months in lettuce, 3 months in muskmelon and summer squash, and 6 months in apple, cucumber, and strawberry.

For the following commodities, stability of residues during storage was not demonstrated for any time period: cabbage, mustard greens, Swiss chard, and tomato.

Definition of the residue

In the lactating goat metabolism study, TRR were significantly higher in liver than in any other matrix, including milk. Triflumizole was not detected in liver or milk. In liver, free and conjugated FA-1-1 constituted nearly 80% of the residue, with FA-1-5-sulphate making up an additional 12%. In milk, sulphate and glucuronide conjugates of FA-1-5 account for 40% of the residue; the only other major residues were FD-2-1 (10.4% TRR) and FM-8-1-sulphate (12.6% TRR).

In the laying hen metabolism study, TRR were highest in liver, kidney, and egg. Liver contained only FA-1-1 (or a metabolite converted to FA-1-1 during proteolytic digestion). In egg, major residues were triflumizole (13.4% TRR in whites), FD-6-1 or FD-4-1 (12.6% TRR in white), and FA-1-1 (up to 35% TRR in white and 22% TRR in yolk). Hen kidney was not subjected to analysis for residue identification.

In the lactating cattle feeding study, samples were analysed using a common-moiety method, which would have captured all of the major residues observed in the lactating goat and laying hen metabolism studies except for FA-1-5-sulphate, which was the major metabolite in milk observed in the metabolism study. However, in the feeding study, residues of FA-1-5-sulphate were < 0.01 mg/kg in milk and < 0.03 mg/kg in liver and kidney.

Analytical methods for animal matrices are available for the analysis of residues convertible to FA-1-1 or for analysis of FA-1-5-sulphate.

The Meeting agreed that residues converted to 4-chloro-2-(trifluoromethyl)aniline (FA-1-1) and expressed as parent triflumizole are suitable for enforcement and dietary risk purposes in animal commodities.

The log P_{OW} of the residues in animal commodities will be determined by the composition and relative amounts of the metabolite residues in the various matrices. In the lactating cattle feeding study, total residues of triflumizole in fat were, on average, approximately 3.5 times greater than those in muscle.

The Meeting concluded that the residue is fat soluble.

In metabolism studies with apple (leaves only), pear, cucumber, and grape, triflumizole and FM-6-1 constitute the vast majority of the identified residues, and no other residues consistently occur at greater than 10% TRR. The FM-6-1 metabolite was observed in the rat.

The analytical method for plant matrices is a common-moiety method that quantifies all residues convertible to FA-1-1, including FM-6-1.

The Meeting agreed that residues converted to 4-chloro-2-(trifluoromethyl)aniline (FA-1-1) and expressed as parent triflumizole are suitable for enforcement and dietary risk purposes in plant commodities.

The Meeting recommended the following residue definition:

For plants and animals:

Definition of the residue (for compliance with the MRL and for estimation of dietary intake):

Residues analysed as 4-chloro-2-(trifluoromethyl)aniline and expressed as parent triflumizole.

Results from supervised residue trials on crops

The Meeting received supervised trial data for the foliar application of triflumizole on apple, pear, cherry, grape, strawberry, papaya, broccoli, cabbage, cucumber, muskmelon, squash, tomato, lettuce (head and leaf), mustard green, Swiss chard, turnip green, hazelnuts and hops. Residue trial data were made available from the USA for all crops as well as Japan (cucumber, apple and pear), Netherlands (cucumber and tomato), and Belgium (tomato).

Labels for end-use products containing triflumizole were available from the USA and the Netherlands (glasshouse use on tomato and cucumber only) describing the registered uses of triflumizole.

For most crops, the residues were determined by the common-moiety method and reflect the sum of all residues convertible to the aniline moiety, expressed as triflumizole. For the trials in Japan (cucumber), the Netherlands (cucumber and tomato) and Belgium (tomato), the reported residues are the sum of triflumizole and FM-6-1. Side-by-side data reflecting analysis by both common-moiety and residue-specific (triflumizole + FM-6-1) methods are available for hops. In those samples, residues from the common-moiety method were considerably greater than those from the residue-specific method. As the residue definition is for residues convertible to the FA-1-1 metabolite, only residues determined as total triflumizole are suitable for making residue estimates.

Pome fruits

The GAP in the USA on pome fruit is foliar application at a maximum rate of 0.56 kg ai/ha and a PHI of 14 days. Applications may be made at a 7- to 10-day interval with a maximum seasonal rate of 2.24 kg ai/ha.

Apple

Data were available from supervised trials on apple in the USA. Data were also provided from Japan; however, there is no GAP in Japan.

Eighteen supervised trials were conducted in the USA at GAP and residues were obtained by the common-moiety method. Using trials with a supported storage interval, the Meeting selected the following data for consideration (n=3): < 0.02, 0.26, 0.30 mg/kg.

The meeting agreed that the data for apples were insufficient to make a recommendation.

Pear

Data were available from supervised trials on pear in the USA. Data were also provided from Japan; however, there is no GAP in Japan.

Seven supervised trials were conducted in the USA at GAP and residues were obtained by the common-moiety method. Using trials with a supported storage interval, the Meeting selected the following datum for consideration (n=1): 0.28 mg/kg.

The Meeting agreed that the data for pear were insufficient to make a recommendation.

Cherries

The GAP in the USA on cherry is foliar application at a maximum rate of 0.56 kg ai/ha and a PHI of 1 day. Applications may be made at a 7- to 14-day interval with a maximum seasonal rate of 3.36 kg ai/ha.

Eight supervised trials were conducted in the USA at GAP and residues were obtained by the common-moiety method. The residue results are supported by the available storage stability data. The trials resulted in the following eight independent residue values: 0.59, 0.96, 1.1, 1.1, 1.2 (2), 1.3, 1.5 mg/kg.

The Meeting estimated a maximum residue level, STMR, and HR for triflumizole residues in cherries (Subgroup 003A) of 4 mg/kg, 1.2 mg/kg, and 1.5 mg/kg, respectively.

Berries and other small fruits

The GAP in the USA on grapes and strawberries is foliar application at a maximum rate of 0.28 kg ai/ha and a PHI of 7 days for grapes and 1 day for strawberry. Applications may be made at a minimum interval of 14 days, with a maximum seasonal rate of 1.12 kg ai/ha.

Grape

Nineteen supervised trials were conducted in the USA at GAP for grapes and residues were obtained by the common-moiety method. The residue results are supported by the available storage stability data. The trials resulted in the following 12 independent residue values: 0.09, 0.1, 0.15, 0.16, 0.18, 0.21, 0.31, 0.50, 0.90, 0.94, 1.4, and 2.0 mg/kg.

Based on these data, the Meeting estimated a maximum residue level, STMR, and HR for triflumizole residues in grapes of 3 mg/kg, 0.26 mg/kg, and 2.0 mg/kg, respectively.

Strawberry

Eight supervised trials were conducted in the USA. The residue data for strawberry are not supported by the available storage stability data.

The Meeting agreed not to make a recommendation for strawberry.

Papaya

The GAP in the USA on papaya is foliar application at a maximum rate of 0.35 kg ai/ha on a 14-day interval, with a PHI of 0 days. The maximum seasonal rate is 0.84 kg ai/ha.

Four supervised trials were conducted in the USA. Each treated plot received five applications at approximately 0.42 kg ai/ha on a 12- to 14-day interval for a total rate of approximately 2.1 kg ai/ha. Papaya were harvested 0 DAT.

The Meeting agreed that although application in the papaya field trials reflects an over dosing relative to GAP due to the number of applications, the retreatment interval (12 to 14 days) combined with residue decline and the rapid growth of the papaya fruit which would be occurring during the first two applications, the early applications are unlikely to have contributed significantly to the residue level at harvest. Therefore, the available trials are suitable for estimation of residue levels resulting from GAP applications. The residue data (n=4) are: 0.22, 0.53, 0.88, and 0.89 mg/kg.

Based on the trials for papaya in the USA, the Meeting estimated a maximum residue level, STMR, and HR for triflumizole residues in papaya of 2 mg/kg, 0.71 mg/kg, and 0.89 mg/kg, respectively.

Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead brassica

The GAP in the USA on Brassica vegetables is foliar application at a maximum rate of 0.28 kg ai/ha, at a 14-day interval, and a PHI of 1 day. The maximum seasonal rate is 0.63 kg ai/ha.

Broccoli

Ten supervised trials were conducted in the USA. The residue data for broccoli are not supported by the available storage stability data.

The Meeting agreed not to make a recommendation for broccoli.

Cabbage

Nine supervised trials were conducted in the USA. The residue data for cabbage are not supported by the available storage stability data.

The Meeting agreed not to make a recommendation for cabbage.

Fruiting vegetables, Cucurbits

The GAP in the USA on cucurbit vegetables is foliar application at a maximum rate of 0.28 kg ai/ha at a 7- to 14-day interval, and a PHI of 0 days. The maximum seasonal rate is 1.4 kg ai/ha.

The GAP in the Netherlands on cucumber and summer squash is foliar application at a maximum rate of 0.225 kg ai/ha and a PHI of 1 day. One to six applications may be made per season at a 7-day interval.

Cucumber-Outdoor Crops

Six supervised trials were conducted in the USA at GAP and residues were obtained by the common-moiety method. The residue results supported by the available storage stability data are as follows (n=4): 0.13 (2), 0.17, and 0.18 mg/kg.

The Meeting agreed that the data from field-grown cucumber were insufficient to make a recommendation.

Cucumber-Indoor Crops

Four supervised trials were conducted in the USA at GAP and residues were obtained by the common-moiety method. The residue results supported by the available storage stability data are as follows (n=3): 0.10, 0.11, and 0.21 mg/kg.

An additional four trials were conducted in the Netherlands according to the Netherlands GAP. The trials measured only triflumizole and FM-6-1; therefore the residues did not match the residue definition.

The Meeting agreed that the data from indoor-grown cucumber were insufficient to make a recommendation.

Residues from the indoor and outdoor trials on cucumbers from the USA matching the USA GAP are from the same population (Mann-Whitney U test). Using the combined data set (n=7): 0.10, 0.11, 0.13 (2), 0.17, 0.18 and 0.21 mg/kg, the Meeting estimated a maximum residue level, STMR, and HR for triflumizole residues in cucumber of 0.5 mg/kg, 0.13 mg/kg, and 0.21 mg/kg, respectively.

Melon

Six supervised trials were conducted on muskmelon in the USA at GAP. The residue data for muskmelon are not supported by the available storage stability data.

The Meeting agreed not to make a recommendation for muskmelon.

Summer squash

Five supervised trials were conducted in the USA at GAP and residues were obtained by the common-moiety method. The residue data for summer squash are not supported by the available storage stability data.

The Meeting chose not to make a recommendation for summer squash.

Tomato

The GAP in the USA on tomato is foliar application at a maximum rate of 0.28 kg ai/ha at a 7- to 14-day interval and a PHI of 0 days. The maximum seasonal rate is 1.4 kg ai/ha. The USA GAP is the Critical GAP.

Four supervised trials were conducted in the USA at GAP and residues were obtained by the common-moiety method. The residue data for tomato are marginally supported by the storage stability data and are as follows (n=4): < 0.5 (2), 0.59, and 0.76 mg/kg.

The Meeting agreed that the data for tomato from the USA were insufficient to make a recommendation.

The GAP in the Netherlands on tomato is foliar application at a maximum rate of 0.015 kg ai/hL and a PHI of 1 day. One to five applications may be made per season at a 7-day interval.

Four supervised trials were conducted in each of the Netherlands and Belgium. Treated plot received three applications each at 0.016 kg ai/hL on a 7-day interval and fruits were harvested 3 DAT.

The trials in the Netherlands and Belgium were conducted according to the Netherlands GAP. The Netherlands trials measured only triflumizole and FM-6-1; therefore the residues do not reflect the residue definition.

The Meeting agreed not to make a recommendation for tomato.

Leafy vegetables (including Brassica leafy vegetables)

The GAP in the USA on leafy vegetables is foliar application at a maximum rate of 0.28 kg ai/ha at a 14-day interval and a PHI of 0 days. The maximum seasonal rate is 0.63 kg ai/ha.

Lettuce

Data were available from supervised trials on lettuce in the USA.

Seventeen supervised trials were conducted in the USA on lettuce (head lettuce = seven field trials; leaf lettuce = seven field trials + two greenhouse trials; unspecified = one field trial). In 16 trials, treated plot received four applications each at approximately 0.28 kg ai/ha on a 6- to 9-day interval. The total application rate was approximately 1.12 kg ai/ha. In the remaining trial on the unspecified lettuce variety, five applications were made at approximately 0.57 kg ai/ha, for a total rate of approximately 2.85 kg ai/ha. Lettuce was harvested 0 DAT.

The Meeting agreed that in both the number and interval of applications, the residue trials for lettuce did not match the GAP for lettuce in the USA, and that the proportionality concept could not be used.

The Meeting agreed not to make a recommendation for lettuce.

Mustard greens

Ten supervised trials were conducted in the USA on mustard greens at GAP. The residue trials are not supported by the available storage stability data.

The Meeting agreed not to make a recommendation for mustard greens.

Swiss chard

Data were available from supervised trials on Swiss chard in the USA at GAP. The residue trials are not supported by the available storage stability data.

The meeting agreed not to make a recommendation for Swiss chard.

Turnip greens

The GAP in the USA for triflumizole on turnip greens is foliar application at a maximum rate of 0.28 kg ai/ha and a PHI of 1 day. Two to three applications may be made per season at a 14-day interval with a maximum seasonal rate of 0.63 kg ai/ha.

In one trial conducted in USA, where five applications of 0.27–0.3 kg ai/ha triflumizole were made on a 7-day schedule, total residues in turnip greens 1 day after the last application were 7.1 mg/kg.

The Meeting agreed that the supporting data for turnip greens did not match the GAP in USA and are of insufficient quantity. The Meeting agreed not to make a recommendation for turnip greens.

Hazelnuts/Filberts

The GAP in the USA on hazelnut is foliar application at a maximum rate of 0.21 kg ai/ha and a PHI of 18 days. Four to six applications may be made per season at a 10- to 14-day interval with a maximum seasonal rate of 0.84 kg ai/ha.

All of the field trials in the USA (n=3) were conducted at an exaggerated rate of 6.25× GAP. Per-trial average triflumizole residues (via common moiety) were < 0.05 mg/kg for all samples. The Meeting noted that all three trials were conducted in the same year and in the same orchard complex.

The Meeting noted that the trials are not independent and agreed not to make a recommendation for hazelnuts.

Hops

The GAP in the USA on hops is foliar application at a maximum rate of 0.42 kg ai/ha and a PHI of 7 days. Three applications may be made per season at a 14-day interval with a maximum seasonal rate of 1.26 kg ai/ha.

Data were available from supervised trials on hops in the USA.

Four supervised trials were conducted in the USA at GAP and residues were obtained by the common-moiety method. The residue results are supported by the available storage stability data. The trials resulted in the following 4 independent residue values for dried hops: 7.0, 7.8, 10, and 11 mg/kg.

Based on the trials for hops in the USA, the Meeting estimated a maximum residue level, STMR, and HR for triflumizole residues in hops, dried of 30 mg/kg, 8.9 mg/kg, and 11 mg/kg, respectively.

Fate of residues during processing

The Meeting received data depicting the effects of processing on residue levels in apple (juice, sauce, and wet/dry pomace) and grape (juice, raisins (and related commodities), stems, and wet/dry pomace). The estimated processing factors for grape commodities are 0.42 for juice; 0.22 for grape, dried; and 4.3 for wet pomace.

The Meeting estimated an STMR and HR for grapes of 0.41 mg/kg and 2.0 mg/kg, respectively. Application of the estimated processing factors results in an estimated STMR-P and HR-P, respectively, of 0.06 mg/kg and 0.44 mg/kg for grape, dried; an STMR-P of 0.17 mg/kg for grape juice; and an STMR-P of 1.2 mg/kg for wet grape pomace.

Residue in animal commodities*Farm animal dietary burden*

The Meeting estimated the dietary burden of triflumizole in farm animals on the basis of the diets listed in Appendix IX of the FAO Manual 2009. Calculation from highest residue, STMR (some bulk commodities) and STMR-P values provides levels in feed suitable for estimating MRLs, while calculation from STMR and STMR-P values for feed is suitable for estimating STMR values for animal commodities.

Estimated maximum and mean dietary burdens of farm animals

Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are provided in Appendix IX of the FAO manual. The calculations were made according to the animal diets from US-Canada, EU, Australia and Japan in the Table (Appendix IX of the FAO manual). The diets are based on residues in wet grape pomace.

Livestock dietary burden, triflumizole, ppm of dry matter diet ^a

US-Canada	EU	Australia	Japan

	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	—	—	—	—	1.49 ^a	1.49 ^c	—	—
Dairy cattle	—	—	—	—	1.49 ^b	1.49 ^d	—	—
Poultry—broiler	—	—	—	—	—	—	—	—
Poultry—layer	—	—	—	—	—	—	—	—

^a Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian meat

^b Highest maximum dairy cattle dietary burden suitable for MRL estimates for mammalian milk

^c Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat.

^d Highest mean dairy cattle dietary burden suitable for STMR estimates for milk.

Farm animal feeding studies

The Meeting received lactating dairy cow feeding studies, which provided information on likely residues resulting in animal commodities and milk from triflumizole residues in the animal diet.

Lactating dairy cows

Lactating dairy cows were dosed with triflumizole for 28 days at the equivalent of 10 or 50 ppm in the diet. Analysis was for residues convertible to FA-1-1 and FA-1-5 (high-dose group only). Residues for all analyses and tissues were < 0.02 for control animals.

From the high-dose group, milk samples from even-numbered treatment days (except Day 24) were analysed. Residues of FA-1-5 were < 0.01 mg/kg in all milk samples and < 0.03 mg/kg in liver and kidney, which were the only tissue analysed for this compound. Total triflumizole residues were < 0.02 mg/kg in milk on Day 0 and were then rather consistent, ranging from, on average, 0.03 to 0.06 mg/kg. In the low- and high-dose tissue samples, respectively, average residues were 0.06 to 0.33 mg/kg in fat, 0.31 to 1.55 mg/kg in kidney, 0.48 to 4.25 mg/kg in liver, < 0.02 to 0.94 in muscle, and < 0.02 to 0.04 mg/kg in milk.

Animal commodities maximum residue levels

For MRL estimation, the residue in the animal commodities is residues analysed as 4-chloro-2-(trifluoromethyl)aniline and expressed as parent triflumizole.

Residues in tissues and milk at the expected dietary burden for beef cattle in Australia are shown in the Table below. The residue in milk was relatively consistent from Day 2 through Day 28 and the mean estimated residue in milk was calculated using the residue values from Day 4 to the final day.

Triflumizole feeding study	Feed level (ppm) for milk residues	Residues (mg/kg) in milk	Feed level (ppm) for tissue residues	Residues (mg/kg) in			
				Muscle	Liver	Kidney	Fat
MRL beef or dairy cattle							
Feeding study ^a	10	< 0.02	10	< 0.02	0.496	0.460	0.115
	50	0.041	50	0.106	4.602	1.717	0.478
Dietary burden and high residue	1.49	< 0.02	1.49	< 0.02	0.07	0.69	0.03
STMR beef or dairy cattle							
Feeding study ^b	10	< 0.02	10	< 0.02	0.484	0.307	0.056
	50	0.041	50	0.094	4.248	1.552	0.330
Dietary burden and residue estimate	1.49	< 0.02	1.49	< 0.02	0.072	0.046	0.008

^a Highest residues for tissues and mean residues for milk

^b Mean residues for tissues and mean residues for milk

The Meeting estimated the following maximum residue levels: Milk = 0.02(*) mg/kg, meat = 0.03 (fat) mg/kg and edible offal = 0.1 mg/kg.

The Meeting estimated the following STMR levels: Milk = 0 mg/kg, meat = 0 mg/kg, fat = 0.008 mg/kg and edible offal = 0.072 mg/kg.

The Meeting estimated the following HR levels: Milk = 0mg/kg, meat = 0 mg/kg, fat = 0.017 mg/kg and edible offal = 0.074 mg/kg.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue levels listed below are suitable for estimating maximum residue limits and for IEDI and IESTI assessments.

Plant and animal commodities:

Definition of the residue for plant and animal commodities (for compliance with the MRL and for estimation of dietary intake): *Residues analysed as 4-chloro-2-(trifluoromethyl)aniline and expressed as parent triflumizole.*

The residue is fat soluble

Commodity		Recommended MRL, mg/kg	STMR or STMR-P, mg/kg	HR or HR-P, mg/kg
CCN	Name	New		
FS 0013	Cherries	4	1.17	1.5
VC042 4	Cucumber	0.5	0.13	0.21
FB 0269	Grapes	4	0.41	2.0
FI 0350	Papaya	2	0.71	0.89
DH 1100	Hops, Dried	30	8.9	11
ML 0106	Milks	0.02(*)	0	0
MM 0095	Meat (from mammals other than marine mammals)	0.05 (fat)	0 Muscle 0.008 Fat	0 Muscle 0.017 Fat
MO 0105	Edible Offal (mammalian)	0.2	0.072	0.072
JF 0269	Grape, Juice	Covered by grapes	0.11	
	Grape, pomace (wet)	—	1.2	
DF 0269	Dried grapes (=currants, raisins and sultanas)	Covered by grapes	0.06	0.44

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDIs) of triflumizole were calculated for the 13 GEMS/Food cluster diets using STMRs/STMR-Ps estimated by the current Meeting (see Annex 3 of

the 2013 JMPR Report). The ADI is 0–0.04 mg/kg bw and the calculated IEDIs were 0–2% of the maximum ADI (0.04 mg/kg bw). The Meeting concluded that the long-term intakes of residues of triflumizole, resulting from the uses considered by the current JMPR, are unlikely to present a public health concern.

Short-term intake

The International Estimated Short-Term Intakes (IESTI) of triflumizole were calculated for food commodities and their processed commodities using HRs/HR-Ps or STMRs/STMR-Ps estimated by the current Meeting (see Annex 4 of the 2013 JMPR Report). The ARfD is 0.3 mg/kg bw and the calculated IESTIs were $\leq 100\%$ of the ARfD for all commodities. The Meeting concluded that the short-term intake of residues of triflumizole, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

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UR-01-89	Eckert, J	1990	Freezer Storage Stability Analysis of Triflumizole (A-815) and Metabolite FA-1-1 in Cow Tissues and Milk. Uniroyal Chemical Company, Inc. Report No. UR-01-89. Unpublished.
GRL-FR-11321	Friedlander, BT	1998	Determination of the Oxidizing and Reducing Characteristics of Procure 50 WG. Uniroyal Chemical Co. Report No. GRL-FR-11321. Unpublished.
RP-97007	Gaydosh, K	1999	Procure®50WS on Squash: Magnitude of Residue Study. Uniroyal Chemical Company, Inc. Report No. RP-97007. Unpublished.
RP-97005	Gaydosh, K, Maselli, C & Puhl, J	1999	Procure® 50WS on Muskmelon: Magnitude of the Residue Study. Uniroyal Chemical Company, Inc. Report No. RP-97005. Unpublished.
RP-95012	Gaydosh, KA	1997	Procure 50WS® on Sweet Cherries: Magnitude of the Residue Study. Uniroyal Chemical Company, Inc. Report No. RP-95012. Unpublished.
RP-98023	Gaydosh, KA	2000a	Residue Analytical Method Validation for Triflumizole and its Metabolites in Wheat, Turnip, and Lettuce. Uniroyal Chemical Company, Inc. Report No. RP-98023. Unpublished.
RP-98017	Gaydosh, KA	2000b	Procure 50WS Rotational Crop Study: Procure 50WS Treated Cucumbers Rotated with Wheat, Lettuce, and Turnips 30, 60, 90, and 180 Days After Harvest. Uniroyal Chemical Co., Inc. Report No. RP-98017. Unpublished.
RP-99005	Gaydosh, KA	2001	Procure® 50WS on Strawberries: Magnitude of the Residue Study. Uniroyal Chemical Company, Inc. Report No. RP-99005. Unpublished.
RP-03006	Gaydosh, KA	2004a	PROCURE® 50WS in Broccoli: Magnitude of the Residue Study. Crompton Corp. Uniroyal Chemical. Report No. RP-03006. Unpublished.
RP-03005	Gaydosh, KA	2004b	PROCURE® 50WS in Lettuce: Magnitude of the Residue Study. Crompton Corp. Uniroyal Chemical. Report No. RP-03005. Unpublished.
RP-03004	Gaydosh, KA	2004c	PROCURE® 50WS in Turnip: Magnitude of the Residue Study. Crompton Corp. Uniroyal Chemical. Report No. RP-03004. Unpublished.
F-93-30-NL-00/02	Geuijen, I	1994	Determination of the magnitude of residues triflumizole on the raw agricultural commodity cucumber, from Rocket EC by ground-equipment in the Netherlands (field phase). Certis. Report No. F-93-30-NL-00/02. Unpublished.
EC-326; RD-9118	Gomyo, T	1991	Analytical Method for Total Content of Triflumizole and Its Degradates in Water by Gas Chromatography and Gas Chromatography Mass Spectrometry. Nippon Soda Co., Ltd. Report No. EC-326; RD-9118. Unpublished.
RD-9235	Gomyo, T	1992	Residue Analysis of Triflumizole in Pome Fruits. Nippon Soda Co., Ltd. Report No. RD-9235. Unpublished.
RD-9331	Gomyo, T	1993	The Results of the Supervised Residue Trials of Triflumizole on Cucumber in Japan. Nippon Soda Co., Ltd. Report No. RD-9331. Unpublished.
EC-311; RD-9112	Gomyo, T, Morishima, Y & Ono, S	1990	Analytical Method for Individual and Total Content of Residues of Triflumizole Fungicide and Its Metabolites in Crops by High Performance Liquid and Gas Chromatography. Nippon Soda Co., Ltd. Report No. EC-311; RD-9112. Unpublished.
EC-322; RD-9114	Gomyo, T, Morishima, Y, Tachibana, T, Kobayashi, S & Ono, S	1991	Analytical Method for Residues of Triflumizole Fungicide and Its Main Metabolite in Crops by High Performance Liquid and Gas Chromatography. Nippon Soda Co., Ltd. Report No. EC-322; RD-9114. Unpublished.
EC-323; RD-9115	Gomyo, T, Morishima, Y, Yamazaki, S, Dairiki, H & Ono, S	1991	Analytical Method for Total Content of Residues of Triflumizole Fungicide and Its Metabolites in Crops by High Performance Liquid and Gas Chromatography. Nippon Soda Co., Ltd. Report No. EC-323; RD-9115. Unpublished.
84253	Harned, WH,	1985	Aerobic Soil Metabolism study of [¹⁴ C]A815 in Sandy Loam Soil.

Code	Author	Year	Title, Institute, Report reference
	Tortora, NJ & Sullivan, EA		Uniroyal Chemical. Report No. 84253.
RD-9862	Higashida, S & Tanaka, T	1998	Partition Coefficient (n-octanol/water) of Triflumizole. Nippon Soda Co., Ltd. Report No. RD-9862. Unpublished.
09300	Homa, K	2012	Triflumizole: Magnitude of the Residue on Greenhouse Cucumber. Rutgers, The State University of NJ. Report No. 09300. Unpublished.
TL-6362, RD-8841	Iguchi, K	1988a	Triflumizole—Density, bulk density or specific gravity. Nippon Soda Co., Ltd. Report No. TL-6362, RD-8841. Unpublished.
TL-6361, RD-8840	Iguchi, K	1988b	Triflumizole—Melting Point. Nippon Soda Co., Ltd. Report No. TL-6361, RD-8840. Unpublished.
RD-II02245	Knight, LJL	2002	Triflumizole—Photodegradation in Water. Nippon Soda Co., Ltd. Report No. RD-II02245. Unpublished.
8517-A	Knipe, JO	1986	Further Analysis of the Metabolism of (¹⁴ C)-A815 (Triflumizole) in a Lactating Goat. Uniroyal Chemical Company, Inc. Report No. 8517-A. Unpublished.
8517	Knipe, JO & Harned, WH	1985	The Metabolism of (¹⁴ C)-A815 in a Lactating Goat. Uniroyal Chemical Company, Inc. Report No. 8517. Unpublished.
8635	Knipe, JO & Lengen, MR.	1986	The Disposition of (¹⁴ C)-A815 (Triflumizole) in Chickens. Uniroyal Chemical Company, Inc. Report No. 8635. Unpublished.
2010-020	Marin, JE	2011	Storage Stability of Triflumizole Metabolites in Plant Matrices. PTRL Report No. 2122W, Chemtura Report No. 2010-020. Unpublished.
RP-95013	Maselli, CV	1997	Procure 50WS on Tart Cherries: Magnitude of the Residue. Uniroyal Chemical Company, Inc. Report No. RP-95013. Unpublished.
RP-97006	Maselli, CV	1999	Procure® 50WS on Cucumbers: Magnitude of the Residue Study. Uniroyal Chemical Company, Inc. Report No. RP-97006. Unpublished.
EC-99, RD-8762	Nomura, O & Nakashima, N	1987	Triflumizole—Octanol/Water Partition Coefficient. Nippon Soda Co., Ltd. Report. No. EC-99, RD-8762. Unpublished.
20	Noon, P	1993	Method Validation: Determination of Residues of 2-Hydroxy-4-Chloro-6-Trifluoromethylaniline, FA-1-5, and Its Conjugates in Meat and Milk. Uniroyal Chemical Company, Inc. Report No. 20.028: 9308. Unpublished.
8772	Parkins, MD	1988	Triflumizole Cow Feeding Study. Uniroyal Chemical Company, Inc. Report No. 8772. Unpublished.
9308: EPA3/EH/H701/3	Parkins, MD	1993	Proposed Enforcement Procedure for the Determination of Conjugates of 2-hydroxy-4-chloro-6-trifluoromethylaniline, FA-1-5, in Liver and Milk. Uniroyal Chemical Company, Inc. Report No. 9308: EPA3/EH/H701/3. Unpublished.
8659	Parkins, MD & Polakoff, BM	1986	Methods for Analyzing Meat, Milk and Egg Residues Resulting from Feed Containing Triflumizole (A815). Uniroyal Chemical Company, Inc. Report No. 8659. Unpublished.
94181	Pierce, JP	1994	Calculation of Henry's Law Constant. Uniroyal Chemical Company. Report No. 94181. Unpublished.
2006/004, 1512W	Ponte, M	2006	Photodegradation of [¹⁴ Carbon] Triflumizole in/on Soil by Simulated Sunlight: Final Report. PTRL West, Inc. Report No. 2006/004, 1512W. Unpublished.
RP-03008	Puhl, J	2005	Procure® 50WS Treated Squash Rotated with Wheat, Onion, Tomato, Cabbage, and Cotton: Rotational Crop Study. Crompton Corporation. Report No. RP-03008. Unpublished.
RD-01201	Rijsbergen, L	2002	Determination of the Vapour Pressure of TRIFLUMIZOLE. Nippon Soda Co., Ltd. Report No. RD-01201.
EC-211, RD-9004	Saito, H	1990	Triflumizole—Solubility in Organic Solvents. Nippon Soda Co., Ltd. Report No. EC-211, RD-9004. Unpublished.
V 94	Schouten, .	1994	The determination of residues of triflumizole (NF-114) and its main metabolite (FM-6-1) in cucumber by high performance liquid chromatography. Certis. Report No. V 94.326. Unpublished.
RD-8246	Shiotani, H	1982	Fate of ¹⁴ C-NF-114 in Soil. Nippon Soda Co., Ltd. Report No. RD-8246. Unpublished.
ML-1, RD-8359	Soeda, Y	1983	Fate of NF-114 in Cucumber Plants. Nippon Soda Co., Ltd. Report No. ML-1, RD-8359. Unpublished.
RD-8845	Soeda, Y	1988	Triflumizole—Oxidizing or reducing. Nippon Soda Co., Ltd. Report No. RD-8845. Unpublished.
EC-80, RD-8708	Soeda, Y & Hashimoto, Y	1987a	Triflumizole Fate in Pear Plants. Nippon Soda Co., Ltd. Report No. EC-80, RD-8708. Unpublished.
EC-81, RD-8709	Soeda, Y & Hashimoto, Y	1987b	Triflumizole Fate in Apple Plants. Nippon Soda Co., Ltd. Report No. EC-81, RD-8709. Unpublished.
EC-82, RD-8710	Soeda, Y & Hashimoto, Y	1987c	Triflumizole Fate in Grape Plants. Nippon Soda Co., Ltd. Report No. EC-82, RD-8710. Unpublished.

Code	Author	Year	Title, Institute, Report reference
EC-129, RD-8833	Soeda, Y & Nomura, O	1988	Triflumizole—Solubility in Organic Solvents. Nippon Soda Co., Ltd. Report No. EC-129, RD-8833. Unpublished.
EC-111	Soeda, Y & Shiotani, H	1987a	Triflumizole—Hydrolysis. Nippon Soda Co., Ltd. Report No. EC-111. Unpublished.
EC-113, RD-8783	Soeda, Y & Shiotani, H	1987b	Triflumizole—Photodegradation in Water. Nippon Soda Co., Ltd. Report No. EC-113, RD-8783. Unpublished.
EC-130, RD-8834	Soeda, Y & Shiotani, H	1988	Triflumizole—Dissociation Constant. Nippon Soda Co., Ltd. Report No. EC-130, RD-8834. Unpublished.
RD-II02419	Tanaka, T	2002	Validation of Analytical Method for Technical Grade Triflumizole. Nippon Soda Co., Ltd. Study No. 1-0206; Report No. RD-II02419. Unpublished.
07996	Thompson, DC	2002	Triflumizole: Magnitude of the Residue on Filbert. Rutgers, The State University of NJ. Report No. 07996. Unpublished.
91469	Tutty, DG	1994	Determination of the Solubility of Triflumizole in Water at 25 °C. Uniroyal Chemical Ltd. Report No. 91469. Unpublished.
GRL-FR-11330	Tutty, DG	1998	Thermal Explodability of Procure 50WG. Uniroyal Chemical Co. Report No. GRL-FR-11330. Unpublished.
RD-8225N	Unknown	1983	Physical and Chemical Properties of NF-114. Nippon Soda Co., Ltd. Report No. RD-8225N. Unpublished.
RD-8409N	Unknown	1984	Physical and Chemical Properties of NF-114 Technical. Nippon Soda Co., Ltd. Report No. RD-8409N. Unpublished.
3096040731	van de Ruit, ANR	1997	Field residue study of Rocket EC (a.i.: 150 g/L triflumizole) in greenhouse tomatoes in the Netherlands and Belgium. Certis. Report No. 3096040731. Unpublished.
98201	Yu, WC, Dzialo, DG, Whitright, RR & Regis, RR	2001	Confined Accumulation Study on Rotational Crops with ¹⁴ C-Triflumizole (Procure®). Uniroyal Chemical Company, Inc. Report No. 98201. Unpublished.

TRINEXAPAC-ETHYL (271)

First draft prepared by Dr Paul Humphrey, Australian Pesticides and Veterinary Medicines Authority, Canberra, Australia

EXPLANATION

At the Forty-fourth Session of the CCPR (2012), trinexapac-ethyl was scheduled for evaluation as a new compound by 2013 JMPR.

Trinexapac-ethyl is a synthetic plant growth regulator that is derived from cyclohexanecarboxylate. It is applied as a foliar spray, post-emergence and approved for use on cereal crops such as barley, durum wheat, oats, rye, triticale and wheat, oilseed rape and sugarcane as well as grassland, amenity turf and managed turf.

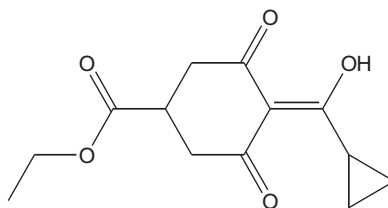
The manufacturer supplied information on identity, metabolism, methods of residue analysis, freezer storage stability, registered use patterns, supervised residue trials, fate of residues in processing and farm animal feeding studies.

SPECIFICATIONS

Specifications for trinexapac-ethyl have not been developed by FAO.

IDENTITY

ISO common name:	Trinexapac-ethyl
IUPAC name:	4-(cyclopropyl-hydroxy-methylene)-3,5-dioxo-cyclohexanecarboxylic acid ethyl ester
Chemical Abstract name:	4-(cyclopropylhydroxymethylene)-3,5-dioxo-cyclohexanecarboxylic acid ethyl ester
CAS Index Name: (alternative)	
CAS No.:	95266-40-3
CIPAC No.:	Not allocated
Manufacturer's experimental name:	CGA 163935
Molecular Formula:	C ₁₃ H ₁₆ O ₅
Structural Formula:	



Molecular Weight:	252.3 g/mol

PHYSICAL AND CHEMICAL PROPERTIES***Pure Active Ingredient (except as noted)***

Physical-Chemical Property	Results	Test material purity and specification	Reference
<i>Trinexapac-ethyl</i>			

Physical-Chemical Property	Results			Test material purity and specification	Reference
Melting point	36.1–36.6 °C.			AMS 265/102, purity 99.6%	Das 1998, CGA163935/0537
Boiling point	Trinexapac-ethyl has no boiling point at atmospheric pressure. Trinexapac-ethyl decomposed at a temperature of approximately 310 °C.			AMS 265/102, purity 99.6%	Das 2000, CGA163935/0631
Thermal stability	Trinexapac-ethyl shows no thermal effect between room temperature and 150 °C.			P.912005, TGAI	Schürch 1993, CGA163935/0299
Relative Density	Active substance, pure: 1.31 g/mL at 22 °C			AMS 265/102, purity 99.6%	Földner 2000, CGA163935/0651
Vapour pressure	Vapour pressure curve $^{10}\text{Log P (Pa)} = 16.244 - 5637.9 \times 1/T \text{ (K)}$ extrapolated from vapour pressure curve obtained between 38 °C and 170.2 °C. Vapour pressure = 2.16×10^{-3} Pa at 25 °C			AMS 265/101, purity 99.3%	Rordorf 1990, CGA163935/0241
Henry's law constant	Henry's law constants at 25 °C: 5.4×10^{-4} Pa $\times$ m ³ $\times$ mol ⁻¹ . A vapour pressure of 2.16×10^{-3} Pa and a water solubility of 1.1 g/L (measured) were used to calculate the Henry's Law constant.				Burkhard 1995, CGA163935/0432
Description of the physical state and colour, purity of the ai. and of technical grade	Active substance, pure: white odourless powder			AMS 265/102, purity 99.6%	Das 2000a, CGA163935/0629
	Active substance as manufactured: red-brown solidified melt with weak odour			P.306042, TGAI purity 96.8%	Das 2000b, CGA163935/0628
UV absorption	Solution	Wavelength [nm]	Molar Extinction Coefficient [L/mol $\times$ cm]	AMS 265/102, 99.6%	Roth 1997, CGA163935/0504
	Neutral	240.2	9335		
		277.4	13976		
	Acidic	240.0	11712		
		280.4	12368		
	Basic	270.8	21320		
Solubility of purified active substance in water	pH 4.9	2.8 g/L at 25 °C		AMS 265/101, purity 99.3%	Rodler 1990, CGA163935/0238
	pH 5.5	10.2 mg/L at 25 °C			
	pH 8.2	21.1 mg/L at 25 °C			
	pH 3.5	1.1 g/L at 25 °C (distilled water)		AMS 265/102, purity 99.6%	Stulz 1991 CGA163935/0351

Physical-Chemical Property	Results	Test material purity and specification	Reference
Solubility in organic solvents	[g/L at 25 °C] acetone > 500 dichloromethane > 500 ethyl acetate > 500 hexane 45 methanol > 500 octanol 420 toluene > 500	P.306042, TGA1 96.0%	Stulz 1998, CGA163935/0561
n-Octanol/ water partition coefficient	log K _{ow} at 25 °C pH 5 log K _{ow} 1.5 pH 6.9 log K _{ow} -0.29 pH 8.9 log K _{ow} -2.1	AMS 265/102, purity 99.6%	Kettner 1999, CGA163935/0621
Hydrolysis rate at pH 5, 7 and 9 under sterile and dark conditions	pH 5 t _{0.5} 485–562 days pH 7 t _{0.5} 828–908 days pH 9 t _{0.5} 8.1 days It is considered that trinexapac-ethyl is hydrolysed to the free acid in basic solutions. Therefore hydrolysis may be a major degradation pathway in the environment in basic media with substantially slower degradation in neutral and acid environments.	PAIRA (pure active ingredient radiocarbon labelled [1, 2, 6- ¹⁴ C-cyclohexyl] trinexapac-ethyl), radiochemical purity 99.3%	Spare 1989, CGA163935/0021 Spare 1990, CGA163935/0022 Spare 1992, CGA163935/0274
Direct phototransformation in sterile water using artificial light	Trinexapac-ethyl was significantly degraded in irradiated samples (pH 7.0, 20 °C, Xenon arc light) reaching 13% of the applied dose after 15 days of irradiation. Assuming a pseudo-first order kinetic, a half-life of 6.5 days was calculated, equivalent to a half-life of 21.3 equivalent days of midday summer sunlight. There was negligible degradation of the test compound in dark control vessels (< 4% in 15 days). $\Phi = 1.86 \times 10^{-3}$ at pH 7.0	Radiolabelled: [Hydroxymethylene- ¹⁴ C] trinexapac-ethyl, radiochemical purity > 98% Non-radiolabelled: AMS 265/102, purity 99.6%	Millais 2001, CGA163935/0724
Quantum yield	The quantum yield of direct photolysis was found to be: $\Phi = 1.00 \times 10^{-3}$ at pH 7 (anionic form) $\Phi = 8.32 \times 10^{-3}$ at pH 2.3 (undissociated)	AMS 265/102, purity 99.6%	Zetzsch 1994 CGA163935/0480

Physical-Chemical Property	Results	Test material purity and specification	Reference
Dissociation in water of purified active substance	pKa = 4.57 at 20 °C	AMS 265/101, purity 99.3%	Jäkel 1990, CGA163935/0535 Burkhard 1999, CGA163935/0566
Surface tension	55.5 mN/m at 20 °C	P.306042, 96.8%	Martin 2000, CGA163935/0630
<i>Trinexapac acid</i>			
Hydrolysis rate at pH 4, 5, 7 and 9 under sterile and dark conditions	pH 4 $t_{0.5}$ 79.1 days at 20°C pH 5 $t_{0.5}$ 74.4 days at 20°C pH 4 $t_{0.5}$ 3.4 days at 44°C pH 5 $t_{0.5}$ 3.2 days at 44°C pH 4 $t_{0.5}$ 40 days at 25°C* pH 5 $t_{0.5}$ 37 days at 25°C* *Extrapolated values using the Arrhenius equation Trinexapac acid was found to be stable in buffer solutions at pH 7 and 9. No degradation was observed after 5 days of incubation at 50 °C in the dark.	ILA-47.2A, radiochemical purity > 99.4%	Mamouni 2006, CGA179500/0034

Formulations

Formulation type	Active substance and content
EC (Emulsifiable Concentrate)	Trinexapac-ethyl 250 g/L
EC	Trinexapac-ethyl 249 g/L
EC	Trinexapac-ethyl 120 g/L
ME (Micro-emulsion)	Trinexapac-ethyl 250 g/L

METABOLISM AND ENVIRONMENTAL FATE

General

The studies for plant metabolism, animal metabolism and confined rotational crops were conducted with the test materials shown below, with the label position/s indicated in the following structural formulae:

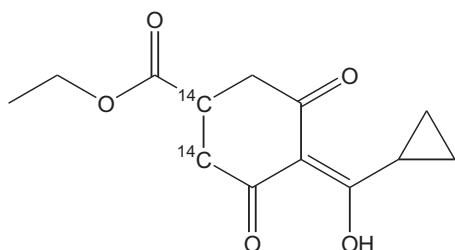
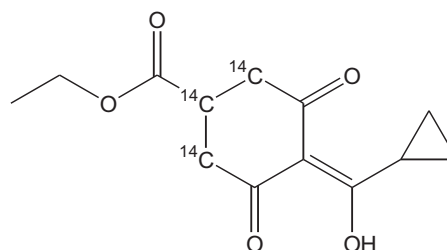
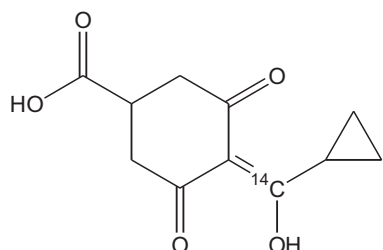
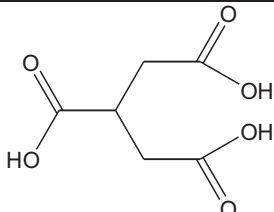
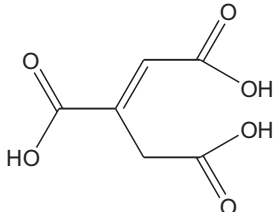
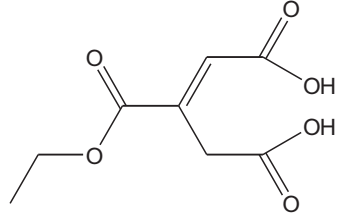
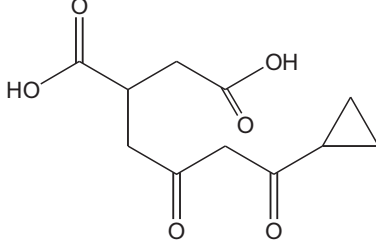
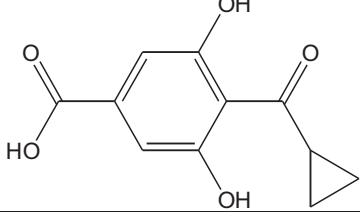
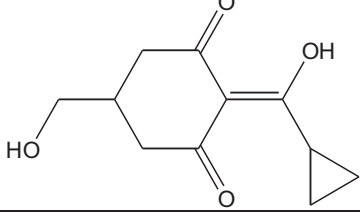
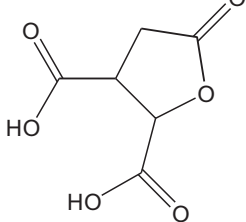
[1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl[1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl[Hydroxymethylene ¹⁴C] trinexapac-acid

Table 1 summarises the names, codes, and structures of the parent and principle metabolites found in plant, livestock, rat and rotational crop studies.

Table 1 Trinexapac-ethyl and metabolites/degradates found in metabolism and environmental fate studies

Abbreviation or Code	Chemical Structure	IUPAC Name	Found in
Active substance: Trinexapac-ethyl CGA 163935		4-(cyclopropyl-hydroxy-methylene)-3,5-dioxocyclohexanecarboxylic acid ethyl ester	Wheat, Rapeseed, Rice, Hen (egg only)
CGA 179500 Trinexapac acid		4-(cyclopropyl-hydroxy-methylene)-3,5-dioxocyclohexanecarboxylic acid	Wheat, Rapeseed, Rice, Grass, Rotational wheat, Goat, Hen
CGA 113745		3-hydroxy,5-oxocyclohexanecarboxylic acid	Goat

Abbreviation or Code	Chemical Structure	IUPAC Name	Found in
CGA 275537 Tricarballic acid		3-carboxy-pentanedioic acid	Wheat, Rice, Grass
CGA 312753 Trans aconitic acid		(E)-3-carboxy-pent-2-enedioic acid	Rapeseed, Rice, Rotational wheat
CGA 312753 mono-ethyl ester		(E)-3-ethoxycarbonylpent-2-enedioic acid	Wheat
CGA 313458		2-(4-cyclopropyl-4-hydroxy-2-oxo-but-3-enyl)-succinic acid	Rapeseed, Rice
CGA 329773		4-cyclopropanecarbonyl-3,5-dihydroxy-benzoic acid	Wheat, Rice
CGA 351210		2-(cyclopropyl-hydroxymethylene)-5-hydroxymethylcyclohexane-1,3-dione	Rapeseed
– Isocitric acid lactone		5-oxo-tetrahydro-furan-2,3-dicarboxylic acid	Rapeseed (tentative identification)

Animal metabolism

Metabolism in rats

Evaluation of the metabolism studies in rats was carried out by the WHO Core Assessment Group.

Trinexapac-ethyl undergoes limited metabolism in the rat, involving predominantly ester hydrolysis of trinexapac-ethyl to trinexapac acid. The predominant urinary metabolite was trinexapac acid (up to 100% of total urinary radioactivity), with low levels of a conjugated derivative of trinexapac acid detected only in the urine of bile-duct cannulated rats (6.3% of the administered dose). In faeces, the parent compound accounted for 5–22% of total faecal radioactivity (1–2.5% of the administered dose), with the balance comprising trinexapac acid. Bile contained mainly a conjugated derivative of trinexapac acid (2.9% of the administered dose), with low levels of the parent compound also detected (0.2% of the administered dose).

Metabolism in lactating goats

Two studies were conducted on lactating goats using [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl.

[1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl was orally administered by capsule to two lactating goats (British Saanen, 43.0–47.5 kg bw during acclimatisation and 42.0–45.5 kg bw at sacrifice) at a level of either 7.2 ppm or 694 ppm in the feed for 4 consecutive days (Cameron *et al.* 1992, CGA163935/0276).

Actual doses were 7.17 or 694.0 ppm in feed based on feed consumption of 1.39 or 1.30 kg dry matter/ day or 0.20 or 19.9 mg/kg bw/day respectively. Urine, faeces and blood were collected throughout the study. Milk was sampled twice daily, in the morning and afternoon. The mean milk yield during the dosing period was 536 or 586 mL/day. Animals were sacrificed approximately 4 hours after the last dose. Samples of liver, kidney, muscle (tenderloin, hindquarter and forequarter), fat (omental, subcutaneous and renal) and rumen contents were collected.

The low dose goat eliminated 0.02%, 16.3% and 50.0% via milk, faeces and urine of the total dose applied respectively, while the corresponding values of the high dosed goat were 0.02%, 19.0% and 62.2% at 76 hours in the study.

The tissue residues of the low dosed goat were 0.035–0.043 mg/kg trinexapac-ethyl equivalents in muscles, 0.017–0.094 mg/kg trinexapac-ethyl equivalents in fat, 0.25 mg/kg equiv. in liver and 0.50 mg/kg equiv. in kidney. In the high dosed goat the residues were correspondingly higher *i.e.* 1.90–2.49 mg/kg trinexapac-ethyl equivalents in muscles, 1.20–1.55 mg/kg equiv. in fat, 12.1 mg/kg equiv. in liver and 41.9 mg/kg equiv. in kidney. The residue in the milk of the low dosed goat reached a plateau on the second day of dosing, with 0.002 mg/kg trinexapac-ethyl equivalents (am) and 0.007 mg/kg equiv. (pm). In the milk of the high dosed goat the plateau was reached on the third day when the total of am and pm is considered.

Residue levels in the corresponding tissues of the high dose goat were generally proportional but by a factor of 48 (liver)–84 (kidney) rather than the feed concentration factor of 96. An exception was subcutaneous fat, in which high dose residues were approximately 13 times the low dose residues, although it was postulated that the low dose subcutaneous fat result was an outlier.

Table 2 Recovery of radioactivity from goats dosed with [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl at 7.2 ppm (low dose) and 694 ppm (high dose) in the feed for 4 consecutive days

Sample	Interval (hours)	Low dose		High dose	
		mg/kg trinexapac-ethyl equiv.	% total dose	mg/kg trinexapac-ethyl equiv.	% total dose
Total Faeces	0–76		16.3		19.0
Total Urine	0–76		50.0		62.2
Cage Wash	0–76		8.69		5.90
Total Milk	0–76		0.02		0.02
Total Eliminated	0–76		75.0		87.1

Sample	Interval (hours)	Low dose		High dose	
		mg/kg trinexapac-ethyl equiv.	% total dose	mg/kg trinexapac-ethyl equiv.	% total dose
Hindquarter muscle	76	0.035		1.90	
Forequarter muscle	76	0.043		2.49	
Tenderloin	76	0.035		2.15	
Total Muscle	76		2.17 ^a		1.20 ^a
Omental fat	76	0.024		1.55	
Subcutaneous Fat	76	0.094		1.20	
Renal fat	76	0.017		1.41	
Total Fat	76		0.34 ^a		0.10 ^a
Kidney	76	0.50	0.18	41.9	0.14
Liver	76	0.25	0.55	12.1	0.27
Total Tissue	76		3.24		1.71
Blood cells	76	0.29	1.20	17.9	0.59
Plasma	76	0.79	3.78	44.1	2.35
Bile	76	0.21	0.0	8.17	0.0
Rumen	76	0.27	3.88	31.4	3.12
Total Recovery	0–76		87.1		94.9

^a Value calculated using mean data from the three regions taken

Table 3 Radioactivity in the milk from goats dosed with [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl at 7.2 ppm (low dose) and 694 ppm (high dose) in the feed for 4 consecutive days

Study day	Low dose				High dose			
	(mg/kg trinexapac-ethyl equiv.)		% Daily Dose		(mg/kg trinexapac-ethyl equiv.)		% Daily Dose	
	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.
1	NA	0.004	NA	0.01	NA	0.45	NA	0.01
2	0.002	0.007	0.01	0.01	0.31	0.66	0.01	0.01
3	0.002	0.006	0.01	0.01	0.22	0.83	0.01	0.01
4	0.002	0.008 ^a	0.01	0.01 ^a	0.11	0.80 ^a	0.01	0.01 ^a

^a Milk collected pre-sacrifice (*i.e.* 4 hours after administration of the fourth daily dose)

NA = Not Applicable

In a second study (Müller 1993, CGA163935/0305) the nature of the metabolites of trinexapac-ethyl from the previously described goat metabolism study was determined.

Radioactivity in faeces was almost completely extractable with acidified methanol/water (1:1 v/v). The extractability of the muscle, liver and kidney samples was high (> 89% of the total radioactive residues). Extraction from these matrices was by using acetonitrile/water for the low dosed goat and liver of the high dosed goat, or acetonitrile and acetonitrile/water (1:1 v/v) for kidney and muscle in the high dosed goat. In milk 53–85% of the radioactivity was recovered in the supernatants after precipitation of the proteins and lipids with acetonitrile.

In the fat pools the majority of the radioactivity (70–82%) was extracted with chloroform/methanol (4:1 v/v for the low dose pool and 2:1 v/v for the high dose pool). In order to separate acidic from neutral compounds the extract was then partitioned with basic phosphate buffer and re-transferred into methylene chloride after acidification. Approximately 39% of the radioactivity remained in the organic layer in the low dosed pool, whereas in the high dosed pool the radioactivity of the extract was completely transferred into the basic aqueous layer and re-transferred in the methylene chloride phase for TLC analysis. It was assumed that the poor extractability from the chloroform phase of the low dose goat was due to the low residual radioactivity in a complex matrix, rather than due to differences in the nature of the metabolites present.

Trinexapac acid was the main component of TRR in urine, faeces and bile fluid of both low and high dose goats (81.6–96.1% of extractable radioactivity). Residues in muscle and kidney were also mostly trinexapac acid (80.7–89.6% TRR). In milk, trinexapac acid accounted for 45.5–76.0 % TRR. In liver and fat trinexapac acid was 30.8–67.3% TRR although for fat this represented 87.3–96.1% of the extractable radioactivity. For liver this represented only 34.1–47.2% of the extractable radioactivity, although other distinct metabolites observed in liver did not co-chromatograph with any of the reference compounds.

Table 4 Distribution of metabolites in goat tissues and milk after multiple applications of [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl in the feed for 4 consecutive days

Dose Level (ppm in the feed)	Tissues	% Extracted	Quantitation (TLC)			Total residues (mg/kg)
			Trinexapac acid % of radioactivity analysed	% of TRR	mg/kg	
Low (7.2)	Muscles ^a	95.4	94.0	89.6	0.034	0.038
	Fat ^b	82.1	87.3	30.8	0.014	0.045
	Liver	88.8	47.2	41.9	0.11	0.25
	Kidney	96.4	83.8	80.8	0.40	0.50
	Milk pm ^c	71.1	88.7	63.1	0.004	0.006
High (694)	Milk am ^d	52.8	86.1	45.5	0.001	0.002
	Muscles ^a	95.9	84.1	80.7	1.76	2.18
	Fat ^b	70.0	96.1	67.3	0.93	1.39
	Liver	95.8	34.1	32.7	3.96	12.1
	Kidney	97.1	84.2	81.7	34.2	41.9
	Milk pm ^c	84.6	89.8	76.0	0.49	0.65

^a Equal amounts of fore-, hindquarter and tenderloin muscle

^b Equal amounts of omental, subcutaneous and renal fat

^c Pool of equal amounts collected pm on days 1, 2 and 4

^d Pool of equal amounts collected am on days 2 and 4

ND = Not Determined

The residual radioactivity present in the rumen content 4 hours after the last dose was readily extractable (98 and 99% for the low and high dose goats respectively). The extracts contained only trinexapac acid, indicating rapid hydrolysis of trinexapac-ethyl to the corresponding carboxylic acid, under conditions present in the rumen.

In another study [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was orally administered by gelatin capsule to two lactating goats (*Capra hircus*, 47.0 and 51.5 kg bw) at a level of 95 and 125 ppm in the feed for 4 consecutive days based on feed consumption of 1.50 kg feed/ day (Ray 2002, CGA163935/0944).

Urine and faeces were collected daily and blood samples just prior to sacrifice. Milk was sampled twice daily. Animals were sacrificed approximately 6 hours after the last dose. Samples of liver, kidney, muscle (leg and tenderloin), fat (omental and perirenal), bile and gastrointestinal contents were collected. Muscle and fat samples were combined.

Approximately 90% of the total administered radioactivity was recovered; 2.54% in the faeces, 80.5% in urine, < 0.01% in the bile, 2.19% in the blood, 1.19% in the combined tissues, 3.37% in the GI tract and 0.05% in milk. The ¹⁴C residue levels in composite tissues ranged from 0.106 mg/kg equiv. in the fat to 5.903 mg/kg equiv. in the kidney. The ¹⁴C residue levels in composite milk ranged from 0.018 mg/kg equiv. (7–24 hour, day 1 am) to 0.078 mg/kg equiv. (0–7 hour, day 1 pm).

The extractability of the muscle, liver and kidney samples was high (> 95% of the TRRs). Extraction from these matrices was by using acetonitrile/water. The extractability of the fat samples using chloroform/methanol was 98% of the TRR. In milk 90% of the radioactivity was recovered in the supernatants after precipitation of the proteins and lipids with acetonitrile.

Parent compound was not detected in any tissue or milk. After isolation and analysis by co-chromatography and mass spectrometry, two tissue and milk metabolites were identified. Residues of trinexapac acid accounted for 66.0–96.8% TRR in milk and tissues (Table 5). CGA 113745 (formed from further hydrolysis of trinexapac acid) was a major metabolite in liver, kidney and fat (6.0–16.3% TRR) but was not detected in muscle and milk. Post-extraction solids in tissues and milk represented 4.0–9.0% TRR.

Table 5 Quantitation of metabolites in tissues and milk after multiple applications of [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl in the feed

	Liver		Kidney		Muscle		Fat		Milk (Day 2 pm)	
	mg/kg equiv.	% TRR	mg/kg equiv.	% TRR	mg/kg equiv.	% TRR	mg/kg equiv.	% TRR	mg/kg equiv.	% TRR
	0.802	100	5.903	100	0.275	100	0.106	100	0.076	100
Extractable Metabolites	0.758	94.5	5.61	95.0	0.285	103.6	0.104	97.8	0.069	90.3
CGA113745	0.131	16.3	0.354	6.0	ND	ND	0.012	11.4	ND	ND
CGA179500	0.529	66.0	5.04	85.3	0.266	96.8	0.089	83.9	0.065	85.3
Unknown G3	0.041	5.1	ND	ND	0.010	3.5	ND	ND	ND	ND
Unknown G4	0.012	1.5	ND	ND	ND	ND	0.002	1.5	ND	ND
Unidentified	0.044	5.5	0.212	3.6	ND	ND	ND	ND	0.002	2.0
Total Identified	0.660	82.3	5.39	91.3	0.266	96.8	0.101	95.3	0.065	85.3
PES	0.064	8.0	0.266	4.5	0.011	4.0	NS	NS	0.007	9.0
Total Characterised	0.724	90.3	5.66	95.8	0.277	100.8	0.101	95.3	0.072	94.3

ND = Not detected

NS = No PES sample after extraction

Metabolism in Poultry

Two studies were conducted in laying hens using [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl.

In the first study [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl was orally administered daily to laying hens (White Leghorn, 1.26–1.45 kg bw prior to the start of acclimatisation until the last day of acclimatisation and 1.30–1.51 kg bw at sacrifice) using gelatine capsules at a low dose level (two hens, 0.4 mg/kg body weight equivalent to 3.8 ppm in feed) or a high dose level (four hens, 20.3 mg/kg body weight equivalent to 180 ppm in feed) for 4 consecutive days (Cameron *et al.* 1992, CGA163935/0277).

Excreta, blood and cage washes were collected throughout the study. Eggs were collected throughout the day and in the morning before subsequent administration. Egg yield for the low dose hens was 71–86% for the acclimatisation period (100% = 1 egg per hen per day) and 25–75% for the dose period, while for the high dose hens the egg yield was 86–100% for the acclimatisation period and 50–75% for the dose period. Animals were sacrificed approximately 4 hours after the last dose. Samples of lean meat (mixture of leg, thigh and breast), skin (including attached fat), peritoneal fat, liver and kidney and gizzard and crop contents were collected.

Over the period of the experiment (76 hours), 85–89% (high and low doses respectively) of the total administered dose was eliminated in excreta. Transfer of radioactivity into eggs accounted for only 0.01% and 0.02% of the total administered dose for the low and high dosed hens, respectively. A plateau was reached on Day 2 of the dosing period. Concentrations of radioactivity in egg yolk were generally less than in egg whites. Radioactivity did not accumulate in eggs with time over the period of the experiment. Concentrations of radioactivity in egg white and egg yolk in the low-dosed hens did not exceed 0.007 and 0.002 mg/kg trinexapac-ethyl equivalents, respectively. In the high dosed hens the corresponding values were 0.33 and 0.055 mg/kg trinexapac-ethyl equivalents.

Mean radioactive residues in tissues of the low-dosed hens were 0.002 mg/kg trinexapac-ethyl equivalents in lean meat (0.12 mg/kg equiv. high dose), 0.011 mg/kg equiv. in skin (including attached fat) (0.37 mg/kg equiv.), 0.003 mg/kg equiv. in peritoneal fat (0.18 mg/kg equiv.), 0.013 mg/kg equiv. in liver (0.60 mg/kg equiv.) and 0.043 mg/kg in kidney (1.77 mg/kg equiv.).

Residue levels in tissues of the high dose hens compared with levels observed in the low dose hens were greater by a factor of 33–61, which is comparable with the feed concentration factor of 47.

Table 6 Cumulative excretion of radioactivity following four consecutive daily doses of [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl at an average of 3.8 ppm (low dose) and 180 ppm (high dose) in the feed

Interval (hours)	Sample	Low dose ^a	High dose ^b
		% total administered dose	% total administered dose
0–24	Excreta	24.0	20.9
	Eggs	0.01	0.01
	Cage wash	0.16	0.26
	Total excreted	24.2	21.4
0–48	Excreta	47.9	42.3
	Eggs	0.01	0.02
	Cage wash	0.97	1.04
	Total excreted	48.9	43.4
0–72	Excreta	72.2	63.0
	Eggs	0.01	0.02
	Cage wash	1.73	2.46
	Total excreted	74.0	65.5
0–76	Excreta	88.7	85.4
	Eggs	0.01	0.02
	Cage wash	4.24	4.36
	Total excreted	92.9	89.9
Gizzard contents		0.11	0.06
Crop contents		1.08	1.08
Tissues (all)		0.11	0.15
Total calculated recovery		94.2	91.1

^a mean of two animals

^b mean of four animals

Table 7 Radioactivity in eggs from hens dosed with [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl at 3.8 ppm (low dose) and 180 ppm (high dose) in the feed for 4 consecutive days

Interval (hours)	Low dose (mg/kg equiv.) ^a		High dose (mg/kg equiv.) ^b	
	Yolk	White	Yolk	White
0–24	< 0.001	0.005	0.020	0.22
0–48	0.001	0.007	0.048	0.33
0–72	0.001	0.004	0.055	0.31
0–76	0.002	0.001	-	-

^a mean of two animals

^b mean of four animals

Table 8 Distribution of the radioactivity in the tissues of laying hens from hens dosed with [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl at 3.8 ppm (low dose) and 180 ppm (high dose) in the feed for 4 consecutive days

Sample	Low dose (mg/kg equiv.) ^a		High dose (mg/kg equiv.) ^b	
	mg/kg trinexapac-ethyl equiv.	% total dose	mg/kg trinexapac-ethyl equiv.	% total dose
Lean meat	0.002	0.04	0.12	0.06
Skin (incl. attached fat)	0.011	NC	0.37	NC
Peritoneal fat	0.003	0.01	0.18	0.01
Liver	0.013	0.02	0.60	0.03
Kidney	0.043	0.02	1.77	0.02

Sample	Low dose (mg/kg equiv.) ^a		High dose (mg/kg equiv.) ^b	
	mg/kg trinexapac-ethyl equiv.	% total dose	mg/kg trinexapac-ethyl equiv.	% total dose
Blood cells	0.006	0.01	0.28	0.01
Plasma	0.014	0.02	0.75	0.03
Total Tissue and Blood	NA	0.11	NA	0.15
Gizzard content	0.22	0.11	5.21	0.06
Crop content	0.96	1.08	15.8	1.08
Total	NA	1.30	NA	1.29

^a mean of two animals

^b mean of four animals

NC = Not calculable as total weight of skin (including attached fat) is not known

NA = Not applicable

In the second study (Müller 1993a, CGA163935/0306) the nature of the metabolites of trinexapac-ethyl from the previously described hen metabolism study was determined.

A high proportion (> 97%) of the radioactivity in the excreta of low and high dosed hens was extractable using acetonitrile and acetonitrile/water (1:1 v/v), more than 90% of which was trinexapac acid. All other metabolites contributed to less than 10% of the total radioactivity.

The extractability of the radioactivity in lean meat, liver and kidney samples of low and high-dose hens was high ($\geq 83\%$ of the total radioactive residues using acetonitrile/water (1:1 v/v)).

In the fat pools the majority of the radioactivity (59–64%) was extracted with chloroform/methanol (4:1 v/v). In order to separate acidic from neutral compounds the extract was then partitioned with basic phosphate buffer and re-transferred into methylene chloride after acidification. Approximately 11% of the radioactivity remained in the organic layer in the high dosed pool whereas in the low dosed pool the radioactivity of the extract was completely transferred into the basic aqueous layer and re-transferred in the methylene chloride phase for TLC analysis.

Radioactive residues in muscle (lean meat), liver, kidney and fat samples of low and high-dosed hens were predominantly trinexapac acid (44–84% of the total residues or 54–92% of the extractable radioactivity).

In skin including attached fat the extractability (chloroform/ methanol (4:1 v/v)) was only 14–30%. No additional radioactivity could be released from the non-extractable solid of the high-dose pool when heated in acetonitrile/ formic acid (99:1 v/v) under reflux for 2 hours. The extract was then partitioned with basic phosphate buffer and re-transferred into methylene chloride after acidification. In skin with attached fat, trinexapac acid was also the major metabolite accounting for 64–80% of the extractable radioactivity. However as the extractability was rather low, the contribution to the total radioactivity was only 9–24%.

The extractability (acetonitrile) in eggs from hens of both feed levels was 55–68% of the total radioactivity in the egg white and 45–49% in the yolk. In the yolk the major metabolite was again trinexapac acid amounting to 57–76% of the extractable radioactivity, while parent trinexapac-ethyl was present at only 10–25%. In egg white the major residue was parent accounting for 64–78% of the extractable TRR. Trinexapac acid was either not detected (high dose) or accounted for only 13% of the extractable TRR (low dose).

The gizzard contents of the low and high-dose hens, which were extracted with acetonitrile, contained unchanged parent compound (43–65%) and trinexapac acid (25–39%) indicating that hydrolysis already occurs partially in the digestive tract.

Table 9 Distribution of the radioactivity in the tissues of laying hens from hens after multiple applications with [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl in the feed for 4 consecutive days

Dose Level	Tissues	% Extracted	Quantitation	
			Trinexapac acid	Other metabolites

(ppm in the feed)			% of total residues	mg/kg trinexapac-ethyl equiv.	(mg/kg)
Low (3.8)	Lean meat	90.3	59.5	0.001	0.001
	Fat	63.9	53.5	0.002	0.001
	Skin/ fat	29.9	24.0	0.003	0.008
	Liver	83.4	69.0	0.009	0.004
	Kidney	91.1	84.2	0.036	0.007
High (180)	Lean meat	90.9	49.1	0.058	0.060
	Fat	59.4	43.7	0.080	0.103
	Skin/ fat	14.1	9.0	0.033	0.332
	Liver	88.4	48.7	0.293	0.308
	Kidney	89.1	53.0	0.938	0.832

Table 10 Quantitative distribution of metabolites and parent in eggs and gizzard content after multiple applications of [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl in the feed of hens for 4 consecutive days

Dose Level (ppm in the feed)	Tissues	% Extracted	Trinexapac acid		Trinexapac-ethyl	
			mg/kg trinexapac-ethyl equiv.	% of extracted	mg/kg trinexapac-ethyl equiv.	% of extracted
Low (3.8)	Egg white	55.1	0.0003	13.5	0.0017	77.8
	Egg yolk	45.4	0.0003	76.1	< 0.0001	10.2
	Gizzard content	96.5	—	38.8	—	ca. 43
High (180)	Egg white	68.3	—	ND	0.124	63.9
	Egg yolk	49.4	0.011	57.1	0.005	25.2
	Gizzard content	96.7	—	25.6	—	65.0

ND = Not Detectable

In another hen metabolism study [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was orally administered daily to five laying hens (White Leghorn, 50 weeks at acclimatisation, 1.45–1.61 kg bw at the start of acclimatisation and 1.47–1.62 kg bw at sacrifice) by gelatine capsule at 10 ppm (based on mean feed consumption of 0.125 kg/day, 1.27 mg/animal/day) in feed for 10 consecutive days (Powell 2006, CGA163935/1048).

Actual doses corresponded to 8.1–10.4 ppm feed, based on the quantity of diet consumed by each hen. Eggs were collected at 24 hour intervals throughout the morning before subsequent administration. Faeces samples were collected daily. Animals were sacrificed approximately 22 hours after the last dose. Samples of fat (skin and attached fat and peritoneal), muscle (breast and thigh), kidney, liver and gastrointestinal tract and contents were collected.

Between 87.5% and 90.6% of the administered dose was recovered in the excreta (mean 89.1%), indicating that the radioactivity was rapidly excreted. The total radioactive recoveries for the five hens ranged from 89.0–91.3% (mean 90.4%).

Table 11 Distribution of radioactivity following multiple doses of [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl in the feed

Sample	Hen 1043	Hen 1044	Hen 1045	Hen 1046	Hen 1047	Mean
	% total administered dose	% total administered dose	% total administered dose	% total administered dose	% total administered dose	% total administered dose
Egg white	0.04	0.02	0.02	0.06	0.04	0.036
Egg Yolk	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Muscle	0.2	< 0.1	< 0.1	0.1	< 0.1	< 0.12
Liver						
Skin with attached fat						
Peritoneal fat pad						
Whole blood						

Sample	Hen 1043	Hen 1044	Hen 1045	Hen 1046	Hen 1047	Mean
	% total administered dose	% total administered dose	% total administered dose	% total administered dose	% total administered dose	% total administered dose
GI tract						
Excreta	88.1	87.5	89.4	89.7	90.6	89.1
Cage wash	2.3	1.5	0.8	0.9	0.6	1.22
Total	90.6	89.0	90.3	90.7	91.3	90.4

Residue levels in the various tissue samples were all < 0.01 mg/kg equiv., indicating very little retention of the compound. Overall retention of the radioactivity in the tissues was < 0.2% of the administered dose.

Table 12 Total radioactive residues in tissue samples (expressed as trinexapac-ethyl equivalents) following multiple doses of [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl in the feed

Matrix	Hen 1043	Hen 1044	Hen 1045	Hen 1046	Hen 1047	Mean
	mg/kg equiv.	mg/kg equiv.	mg/kg equiv.	mg/kg equiv.	mg/kg equiv.	mg/kg equiv.
Muscle	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
Liver	< 0.003	0.005	0.008	0.006	< 0.003	0.005
Skin with attached fat	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
Peritoneal fat pad	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003

Total radioactive residues (TRRs), expressed as mg/kg trinexapac-ethyl equivalents in egg yolk were very low, ranging from < 0.003–0.009 mg/kg equiv. (mean values < 0.003–0.008 mg/kg equiv.). Egg white residues ranged from 0.005–0.031 mg/kg equiv. (mean values 0.011–0.018 mg/kg equiv.). The maximum residue levels of 0.009 and 0.031 mg/kg equiv. were reached by Day 8 of the dosing period (Table 13). Overall retention of the radioactivity in eggs was < 0.1% of the administered dose.

Table 13 Total radioactive residues in eggs (expressed as trinexapac-ethyl equivalents) following multiple doses of [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl in the feed

Matrix	Hen 1043	Hen 1044	Hen 1045	Hen 1046	Hen 1047	Mean
	mg/kg equiv.	mg/kg equiv.	mg/kg equiv.	mg/kg equiv.	mg/kg equiv.	mg/kg equiv.
Egg white						
1	0.006	0.005	0.014	0.027	0.024	0.015
2	0.012	0.007	YB	NS	0.013	0.011
3	0.014	0.009	0.016	0.021	NS	0.015
4	NS	NS	NS	0.013	0.011	0.012
5	0.006	0.007	0.011	0.014	0.026	0.013
6	0.014	0.008	0.010	0.015	0.019	0.013
7	NS	0.007	NS	0.021	0.018	0.015
8	0.014	0.008	0.012	0.031	NS	0.016
9	0.013	0.010	0.010	0.025	0.013	0.014
10	0.014	0.011	0.012	0.027	0.026	0.018
Maximum	0.014	0.011	0.016	0.031	0.026	
Egg yolk						
1	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
2	< 0.003	0.003	YB	NS	< 0.003	< 0.003
3	0.004	< 0.003	0.004	0.003	NS	0.003
4	NS	NS	NS	0.004	0.003	0.004
5	0.006	0.005	0.005	0.007	0.006	0.006
6	0.007	0.006	0.006	0.008	0.007	0.007
7	NS	0.007	NS	0.008	0.008	0.008
8	0.007	0.007	0.007	0.009	NS	0.008
9	0.007	0.007	0.008	0.009	0.008	0.008
10	0.008	0.007	0.007	0.008	0.007	0.007
Maximum	0.008	0.007	0.008	0.009	0.008	

YB = Yolk broke during separation from white, sample discarded

NS = No sample collected

TRR values for edible tissues and egg yolks were below 0.01 mg/kg trinexapac-ethyl equivalents, so no further analysis was undertaken.

A composite egg white sample (two hens, days 6–10 inclusive) was extracted with acetonitrile/ water (80:20 v/v) and acetone. After removal of acetonitrile and acidification with concentrated HCl, a liquid-liquid partition with ethyl acetate separated free organosoluble metabolites from polar residues. The major metabolites identified in the organosoluble residue were parent trinexapac-ethyl and trinexapac acid which accounted for 31.0% TRR (0.005 mg/kg equiv.) and 20.2% TRR (0.003 mg/kg equiv.) respectively (Table 14). The extract also contained at least two other components, none of which was > 0.001 mg/kg. No further analytical work was carried out on the solid debris or the aqueous fractions.

Table 14 Characterisation of ^{14}C -residues from egg whites after multiple applications with [1, 2, 6- ^{14}C -cyclohexyl] trinexapac-ethyl in the feed

Components	Egg White	
	mg/kg equiv. trinexapac-ethyl	% TRR
Total Radioactive Residue	0.016	100.0
Identified		
Parent	0.005	31.0
Trinexapac acid	0.003	20.2
Total identified	0.008	51.2
PES	0.002	10.6
Unanalysed Aqueous Fractions	0.003	18.3
Other unanalysed fraction	0.001	3.3
Chromatographed samples	–	–
Unknown components	0.001	3.3
Remainder	0.001	6.7
Losses during work-up	0.001	6.6
Grand total	0.017 ^a	100.0

^a Slight discrepancy due to rounding of the calculated residues

Summary of animal metabolism

Animal metabolism studies were carried out with [1, 2- ^{14}C -cyclohexyl] trinexapac-ethyl (goat and hens) or [1, 2, 6- ^{14}C -cyclohexyl] trinexapac-ethyl (goats, hens and rats). No accumulation of residues was observed in any organ, tissue or animal commodity.

In the goat [1, 2- ^{14}C -cyclohexyl] trinexapac-ethyl study, parent was hydrolysed to a significant extent prior to absorption. The acid was then efficiently absorbed and excreted via urine and faeces. Of the total dose 66–81% was eliminated in milk, faeces and urine. Trinexapac acid was the main component of urine and faeces (81–96%) and accounted for 81–90% of the total residues in muscle and kidney, 46–76% of the TRRs in milk, while accounting for lower proportions in liver and fat (31–67% of the TRRs), although for fat this represented 87–96% of the extractable radioactivity. In liver this represented only 34–47% of the extractable radioactivity, although other distinct metabolites observed in liver did not co-chromatograph with any of the reference compounds.

In another study in which [1, 2, 6- ^{14}C -cyclohexyl] trinexapac-ethyl was orally administered by gelatin capsule to two lactating goats, approximately 83% was eliminated in the milk, faeces and urine. Parent compound was not detected in any tissue or milk. Residues of trinexapac acid accounted for 66.0–96.8% TRR in milk and tissues. CGA-113745 (formed from further hydrolysis of trinexapac acid) was a major metabolite in liver, kidney and fat (6.0–16.3% TRR), but was not detected in muscle and milk. The metabolite pattern in urine and bile was similar to that of tissues.

In the hen parent trinexapac-ethyl was hydrolysed to the acid in the gizzard prior to absorption. The gizzard of the low and high-dose hens contained unchanged parent compound (43–65% of extractables) and trinexapac acid (25–39% of the extractables). The acid was efficiently absorbed and excreted. Over the period of the experiment, 85–89% of the total administered dose was eliminated in excreta. A high proportion (> 97%) of the radioactivity in the excreta of low and high dosed hens was extractable, more than 90% of which was trinexapac acid. All other metabolites contributed to less than 10% of the total radioactivity. Residues in muscle (lean meat), liver, kidney and fat samples of low and high-dosed hens were predominantly trinexapac acid (44–84% of the total residues or 54–92% of the extracted radioactivity). In the skin (with subcutaneous fat) only 14–30% of the total radioactivity was extractable. Trinexapac acid was the major metabolite in the extracts (64–80% of extracted radioactivity). The major metabolite found in egg yolks was trinexapac acid (57–76% of extracted radioactivity) while parent was present at 10–25%. In egg whites the major residue was parent accounting for 64–78% of extracted radioactivity, with acid only present at up to 13%. In another study the major metabolites identified in the organosoluble residue from egg whites were parent trinexapac-ethyl and trinexapac acid which accounted for 31.0% TRR and 20.2% TRR respectively.

In the rat, residues of trinexapac-ethyl were eliminated almost completely in the urine in the form of trinexapac acid (up to 100% of total urinary radioactivity), with low levels of a conjugated derivative of trinexapac acid detected in the urine of bile-duct cannulated rats (6.3% of the administered dose). In faeces, the parent compound accounted for 5–22% of total faecal radioactivity (1–2.5% of the administered dose), with the balance comprising trinexapac acid. Bile contained mainly a conjugated derivative of trinexapac acid (2.9% of the administered dose), with low levels of the parent compound also detected (0.2% of the administered dose).

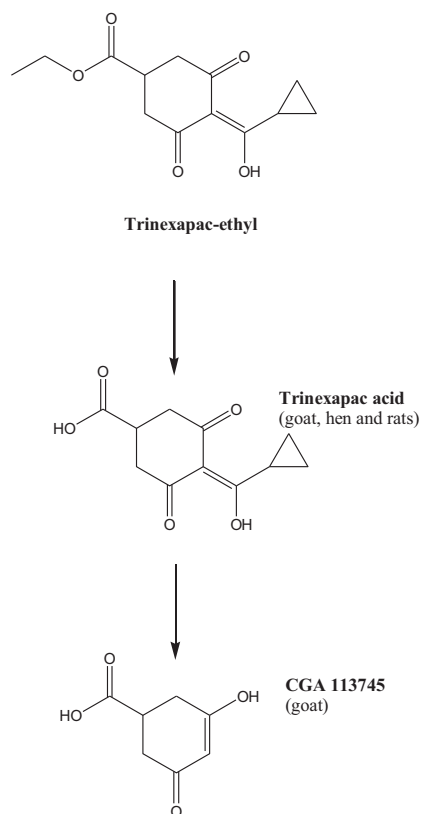


Figure 1 Proposed metabolic pathway for trinexapac-ethyl in animals

Plant metabolism

The metabolism of trinexapac-ethyl in spring wheat, spring rape, paddy rice and grass was investigated. The radiolabelled material was either [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl or [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl.

Rice

[1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was applied by foliar methods to paddy rice (Koshihikari) in water at rates of 40 and 160 g ai/ha (Gross 1996, CGA163935/0482). Applications were made at the lower rate 42 days after transplantation (stem elongation and stem node formation BBCH 37–41), or at the higher rate 64 days after transplantation (early panicle emergence). For the low application rate samples of rice plants were taken one hour as well as 7 and 21 days (full panicle emergence) after treatment. At maturity (82 days after treatment) the rest of the plant material was harvested and divided into grains, husks and straw.

The total radioactive residues (TRRs) are summarized below in Table 15. Total residues at harvest were 0.085 mg/kg trinexapac-ethyl equivalents in grain, 0.168 mg/kg equiv. in husks and 0.161 mg/kg equiv. in straw, indicating translocation of radioactivity from treated plants (foliage) into new growths. At maturity the parent content was less than 0.003 mg/kg in all plant parts. Non-extractable residues at maturity accounted for 40.5%, 41.1% and 72.0% of the total radioactivity in straw, husks and grain respectively.

Table 15 Distribution of radioactivity in various plant parts of rice, paddy water and soil after foliar application of [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl at 40 g ai/ha

Interval after application	Matrix	TRRs		Parent (mg/kg trinexapac-ethyl equiv.)	Extracted radioactivity (%) ^b		Non-extracted (%) ^b	Total (%) ^b
		(mg/kg trinexapac-ethyl equiv.)	(%) ^a		Cold extract ^c	Microwave ^d		
1 hour	Foliage	0.565	100	0.373	97.2	1.2	1.4	99.8
	Paddy water	0.020		NA				
7 days (Flowering)	Foliage	0.138	100	0.008	88.6	3.7	8.1	100.4
	Paddy water	0.002		NA				
21 days	Foliage	0.066	100	0.001	82.1	5.5	15.7	103.2
	Paddy water	< 0.001		NA				
82 days (Maturity)	Straw	0.161	100	0.002	56.5	10.4	40.5	107.4
	Husks	0.168	100	0.002	55.0	8.3	41.1	104.4
	Grain	0.085	100	< 0.001	16.2	12.5	72.0	100.7
	Soil	0.014		< 0.001	NA	5.1	96.2	101.3

^a % of radioactivity found in plant part

^b % of radioactivity found in plant part and determined by combustion

^c Using methanol/ water (8:2 v/v)

^d Using n-propanol/ water (8:2 v/v)

NA = not analysed

In the case of the 160 g ai/ha treatment plant samples were taken only at maturity (60 days after treatment) and divided into grains, husks and straw. The extractability of the residues from harvested material treated with 160 g ai/ha is summarized in Table 16.

Table 16 Distribution of radioactivity in various plant parts of rice after foliar application of [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl at 160 g ai/ha

Interval after application	Matrix	TRRs		Parent (mg/kg trinexapac-ethyl equiv.)	Extracted radioactivity (%) ^b		Non-extracted (%) ^b	Total (%) ^b
		(mg/kg trinexapac-ethyl equiv.)	(%) ^a		Cold extract ^c	Microwave ^d		
60 days	Straw	1.584	100	0.011	73.2	8.2	19.1	100.5
(Maturity)	Husks	2.223	100	0.078	78.0	5.3	16.0	99.3
	Grain	1.067	100	0.004	33.9	19.6	45.0	98.5

^a % of radioactivity found in plant part^b % of radioactivity found in plant part and determined by combustion^c Using methanol/ water (8:2 v/v)^d Using n-propanol/ water (8:2 v/v)

In foliage unchanged parent compound decreased from 66.0% of the TRR at one hour after application, to 5.5% TRR after 7 days which indicated rapid degradation of the molecule. In addition to parent, up to ten metabolite fractions were observed, the major component being trinexapac acid (17.8–26.1% of TRR). Other metabolites observed included CGA 313458 (2.2–5.1% of the TRR), CGA 275537 or tricarballic acid (0–4.0% of the TRR) and CGA 312753 or trans aconitic acid (0–2.6% of the TRR).

Table 17 Summary of identified components in rice foliage after treatment with [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl (40 g ai/ha treatment)

Metabolite	Rice matrix					
	Foliage E ₁ ^a (1 hr after application)		Foliage E ₁ ^a (7 days after application)		Foliage E ₁ ^a (21 days after application)	
	(mg/kg trinexapac-ethyl equiv.)	% TRR	(mg/kg trinexapac-ethyl equiv.)	% TRR	(mg/kg trinexapac-ethyl equiv.)	% TRR
	0.565	100	0.138	100	0.066	100
II ₁			0.025	18.3	0.014	21.8
II ₂			0.008	6.0	0.004	5.4
II ₃ CGA312753 (Aconitic acid)			0.004	2.5	0.002	2.6
II ₄			0.004	2.9	0.002	2.7
II ₅ CGA 275537 (Tricarballic acid)			0.006	4.0	0.003	3.9
II ₆			0.009	6.5	0.005	7.1
II ₇			0.003	1.9		
II ₈ CGA 313458	0.012	2.2	0.007	5.1	0.002	2.6
II ₉ CGA 329773						
II ₁₀ Trinexapac acid	0.101	17.8	0.036	26.1	0.017	25.5
II ₁₁ Trinexapac-ethyl	0.373	66.0	0.008	5.5	0.001	1.6
Unresolved	0.043	7.6	0.014	9.8	0.006	8.9
Non-extractables	0.008	1.4	0.011	8.1	0.010	15.7
Total		95.0		96.7		97.8

^a E₁ = cold extract

Extractability of residues in grain was low. Only 16.2% of the radioactivity could be extracted with methanol/ water and another 12.5% were extracted with aqueous propanol under harsh microwave conditions. The extractable radioactivity consisted mainly of trinexapac acid with 11.6% of the TRR. Absolute amounts were low, all fractions being significantly below 0.01 mg/kg, except trinexapac acid with exactly 0.01 mg/kg (Table 18).

Table 18 Summary of identified components in rice grain, husks and straw 82 days after treatment with [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl (40 g ai/ha treatment)

Metabolite	Rice matrix												Soil	
	Grain				Husks				Straw					
	E ₁ ^a	E ₂ ^b	Σtr ₁ + E ₂		E ₁ ^a	E ₂ ^b	Σ E ₁ + E ₂		E ₁ ^a	E ₂ ^b	Σ E ₁ + E ₂		E ₁	
	% TRR	% TRR	mg/kg equiv.	% TRR	% TRR	% TRR	mg/kg equiv.	% TRR	% TRR	% TRR	mg/kg equiv.	% TRR	mg/kg equiv.	% TRR
			0.085	100			0.168	100			0.161	100	0.014	100
II ₁	0.7	6.5	0.007	8.0	30.0	4.5	0.058	34.5	24.9	4.6	0.048	29.5	—	—
II ₂	0.4								16.4	3.0	0.031	19.4	—	—
II ₃	0.4												—	—
CGA312753	0.4												—	—
II ₄	—				—	—	0.003	—					—	—
II ₅ CGA 275537 (Tricarballic acid)	0.5		< 0.001	0.5	3.2	—	0.005	3.2					—	—
II ₆	1.3	1.2	0.003	2.9	3.9	0.5	0.007	4.4	2.0	0.4	0.004	2.4	—	—
II ₇	—				1.3	—	0.002	1.3	—	—	—	—	—	—
II ₈ CGA 313458	—				—	—	—	—	3.9	0.7	0.007	4.6	—	—
II ₉ CGA 329773	0.4				0.7	—	0.001	0.7	—	—	—	—	—	0.6
II ₁₀ Trinexapac acid	10.0	1.6	0.010	11.6	8.3	0.6	0.015	8.9	4.2	0.7	0.008	4.9		0.7
II ₁₁ Trinexapac-ethyl	0.1		< 0.001	0.1	1.8	—	0.003	1.8	0.9	—	0.001	0.9		0.5
Unresolved	3.8		0.004	5.6	9.5	0.5	0.007	10.0	5.2	1.0	0.006	6.2		1.0
Non-extractables	—		0.061	72.0	—	—	0.069	41.1	—	—	0.065	40.5		96.2
Total				99.4				100.2				106.0		101.3

^a E₁ = cold extract^b E₂ = microwave extract

Due to the low residues and high % of non-extractable radioactivity in grain, the matrices of the 160 g ai/ha experiment were used for further characterisation. As also observed for the 40 g ai/ha treatment, trinexapac acid was the major component. Together with the microwave fraction this metabolite accounted for 28.1% of the total residues in grain. Other metabolites observed included parent trinexapac-ethyl (0.7% of the TRR), CGA 329773 (0.7% of the TRR), CGA 313458 (1.6% of the TRR) and CGA 275537 or tricarballic acid (2.1% of the TRR) (Table 19). Partition of the aqueous residues of E₁ with diethyl ether at pH 4 gave 73% of the radioactivity in the organic phase and 27% in the water phase. The organic phase consisted mainly of trinexapac acid and the water phase the polar fractions II₁, II₂ and II_{3a}. Further enzymatic and mild chemical treatment (0.1 N NaOH) showed that fractions II₁ and II₂ in grain consisted mainly of trinexapac acid in various conjugated forms, probably as esters of sugars and/ or plant constituents.

To characterise the methanol/water insoluble radioactivity in grain the residue R₁ (before microwave extraction) was analysed by digestion with 0.5 N NaOH followed by hydrolysis of the starch at pH 1. 70.1% of the radioactivity was eluted as a weakly acidic fraction. This radioactivity showed a similar TLC pattern to that already observed for the extractable radioactivity with fraction II₁-II₂ and II₁₀ as major spots. Formation of [¹⁴C]-osazone (8% of TRR) from the neutral water eluate indicated incorporation of carbon fragments into the sugar pool of the plant (Table 20).

In husks, extractable radioactivity of 160 g ai/ha treatment consisted mainly of II₁ (20.9% of the TRR), II₂ (8.5% of the TRR), trinexapac acid (13.8% TRR), tricarballic acid (8.2% TRR) and trinexapac-ethyl (6.1% TRR) (Table 19). Partition of the aqueous residues with diethyl ether at pH 4 showed 26% of the radioactivity in the organic phase and 74% in the water phase. The organic phase consisted mainly of trinexapac acid and parent whereas the water phase consisted mainly of the polar fractions II₁, II₂ and II_{3a} as well as tricarballic acid. The polar fractions II₁ through II_{3a} consisted mainly of acid and hydrolysis product of trinexapac acid, tricarballic acid and CGA 313458 in various conjugated forms, most probably as esters of sugars and/or plant constituents.

In straw from the 160 g ai/ha treatment besides the dominant fractions II₁ (21.2% of the TRR) and II₂ (17.0% of the TRR), tricarballic acid (10.7% of the TRR) was a major metabolite followed by trinexapac acid (6.9% TRR) and CGA 313458 (7.8% of the TRR) (Table 19).

Partition of the aqueous residues of E₁ of 160 g ai/ha treatment with diethyl ether at pH 4 gave 22% of the radioactivity in the organic phase and 78% in the water phase. The organic phase consisted mainly of trinexapac acid, II₈ = CGA313458, II₉ = CGA329773 and parent whereas the water phase consisted mainly of the polar fractions II₁, II₂, and II₈ as well as tricarballic acid. Chemical hydrolysis of the water phase (0.1 N NaOH) cleaved metabolite fraction II₂ (17.0% TRR) completely in favour of tricarballic acid and trinexapac acid proving that II₂ in straw consisted of conjugate esters of the tricarballic acid and trinexapac acid. Fraction II₁ was not altered by acid or base treatment. To characterise the non-extractable radioactivity in straw of 160 g ai/ha treatment after cold methanol and microwave extraction the residue R₂ was analysed. After boiling in water, 35% of the residual radioactivity was extracted, containing mainly water-soluble polysaccharides of the cell wall material. The remaining insoluble part was solubilised with boiling 2 N NaOH. Using this procedure another 49.5% was released from the non-extractable radioactivity containing mainly hemicellulose and lignin of the cell wall material. Quantitation of the fractions originating from the non-extractable radioactivity in straw is given in Table 20.

Table 19 Summary of identified components in rice grain, husks and straw 60 days after treatment with [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl (160 g ai/ha treatment)

Metabolite	Rice matrix											
	Grain				Husks				Straw			
	E ₁ ^a	E ₂ ^b	Σtr ₁ +E ₂		E ₁ ^a	E ₂ ^b	Σ E ₁ +E ₂		E ₁ ^a	E ₂ ^b	Σ E ₁ +E ₂	
	% TRR	% TRR	mg/kg equiv.	% TRR	% TRR	% TRR	mg/kg equiv.	% TRR	% TRR	% TRR	mg/kg equiv.	% TRR
			1.067	100			2.223	100			1.584	100
II ₁	2.6	2.6	0.055	5.2	20.2	0.7	0.465	20.9	18.4	2.8	0.336	21.2
II ₂	0.9	—	0.010	0.9	7.4	1.1	0.189	8.5	16.5	0.5	0.269	17.0
II _{3a}	1.3	0.5	0.019	1.8	5.1	—	0.113	5.1	—	—	—	—
II _{3b}	—	—	—	—	3.4	—	0.076	3.4	—	—	—	—
II ₄	—	—	—	—	—	—	—	—	2.1	—	0.033	2.1
II ₅ CGA 275537 (Tricarballic acid)	1.9	0.2	0.022	2.1	8.0	0.2	0.182	8.2	10.4	0.3	0.169	10.7
II ₆	0.8	—	0.009	0.8	2.7	—	0.060	2.7	0.6	—	0.010	0.6
II ₇	0.3	1.0	0.014	1.3	1.3	0.3	0.036	1.6	—	—	—	—
II ₈ CGA 313458	—	1.6	0.017	1.6	1.4	0.5	0.042	1.9	7.0	0.8	0.124	7.8
II ₉ CGA 329773	—	0.7	0.007	0.7	0.8	0.3	0.024	1.1	0.8	—	0.013	0.8
II ₁₀ Trinexapac acid	23.0	5.1	0.30	28.1	13.4	0.4	0.307	13.8	6.7	0.2	0.109	6.9
II _{10a}	—	1.4	0.015	1.4	—	0.2	0.004	0.2	—	—	—	—
II _{10b}	—	1.7	0.018	1.7	—	0.7	0.016	0.7	—	—	—	—
II ₁₁ Trinexapac-ethyl	0.4	0.3	0.007	0.7	6.1	—	0.136	6.1	1.3	0.1	0.022	1.4
Unresolved	2.7	3.9	0.070	6.6	7.5	0.9	0.187	8.4	7.5	2.1	0.152	9.6
Non-extractables			0.48	45.0			0.356	16.0			0.303	19.1
Total				97.9				98.6				97.2

^a E₁ = cold extract

^b E₂ = microwave extract

Table 20 Summary of identified components in rice grain, husks and straw after solvent partition, 0.1 N NaOH treatment of cold extract E₁ and non-extractable analysis (160 g ai/ha treatment with [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl)

Metabolite Fractions	Rice matrix											
	Grain				Husks				Straw			
	E ₁ Org. phase	E ₁ Water Phase ^a	NE Non-extr. ^b	Σ	E ₁ Org. phase	E ₁ Water Phase ^a	NE Non-extr. ^b	Σ E N ₁ Org. phase	E ₁ Org. Phase	E ₁ Water Phase ^a	Σ E Non extr. ^b	Σ
	% TRR	% TRR	% TRR	% TRR	% TRR	% TRR	% TRR	% TRR	% TRR	% TRR	% TRR	% TRR
II ₁		0.9	13.2	14.1		9.2	0.7	9.9		28.0	2.5	31.3
II ₂									0.2		1.0	1.2
II ₃ CGA312753 (Aconitic acid)							1.1	1.1				
II _{2a}											0.8	0.8
II _{3a}		1.3		1.3		3.0		3.0				
II ₄										2.3		2.3
II ₅ CGA 275537 (Tricarballic acid)	0.3	1.6	1.3	3.2		16.8	0.2	17.0	0.8	12.2	0.6	13.6
II ₆	0.3	0.4	0.9	1.6	0.4			0.4	0.6	0.8		1.4
II ₇			1.2	1.2			0.3	0.3		0.8		0.8
II ₈ CGA 313458		0.2	3.1	3.3	0.4	6.5	0.5	7.4	4.1	2.3		6.4
II ₉ CGA 329773	0.8		1.7	2.5	0.9		0.3	1.2	0.8		0.3	1.1
II ₁₀ Trinexapac acid	20.2	3.8	11.6	35.6	11.0	18.5	0.4	29.9	6.7	1.7	0.2	8.6
II _{10a}							0.2	0.2				
II _{10b}							0.7	0.7				
II ₁₁ Trinexapac-ethyl	0.4		6.0	6.4	6.2			6.2	1.3			1.3
STR6 ^c											8.9	8.9
Pectine Lignin Cellulose ^d											1.6	1.6
¹⁴ C-glucose			8.0	8.0								
Unresolved	2.2	1.0	6.3	9.5	1.5	3.8	0.9	6.2	1.6	8.9	1.0	11.5
Characterised				77.2				72.9				79.3
Identified				59.0				60.3				41.5
Non-extractables								16.0				
Total				86.7				99.5				90.8

^a After 0.1 N NaOH treatment

^b After basic/acid treatment of R₁ (grain) and R₂ (straw)

^c Fractions STR-E₅(E₄) 6.8%, STR-E₇(E₆) 1.4% and STR-R₆(R₅) 0.7%

^d Pectine 0.1%, Cellulose 1.4% and Lignin 0.1%

E₁= cold extract

NA = not analysed

The proposed metabolic pathways of trinexapac-ethyl in rice are mainly by hydrolysis of the ester bond to give trinexapac acid, aromatisation of the C₆ ring of trinexapac acid presumably by hydroxylation followed by elimination of water and keto-enol tautomerisation, yielding 4-cyclopropanecarbonyl-3,5-dihydroxy-benzoic acid (CGA 329773), cleavage of the C₆ ring of trinexapac acid to 2-(4-cyclopropyl-4-hydroxy-2-oxo-but-3-enyl)-succinic acid (CGA 313458) and stepwise oxidation/decarboxylation after cleavage of the C₆ ring of trinexapac acid yielding saturated and unsaturated tricarboxylated acids such as 3-carboxy-pentanedioic acid (tricarballic acid = CGA 275537) and 3-carboxy-pent-2-enedioic acid (trans aconitic acid = CGA 312753) and conjugation of trinexapac acid, CGA 313458 and CGA 275537 with sugars and/ or other plant constituents.

Spring wheat

[1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl formulated as an emulsion concentrate was applied to spring wheat (Besso) by foliar spraying at a rate of 150 g ai/ha (Krauss 1990, CGA163935/0086). Applications were made to two week old plants (greenhouse experiment) and six week old plants (one-node stage, field experiment). In the greenhouse experiment samples were taken at seven time intervals from 0.5 hours, 4 hours, 1, 2, 7, 14 and 21 days. Plants were separated into leaves and roots. In the field experiment samples were taken at 0 days (tops), 25-days (ears and leaves at ear emergence), 48 days (ears and leaves at milky stage) and 71 days (grain, husks, straw at maturity). Soil samples were also taken.

Incorporation of radioactivity into the greenhouse grown plants is summarized below. After rapid initial dissipation of radioactivity from the leaf surface during the first day, subsequent decrease was slow for the next 20 days.

Table 21 Distribution of radioactivity in wheat whole tops and roots after foliar application of [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl (greenhouse short term experiment)

Interval	Plant part	TRRs		Parent (mg/kg trinexapac- ethyl equiv.)	Recovered (%) ^b	Surface (%) ^a	Penetrated		Total (%) ^c
		(mg/kg trinexapac- ethyl equiv.)	% ^a				Cold ext. (%)	NE (%) ^a	
30 minutes	Whole tops	5.476	60.8	4.421	60.8	83.6	16.3	0.1	100.0
	Roots	0.153	0.2	0.015	0.2		68.5	31.5	100.0
	Plant Total		61.0		61.0				
	Soil Whole Pot	0.066	39.0	0.013	39.0		31.7	68.3	100.0
	Soil Total		39.0		39.0				
	Total		100.0		100.0				
4 hours	Whole tops	2.446	44.2	1.028	28.5	43.3	54.7	2.0	100.0
	Roots	0.756	1.7	0.024	1.1		59.9	40.1	100.0
	Plant Total		45.9		29.6				
	Soil Whole Pot	0.057	54.1	0.004	34.9		18.4	81.6	100.0
	Soil Total		54.1		34.9				
	Total		100.0		64.5				
1 day	Whole tops	1.721	33.3	0.226	22.3	20.1	75.5	4.5	100.1
	Roots	2.080	5.3	0.256	3.5		60.4	39.6	100.0
	Plant Total		39.2		25.8				
	Soil Whole Pot	0.066	60.8	< 0.001	40.1		12.7	87.3	100.0
	Soil Total		60.8		40.1				
	Total		100.0		65.9				
2 days	Whole tops	1.118	28.5	0.145	18.1	20.3	74.1	5.6	
	Roots	1.163	3.9	0.015	2.5		54.9	45.1	
	Plant Total		32.4		20.6				
	Soil Whole Pot	0.069	67.6	< 0.001	43.0		13.8	86.2	100.0
	Soil Total		67.6		43.0				
	Total		100.0		63.6				
7 days	Whole tops	0.587	28.7	0.012	14.5	8.3	83.4	8.3	100.0
	Roots	0.411	3.6	< 0.001	1.8		38.1	61.9	100.0
	Plant Total		32.2		16.3				
	Soil Whole Pot	0.057	67.8		34.3		15.3	84.7	100.0
	Soil Total		67.8		34.3				
	Total		100.0		50.6				
14 days	Whole tops	0.466	47.1	0.002	25.1	6.2	83.6	10.3	100.1
	Roots	0.121	4.1	< 0.001	2.2		12.7	87.4	100.1
	Plant Total		51.2		27.3				
	Soil Whole Pot	0.044	48.8		26.0		13.5	86.6	100.1

Interval	Plant part	TRRs		Parent (mg/kg trinexapac- ethyl equiv.)	Recovered (%) ^b	Surface (%) ^a	Penetrated		Total (%) ^c
		(mg/kg trinexapac- ethyl equiv.)	% ^a				Cold ext. (%)	NE (%) ^a	
	Soil Total		48.8		26.0				
	Total		100.0		53.3				
21 days	Whole tops	0.305	39.2	< 0.001	19.6	5.1	81.1	13.8	100.0
	Roots	0.127	4.4	< 0.001	2.2		11.1	88.9	100.0
	Plant Total		43.6		21.8				
	Soil Whole Pot	0.049	56.4	< 0.001	28.2		12.7	87.3	100.0
	Soil Total		56.4		28.2				
	Total		100.0		50.0				

^a % of radioactivity found in sub-balanced plant parts/soil system; non-extractables (NE) is residual radioactivity determined after cold solvent extraction

^b % of radioactivity recovered at interval 1

^c % of radioactivity found in plant parts/ soil, determined by the sum of extractable and non-extractable radioactivity

The characterisation of the leaf rinse radioactivity is shown in the following table. Once penetrated, trinexapac-ethyl was hydrolysed to trinexapac acid. Parent concentration dropped to less than 2% of TRR 7 days after application, whereas the acid metabolite accounted for 30–40% of TRR in the leaf extract after 1 day and the following twenty days. After the first 24 hours approximately 80% of the recovered radioactivity had penetrated the plant surface. Translocation of radioactivity from treated plant parts into newly grown parts could be demonstrated by autoradiography.

Table 22 Residues of parent and trinexapac acid in wheat whole tops after foliar application of [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl (greenhouse short term experiment)

Interval	Parent trinexapac-ethyl		Trinexapac acid	
	Surface (%) ^a	Plant extract (%) ^a	Surface (%) ^a	Plant extract (%) ^a
30 minutes	68.8	11.9	0.6	0.8
4 hours	31.4	10.6	5.0	26.0
1 day	11.9	1.2	2.0	37.0
2 days	10.5	2.5	2.0	35.6
7 days	1.7	0.3	1.5	37.2
14 days	0.5	< LD ^b	0.5	34.7
21 days	0.1	< LD ^b	0.8	29.8

^a In % of radioactivity recovered at each interval

^b LD = Limit of Detection (< 0.1% of radioactivity)

The incorporation of the radioactivity into the field grown spring wheat plants is summarized in the following table. Translocation of radioactivity from aerial plant parts to ears was significant. Total radioactive residues in the ears increased from 0.256 mg/kg at ear emergence (25 days after application) to approximately 0.47 mg/kg at milky stage and maturity. This behaviour of the TRR was confirmed by autoradiography. The TRR in grain, husks and straw at maturity was 0.462, 0.440 and 0.542 mg/kg respectively. Parent was always less than the limit of detection (0.001 mg/kg).

Table 23 Distribution of radioactivity in wheat whole tops, ears, grain, husks and straw after foliar application of [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl (field long term experiment)

Interval	Plant Parts/ Soil Layers	TRRs		Parent (mg/kg trinexapac- ethyl equiv.)	Extracted radioactivity (%) ^b		Non-extracted (%) ^b	Total (%) ^b
		(mg/kg trinexapac- ethyl equiv.)	% ^a		Cold extraction ^d	Soxhlet ^e		
0 days	Whole tops	0.801	100	0.209	84.1	2.5	12.2	98.8
	Soil							
	0–5 cm	0.274	82.5	0.002	14.5	0.9	82.6	98.0
	5–10 cm	0.044	16.1	< 0.001	12.9	0.8	85.8	99.5
	10–20 cm	< 0.001	1.1	NA ^c	NA ^c	NA ^c	NA ^c	
	20–30 cm	< 0.001	0.3	NA ^c	NA ^c	NA ^c	NA ^c	
	Soil Total	0.034	100.0					
25 days (Ear emergence)	Ears	0.256	100	< 0.001	84.3	2.0	12.5	98.8
	Leaves	0.225	100	< 0.001	87.2	2.8	14.7	104.7
48 days	Ears	0.473	100	< 0.001	83.2	3.0	18.3	104.5
(Milky stage)	Leaves	0.438	100	< 0.001	73.5	3.0	25.3	101.8
71 days	Grain	0.462	100	< 0.001	68.4	1.7	25.1	95.2
	Husks	0.440	100	< 0.001	46.6	1.5	50.8	98.9
	Straw	0.542	100	< 0.001	41.0	4.1	61.9	107.0
	Soil							
	0–5 cm	0.071	81.0	< 0.001	6.3	0.6	92.2	99.1
	5–10 cm	0.008	11.7	NA ^c	NA ^c	NA ^c	NA ^c	
	10–20 cm	0.001	4.1	NA ^c	NA ^c	NA ^c	NA ^c	
	20–30 cm	< 0.001	3.3	NA ^c	NA ^c	NA ^c	NA ^c	
	Soil Total	0.011	100.1					

^a In % of the radioactivity found in the sub-balanced plant parts/ soil layers^b In % of radioactivity found in the plant part/ soil layers and determined by combustion^c NA = not analysed^d Using methanol/ water (8:2 v/v)^e Using methanol

Characterisation of the TRR in the growing plants and at maturity is shown in the following table. The portion of the organosoluble radioactivity decreased from approximately 70% in the fresh green plant parts to 20–40% in straw and grain of the extractable radioactivity. The non-extractable residues increased from a few percent of the TRR in the fresh green plant parts to 25–50% of the TRR in grain and husks and 62% of the TRR in the straw at maturity.

Apart from the samples taken shortly after application, no parent compound could be detected in any plant part at later intervals. However the trinexapac acid was present in varying amounts in all plant parts. In the 25 and 48 day ears its relative amount was higher (28 and 25% of TRR respectively) than in the leaves (13 and 3% of TRR respectively). Likewise its content in grain (24% of TRR) was higher than in husks (10.0% of TRR) or in straw (4.5% of TRR).

Table 24 Extractability and residues of parent and trinexapac acid in whole tops, ears, grain, husks, straw and soil after foliar application of [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl (field long term experiment)

Interval	Matrix	Organic phase (%) ^a	Water phase (%) ^a	Parent (%) ^b	Trinexapac acid (%) ^b
Application	Whole tops	69.9	28.8	31.0	24.1
0 days	Soil (0–5 cm)			4.3	7.4
	Soil (5–10 cm)			2.9	6.1
25 days	Ears	45.0	52.8	< LD ^c	28.0

Interval	Matrix	Organic phase (%) ^a	Water phase (%) ^a	Parent (%) ^b	Trinexapac acid (%) ^b
(Ear emergence)	Leaves	23.6	75.6	< LD ^c	13.3
48 days	Ears	49.2	45.8	< LD ^c	24.8
(Milky stage)	Leaves	11.0	87.2	< LD ^c	2.8
71 days	Grain	39.1	60.8	< LD ^c	24.2
(Maturity)	Husks	33.8	61.2	< LD ^c	10.0
	Straw	20.9	75.4	< LD ^c	4.5
	Soil (0–5 cm)			< LD ^c	~0.3

^a In % of the extracted radioactivity

^b in % of the total radioactivity found in plant parts and soil layers and determined by combustion

^c LD = Limit of Detection (< 0.3% of radioactivity)

Eight significant metabolite fractions were characterised originating from the extracts of the field samples (see Table 25). The major metabolite fraction I₅ was identified as trinexapac acid.

The metabolite pattern in leaves, ears and husks was qualitatively similar, showing the presence of the metabolite fractions I₁, I₂, I₄ and I₅. In grain, metabolites I₁ and I₂ were not found. The water soluble metabolite fractions II₁ and II₃ were cellulase resistant. The upper soil layer at plant maturity contained trinexapac acid at 0.3% of the total radioactivity. Non-extractable radioactivity ranged from 26–92% of total residues under the extraction conditions used.

Table 25 Quantification of metabolite fractions in plant parts at maturity (field long term experiment)

Metabolite	Wheat matrix			Soil (0–5 cm) (%)
	Grain (%) ^a	Husks (%) ^a	Straw (%) ^a	
II ₁	6.8	10.0	8.0	4.4
II ₂	3.1	NA	2.4	NA
II ₃	10.9	NA	3.1	NA
II ₄	1.7	NA	NA	NA
I ₁	–	6.1	~0.5	NA
I ₂	–	3.3	~0.2	NA
I ₄	~0.7	~0.6	~0.1	~0.4
I ₅ Trinexapac acid	24.2	10.0	4.5	~0.3
Unresolved and soxhlet	25.4	14.9	21.4	1.2
Soxhlet	1.7	1.5	3.8	0.6
Non-extractable radioactivity	26.4	51.4	57.9	92.2
Total	100.9	97.8	101.9	99.1

^a In % of the radioactivity totally found in plant parts

NA = Not analysed

A stem-injection experiment was conducted on six week old plants grown under greenhouse conditions and an incubation experiment (45 days at room temperature) of a cell suspension of treated leaves. The injection occurred with approximately 40–50 µg of [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl per plant. All injected plants were harvested at maturity, 69 days after treatment (Krauss 1993, CGA 163935/0303).

In addition to the analytical methods used in the previous report silicagel column chromatography run was applied as flash chromatography under pressure, for fractionation of samples the column was eluted with a step gradient using ethylene chloride/ methanol mixtures and for isolation, purification and analysis different HPLC systems were applied. For the analysis of the non-extractable radioactivity in grain, husks and straw, various procedures were used. After extraction at high temperature and purification by partitioning and filtration, the water phase was dialysed in membrane bags. Further techniques for the characterisation and identification of the metabolites were high voltage electrophoresis and chemical derivatisation (methylation and acetylation).

Trinexapac acid was the dominant metabolite observed in grain (27.9% of the TRR). Other important metabolites observed included II₄, CGA 275537 (II₂) and II₃ which after methylation was identified as 4-cyclopropanecarbonyl-3, 5 dihydroxy-benzoic acid (CGA 329773). Approximately 85% of the TRR was characterised in grain and 51% could be identified.

The major metabolite observed in husks was trinexapac acid (16.7% of the TRR). Other metabolites observed included CGA 275537 (II₂). Approximately 86% of the TRR was characterised in husks and 37% could be identified.

In straw, the major fraction observed in the methylene chloride extract was trinexapac acid. Metabolite fraction I₂ which contained the mono ethyl ester of the aconitic acid was also present in the organic phase. After purification of the fraction which was generated from the water phase by partition with ethyl acetate, three major fractions were obtained which corresponded to the metabolite fractions II₃, trinexapac acid and II₄. Heating a suspension of non-extractables in a propanol/water mixture released a further 47% of TRR. From these fractions the metabolite fractions I₂, I₄ and trinexapac acid could be identified. Approximately 94% of the TRR was characterised in straw and 31% could be identified. The major metabolite observed in straw was trinexapac acid (12.8% of the TRR).

Only 6.9% of the total residues in the 0–5 cm soil layer could be extracted by methanol/water extraction followed by soxhlet extraction as previously reported (Table 25), with trinexapac acid only approximately 0.3% of the total residues. Analysis of the non-extractable radioactivity was performed by microwave extraction. The major part of the soil non-extractables (55% of the total residues) was released and partitioned with ethyl acetate. Trinexapac (2.2% of the total residues) and some minor fractions were in the combined organic phase.

Table 26 Summary of identified components in spring wheat matrices at maturity after treatment with [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl

Metabolite	Wheat matrix					
	Grain		Husks		Straw	
	mg/kg equiv.	% TRR ^a	mg/kg equiv.	% TRR ^a	mg/kg equiv.	% TRR ^a
II ₁ ^b	0.031	6.8 ^d	0.044	10.0	0.043	8.0
II ₂ CGA275537	0.014	3.1		NA ^c	0.013	2.4
II ₃ CGA329773	0.050	10.9		NA ^c	0.017	3.1
II ₄	0.0078	1.7		NA ^c		NA ^c
I ₁		NA ^c	0.027	6.1	0.0027	0.5
I _{2a} CGA 312753 mono-ethyl ester		NA ^c	0.019	4.3	0.0097	1.8
I ₄ ^c	0.0032	0.7	0.0026	0.6	0.013	2.4
I ₅ Trinexapac acid	0.129	27.9	0.073	16.7	0.069	12.8
Unresolved and soxhlet		33.6		48.7		63.4
Non-extractables ^f	0.070	15.1	0.050	11.4	0.061	11.2
Characterised		84.7		86.4		94.4
Identified		51.1		37.7		31.0
Total	0.462 ^g	99.8 ^h	0.440 ^g	97.8 ^h	0.542 ^g	105.6 ^h

^a In % of the total radioactivity found in plant parts

^b Radioactivity remaining at the start in TLC analysis

^c NA = Not Analysed

^d Includes sugar conjugate of trinexapac acid

^e Acidic compound

^f Obtained after alkaline hydrolysis

^g TRR

^h Sum of characterised and non-extractables

The proposed transformation of trinexapac-ethyl in spring wheat is mainly by hydrolysis of the ester bond to give trinexapac acid. Conjugation of trinexapac acid with sugar occurs to a small extent in grain. Aromatisation of the C₆ ring of trinexapac acid presumably by hydroxylation followed by elimination of water and keto-enol tautomerisation, yielding CGA 329773 also occurs. Cleavage of

the C₆ ring of trinexapac-ethyl was postulated as an alternative pathway. Stepwise oxidation/decarboxylation after cleavage of the 6-membered ring yielded saturated and unsaturated tricarboxylic acids such as tricarballic acid (CGA 275537) and the mono ethyl ester of aconitic acid (CGA 312753).

Rape

[1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was applied to spring rape (*Tobin Canola*) under greenhouse conditions in plastic containers filled with soil (Nicollier 1991, CGA163935/0209). One treatment was made to 37 day old spring rapeseed (stem elongation) at an application rate of 400 g ai/ha. Plants were sampled at 30 minutes (whole plants), 14 days (green and flowering parts) and 65 days (maturity - stalks, pods and seeds) after application. Soil samples were also taken.

The TRRs are summarized in Table 27. TRRs of 5.74 mg/kg trinexapac-ethyl equivalents, 1.43 mg/kg equiv. and 3.14 mg/kg equiv were found in the pods, seeds and stalks respectively. No parent compound was detected (< 0.002 mg/kg) in any plant part at harvest. After processing into oil and meal only 2.4% of the radioactivity was present in the oil (TRRs 0.11 and 2.11 mg/kg equiv. respectively).

Residues in soil at maturity reached 0.064 mg/kg for the 0–5 cm layer, 0.012 mg/kg for the 5–10 cm layer and 0.012 mg/kg for the 10–20 cm layer. Parent compound was below the limit of detection (0.002 mg/kg). Non-extractable residues accounted for 93.2, 97.3 and 99.0% of the total radioactivity in the 0–5 cm, 5–10 cm and 10–20 cm soil layers respectively.

Table 27 Distribution of radioactivity in various plant parts of rapeseed after foliar application of [¹⁴C] trinexapac-ethyl

Interval	Matrix	TRRs		Parent (mg/kg equiv.)	Extracted radioactivity (%) ^b		Non-extracted (%) ^b	Total (%) ^b
		(mg/kg equiv.)	% ^a		Cold extraction ^c	Soxhlet ^d		
30 minutes (Stem elongation)	Whole tops	6.24	100	1.18	95.2	0.6	3.3	99.1
	Soil							
	0–5 cm	0.030	100	< 0.002	9.0	1.3	93.0	103.3
	Soil Total		100					
14 (Flowering)	Green parts	0.82	100	0.012	92.4	1.0	10.4	103.8
	Flowering parts	6.79	100	0.068	100.7	0.4	0.8	101.9
	Soil							
	0–5 cm	0.063	73.7	< 0.002	10.2	0.4	92.9	103.5
	5–10 cm	0.009	10.1	NA	NA	NA	NA	
	10–20 cm	0.009	16.3	NA	NA	NA	NA	
	Soil Total	0.025	100.0					
65 (Maturity)	Stalks	3.14	100	< 0.002	66.1	1.6	27.2	94.9
	Pods	5.74	100	< 0.002	80.2	1.3	17.3	98.8
	Seeds	1.43	100	< 0.002	NA	NA	NA	
	Meal	2.11	97.6	< 0.002	67.5	1.9	27.6	
	Oil	0.11	2.4	< 0.002	100	–	–	
	Soil							
	0–5 cm	0.064	66.3	< 0.002	8.1	0.3	93.2	101.6
	5–10 cm	0.012	13.4	NA	5.9	0.4	97.3	103.6
	10–20 cm	0.012	20.3	NA	7.1	0.4	99.0	106.5
	Soil Total		100.0					

^a In % of the radioactivity found in the sub-balanced plant parts/ soil layers

^b In % of radioactivity found in the plant part/ soil layers and determined by combustion

^c Using methanol/ water (8:2 v/v)

^d Using methanol

NA = Not Analysed

Partitioning behaviour (pH 4) of the extractable residues in pods and stalks showed that the major part of the radioactivity was located in the water phase (57.9% in pods and 67.4 % in stalks) with 39.4% (pods) and 29.0% (stalks) located in the organic phase.

At harvest no parent compound was detected in pods, seeds and stalks. Approximately 16 metabolite fractions were found in plant, seeds processed parts and soil extracts. The major metabolite observed was trinexapac acid representing 26.9, 16.2 and 8.9% of the total radioactivity in meal, pods and stalks respectively (Table 28). Aqueous fractions obtained after partition were treated with cellulase which released aglycones indicating the presence of sugar conjugates. The major metabolite fractions that were released as aglycones were II₇ and II₁–II₂. The aglycones released were chromatographed and revealed the presence of trinexapac acid (I₅) and I₄. Non-extractable radioactivity accounted for 93.2% of the radioactivity in the 0–5 cm soil extract, with one minor metabolite, I₇, being observed only in soil.

The metabolite pattern observed in spring rape compared with that obtained in spring wheat, revealed the presence of crop specific metabolite fractions.

Table 28 Summary of identified components in plants parts, processed fractions and soil at harvest after treatment with [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl (400 g ai/ha treatment)

Metabolite	Rapeseed matrices			Soil (0–5 cm)
	Seeds—Meal	Pods	Stalks	% TRR ^a
	% TRR ^a	% TRR ^a	% TRR ^a	
II ₁	—	3.5	2.6	4.8
II ₂	—	0.9	1.2	
II ₃		1.9	2.2	
II ₄		1.3	2.3	
II ₅		2.2		
II ₆	19.0	0.9	1.5	
II ₇ ^b		11.0	11.8	ND
II ₈		1.1		
II ₉		1.7		
II ₁₀	—	1.9	4.9	
I ₂	6.3	3.0	0.5	
I ₃	—	—	—	
I ₄	2.6	7.7	6.0	0.2
I ₅ Trinexapac acid	26.9	16.2	8.9	0.4
I ₆	—	0.4	0.7	0.4
I ₇	—	—	—	0.3
Unresolved	12.6	24.3	21.0	2.0
Sub-total	67.4	78.0	63.7	8.1
Soxhlet	1.9	1.3	1.6	0.3
Non-extractables	27.6	17.3	27.2	93.2
Total	96.5	98.8	92.5	101.6

^a % of radioactivity found in plant parts, processed parts and in soil

^b Treatment with cellulase released aglycones I₄ and I₅ (trinexapac acid)

ND = Not Detected

In a subsequent study (Nicollier 1993, CGA163935/0308) with application of the radio-labelled trinexapac-ethyl and sampling of specimens as described above, additional analytical techniques were employed.

Metabolites identified are summarized below in Table 29. Forty to 46% of the TRR was identified in stalks, pods, seed meal and whole seeds while 89% of the TRR was identified in oil. In all plant parts 65–100% TRR was characterised.

In stalks organo-soluble radioactivity contained CGA 351210 and trinexapac acid while water soluble radioactivity (from a water/ methanol gradient) yielded six fractions which included trans aconitic acid (CGA 312753) and CGA 313458. Metabolite II_{3b} was tentatively identified as isocitric acid lactone while metabolite II₉ was postulated to be CGA 329773. The major fraction of the water

phase was enzymatically hydrolysed with cellulase. Two aglycones were released, one co-chromatographed with metabolite I_{4b} (CGA 351210) and the second one with metabolite I₅ (trinexapac acid).

In pods organo-soluble radioactivity again contained CGA 351210 and trinexapac acid while water soluble radioactivity (from a water/ methanol gradient) yielded four fractions which included trans aconitic acid (CGA 312753). After enzymatic hydrolysis with cellulase two aglycones, metabolites I_{4b} (CGA 351210) and I₅ (trinexapac acid) were released.

In seeds residues in oil were extracted with hexane. The two major metabolite fractions co-chromatographed were metabolite I_{4b} (CGA 351210) and metabolite I₅ (trinexapac acid). Of the oil radioactivity, 69.5% (or 1.7% of the TRR in the seed) remained attached to the lipid fraction. The meal fraction was extracted with 80% methanol. The major fractions again were metabolites I_{4b} (CGA 351210) and I₅ (trinexapac acid). Water soluble radioactivity (from a water/ methanol gradient) yielded four fractions which included trans aconitic acid (CGA 312753). After enzymatic hydrolysis with cellulase, metabolites I_{4b} (CGA 351210) and trinexapac acid were released. About 48% of the non-extractable radioactivity in meal could be solved in alkaline propanol after heating in a microwave. The major fraction of this organic phase was again trinexapac acid.

Table 29 Summary of identified components in plants parts and processed fractions at harvest after treatment with [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl (400 g ai/ha treatment)

Metabolite	Rapeseed Matrices										Soil (0– 5 cm)
	Seeds						Pods		Stalks		
	Meal		Oil		Whole						
	mg/kg equiv. ^a	% TRR ^a	mg/kg equiv. ^a	% TR R ^a	mg/kg equiv. ^a	% TRR ^a	mg/kg equiv. ^a	% TRR ^a	mg/kg equiv. ^a	% TRR ^a	% TRR ^a
II ₁	0.097	4.6			0.064	4.5	0.201	3.5	0.082	2.6	8.2
II ₂		ND			–	ND	0.051	0.9	0.038	1.2	
II _{3b} ^c	0.038	1.8			0.026	1.8	0.109	1.9	0.069	2.2	
II ₄	0.061	2.9			0.040	2.8	0.075	1.3	0.072	2.3	
II ₅							0.126	2.2			
II ₆ CGA312753	0.019	0.9			0.013	0.9	0.051	0.9	0.047	1.5	
II ₇ ^b			–	ND			0.069	1.2	0.107	3.4	
II ₈		ND			–	ND	0.063	1.1	–	ND	
II ₉		ND			–	ND	0.097	1.7	–	ND	
II ₁₀ CGA313458	0.023	1.1			0.016	1.1	0.109	1.9	0.154	4.9	
I ₂	0.015	0.7			0.010	0.7	0.017	0.3	0.016	0.5	
I _{2b}	0.057	2.7			0.037	2.6	0.172	3.0	–	ND	
I ₃	0.004	0.2	0.0007	0.6	0.003	0.2	0.006	0.1	–	ND	
I _{4b} free 351210	0.036	1.7	0.0184	16.0	0.030	2.1	0.442	7.7	0.188	6.0	0.2
I _{4b} conjugated 351210	0.074	3.5	–	ND	0.048	3.4	0.476	8.3	0.681	21.7	ND
I ₅ free trinexapac acid	0.624	29.5	0.004	3.5	0.415	29.0	1.039	18.1	0.279	8.9	10.2
I _{5b} conjugated trinexapac acid	0.023	1.1	–	ND	0.016	1.1	0.023	0.4	0.025	0.8	ND
I ₆	0.038	1.8	0.0025	2.2	0.026	1.8	–	ND	0.022	0.7	0.4
I ₇		ND		ND		ND				ND	5.7
I ₈		ND	0.0799	69.5	0.024	1.7			–	ND	ND
Unresolved + Soxhlet	0.609	28.8	0.0094	8.2	0.405	28.3	1.740	30.3	0.710	22.6	21.4
Non-	0.302	14.3	–	–	0.200	14.0	0.626	10.9	0.854	27.2	55.2

Metabolite	Rapeseed Matrices										Soil (0–5 cm)
	Seeds						Pods		Stalks		
	Meal		Oil		Whole		mg/kg equiv.	% TRR ^a	mg/kg equiv.	% TRR ^a	% TRR ^a
	mg/kg equiv.	% TRR ^a	mg/kg equiv.	% TRR ^a	mg/kg equiv.	% TRR ^a					
extractables ^d											
Characterised		81.3		100		82.0		84.8		65.3	
Identified		39.6		89.0		41.1		39.9		46.0	
Total	2.115	95.6	0.115	100	1.430	96.0	5.742	95.7	3.141	92.5	101.6

^a % of radioactivity found in plant parts, processed parts and in soil

^b Treatment with cellulase released aglycones I₄ and I₅

^c Tentatively identified as isocitric acid lactone

^d For meal, pods and soil after hydrolysis of the non-extractables

ND = Not detected

The proposed transformation of trinexapac-ethyl in rape seed is mainly by hydrolysis of the ester bond to give trinexapac acid. The sum of free and sugar conjugated trinexapac acid accounted for 30.6%, 3.5%, 18.5% and 9.7% of total radioactivity in meal, oil, pods and stalks respectively. Reduction of trinexapac acid to 2-(cyclopropyl-hydroxymethylene)-5-hydroxymethylcyclohexane-1,3-dione (CGA 351210) and subsequent conjugation with sugar occurs. Additional oxidation of trinexapac acid gives 2-(4-cyclopropyl-4-hydroxy-2-oxo-but-3-enyl)-succinic acid (CGA 313458) while cleavage of the C₆ ring of trinexapac-ethyl followed by stepwise oxidation/decarboxylation after cleavage of the 6-membered ring yielded isocitric acid and dehydration to trans aconitic acid (CGA 312753).

The observed metabolic pathway for rapeseed is comparable with those of wheat, grass and rice with the exception of one rape specific metabolite (CGA 351210) formed by the reduction of trinexapac acid.

Grass

[1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was applied by foliar methods to tall fescue grass at rates of 560.4 g ai/ha (Ray and May-Hertl 2003, CGA163935/0862). One foliar broadcast spray was made 46 days prior to swath the grass for harvest of mature grass seed. Pre-forage samples were taken 22-days after application and hay samples were collected 46 days after application. The hay samples were dried and separated into straw, seed and seed screenings. Forage regrowth was collected 105 days after application. Soil samples were also taken at each of the harvest intervals listed above.

The TRRs and extractable and non-extractable radioactivity are summarized in Table 30. TRRs of 5.45 mg/kg trinexapac-ethyl equivalents, 7.13 mg/kg equiv. and 4.78 mg/kg equiv. were found in seeds, seed screenings and straw respectively. TRRs of 2.03 mg/kg equiv. and 0.054 mg/kg equiv. were observed for the 22 and 105 day forage samples respectively. Radioactivity extracted from 22 day forage, straw, seeds and seed screenings using acetonitrile/ water (4:1 v/v) or from 105 day regrowth forage using chloroform/methanol (4:1 v/v), ranged from 45% (seed screenings and seeds) to 75.5% (22 day forage).

Table 30 Total radioactive residues in various parts of grass after foliar application of [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl

Days After Treatment	Matrix	TRRs (mg/kg equiv.)	Extracted radioactivity (%) ^a	PES radioactivity (%) ^b	Recovery (%)
After 1 st application	Soil	0.374	70.7	28.2	99.0
45	Soil	0.079	7.72	67.9	75.7
105	Soil	0.083	8.78	62.4	71.2

Days After Treatment	Matrix	TRRs (mg/kg equiv.)	Extracted radioactivity (%) ^a	PES radioactivity (%) ^b	Recovery (%)
22	Forage	2.03	75.5	20.2	95.8
46	Seeds	5.45	45.6	53.6	99.2
Swathing of mature grass	Seed screenings	7.13	45.0	53.4	98.4
seeds	Straw	4.78	70.4	28.2	98.6
105	Forage	0.054	55.5	34.8	90.4

^a % of radioactivity found in plant part

^b % of radioactivity found in plant part and determined by combustion

In-depth isolation procedures of extractable and non-extractable material, followed by analysis of purified metabolites enabled identification of five metabolites which are summarized below in Table 31. Degradation of parent compound was rapid as none was detected in any plant part at harvest. Eleven metabolite fractions were found, of which five major metabolites were present in all plant samples. In the various plant matrices, the two main metabolites observed were trinexapac acid representing 10.2–22.4% of the TRR and CGA 275537 (tricarballic acid) representing 9.3–17.0% of the TRR. Radioactive residues left after solvent extraction (PES) ranged from 10.2–34.8% TRR.

Table 31 Summary of identified components in grass after treatment with [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl

Metabolite	Grass matrix									
	Forage (22 day)		Straw		Seeds		Seed Screenings		Regrowth Forage	
	mg/kg equiv.	% TRR	mg/kg equiv.	% TRR	mg/kg equiv.	% TRR	mg/kg equiv.	% TRR	mg/kg equiv.	% TRR
	2.03	100	4.78	100	5.45	100	7.13	100	0.054	100
Metabolite A	0.15	7.46	0.49	10.3	0.10	1.90	0.27	3.76	0.002	4.40
CGA 275537	0.28	13.8	0.81	17.0	0.91	16.6	1.18	16.6	0.005	9.34
Metabolite B	0.17	8.58	0.27	5.60	0.45	8.32	0.70	9.84	0.001	2.72
Metabolite C (terephthalic acid)	0.20	9.74	0.45	9.43	0.52	9.55	0.84	11.7	0.004	6.61
Trinexapac acid	0.33	16.3	1.07	22.4	0.80	14.7	0.91	12.7	0.006	10.2
Unknown Region 1	0.11	5.55	0.15	3.15	0.14	2.65	0.22	3.01	0.005	10.0
Unknown Region 2	0.16	7.95	0.38	8.00	0.14	2.53	0.22	3.08	NA	NA
Unknown Region 3	NA	NA	0.22	4.69	NA	NA	NA	NA	0.001	2.69
Unknown Region 4	0.32	16.0	0.43	8.93	0.52	9.50	0.64	8.95	0.004	6.85
Unknown Region 5	0.15	7.31	0.30	6.30	0.38	7.01	0.48	6.78	0.001	2.66
Unknown Region 6	0.057	2.79	0.080	1.68	0.14	2.55	0.11	1.49	0.001	2.63
Identified	1.13	55.9	3.09	64.6	2.79	51.1	3.89	54.6	0.018	33.3
PES ^a	0.21	10.2	0.51	10.6	1.32	24.2	1.36	19.1	0.019	34.8
Characterised	1.34	66.1	3.60	75.3	4.11	75.3	5.26	73.7	0.037	68.1

Metabolite % TRRs and mg/kg are a summation of the individual values from their identification in the initial extracts, enzyme treatments plus the PES extracts (unknown regions not included in this summation).

^a PES values obtained by subtracting total metabolites identified from the original PES values.

NA = Not Applicable

The proposed transformation of trinexapac-ethyl in grass was mainly determined by exhaustive analyses of the straw and 22 day forage samples. The major biotransformation is by hydrolysis of the ester bond to give trinexapac acid. Trinexapac acid undergoes hydrolytic ring opening and a Baeyer-Villiger like oxidation of the cyclopropylketone moiety to yield open chain metabolite A. Subsequent retro Claisen condensation provides tricarballic acid (CGA 275537). An observed minor pathway starting from trinexapac-ethyl involves reductive elimination of one ring carbonyl group and Baeyer-Villiger like oxidation of the cyclopropyl-ketone moiety to yield metabolite B. An additional reductive elimination followed by aromatisation provides metabolite C (terephthalic acid).

Summary of plant metabolism

Rice, wheat, rape and grass (foliar treatment) metabolism studies were carried out with [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl or [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl. Metabolic pathways in rice, wheat, rape and grass were comparable in all four crops.

Between 85–94%, 23–79%, 65–100% and 66–75% of TRR was characterised in the various plant parts of wheat, rice, oilseed rape and grass respectively depending on the plant part and the sampling interval after application. The portion of identified metabolites was 31–51%, 10.4–60.3%, 39.6–89.0% and 33.3–64.6% of TRR in wheat, rice, oilseed rape and grass, respectively.

Seven metabolites were identified. Trinexapac acid was the major metabolite which was present in all species and all plants parts at harvest. Parent compound was completely degraded and was not detectable (< 0.001 / < 0.002 mg/kg) in any plant part of wheat, rapeseed and grass at harvest time. In rice only traces (0.001 and 0.003 mg/kg) were observed in straw and husks respectively. Further degradation of trinexapac acid proceeded *via* stepwise oxidation/ decarboxylation after cleavage of the 6-membered ring yielding saturated and unsaturated tricarboxylated acids such as tricarballic acid (CGA 275537) and trans aconitic acid (CGA 312753), the latter compound an intermediate in the citric acid cycle (Krebs cycle). From the intermediates of the citric acid cycle and their breakdown products, sugars, fatty acids and certain amino acids were formed by de-novo synthesis. Consequently high non-extractable residues are formed (for example 72.0% in rice grains). High unresolvable radioactivity in TLC-analysis after extraction may also be in part attributed to radio-labelled matrix products or breakdown products thereof. In wheat, the ring cleavage occurred also on the parent molecule yielding the mono-ethyl ester of the aconitic acid. Further minor steps were aromatisation of the 6 membered ring of trinexapac acid and keto-enol tautomerism to 4-cyclopropanecarbonyl-3,5-dihydroxybenzoic acid (CGA 329773) and in rape reduction of trinexapac acid to 2-(cyclopropylhydroxy-methylene)-5-hydroxymethyl-cyclohexane-1,3-dione (CGA 351210) and subsequent conjugation with sugar.

Sugar conjugates of trinexapac acid were hydrolysed in some crop parts to yield free acid. Trinexapac acid sugar conjugates accounted for an increase in trinexapac acid of 11.6% TRR in rice grain and 10% and 14% TRR in grass forage and straw, respectively. Levels of sugar conjugates of trinexapac acid were not significant in oilseed rape, rice straw or wheat grain and were not investigated in wheat straw or husk.

Although not all metabolites were found in every plant species, all observed degradation and transformation steps (oxidation, decarboxylation, ring cleavage and conjugation) occurred in all crops. Therefore, the metabolic profiles revealed comparable pathways in all crops.

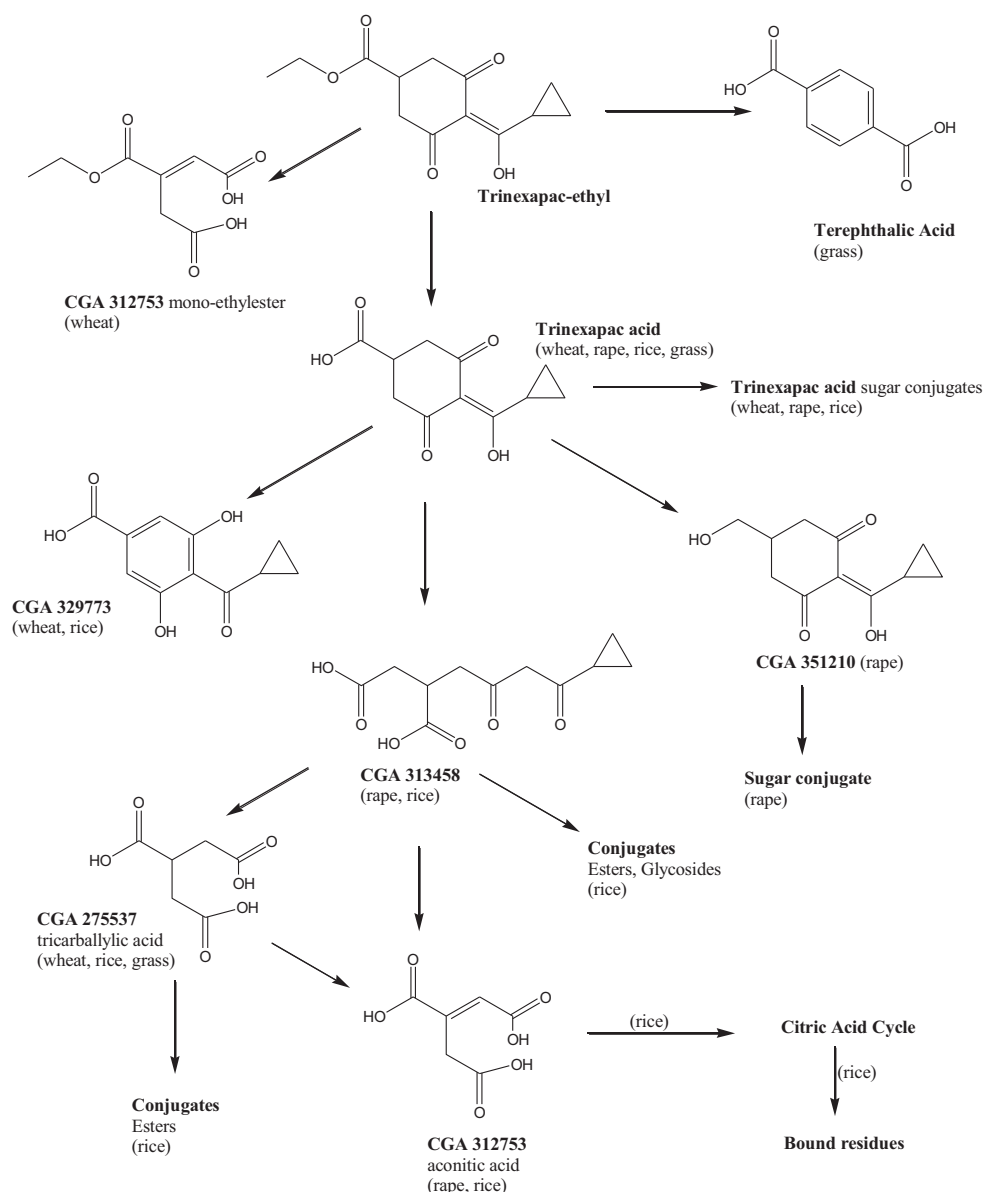


Figure 2 Proposed metabolic pathways for trinexapac-ethyl in plants

Confined Rotational Crop Studies

The metabolism of trinexapac-ethyl was investigated in three representative succeeding crops—lettuce (representative of leafy vegetables), radish (root and tuber vegetables) and wheat (cereals) (Quistad and Kovatchev 2010, CGA163935_50024). The study was performed with the test substance, [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl, applied to bare sandy loam soil, at a rate of 350 g ai/ha, followed by soil aging intervals of 30, 120 and 270 days. Crops were planted at each of the above intervals after application, to determine whether trinexapac-ethyl residues or degradates appear in follow crops. In addition radishes were sown at 309 days after soil treatment because the 270 plant back interval (PBI) crop did not produce root bulbs, due to the high summer temperatures during the cultivation interval.

Table 32 Schedule for planting/ seeding and harvest

Representative Crop Type	Crop	Planting/ Sowing [Days after Treatment]	Harvest [Days after Treatment]	Plant parts
Leafy Vegetable	Lettuce	30	86	Heads (immature)
			113	Heads (mature)
		120	183	Heads (immature)
			198	Heads (mature)
		270	290	Heads (immature)
			309	Heads (mature)
		30	83	Foliage, Roots
			183	Foliage, Roots
Root Vegetable	Radish	120	183	Foliage, Roots
		309	350	Foliage, Roots
		30	83	Forage
			168	Hay
Cereal	Wheat	120	231	Straw, Grain
			168	Forage
			209	Hay
			251	Straw, Grain
		270	296	Forage
			315	Hay
			352	Straw, Grain

Lettuce heads were harvested at immaturity (20–63 days after transplantation) and maturity (39–83 days after transplantation). Radish foliage and roots were harvested at maturity (41–63 days after sowing). Wheat was sampled as forage (26–53 days after sowing), as hay (45–138 days after sowing) and as straw and grain at maturity (82–201 days after sowing).

Total radioactive residues detected in rotational crops following soil application of [^{14}C] cyclohexyl trinexapac-ethyl were found to be:

- 0.011 mg/kg trinexapac-ethyl equivalents in lettuce head samples at immaturity (86 days after application) and 0.017 mg/kg equiv. in lettuce heads sampled at 100% maturity (113 days after application); for lettuce planted at 30 days PBI; 0.004 mg/kg equiv. and 0.007 mg/kg equiv. in immature lettuce heads of plants with 120 and 270 days PBI and 0.004 mg/kg equiv. and 0.001 mg/kg equiv. in mature lettuce heads of plants with 120 and 270 days PBI
- 0.005 mg/kg equiv., 0.007 mg/kg equiv. and 0.001 mg/kg equiv. for radish foliage of radish sown at 30, 120 and 309 days PBI respectively; 0.002 mg/kg equiv., 0.002 mg/kg equiv. and 0.001 mg/kg equiv. for radish roots sown at 30, 120 and 309 days PBI respectively
- 0.010 mg/kg equiv. in wheat forage sampled at 83 days after application and 0.011 mg/kg equiv. in wheat hay sampled 168 days after application, for plants with 30 days PBI; 0.004 mg/kg equiv. and 0.002 mg/kg equiv. for wheat forage of plants with 120 and 270 days PBI; 0.009 mg/kg equiv. and 0.008 mg/kg equiv. for wheat hay of plants with 120 and 270 days PBI, 0.003 mg/kg equiv., 0.004 mg/kg equiv. and 0.004 mg/kg equiv. for wheat straw samples and 0.005 mg/kg equiv., 0.008 mg/kg equiv. and 0.003 mg/kg equiv. for wheat grain samples of plants with 30, 120 and 270 days PBI respectively.

RACs were initially extracted with acetonitrile: water (1:1, 2 $\times$) followed by acetonitrile (1 $\times$). The combined acetonitrile: water extract supernatants were analysed by HPLC and/ or TLC. Post extraction solids were further extracted with other solvents if their total radioactive residues (TRR) were > 10%. The TRR of the final PES was determined by combustion.

The TRRs detected in rotational crops following soil application of [^{14}C] cyclohexyl trinexapac-ethyl at 350 g ai/ha are shown in Table 33.

Table 33 TRR values determined for trinexapac-ethyl confined accumulation in rotational crops

Crop	RAC	30 Days After Treatment (mg/kg trinexapac-ethyl equiv.)	120 Days After Treatment (mg/kg trinexapac-ethyl equiv.)	270 Days After Treatment (mg/kg trinexapac-ethyl equiv.)
Lettuce	Immature	0.011 ^a	0.004	0.007
	Mature	0.017 ^a	0.004	0.001
Radish ^b	Foliage	0.005	0.007	0.001
	Roots	0.002	0.002	0.001
	Forage	0.010 ^a	0.004	0.002
Wheat	Hay	0.011 ^a	0.009	0.008
	Straw	0.003	0.004	0.004
	Grain	0.005	0.008	0.003

^a Sum of fractions (combined acetonitrile/water extracts + further PES extracts + PES). Other TRR values were determined by combustion

^b 270 day PBI radish did not produce a root bulb, so re-sown at 309 days after treatment within the same plot

Radish RACs were not extracted with acetonitrile for analysis of residue distribution and extractable radioactivity because the TRRs were < 0.01 mg/kg. For lettuce only RACs with TRR ≥ 0.010 mg/kg were extracted (RACs with 30 days PBI). For wheat, only forage and hay specimens from plants of 30 and 120 days PBI were extracted. The extractability of radioactivity in lettuce and wheat RACs with acetonitrile was generally low at < 50% TRR. Residues of parent trinexapac-ethyl were not detectable by HPLC-UV (LOQ = 0.001 mg/kg). Residues of trinexapac acid from hydrolysis of parent and CGA 312753, formed by cleavage of the cyclohexanedione ring of trinexapac acid, were only detectable in wheat hay and forage in the range of 0.001–0.002 mg/kg.

The distribution of residual trinexapac-ethyl and extractable radioactivity in rotational crops (lettuce and wheat) is shown in Table 34.

Table 34 Summary of identified components in rotational lettuce and wheat following cultivation in soil treated with [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl after plant back intervals of 30, 120 and 270 days.

Metabolite	Crop parts											
	Immature lettuce heads		Mature lettuce heads		Wheat Forage		Wheat Hay		Wheat Straw		Wheat Grain	
	mg/kg ^a	% TRR ^b	mg/kg ^a	% TRR ^b	mg/kg ^a	% TRR ^b	mg/kg ^a	% TRR ^b	mg/kg ^a	% TRR ^b	mg/kg ^a	% TRR ^b
Plant back interval: 30 DAT												
TRR	0.011		0.017		0.010		0.011		NA		NA	
Parent	ND		ND		ND		ND		NA		NA	
Trinexapac acid	ND		ND		0.002	20.0	0.001	9.1	NA		NA	
CGA 312753	ND		ND		ND		0.002	18.2	NA		NA	
Extractable radioactivity	0.004	36.4	0.007	41.2	0.005	50.0	0.004	36.4		NA		NA
Plant back interval: 120 DAT												
TRR	NA		NA		0.004		0.009		NA		0.007	
Parent	NA		NA		ND		ND		NA		NA	
Trinexapac acid	NA		NA		ND		ND		NA		NA	
CGA 312753	NA		NA		ND		0.001	11.1	NA		NA	
Extractable radioactivity		NA		NA		50.0	0.003	33.3		NA	0.001	14.3
Plant back interval: 270 DAT												
TRR	NA		NA		NA		NA		NA		NA	
Parent	NA		NA		NA		NA		NA		NA	
Trinexapac acid	NA		NA		NA		NA		NA		NA	
CGA 312753	NA		NA		NA		NA		NA		NA	

Metabolite	Crop parts											
	Immature lettuce heads		Mature lettuce heads		Wheat Forage		Wheat Hay		Wheat Straw		Wheat Grain	
	mg/kg ^a	% TRR ^b	mg/kg ^a	% TRR ^b	mg/kg ^a	% TRR ^b	mg/kg ^a	% TRR ^b	mg/kg ^a	% TRR ^b	mg/kg ^a	% TRR ^b
Extractable radioactivity		NA		NA		NA		NA		NA		NA

^a Trinexapac-ethyl equivalents

^b In % of radioactivity found in the plant part, determined by combustion

ND = Not detectable

NA = Not Applicable (RACS were not extracted due to low TRR detected by combustion)

The uptake of residues by the rotational crops lettuce, radish and wheat planted or sown after several intervals after application of trinexapac-ethyl to bare ground was very low. No accumulation was observed. Residues of trinexapac-ethyl in the rotational crop RACs were below the LOQ (< 0.001 mg/kg). The residues of trinexapac acid and CGA 312753 were very close to or below the LOQ (< 0.001–0.002 mg/kg). The very limited uptake of radioactive material in succeeding crops clearly indicates the lack of systemic behaviour of trinexapac-ethyl. It was concluded that residues in rotational crops are negligible.

Field Accumulation in Rotational Crops

Field rotational crop studies for trinexapac-ethyl were conducted in both the USA and Switzerland.

USA Study—application to wheat (rotational crops—wheat, radish, spinach)

In a study conducted in the USA in the 2004–2005 growing season, a 250 g/L EC formulation of trinexapac-ethyl was applied once as a broadcast spray to wheat at 203 g ai/ha (Ediger 2006b, CGA163935/1054). Radish, wheat and spinach were planted after 3 different plant back intervals (14, 30 and 45 days).

Table 35 Schedule for planting/ seeding and harvest

Representative Crop Type	Crop [Varieties]	Planting/ Sowing [Days after Treatment]	Harvest [Days after Treatment]	Plant parts
	Spinach (Tyee, Melody)	14	60–73	Leaves
Leafy Vegetable		30	75–90	Leaves
		45	91–107	Leaves
		14	55–75	Tops
			55–75	Roots
Root Vegetable	Radish	30	73–90	Tops
	(Champion, Cherry Belle)		73–90	Roots
		45	79–106	Tops
			79–106	Roots
			73–75	Forage (fall)
			235–274	Forage (spring)
		14	266–287	Hay
			300–310	Straw
			300–310	Grain
			90	Forage (fall)
			250–274	Forage (spring)
Cereal	Spring and Winter Wheat	30	281–287	Hay
	(Barrie, Caledonia, Kaskaskia)		310–315	Straw
			310–315	Grain
			106–107	Forage (fall)
			266–303	Forage (spring)
		45	297–345	Hay
			331–368	Straw

Representative Crop Type	Crop [Varieties]	Planting/ Sowing [Days after Treatment]	Harvest [Days after Treatment]	Plant parts
			331–368	Grain

Spinach leaves were harvested 45–62 days after sowing. Radish tops and roots were harvested 34–61 days after sowing. Wheat was sampled as fall forage (59–62 days after sowing), spring forage (220–260 days after sowing), hay (253–300 days after sowing), straw (280–323 days after sowing) and grain (280–323 days after sowing).

Samples were stored frozen for a maximum of 23 months. Trinexapac residues in rotational crop samples were quantitated as trinexapac acid by LC/MS/MS (Method 110-01). The LOQ is 0.05 mg/kg for trinexapac acid. Concurrent method recovery data were collected in rotational crop matrices at spiking levels of 0.05 and 0.50 mg/kg and were acceptable.

The maximum residues observed in specimens from treated crops were all < 0.05 mg/kg except for one Day-14 PBI wheat straw sample at 0.07 mg/kg.

Table 36 Residues of trinexapac acid in rotational crops (spinach, radish and wheat) following application of trinexapac-ethyl to the target crop (wheat) at 203 g ai/ha

Crop	Matrix	Days After Treatment	Trinexapac Acid (mg/kg)		
			Single Values	Mean	RSD (%)
Plant back interval: 14 DAT					
Spinach	Leaves	60–73	< 0.05 (×4)	< 0.05	NA
Radish	Tops	55–75	< 0.05 (×4)	< 0.05	NA
	Roots	55–75	< 0.05 (×4)	< 0.05	NA
	Forage (fall)	73–75	< 0.05 (×4)	< 0.05	NA
	Forage (spring)	235–274	< 0.05 (×4)	< 0.05	NA
Wheat	Hay	266–287	< 0.05 (×4)	< 0.05	NA
	Straw	300–310	< 0.05 (×3), 0.07	0.06 ^a	18 ^a
	Grain	300–310	< 0.05 (×4)	< 0.05	NA
Plant back interval: 30 DAT					
Spinach	Leaves	75–90	< 0.05 (×4)	< 0.05	NA
Radish	Tops	73–90	< 0.05 (×4)	< 0.05	NA
	Roots	73–90	< 0.05 (×4)	< 0.05	NA
	Forage (fall)	90	< 0.05 (×4)	< 0.05	NA
	Forage (spring)	250–274	< 0.05 (×4)	< 0.05	NA
Wheat	Hay	281–287	< 0.05 (×4)	< 0.05	NA
	Straw	310–315	< 0.05 (×4)	< 0.05	NA
	Grain	310–315	< 0.05 (×4)	< 0.05	NA
Plant back interval: 45 DAT					
Spinach	Leaves	91–107	< 0.05 (×4)	< 0.05	NA
Radish	Tops	79–106	< 0.05 (×4)	< 0.05	NA
	Roots	79–106	< 0.05 (×4)	< 0.05	NA
	Forage (fall)	106–107	< 0.05 (×4)	< 0.05	NA
	Forage (spring)	266–303	< 0.05 (×4)	< 0.05	NA
Wheat	Hay	297–345	< 0.05 (×4)	< 0.05	NA
	Straw	331–368	< 0.05 (×4)	< 0.05	NA
	Grain	331–368	< 0.05 (×4)	< 0.05	NA

^a For statistical calculations 0.05 was substituted for < 0.05

DAT = Days After Treatment

NA = Not Applicable

Two control straw samples had residues of 0.05 (confirmed as 0.06) and 0.07 (confirmed as 0.07) mg/kg

The results showed that rotational crops sown 14, 30 and 45 days after application of trinexapac-ethyl to the target crop, are very unlikely to contain residues of trinexapac-ethyl as its main metabolite trinexapac acid, above the LOQ of 0.05 mg/kg.

European study—application to bare soil (rotational crops—lettuce, winter wheat, sugar beet and corn)

A trial was conducted in Switzerland during 1989 to investigate residues of trinexapac-ethyl in succeeding crops, grown in soil previously treated with [^{14}C] cyclohexyl trinexapac-ethyl (Krauss 1992, CGA163935/0265). A 250 g/L EC formulation of trinexapac-ethyl was applied once to bare soil at a rate of 150 g ai/ha. Treated plots (1 m² each) were planted after four different time intervals (69, 119, 299 and 338 days after treatment). The crops investigated were lettuce, winter wheat, sugar beet and maize (corn).

The schedule for seeding/planting and harvesting is shown in Table 37.

Table 37 Schedule for planting/ seeding and harvest

Representative Crop Type	Crop [Varieties]	Planting/ Sowing [Days after Treatment]	Harvest [Days after Treatment]	Plant parts
Leafy Vegetable	Lettuce	69	99	Heads (50% Maturity)
	(Sorraya)		119	Heads (Maturity)
			343	Tops, Roots
Root Vegetable	Sugar Beet	299	407	Tops, Roots
	(KWS)		496	Tops, Roots
			173	Whole tops (fall, cutting) (25% maturity)
Cereal	Winter Wheat	119	299	Whole tops (50% maturity)
	(Zenta)		343	Whole tops (75% maturity)
			407	Stalks, husks, grain (100% maturity)
			369	Whole tops (25% maturity)
	Maize	338	407	Whole tops (50% maturity)
	(Blizzard)		496	Stalks, husks, grain (100% maturity)

Plant samples and soil cores (0–5 cm, 5–10 cm, 10–20 cm and 20–30 cm layers) were collected. Lettuce was harvested at one-half maturity (30 days after transplantation) and maturity (50 days after transplantation). Winter wheat was sampled as a fall cutting, one quarter maturity (54 days after sowing), one half maturity (180 days after sowing), three quarters maturity (224 days after sowing), and at maturity (288 days after sowing). The sugar beets and maize were harvested at one-quarter maturity (44 and 31 days after sowing respectively), one-half maturity (108 and 69 days after sowing, respectively) and at maturity (197 and 159 days after sowing respectively).

The following tables show the distribution of radioactivity in rotational crops (lettuce, winter wheat, sugar beet and maize) and the distribution of residue trinexapac-ethyl in soil.

Table 38 Distribution of radioactivity and residual trinexapac-ethyl in rotational lettuce and soil following application of [^{14}C] cyclohexyl trinexapac-ethyl to bareground

Days After Treatment / Growth Stage of Rotational Crops	Plant Parts / Soil Layers	Total Residues		Parent (mg/kg) ^a	Extractable radioactivity (%)		Non Extractable (%) ^c	Total (%) ^c
		(mg/kg) ^a	(%) ^b		Cold ^c	Soxhlet ^c		
70 days (planting)	Soil							
	0–5 cm	0.071	85.6	NA	14.9	1.8	82.3	99.0
	5–10 cm	0.010	10.6	NA	NA	NA	NA	
	10–20 cm	0.001	2.8	NA	NA	NA	NA	
	20–30 cm	< 0.001	1.0	NA	NA	NA	NA	
	Soil Total	0.012	100.0					
99 days Lettuce 50% Maturity	Heads	0.001	100.0	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.044	95.4	NA	10.4	1.4	87.4	99.3
	5–10 cm	0.002	2.7	NA	NA	NA	NA	
	10–20 cm	< 0.001	1.9	NA	NA	NA	NA	

Days After Treatment / Growth Stage of Rotational Crops	Plant Parts / Soil Layers	Total Residues		Parent (mg/kg) ^a	Extractable radioactivity (%)		Non Extractable (%) ^c	Total (%) ^c
		(mg/kg) ^a	(%) ^b		Cold ^c	Soxhlet ^c		
	20–30 cm	NA	NA	NA	NA	NA	NA	
	Soil Total	0.012	100.0					
119 days Lettuce 100% Maturity	Heads	0.001	100.0	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.080	77.9	NA	10.3	1.6	87.0	98.9
	5–10 cm	0.018	17.9	NA	9.2	1.6	88.0	98.8
	10–20 cm	0.001	3.8	NA	NA	NA	NA	
	20–30 cm	< 0.001	0.4	NA	NA	NA	NA	
	Soil Total	0.015	100.0					

^a in trinexapac-ethyl equivalents; limit of detection for combustion = 0.001 mg/kg

^b in % of radioactivity found in the sub-balanced plant parts/ total soil system

^c in % of radioactivity found in the plant part/ soil layer, determined by combustion

NA = Not Analysed

Table 39 Distribution of radioactivity and residual trinexapac-ethyl in rotational winter wheat and soil following application of [¹⁴C] cyclohexyl trinexapac-ethyl to bare ground

Days After Treatment / Growth Stage of Rotational Crops	Plant Parts / Soil Layers	Total Residues		Parent (mg/kg) ^a	Extractable radioactivity (%)		Non Extractable (%) ^c	Total (%) ^c
		(mg/kg) ^a	(%) ^b		Cold ^c	Soxhlet ^c		
119 days (planting)	Soil							
	0–5 cm	0.072	77.0	NA	12.0	1.7	86.5	100.2
	5–10 cm	0.019	18.0	NA	9.5	1.7	86.9	98.1
	10–20 cm	0.002	4.5	NA	NA	NA	NA	
	20–30 cm	< 0.001	0.6	NA	NA	NA	NA	
	Soil Total	0.016	100.0					
173 days Fall Cutting	Whole Tops	0.001	100.0	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.034	82.2	NA	10.8	1.4	84.0	96.2
	5–10 cm	0.004	10.0	NA	NA	NA	NA	
	10–20 cm	0.001	7.0	NA	NA	NA	NA	
	20–30 cm	< 0.001	0.9	NA	NA	NA	NA	
	Soil Total	0.007	100.0					
299 days Winter Wheat 50% Maturity	Whole Tops	< 0.001	100.0	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.045	72.9	NA	10.1	2.5	84.6	97.2
	5–10 cm	0.008	12.7	NA	NA	NA	NA	
	10–20 cm	0.002	8.4	NA	NA	NA	NA	
	20–30 cm	0.001	6.0	NA	NA	NA	NA	
	Soil Total	0.009	100.0					
407 days Winter Wheat 75% Maturity	Whole Tops	< 0.001	100.0	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.052	74.2	NA	10.1	1.9	78.9	90.9
	5–10 cm	0.012	17.1	NA	8.4	2.5	86.8	97.4
	10–20 cm	0.002	8.2	NA	NA	NA	NA	
	20–30 cm	< 0.001	0.5	NA	NA	NA	NA	
	Soil Total	0.010	100.0					
343 days Winter Wheat 100% Maturity	Stalks	0.002	100	NA	NA	NA	NA	
	Husks	0.001	100	NA	NA	NA	NA	
	Grain	< 0.001	100	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.028	74.4	NA	7.8	2.0	92.5	102.3
	5–10 cm	0.006	16.5	NA	NA	NA	NA	
	10–20 cm	0.001	6.4	NA	NA	NA	NA	
	20–30 cm	< 0.001	2.8	NA	NA	NA	NA	

Days After Treatment / Growth Stage of Rotational Crops	Plant Parts / Soil Layers	Total Residues		Parent (mg/kg) ^a	Extractable radioactivity (%)		Non Extractable (%) ^c	Total (%) ^c
		(mg/kg) ^a	(%) ^b		Cold ^c	Soxhlet ^c		
	Soil Total	0.005	100.0					

^a in trinexapac-ethyl equivalents; limit of detection for combustion = 0.001 mg/kg

^b in % of radioactivity found in the sub-balanced plant parts/ total soil system

^c in % of radioactivity found in the plant part/ soil layer, determined by combustion

NA = Not analysed

Table 40 Distribution of radioactivity and residual trinexapac-ethyl in rotational sugar beet and soil following application of [¹⁴C] cyclohexyl trinexapac-ethyl to bare ground

Days After Treatment / Growth Stage of Rotational Crops	Plant Parts / Soil Layers	Total Residues		Parent (mg/kg) ^a	Extractable radioactivity (%)		Non Extractable (%) ^c	Total (%) ^c
		(mg/kg) ^a	(%) ^b		Cold ^c	Soxhlet ^c		
299 days (planting)	Soil							
	0–5 cm	0.076	73.6	NA	9.6	2.0	86.6	98.2
	5–10 cm	0.018	17.9	NA	8.6	2.1	86.4	97.1
	10–20 cm	0.003	8.0	NA	NA	NA	NA	
	20–30 cm	< 0.001	0.4	NA	NA	NA	NA	
	Soil Total	0.014	100.0					
343 days Sugar Beet 25% Maturity	Tops	< 0.001	100.0	NA	NA	NA	NA	
	Roots	0.001	100.0	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.063	69.2	NA	8.1	2.1	85.8	96.0
	5–10 cm	0.014	17.1	NA	10.1	1.8	86.7	98.6
	10–20 cm	0.004	10.2	NA	NA	NA	NA	
	20–30 cm	0.001	3.5	NA	NA	NA	NA	
	Soil Total	0.014	100.0					
407 days Sugar Beet 50% Maturity	Tops	< 0.001	100.0	NA	NA	NA	NA	
	Roots	< 0.001	100.0	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.042	46.0	NA	7.3	2.0	93.1	102.4
	5–10 cm	0.019	23.8	NA	6.8	1.3	89.0	97.1
	10–20 cm	0.010	27.2	NA	NA	NA	NA	
	20–30 cm	0.001	3.0	NA	NA	NA	NA	
	Soil Total	0.013	100.0					
496 days Sugar Beet 100% Maturity	Tops	< 0.001	100	NA	NA	NA	NA	
	Roots	< 0.001	100	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.044	65.8	NA	7.5	2.4	95.9	105.8
	5–10 cm	0.017	24.0	NA	7.4	1.7	91.5	100.6
	10–20 cm	0.003	8.6	NA	NA	NA	NA	
	20–30 cm	< 0.001	1.5	NA	NA	NA	NA	
	Soil Total	0.010	100.0					

^a in trinexapac-ethyl equivalents; limit of detection for combustion = 0.001 mg/kg

^b in % of radioactivity found in the sub-balanced plant parts/ total soil system

^c in % of radioactivity found in the plant part/ soil layer, determined by combustion

NA = Not analysed

Table 41 Distribution of radioactivity and residual trinexapac-ethyl in rotational maize and soil following application of [¹⁴C] cyclohexyl trinexapac-ethyl to bareground

Days After Treatment / Growth Stage of Rotational Crops	Plant Parts / Soil Layers	Total Residues		Parent (mg/kg) ^a	Extractable radioactivity (%)		Non Extractable (%) ^c	Total (%) ^c
		(mg/kg) ^a	(%) ^b		Cold ^c	Soxhlet ^c		
338 days (planting)	Soil							
	0–5 cm	0.065	72.2	NA	9.8	1.9	87.6	99.3
	5–10 cm	0.019	21.8	NA	7.7	1.7	84.9	94.3
	10–20 cm	0.002	5.1	NA	NA	NA	NA	
	20–30 cm	< 0.001	0.9	NA	NA	NA	NA	
	Soil Total	0.012	100.0					
369 days Maize 25% Maturity	Whole Tops	0.001	100.0	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.051	73.5	NA	8.1	2.0	88.7	98.8
	5–10 cm	0.013	20.6	NA	6.7	1.4	90.0	98.1
	10–20 cm	0.002	5.4	NA	NA	NA	NA	
	20–30 cm	0.001	0.6	NA	NA	NA	NA	
407 days Maize 50% Maturity	Soil Total	0.009	100.0					
	Whole Tops	< 0.001	100.0	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.047	52.4	NA	9.3	2.5	87.7	99.5
	5–10 cm	0.018	39.6	NA	7.5	1.2	92.6	101.3
	10–20 cm	0.002	7.1	NA	NA	NA	NA	
496 days Maize 100% Maturity	20–30 cm	< 0.001	0.9	NA	NA	NA	NA	
	Soil Total	0.011	100.0					
	Stalks	< 0.001	100	NA	NA	NA	NA	
	Cobs	< 0.001	100	NA	NA	NA	NA	
	Grain	< 0.001	100	NA	NA	NA	NA	
	Soil							
	0–5 cm	0.034	55.3	NA	7.1	2.2	98.7	108.0
	5–10 cm	0.015	26.9	NA	5.4	1.5	95.2	102.1
	10–20 cm	0.004	16.0	NA	NA	NA	NA	
	20–30 cm	< 0.001	1.9	NA	NA	NA	NA	
	Soil Total	0.009	100.0					

^a in trinexapac-ethyl equivalents; limit of detection for combustion = 0.001 mg/kg^b in % of radioactivity found in the sub-balanced plant parts/ total soil system^c in % of radioactivity found in the plant part/ soil layer, determined by combustion

NA = Not analysed

Total radioactive residues in rotational crops following soil application of [¹⁴C] cyclohexyl were found to be:

- 0.001 mg/kg in lettuce head samples at 50% maturity (99 days after application) and 100% maturity (119 days after application)
- 0.001 mg/kg in winter wheat whole top samples at fall cutting (173 days after application), < 0.001 mg/kg in whole tops at 50% maturity (299 days after application) and 75% maturity (343 days after application). Harvest stalks, husks and grain taken 407 days after application contained 0.002 mg/kg, 0.001 mg/kg and < 0.001 mg/kg respectively
- 0.001 mg/kg in sugar beet root samples at 25% maturity (343 days after application), < 0.001 mg/kg in sugar beet tops at 25% maturity and tops and roots taken at 50% maturity (407 days after application). and at maturity (496 days after application)

- 0.001 mg/kg in maize whole tops samples at 25% maturity (369 days after application) and < 0.001 mg/kg in whole tops taken at 50% maturity (407 days after application). Harvest stalks, cobs, and grain taken 496 days after application contained < 0.001 mg/kg.

The uptake of residues by the rotational crops lettuce, winter wheat, sugar beet and maize planted or sown after several intervals after application of trinexapac-ethyl to bareground was therefore very low (< 0.001–0.002 mg/kg). No accumulation was observed. Due to the residues in the rotational crop RACs being < 0.01 mg/kg, no characterisation was possible. The very limited uptake of radioactive material in succeeding crops clearly indicates the lack of systemic behavior of trinexapac-ethyl. It was concluded that the residues situation in rotational crops is negligible.

Greater than 90% of the TRR after application of trinexapac-ethyl to bare ground remained in the top 10 cm of soil during the entire cultivation of the succeeding crops. In soil significant residues (TRR) were only observed in the top soil layer (0–5cm) in the range of 0.065–0.076 mg/kg at planting or sowing and at 0.028–0.080 mg/kg at harvest. In layers below, the TRR did not exceed 0.019 mg/kg and was in most cases < 0.010 mg/kg. Extractables in the top soil layer amounted to 7.1–14.9% of TRR after cold extraction using 50% aqueous methanol. An additional 1.4–2.5% of TRR was extractable after a hot Soxhlet extraction with methanol. 78.9–98.7% of TRR in the top soil layer were non-extractables.

The confined and field rotational crop studies suggest that residues of trinexapac-ethyl are unlikely to occur in succeeding crops.

RESIDUE ANALYSIS

Analytical methods

Details of analytical methods including validation data were supplied for the determination of trinexapac acid or trinexapac-ethyl in plant and animal matrices, soil, water and air and are considered satisfactory. A summary of all analytical methods for plants and animals is given in Table 42.

Table 42 Summary of analytical methods developed for plant and animal matrices

Matrix	Analyte	Method No.	Detection system	LOQ	Reference
Plant	Trinexapac acid	110-01	HPLC-MS	Field grown grass (forage, straw, hay, seed) LOQ = 0.05 mg/kg	Lin 2002, CGA163935/0962 Cobin and Pyles 2002, CGA163935/0961 (ILV for 110-01)
Plant	Trinexapac acid (free and conjugated)	GRM020.01A	HPLC-MS/MS	Field grown grass (forage, straw, seed), wheat (grain, forage, straw) LOQ = 0.01 mg/kg	Lin 2008, CGA179500_50010 Thomas 2010, CGA179500_50000 (ILV for GRM020.01A)
Plant	Trinexapac acid	REM 137.02	HPLC-UV	Wheat (grain, straw), barley (grain, straw), rape seed LOQ = 0.02 mg/kg	Forrer 1991, CGA163935/0082 Sack 1999, CGA163935/0588 (Validation for REM 137.02)
Plant	Trinexapac acid	REM 137.11	HPLC-UV	Rape seed oil LOQ = 0.02 mg/kg	Sack 1995, CGA163935/0417
Plant	Trinexapac acid	REM 137.13	HPLC-MS/MS	Beans, apple, potato, wheat grain, oilseed rape LOQ = 0.01 mg/kg	Campbell and Crook 2004, CGA163935/0990 Benazeraf 2004,

Matrix	Analyte	Method No.	Detection system	LOQ	Reference
				LOQ = 0.02 mg/kg (beans)	CGA163935/0988 (ILV for REM 137.13)
Plant	Trinexapac-ethyl	REM 137.01	HPLC-UV	Wheat (grain, straw), barley (grain, straw) LOQ = 0.04 mg/kg	Forrer 1989, CGA163935/0033
Plant	Trinexapac-ethyl	REM 137.05	HPLC-UV	Rape seed LOQ = 0.02 mg/kg	Forrer 1991a, CGA163935/0142
Animal	Trinexapac acid	REM 137.12	HPLC-UV	LOQ = 0.02 mg/kg LOQ = 0.01 mg/kg (milk) LOQ = 0.005 mg/kg (milk – modified method using HPLC-MS/MS in dairy cattle feeding study)	Sack 1995, CGA163935/0440 Gasser 2004, CGA163935/0740 (ILV for REM 137.12)
Animal	Trinexapac acid	REM 137.14	HPLC-MS/MS	LOQ = 0.01 mg/kg LOQ = 0.005 mg/kg (milk)	Kwiatkowski 2004, CGA179500/0039 Benazeraf 2004, CGA163935/0989 (ILV for REM 137.14)

ILV = Independent Laboratory Validation

Plant commodities

Method 110-01

Method 110-01 for the determination of trinexapac as trinexapac acid in plant matrices by means of high performance liquid chromatography with mass spectrometry (HPLC/MS) was reported by Lin (2002, CGA163935/0962). The method includes a reflux extraction procedure which is buffered to pH 7 and therefore does not hydrolyse sugar conjugates. Residues are quantified against a trinexapac acid external standard to give residues of “free” trinexapac acid.

Samples are extracted by refluxing for 1 hour with acetonitrile/ sodium phosphate buffer (70:30, v/v) at pH 7. The sample is passed through a pre-conditioned C₁₈ SPE cartridge for purification and evaporated to an aqueous solution (rotary evaporator). The aqueous solution is acidified and is then passed through a second SPE cartridge (C₈). The cartridge is rinsed with acetonitrile/ 0.05% H₃PO₄ aqueous solution (10:90, v/v) and the analyte is eluted from the column with acetonitrile/ 0.05% H₃PO₄ aqueous solution (30:70, v/v). The eluate is evaporated again to an aqueous solution, acidified and is liquid/liquid partitioned twice against a methyl tertiary butyl ether (MTBE)/hexane (63:35, v/v) with the addition of salt. The organic layers are collected and evaporated to dryness and re-dissolved in ethyl acetate. The ethyl acetate sample is passed through a pre-conditioned silica SPE column and rinsed with methanol/ ethyl acetate (15:85, v/v). The analyte is eluted from the cartridge with methanol/acetonitrile/ ethyl acetate (40:30:30, v/v/v). The eluate is evaporated to near dryness and dissolved in acetonitrile/water (10:90, v/v). The sample is injected onto a reverse phase C₈ column HPLC/MS/MS system for analysis of trinexapac acid using 0.1% acetic acid/acetonitrile (60:40, v/v) as the mobile phase. Detection in the positive ionisation mode was used (mass monitored 225).

Samples of grass (forage, hay/ straw, seed and seed screenings) were spiked with trinexapac acid at levels of 0.05, 1 and 5 mg/kg and then extracted and analysed using Method 110-01. Recoveries were found to be within acceptable ranges. In all matrices tested, the individual recovery values were in the acceptable range of 70–120%. The relative standard deviations (RSD, %) for all commodities and all spiking levels were at or below 20%. The mean recovery data are summarized in Table 43. The LOQ was reported as 0.05 mg/kg in all matrices.

Table 43 Method recoveries for method 110-01: trinexapac acid in field grown grass matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
	0.05	3	72–107	87	20
Forage	1	1	75	–	–
	5	3	76–94	86	11
	0.05	3	72–99	86	16
Hay/straw	1	1	86	–	–
	5	3	90–94	92	2
	0.05	2	84, 95	90	–
Seed	1	1	98	–	–
	5	3	77–92	87	10
	0.05	3	72–87	80	10
Seed screenings	1	1	104	–	–
	5	3	75–102	92	16

The extraction efficiency of Method 110-01 was tested. Grass matrices (forage, straw, seed and seed screenings) samples from the metabolism study were analysed in triplicate.

Table 44 Extractability of residues of [¹⁴C] trinexapac in grass matrices according to Method 110-01

Matrix	TRR (mg/kg) ^a Determined in Study 623-00	LSC Values (mg/kg) ^b Determined in this Study	Method 110-01 Extraction Efficiency ^c	Trinexapac acid residues (mg/kg) ^d Determined by Method 110-01	Accountability (%) ^e
Forage	2.03	1.6	80%	0.12 (4.8%)	5.9%
Straw	4.78	3.6	75%	0.75 (4.3%)	15.7%
Seed	5.45	3.2	58%	0.36 (38.9%)	6.6%
Seed screenings	7.13	4.2	59%	0.61 (16.6)	8.6%

^a TRRs were determined by combustion analyses of radiolabelled samples in Study 623-00 (Ray and May-Hertl 2003, CGA163935/0862)

^b Liquid scintillation counting (LSC) of the radiolabelled extracts in this study (averaged from triplicate samples)

^c Extractability or extraction efficiency = (LSC results ÷ TRR values) × 100%

^d Residues concentrations averaged from triplicate analysis (RSD)

^e Accountability = (Residues found by this method ÷ TRR) × 100%

It was found that the extraction efficiencies determined by Method 110-01 ranged from 58–80% for various grass matrices. Concentrations of trinexapac acid were determined by the method. Accountability ranged from 5.9% in forage to 15.7% in straw.

An independent laboratory validation report for Method 110-01 for the determination of residues of trinexapac acid (Cobin and Pyles 2002, CGA163935/0961) in plants (grass forage, hay, straw and seed) has been submitted. Minor modifications, principally concerning the silica SPE column, were suggested. Grass forage, straw and seed screenings were successfully validated during the first trial and grass hay during the second trial.

Table 45 Recovery results of method 110-01: trinexapac in plant matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Grass Forage	0.05	2	70, 70	70	–
	0.5	2	74, 83	79	–
Grass Hay	0.05	2	42, 49 (Trial 1) 85, 90 (Trial 2)	46 88	– –
	0.5	2	88, 92 (Trial 1) 96, 96 (Trial 2)	90 96	– –
Grass Straw	0.05	2	99, 109	104	–

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
	0.5	1	102	—	—
Grass Seed Screenings	0.05	2	105, 113	109	—
	0.5	2	99, 104	102	—

Note: For hay the method was changed from trial 1 to trial 2 to improve recoveries

Concurrent recovery results obtained during the residues and processing studies are tabulated below.

Table 46 Concurrent recovery results for method 110-01: trinexapac in plant matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid				Reference
		No.	Range [%]	Mean [%]	RSD [%]	
	0.05	4	70–86	79	9	Ediger 2006, 451534
Spring Wheat Forage	0.50	3	75–85	81	7	
	5	1	111	111	—	
	0.05	2	70, 85	78	—	
Spring Wheat Hay	0.5	2	85, 120	103	—	
	5	3	104	104	—	
	0.05	3	70–92	82	14	
Spring Wheat Straw	0.5	1	82	82	—	
	2	1	80	80	—	
	5	1	95	95	—	
	0.05	4	88–94	90	5	
Spring Wheat Grain	0.5	4	72–109	96	17	
	10	1	96	96	—	
	15	1	80	80	—	
Spring Wheat Aspirated	0.5	1	101	101	—	
Grain Fractions	5.0	1	112	112	—	
Spring Wheat Bran	0.5	1	77	77	—	
	25	1	81	81	—	
Spring Wheat Flour	0.05	1	89	89	—	
	5	1	103	103	—	
Spring Wheat Middlings	0.05	1	80	80	—	
	5	1	82	82	—	
Spring Wheat Shorts	0.05	1	94	94	—	
	10	1	78	78	—	
Spring Wheat Germ	0.50	1	70	70	—	
	10	1	94	94	—	
Winter Wheat Forage	0.1	6	70–73	71	2	
	0.5	8	73–120	90	17	
Winter Wheat Hay	0.2	1	69	69	—	
	0.5	9	64–105	85	16	
Winter Wheat Straw	0.1	3	70–88	78	12	
	0.5	8	71–104	89	13	
	1	1	80	80	—	
Winter Wheat Grain	0.05	1	86	86	—	
	0.1	6	72–92	83	8	
	0.5	7	76–99	90	10	
Winter Wheat Aspirated	0.05	1	118	118	—	
Grain Fractions	0.5	1	101	101	—	
Winter Wheat Bran	0.05	1	91	91	—	
	0.5	1	98	98	—	
Winter Wheat Flour	0.05	1	92	92	—	
	0.5	1	118	118	—	
Winter Wheat Middlings	0.05	1	89	89	—	
	0.5	1	87	87	—	
Winter Wheat Shorts	0.05	1	109	109	—	

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid				Reference
		No.	Range [%]	Mean [%]	RSD [%]	
	0.5	1	96	96	—	
Winter Wheat Germ	0.05	1	110	110	—	
	0.5	1	89	89	—	
Stripped Cane	0.05	4	85–104	94	9	Ediger 2006a, 451598
	0.50	4	80–112	95	14	
	0.05	4	82–111	95	16	
Stripped Matured Cane	0.50	4	97–107	102	4	
	2.0	2	94, 99	97	—	
	0.05	1	94	94	—	
Stripped Cane (before processing)	0.5	1	100	100	—	
	1.0	2	114, 124	119	—	
Molasses	0.05	1	87	87	—	
	2.0	2	81, 90	86	—	
Refined Sugar	0.05	1	92	92	—	
Spinach Leaves	0.05	2	71, 78	75	—	Ediger 2006b, CGA163935/1054
	0.5	2	87, 89	88	—	
Radish Tops	0.05	2	60, 107	84	—	
	0.5	2	80, 94	87	—	
Radish Roots	0.05	2	88, 91	90	—	
	0.5	2	89, 100	95	—	
Wheat Forage	0.05	4	74, 76, 79, 104	83	17	
	0.5	4	85, 88, 92, 100	91	7	
Wheat Hay	0.05	2	67, 70	69	—	
	0.5	2	79, 111	95	—	
Wheat Straw	0.05	2	79, 120	100	—	
	0.5	2	102, 117	110	—	
Wheat Grain	0.05	2	111, 111	111	—	
	0.5	2	91, 112	102	—	

Method GRM020.01A

A validated method (GRM020.01A) has been reported for the determination of trinexapac acid in plant matrices using HPLC-MS/MS (Lin 2008, CGA179500_50010). It is a modified version of Method 110-01. This method includes a strong acid hydrolysis procedure to release “conjugated” residues of trinexapac acid from plant matrices. Residues are quantitated against a trinexapac acid external standard to give the sum of “free” and “conjugated” trinexapac acid. Other modifications included reducing the steps for sample clean-up procedures and using HPLC/MS/MS for final determination.

Samples are refluxed for 5 hours with acetonitrile/ 1 N hydrochloric acid (80:20, v/v). An aliquot of the extract supernatant is mixed with water and passed through a C₈ SPE cartridge (pre-conditioned with acetonitrile then 0.5% formic acid). The C₈ SPE cartridge is rinsed with water then water/ acetonitrile (80:20, v/v). The analyte is eluted from the cartridge with formic acid aqueous solution/ acetonitrile (80:20, v/v). The eluent is injected onto a reverse phase ODS-2 column HPLC-MS/MS system for analysis of trinexapac acid. MS/MS detection in the negative ionization mode is used to monitor the ion transition 223→135 (quantitation) for trinexapac. The 223→179 transition can be used for the confirmatory analysis of trinexapac residues.

Samples of field grown grass commodities (forage, straw, seed screenings and seed) were spiked with trinexapac acid at levels of 0.01–1 mg/kg. Samples were extracted and analysed with Method GRM020.01A (HPLC-MS/MS). In the matrices tested the mean recoveries were within 70–120% (Table 47). The relative standard deviations (RSD, %) for all commodities and all spiking levels were below 20%. The LOQ was defined by the lowest spiking level successfully tested, which was 0.01 mg/kg for trinexapac acid in all matrices.

Table 47 Method recoveries for GRM020.01A: trinexapac acid in grass matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Forage	0.01	5	95–101	99	2
	0.1	5	85–105	97	8
	0.2	1	100	–	–
Straw	0.01	5	93–97	94	2
	0.02	5	95–100	98	2
	0.2	5	86–91	89	2
	1	1	107	–	–
Seed screenings	0.01	5	91–99	96	3
	0.1	5	97 (×5)	97	0
	0.2	1	100	–	–
Seed	0.01	5	95–97	96	1
	0.1	5	84–100	92	7

The extraction efficiency (radio-validation) of Method GRM020.01A was tested. Grass matrices (forage, straw and seed screenings) samples from the metabolism study were analysed in triplicate.

Table 48 Extractability of residues of [¹⁴C] trinexapac in grass matrices according to Method GRM020.01A

Matrix	TRR (mg/kg) ^a Determined in Study 623-00	LSC Values (mg/kg) ^b Determined in this Study	Method GRM020.01A Extraction Efficiency ^c	Trinexapac acid residues (mg/kg) ^d Determined in Study 623-00	Trinexapac acid residues (mg/kg) ^e Determined by GRM020.01A
Forage	2.03	2.28	112%	0.329	0.40
Straw	4.78	4.85	101%	1.068	1.3
Seed screenings	7.13	6.37	89%	0.906	2.0

^a TRRs were determined by combustion analyses of radiolabelled samples in Study 623-00 (Ray and May-Hertl 2003, CGA163935/0862)

^b Liquid scintillation counting (LSC) of the radiolabelled extracts in this study

^c Extractability or extraction efficiency = (LSC results ÷ TRR values) × 100%

^d Data reported in Study 623-00 (Ref.)

^e Averaged from triplicate analysis of radiolabelled samples (duplicate for seed screenings) by Analytical Method GRM020.01A LC-MS/MS analysis

It was found that the extraction efficiency and residue concentrations determined by Method GRM020.01A were in general agreement with those reported in the metabolism study. The radio-validation data confirms that the method is capable of accurately quantifying incurred residues of trinexapac acid as the sum of free and conjugated residues.

An independent laboratory validation report for Method GRM020.01A for the determination of residues of trinexapac acid in plants (wheat grain, forage and straw) has been submitted (Thomas 2010, CGA179500_50000).

For trinexapac, the transition 223→135 was used for quantitation, and 223→179 was used for confirmation. Recoveries at fortification levels of 0.01 (LOQ) and 0.1 mg/kg were provided for the quantitation transition and were found to be acceptable (Table 49). All individual recoveries were between 70–120% with a relative standard deviation < 20% for each fortification level / matrix combination. The LOQ was defined by the lowest spiking level successfully tested, which was 0.01 mg/kg for trinexapac in all matrices.

Table 49 Recovery results of method GRM020.01A: trinexapac acid in plant matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Wheat Grain	0.01	5	86–109	95	10
	0.10	5	95–106	100	4
Wheat Forage	0.01	5	79–98	90	8
	0.10	5	85–97	91	5
Wheat Straw	0.01	5	94–108	100	5
	0.10	5	98–105	102	3

The method GRM020.01A was successfully independently validated for measurement of residues of trinexapac acid in wheat forage, straw and grain.

Method and concurrent recovery results obtained for Method GRM020.01A during the residues and processing studies are tabulated in the following tables.

Table 50 Method recoveries for method GRM020.01A: trinexapac acid in plant matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid				Reference
		No.	Range [%]	Mean [%]	RSD [%]	
Wheat Grain	0.01	2	110, 112	111	–	Mäyer 2010, CGA163935_50036
	0.10	2	106, 106	106	–	
Wheat AGFs	0.01	2	82, 83	83	–	
	0.10	2	96, 96	96	–	
Wheat Bran	0.01	2	112, 102	107	–	
	0.10	2	114, 116	115	–	
Wheat Flour	0.01	2	78, 84	81	–	
	0.10	2	95, 111	103	–	
Wheat Middlings	0.01	2	75, 76	76	–	
	0.10	2	83, 85	84	–	
Wheat Shorts	0.01	2	81, 84	83	–	
	0.10	2	84, 89	87	–	
Wheat Germ	0.01	2	93, 108	101	–	
	0.10	2	93, 94	94	–	
Sugarcane	0.01	2	76, 70	73	–	Mäyer 2010b, CGA163935_50038
	0.10	2	80, 76	78	–	
Molasses	0.01	2	101, 89	95	–	
	0.10	2	94, 87	91	–	
Refined Sugar	0.01	2	85, 78	82	–	
	0.10	2	82, 71	77	–	
	2.5	2	71, 79	75	–	Simmons 2010,
Poultry feed	10.0	2	70, 75	38	–	CGA179500_50008
	41.0	2	79, 90	85	–	

Table 51 Concurrent recovery results of method GRM020.01A: trinexapac acid in plant matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid				Reference
		No.	Range [%]	Mean [%]	RSD [%]	
	0.01	5	72–109	96	16	Mäyer 2010a, CGA163935_50026
Barley Hay	0.10	4	100–110	105	4	
	1.0	1	107	107	–	
	7.0	1	98	98	–	
	0.01	5	72–112	95	15	
Barley Straw	0.10	4	81–110	95	13	
	1.0	1	80	80	–	
	0.01	8	82–111	95	12	
Barley Grain	0.10	7	72–92	82	8	
	11.0	1	94	94	–	

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid				Reference
		No.	Range [%]	Mean [%]	RSD [%]	
Pearled Barley	0.01	1	108	108	–	
	20.0	1	114	114	–	
Barley Flour	0.01	1	102	102	–	
	20.0	1	111	111	–	
Barley Bran	0.01	1	91	91	–	
	20.0	1	100	100	–	
Wheat Forage	0.01	9	72–120	93	18	Mäyer 2010,
	0.10	8	84–105	96	7	CGA163935_50036
	10	1	94	94	–	
Wheat Hay	0.01	9	71–118	94	18	
	0.10	8	90–107	100	6	
	11	1	106	106	–	
	0.01	9	71–112	88	19	
Wheat Straw	0.10	8	89–107	96	6	
	1.0	1	111	111	–	
	0.01	12	83–120	101	12	
Wheat Grain	0.10	11	88–113	103	7	
	15	1	113	113	–	
Wheat AGFs	0.01	1	74	74	–	
	20	1	86	86	–	
	0.01	3	94–120	108	12	
Wheat Bran	0.10	2	106, 107	107	–	
	20	1	84	84	–	
Wheat Flour	0.01	1	107	107	–	
	20	1	115	115	–	
	0.01	2	99, 100	100	–	
Wheat Middlings	0.10	1	96	96	–	
	10	1	116	116	–	
	0.01	2	70, 117	94	–	
Wheat Shorts	0.10	1	78	78	–	
	10	1	86	86	–	
	0.01	2	74, 114	94	–	
Wheat Germ	0.10	1	100	100	–	
	15	1	99	99	–	
	0.01	6	71–100	83	14	Mäyer 2010b,
Sugarcane	0.10	5	71–92	84	10	CGA163935_50038
	10.0	1	71	71	–	
Molasses	0.01	1	85	85	–	
	20.0	1	75	75	–	
Refined Sugar	0.01	1	71	71	–	
	20.0	1	71	71	–	
Wheat Germ	0.1	8	79–109	99	11	Brown 2011,
Wheat Bran	0.1	8	85–103	93	8	CGA179500_50012
Wheat Flour	0.1	8	70–107	87	17	
	2.5	3	76, 98, 101	92	15	Simmons 2010,
Poultry feed	10.0	2	70, 81	76	–	CGA179500_50008
	41.0	1	105	–	–	

Method REM 137.02

A validated method (REM 137.02) has been reported for the determination of trinexapac acid in plant matrices using HPLC-UV (Forrer 1991, CGA163935/0082).

In the case of wheat and barley, trinexapac acid is extracted by shaking a homogenised subsample with a pH 7 methanol/aqueous phosphate buffer (30:70, v/v) to analyse for free trinexapac acid. In the case of rapeseed, trinexapac acid is extracted by shaking a homogenised subsample with a pH 7 acetonitrile/aqueous phosphate buffer (80:20, v/v) to analyse for free trinexapac acid. An extract aliquot is transferred to a pre-conditioned (methanol/water 50:50, v/v) solid phase extraction cartridge

(SAX). After washing with methanol/water (30:70, v/v) and water, trinexapac acid is eluted with sulphuric acid (0.1 N) and partitioned into dichloromethane. The organic phase is evaporated to dryness. Additional clean-up and final determination are achieved using a three-column HPLC switching system with UV-detection. The LOQ of this method was given as 0.02 mg/kg trinexapac acid. Recovery data are summarized in Table 52.

Table 52 Method recoveries for method REM 137.02: trinexapac acid in plant matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Wheat Grain	0.04	1	94	—	—
	0.2	1	80	—	—
Wheat Straw	0.04	1	104	—	—
	0.2	1	99	—	—
Barley Grain	0.04	3	96–101	98	3
	0.2	3	89–98	95	5
Barley Straw	0.04	3	96–110	102	7
	0.2	3	89–97	94	5
Rape Seed	0.04	1	105	—	—
	0.2	1	98	—	—

In a validation study for Method 137.02 (Sack 1999, CGA163935/0588) for the final determination the HPLC system was changed from the original 3-column LC system to the 2-column system which follows the same reversed phase principles as the 3-column system. The LOQ was defined by the lowest spiking level successfully tested, which was 0.02 mg/kg for trinexapac acid in all matrices.

Samples of wheat and rape seed matrices were spiked with trinexapac acid at levels of 0.02–0.2 mg/kg. Samples were extracted and analysed with Method REM 137.02 (HPLC-UV). In the matrices tested mean recoveries were within 70–120%. The recovery data are summarized in Table 53. Relative standard deviations (RSD, %) for all commodities and all spiking levels were below 20%. Reproducibility was demonstrated by the successful validation with wheat grain and rapeseed carried out in a second laboratory, fulfilling the requirement for an enforcement method.

Table 53 Method recoveries for method REM 137.02: trinexapac acid in plant matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Wheat Grain	0.02	5	92–102	98	4
	0.20	5	71–93	85	10
Wheat Straw	0.02	5	98–110	104	5
	0.20	5	79–93	89	6
Rape Seed	0.02	5	75–96	90	10
	0.20	5	73–81	78	4
Wheat Grain ^a	0.02	5	75–83	78	4
	0.20	5	70–75	72	3
Rape Seed ^a	0.02	5	76–79	77	2
	0.20	5	68–72	70	3

^a Results from the second laboratory

Method REM 137.11

Details of a method (REM 137.11) for the determination of trinexapac acid in rape seed oil using HPLC-UV have been reported in the rape seed processing studies (e.g. Sack 1995, CGA163935/0417).

Trinexapac acid is extracted from rape seed oil four times by vigorously shaking with methanol. The combined methanol phases are diluted with pH 7 phosphate buffer. This aqueous

sample is pre-cleaned using a C18 SPE column. After acidification of the sample passed through the first column, trinexapac acid is extracted by means of a second C18 SPE column. Final determination is performed using a two column HPLC with UV-detection. Samples of rape seed oil were spiked with trinexapac acid at levels of 0.02 and 0.1 mg/kg (recoveries 88% and 87% respectively).

Method REM 137.13

A validated method (REM 137.13) has been reported for the determination of free trinexapac acid in plant matrices using HPLC-MS/MS (Campbell and Crook 2004, CGA163935/0990). The method was developed from Method 137.02 with the replacement of the HPLC-UV two column switching method by solid phase extraction (SPE) followed by single column HPLC-MS/MS.

Samples are extracted by homogenisation with pH 7 methanol/ water/ phosphate buffer (30:56:14, v/v/v) to analyse for free trinexapac acid. Extracts are centrifuged and aliquots are subsequently diluted with ultra-pure water. A SPE procedure is then carried out to facilitate sample clean up. Final determination is by high performance liquid chromatography with triple quadrupole mass spectrometric detection (LC-MS/MS).

Samples of broad bean seed, broad bean whole plant and broad bean remainder were spiked with trinexapac acid at levels of 0.02–4 mg/kg (whole plant), 0.02–0.2 mg/kg (remainder) and 0.02–10.0 mg/kg (seed) (Table 54). Samples were extracted and analysed using Method REM 137.13. In the matrices tested the mean recoveries were within 70–120%. The relative standard deviations (RSD, %) for all commodities and all spiking levels were $\leq 20\%$. MS/MS detection in the negative ionisation mode is used to monitor the ion transition 223 $\rightarrow$ 83 for trinexapac.

Table 54 Method recoveries for method REM 137.13: trinexapac acid in bean matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Broad Bean (Whole Plant)	0.02	5	91–104	97	5
	4	5	93–102	96	4
Broad Bean (Remainder)	0.02	5	64–96	78	20
	0.2	5	69–111	91	17
Broad Bean (Seed)	0.02	5	75–98	89	10
	10.0	5	87–96	91	4

An independent laboratory validation report for Method REM 137.13 for the determination of residues of trinexapac acid (Benazeraf 2004, CGA163935/0988) in plants has been submitted.

Samples of apple, potato, wheat grain and oilseed rape were spiked with trinexapac acid at levels of 0.01–0.1 mg/kg (apple), 0.01–0.1 mg/kg (potato), 0.01–0.3 (wheat grain) and 0.01–1 mg/kg (oilseed rape). Samples were extracted and analysed using Method REM 137.13. In the matrices tested the mean recoveries were within 70–120% and the relative standard deviations (RSD, %) for all commodities and all spiking levels were $\leq 20\%$ (Table 55).

Table 55 Recovery results of method REM 137.13: trinexapac acid in plant matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Apple	0.01	5	63–100	84	18
	0.1	5	72–98	90	12
Potato	0.01	5	97–111	103	6
	0.1	5	88–104	98	7
Wheat Grain	0.01	5	72–96	84	12
	0.3	5	79–103	92	9
Oilseed Rape	0.01	5	74–90	85	8
	1	5	79–87	83	5

The LOQ was defined by the lowest spiking level successfully tested, which was 0.01 mg/kg each for trinexapac in all matrices.

Method REM 137.01

Method REM 137.01 has been reported for the determination of trinexapac-ethyl in wheat and barley grains and straw using HPLC-UV (Forrer 1989, CGA163935/0033).

Samples are extracted by homogenisation with pH 7 methanol/ aqueous phosphate buffer (30:70, v/v) to analyse for trinexapac-ethyl. Extracts are acidified and the compound re-extracted into dichloromethane. A SPE procedure is then carried out to facilitate sample clean up. Final determination is by a three column high performance liquid chromatography switching system with UV-detection.

Samples of wheat grain and straw were spiked with trinexapac-ethyl at levels of 0.04 and 0.2 mg/kg (Table 56). Samples were extracted and analysed using Method REM 137.01. In the matrices tested the mean recoveries were within 70–120%. The relative standard deviations (RSD, %) for all commodities and all spiking levels were $\leq 21\%$. Supplementary data (wheat and barley grain and straw) for confirmation of the validity of Method REM 137.01, using a simplified chromatographic system with only the first two columns, was presented in the same study. Method REM 137.01 was also validated in this study for quantitation of residues of trinexapac-ethyl in soil.

Table 56 Method recoveries for method REM 137.01: trinexapac-ethyl in cereal matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac-ethyl			
		No.	Range [%]	Mean [%]	RSD [%]
Wheat grain	0.04	6	60–111	87	21
	0.2	9	71–104	87	12
Wheat straw	0.04	2	100, 103	102	–
	0.2	7	99–106	103	3
Wheat grain ^a	0.04	5	70–104	89	16
	0.2	5	83–99	93	7
Wheat straw ^a	0.04	5	73–105	92	13
	0.2	5	82–99	93	8
Barley grain ^a	0.04	4	72–99	87	13
	0.2	4	77–99	89	11
Barley straw ^a	0.04	4	87–104	98	8
	0.2	4	86–101	94	7

^a Supplementary data supplied with Forrer 1989, CGA163935/0033 using a simplified chromatographic system

Method REM 137.05

A validated method (REM 137.05) has been reported for the determination of trinexapac-ethyl in rape seed using HPLC-MS/MS (Forrer 1991a, CGA163935/0142).

Trinexapac-ethyl is extracted by shaking a homogenised sub-sample with a pH 7 mixture of acetonitrile and aqueous phosphate buffer. An aliquot of the extract is washed with hexane, acidified and the compound is re-extracted into dichloromethane or into tert-butyl methyl ether/ethyl acetate. Additional clean-up and final determination are achieved by a three column HPLC switching system with UV-detection. Samples of rape seed were spiked with trinexapac-ethyl at levels of 0.04 – 0.2 mg/kg. Samples were extracted and analysed with REM 137.05 (HPLC-UV). Mean recoveries were within 70–120% (Table 57). The relative standard deviations (RSD, %) for all commodities and all spiking levels were below 20%. The limit of quantitation for trinexapac-ethyl residues in crop commodities using Method REM 137.05 was established at 0.02 mg/kg.

Table 57 Method recoveries for method REM 137.05: trinexapac-ethyl in rape seed

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Rape Seed	0.04	2	80, 91	86	-
	0.2	7	78-103	91	10
Rape Seed ^a	0.04	6	72-84	78	6
	0.2	6	62-82	75	10

^a Recoveries were generated with Method REM 137.01 using a simplified chromatographic system. Instead of the three column HPLC (as described for Method REM 137.05) the first two columns only were used.

Animal commodities

Method REM 137.12

Method REM 137.12 was developed for the determination of trinexapac acid in animal matrices (Sack 1995, CGA163935/0440). This HPLC-UV method was superseded by Method REM 137.14 (LC-MS/MS).

Method REM 137.12 involves the extraction of trinexapac acid from tissues (meat, liver or kidney) using a mixture of water/ methanol/ sodium hydroxide by shaking at room temperature. The extract is centrifuged and an aliquot is acidified. This aliquot is cleaned-up by means of solid phase extraction (SPE) using a C18 column followed by a second clean-up step on a strong anion exchange (SAX) SPE column. For milk, sub-specimens are diluted with water. After addition of sodium hydroxide an aliquot is taken and passed through a C18 SPE column. The entire pre-cleaned aliquot passed through the column is collected and acidified with phosphoric acid. Trinexapac acid is then extracted on a second C18 SPE column. For eggs, a homogenised sub-specimen (liquid part of egg only) is suspended in a mixture of water and methanol and dissolved by addition of sodium hydroxide. An aliquot of this clear solution is cleaned up/ extracted according to the same principles as applied for milk. The final extracts in all cases are analysed using HPLC-UV.

Samples of bovine meat, liver and kidney, milk and eggs were spiked with trinexapac acid at levels of 0.02–0.20 mg/kg (tissues), 0.01–0.10 mg/kg (milk) and 0.02–0.20 mg/kg (eggs). Samples were extracted and analysed using Method REM 137.12. In all the matrices tested the mean recoveries were within 70–120%. The mean recovery data are summarized in Table 58. The relative standard deviations (RSD, %) for all commodities and all spiking levels were < 20%.

The LOQ was defined by the lowest spiking level successfully tested, which was 0.01 mg/kg in milk and 0.02 mg/kg each in animal tissues and eggs.

Table 58 Recovery results of method REM 137.12: trinexapac acid in animal matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Meat	0.02	8	78–88	84	5
	0.20	8	86–95	92	3
Liver	0.02	4	86–94	89	4
	0.20	4	70–86	79	9
Kidney	0.02	4	77–85	82	5
	0.20	4	78–81	79	2
Milk	0.01	8	93–99	95	2
	0.10	8	92–101	97	3
Eggs	0.02	8	78–86	82	4
	0.20	8	78–84	81	2

An independent laboratory validation report for Method REM 137.12 for the determination of residues of trinexapac acid in animal matrices (milk and meat) has been submitted (Gasser 2001, CGA163935/0740).

Samples of meat and milk were spiked with trinexapac acid at levels of 0.01–0.10 mg/kg (milk) and 0.02–0.20 mg/kg (meat). Samples were extracted and analysed using Method REM 137.12. In both matrices tested the mean recoveries were within 70–120% and the relative standard deviations (RSD, %) for both commodities and both spiking levels were $\leq 20\%$ (Table 59). The LOQ was defined by the lowest spiking level successfully tested, which was 0.01 mg/kg in milk and 0.02 mg/kg in meat.

Table 59 Recovery results of method REM 137.12: trinexapac acid in animal matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Milk	0.01	5	92–96	94	2
	0.10	5	87–93	91	3
Meat	0.02	5	81–90	87	4
	0.20	5	85–89	86	2

Concurrent recovery results obtained for Method REM 137.12 during the dairy cattle feeding study (Sack 2000, CGA179500/0030) are tabulated in Table 60. The method was modified to allow determination using HPLC-MS/MS.

Table 60 Mean concurrent recovery data for Method 137.12 in dairy cattle feeding study

Matrix	Spiking level (mg/kg)	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Liver	0.02	1	80	–	–
	0.2	1	83	–	–
Kidney	0.02	1	102	–	–
	0.2	1	88	–	–
Muscle round	0.02	1	97	–	–
	0.2	1	85	–	–
Tenderloin	0.02	1	80	–	–
	0.2	1	81	–	–
Diaphragm	0.02	1	80	–	–
	0.2	1	82	–	–
Fat, perirenal	0.02	1	103	–	–
	0.2	1	75	–	–
Fat, omental	0.02	1	71	–	–
	0.2	1	91	–	–
Blood	0.01	1	93	–	–
	0.1	1	96	–	–
Milk	0.005	12	88–121	104	11
	0.1	11	100–108	103	2

Method REM 137.14

Method REM 137.14 was developed for the determination of trinexapac acid in animal matrices using quantification of residues by LC-MS/MS (Kwiatkowski 2004, CGA179500/0039). It supersedes the previously developed HPLC-UV Method REM 137.12.

Animal tissue and egg matrices are extracted by shaking with water/ methanol (80:20, v/v) containing 0.33% 1M sodium hydroxide solution. Milk is extracted by shaking with water/ methanol (98:2, v/v) containing 0.2% 1M sodium hydroxide solution. Extracts are centrifuged and aliquots are diluted with ultra-pure water. After a solid phase extraction procedure is carried out, final determination is by high performance liquid chromatography with triple quadrupole mass

spectrometric detection (LC-MS/MS). MS/MS detection in the negative ionisation mode is used to monitor ion transitions 223.0→83.0 and 223.0→178.6 (confirmatory transition) for trinexapac acid.

Samples of bovine muscle, kidney, liver, fat and eggs were spiked with trinexapac acid at levels of 0.01 and 0.10 mg/kg. Samples of milk were spiked with trinexapac acid at levels of 0.005 and 0.05 mg/kg. Samples were extracted and analysed with Method REM 137.14. In all matrices tested, the mean recovery values were between 70% and 120% and the relative standard deviations (% RSD) for all commodities and all spiking levels for five tests at each spiking level were ≤ 20%. Mean recovery data for the quantitation transition are given in Table 61.

The LOQ was defined by the lowest spiking level successfully tested which was 0.01 mg/kg for egg, muscle, kidney, liver and fat, and 0.005 mg/kg for milk.

Table 61 Recovery results of method REM 137.14: trinexapac acid in animal matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Muscle (cow)	0.01	5	62–110	95	20
	0.1	5	63–92	81	15
Kidney (cow)	0.01	5	88–114	99	10
	0.1	5	77–96	91	9
Liver (cow)	0.01	5	69–95	86	12
	0.1	5	86–97	92	5
Fat (cow)	0.01	5	94–109	104	6
	0.1	5	93–102	96	4
Milk (cow)	0.005	5	88–114	106	10
	0.05	5	89–99	94	5
Eggs	0.01	5	67–119	96	20
	0.1	5	79–97	90	8

An independent laboratory validation report for Method REM 137.14 has been submitted (Benazeraf 2004, CGA163935/0989).

Samples of bovine muscle were spiked with trinexapac acid at levels of 0.01 and 0.10 mg/kg and samples of milk were spiked with trinexapac acid at levels of 0.005 and 0.05 mg/kg. Samples were extracted and analysed with Method REM 137.14 (HPLC-MS/MS). In all matrices tested, the mean recovery values were between 70% and 120% and the relative standard deviations (% RSD) for all commodities and all spiking levels for five tests at each spiking level were < 20%. Mean recovery data for the quantitation transition are given in Table 62.

Table 62 Recovery results of method REM 137.14: trinexapac acid in animal matrices

Matrix	Spiking level [mg/kg]	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Muscle	0.01	5	93–108	101	5
	0.10	5	71–108	90	17
Milk	0.005	5	91–113	99	9
	0.05	5	77–119	96	17

Method REM 137.14 was successfully independently validated for the analysis of residues of trinexapac acid at an LOQ of 0.01 mg/kg in bovine muscle and 0.005 mg/kg in bovine milk.

Method and concurrent recovery results obtained for Method REM 137.14 during the poultry feeding study (Simmons 2010, CGA179500_50008) are tabulated in Tables 63 and 64.

Table 63 Mean method validation data for Method REM 137.14 (eggs and tissues) from the laying hen feeding study

Matrix	Spiking level (mg/kg)	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Chicken Egg	0.01	3	74–92	81	12
	0.10	3	94–103	97	5
Chicken Fat	0.01	3	86–89	89	6
	0.10	3	75–101	88	15
Chicken Liver	0.01	3	86–109	98	12
	0.10	3	93–98	95	3
Chicken Kidney	0.01	3	100–116	105	9
	0.10	3	95–100	97	3
Chicken Muscle	0.01	3	89–109	102	11
	0.10	3	98–105	102	3

Table 64 Mean concurrent recovery data for Method REM 137.14 (eggs and tissues) from laying hen feeding study

Matrix	Spiking level (mg/kg)	Recoveries for trinexapac acid			
		No.	Range [%]	Mean [%]	RSD [%]
Chicken Egg	0.01	6	70–109	80	19
	0.10	6	79–95	86	8
Chicken Fat	0.01	2	92, 103	98	–
	0.10	2	99, 100	100	–
Chicken Liver	0.01	2	91, 99	95	–
	0.10	2	86, 89	88	–
Chicken Kidney	0.01	2	93, 114	104	–
	0.10	1	100	–	–
	1.0	1	91	–	–
Chicken Muscle	0.01	1	92	–	–
	0.10	1	96	–	–

Stability of pesticide residues in stored analytical samples

Plant Matrices

A freezer storage stability study was carried out on wheat grain, straw and rapeseed fortified with trinexapac acid at approximately 0.5 mg/kg and stored at $\leq -18^{\circ}\text{C}$ (Sack 1998, CGA163935/0562). Samples were analysed using Method REM 137.02 with minor modifications concerning final determination by HPLC. Concurrent recoveries were determined together with the analytical samples. The results are summarized below in Table 65 and indicate that trinexapac acid is stable in frozen storage for at least 24 months in wheat grain and rapeseed although in the case of wheat straw, the amount of trinexapac acid that could be recovered after storage for approximately 2 years dropped to an average of 69% (75% if corrected for average concurrent recovery).

Table 65 Storage stability of trinexapac acid in plant matrices

Matrix ^a	Days Stored	Stability Recoveries [%]	Concurrent Recoveries [%]
	0	(set at) 100	85, 85
	96	85, 85, 92	88, 95
Wheat Grain	180	82, 84, 88	86, 87
	383	77, 79, 82	84, 90
	742	65, 73, 79	80, 82
	0	(set at) 100	93, 93
	93	101, 102, 103	84, 93
Wheat Straw	183	102, 104, 104	105, 106

Matrix ^a	Days Stored	Stability Recoveries [%]	Concurrent Recoveries [%]
	365	89, 89, 92	94, 99
	709	65, 71, 72	90, 94
	0	(set at) 100	91, 91
	96	89, 93, 94	93, 95
Rapeseed	167	82, 82, 89	94, 95
	376	75, 79, 81	84, 88
	720	77, 81, 82	94, 95

^a Average fortification levels 0.55 mg/kg wheat grain and 0.45 mg/kg wheat straw and rapeseed

A freezer storage stability study was carried out on wheat processed fractions (germ, bran and flour) fortified with trinexapac acid at 0.1 mg/kg and stored at $-20 \pm 5^{\circ}\text{C}$ (Brown 2011, CGA179500_50012).

Samples were analysed using Method GRM020.01A with minor method modifications. Recoveries were run concurrently with the analytical samples. The results are summarized below in Table 66 and indicate that trinexapac acid is stable in frozen storage for at least 12 months in wheat processed fractions.

Table 66 Storage stability of trinexapac acid in plant matrices

Matrix	Days Stored	Concurrent Recoveries [%]		Stability Recoveries [%]	
		Found	Average	Found	Average
	0	103, 102	102	109, 100	104
Wheat Germ	101	105, 101	103	104, 105	104
	271	79, 84	82	83, 84	84
	381	106, 109	108	104, 113	108
	0	87, 95	91	95, 75	85
Wheat Bran	99	100, 103	102	80, 93	86
	269	85, 86	86	85, 76	80
	379	97, 88	92	104, 98	101
	0	107, 104	106	110, 105	108
Wheat Flour	102	73, 91	82	79, 81	80
	272	70, 72	71	69, 67	68
	382	87, 95	91	84, 93	88

In the [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl grass metabolism study the storage stability was determined by comparison of the metabolite profiles of extracts of straw, seed screenings and 105 day regrowth forage at the beginning of the analytical phase and at the end of the study, approximately thirteen months later. The qualitative and quantitative metabolite profiles did not change throughout this period. It was concluded that the results of the study were not considered to be affected by the length and conditions of storage.

Animal Matrices

The stability of trinexapac acid in extracts of animal matrices was tested at the same time as the dairy cattle and laying hen feeding studies (Sack 2000, CGA179500/0030 and Simmons 2010, CGA179500_50008 respectively).

In the dairy cattle feeding study, no significant degradation of residues of trinexapac acid was observed in frozen samples of muscle (average recovery 82% corrected for concurrent recoveries), milk (89%), liver (85%), kidney (85%), fat (96%) and blood (102%) stored at $\leq -18^{\circ}\text{C}$ over the storage period from the arrival of specimens until analysis (83-121 days).

Table 67 Storage stability of trinexapac acid in dairy cattle matrices

Matrix	Spiking Level [mg/kg]	Days Stored	Concurrent Recoveries [%]	Recoveries [%]	
				Found ^a	Average ^a
Muscle	0.20	91	83, 81	86, 86, 77, 76, 87	82
Liver	0.20	94	85, 96	84, 83, 85, 87, 86	85
Kidney	0.20	95	89, 88	87, 86, 87, 81, 82	85
Omental Fat	0.10	101	98, 97	96, 96, 98, 93, 95	96
Milk	0.05	121	108, 109	89, 86, 90, 88, 93	89
Blood	0.10	83	99, 109	102, 99, 104, 104, 101	102

^a Recoveries found (and averages) are corrected for concurrent recoveries

In the laying hen feeding study, no significant degradation of residues of trinexapac acid was observed in frozen samples of eggs, chicken fat, chicken liver, chicken kidney and chicken muscle (average recoveries > 70%) stored at $\leq -18^{\circ}\text{C}$ over the storage period from the sample collection until analysis (31–82 days).

Table 68 Storage stability of trinexapac acid in poultry matrices

Matrix	Spiking Level [mg/kg]	Days Stored	Concurrent Recoveries [%]	Stability Recoveries [%]	
				Found	Average
Eggs	0.1	82	85, 84	73, 87	80
Fat	0.1	56	100, 104	93, 99	96
Liver	0.1	57	85, 85	83, 84	84
Kidney	0.1	54	94, 88	92, 97	95
Muscle	0.1	31	100, 101	97, 104	101

The stability of trinexapac acid in extracts of animal matrices was tested with the validation of Method REM 137.14 (Kwiatkowski 2004, CGA179500/0039). The stability of trinexapac acid in extracts of eggs (7 days storage), muscle (8 days storage), kidney (4 days storage), liver (5 days storage) and fat (3 days storage) was assessed by retaining water: methanol (80:20 v/v) containing 0.33% 1M sodium hydroxide and for milk (6 days storage) in water: methanol (98:2 v/v) containing 0.2% 1M sodium hydroxide extraction solutions at $< 7^{\circ}\text{C}$. Overall mean recoveries for trinexapac acid between 70–120% with an overall RSD of $\leq 20\%$ for each matrix tested, indicated that the compound is stable when stored in the extract solution for the period indicated.

The stability of trinexapac acid in the final solution of acetonitrile: water (30:70 v/v) for all matrices was also assessed. Milk, eggs, muscle, kidney, liver and fat aliquots in the final solution were retained, stored at $< 7^{\circ}\text{C}$ and re-analysed after 2 days (kidney and muscle), 3 days (eggs and fat), 4 days (liver) and 5 days (milk) following the original analysis and quantified against freshly calibrated solutions. The compound was shown to be stable when stored in the final solutions for those periods.

In the [1,2- ^{14}C -cyclohexyl] trinexapac-ethyl hen metabolism study the storage stability was determined by comparison of the quantitative metabolite pattern of hen excreta at the beginning of the storage period, with that obtained from the identical sample at the beginning of the analytical work approximately 2 weeks later. The extractability and quantitative metabolite patterns did not change throughout this period. It was concluded that the results of the study were not considered to be affected by the length and conditions of storage. In the hen metabolism study using [1, 2, 6- ^{14}C -cyclohexyl] trinexapac-ethyl, the extract of the egg white sample (taken as a representative of all the commodities) was analysed by TLC twice, approximately 6 months apart. The generated profiles were similar and therefore it was concluded that storage stability was confirmed.

In the [1,2- ^{14}C -cyclohexyl] trinexapac-ethyl goat metabolism study the storage stability was determined by comparison of the quantitative metabolite pattern of goat urine prior to storage and at the beginning of the experimental phase of the study, approximately nine months later. The quantitative metabolite patterns did not change throughout this period. It was concluded that the results of the study were not considered to be affected by the length and conditions of storage.

USE PATTERNS

Information on registered uses made available to this meeting is shown in Table 69.

Table 69 Registered uses of trinexapac-ethyl on cereal grains, grasses for sugar or syrup production and sugarcane

Crop	Country	Formulation		Application				PHI [days]
		g ai/L	Type	Method	Timing	Rate, g ai/ha	Season Max. (no.) or [g ai/ha/season]	
Cereal Grains								
Barley, summer	Belgium	250	EC	Foliar	BBCH 29–32	100–150	(1)	—
Barley, spring	France	250	EC	Foliar	BBCH 25–37	150	(1)	—
Barley, spring	Germany	250	EC	Foliar	BBCH 31–37	150	(1)	—
Barley, winter	Belgium	250	EC	Foliar	BBCH 31–32	125–200	(1)	—
Barley, winter	France	250	EC	Foliar	BBCH 25–39	200	(1)	—
Barley, winter (multi-row varieties)	Germany	250	EC	Foliar	BBCH 31–49	200	(1)	—
Barley, winter (two-row varieties)	Germany	250	EC	Foliar	BBCH 31–49	150	(1)	—
Barley, winter and spring	USA	249	EC	Foliar	Feekes 5–8	90–123	(1)	45
Barley, winter and spring	USA	249	EC	Foliar	Feekes 6–7 and Feekes 8	45	(2)	45
Barley, winter and spring	USA	120	EC	Foliar	Feekes 5–8	101–123	(1)	45
Barley, winter and spring	USA	120	EC	Foliar	Feekes 6–7 and Feekes 8	56	(2)	45
Grasses (grown for seed)	France	250	EC	Foliar	BBCH 31–51	200	(1)	—
Grasses (grown for seed)	USA	249	EC	Foliar	Feekes 5–8	101–560	(1)	35 ^{a,b}
Grasses (grown for seed)	USA	249	EC	Foliar	Feekes 5–8 and 7–10 days later	45–269	(2)	35 ^{a,b}
Grasses (grown for seed)	USA	120	EC	Foliar	Feekes 5–8	101–560	(1)	35 ^{a,b}
Grasses (grown for seed)	USA	120	EC	Foliar	Feekes 5–8 and 7–10 days later	56–280	(2)	35 ^{a,b}
Oat	Belgium	250	EC	Foliar	BBCH 30–31	100	(1)	—
Oat	Germany	250	EC	Foliar	BBCH 31–37	150	(1)	—
Oat	USA	249	EC	Foliar	Feekes 5–8	90–123	(1)	45
Oat	USA	249	EC	Foliar	Feekes 4–5 and Feekes 7	45	(2)	45
Oat	USA	120	EC	Foliar	Feekes 5–8	101–123	(1)	45
Oat	USA	120	EC	Foliar	Feekes 4–5 and Feekes 7	56	(2)	45
Rye	Belgium	250	EC	Foliar	BBCH 31–32	100–125	(1)	—
Rye, winter	Germany	250	EC	Foliar	BBCH 31–39	150	(1)	—
Rye, winter	Germany	250	EC	Foliar	BBCH 39–49	75	(1)	—
Ryegrass (Italian— grass seed cultivation)	Belgium	250	EC	Foliar	BBCH 31–49	100–200	(1)	—
Ryegrass (perennial—grass seed cultivation)	Belgium	250	EC	Foliar	BBCH 31–49	100–200	(1)	—
Spelt	Belgium	250	EC	Foliar	BBCH 31–32	100–125	(1)	—
Triticale	Belgium	250	EC	Foliar	BBCH 31–32	100–125	(1)	—
Triticale	Germany	250	EC	Foliar	BBCH 31–49	150	(1)	—
Triticale	Germany	250	EC	Foliar	BBCH 39–49	75	(1)	—
Triticale	USA	249	EC	Foliar	Feekes 5–8	90–123	(1)	45
Triticale	USA	249	EC	Foliar	Feekes 4–5 and Feekes 7	45	(2)	45
Triticale	USA	120	EC	Foliar	Feekes 5–8	101–123	(1)	45
Triticale	USA	120	EC	Foliar	Feekes 4–5 and Feekes 7	56	(2)	45
Wheat, summer	Belgium	250	EC	Foliar	BBCH 30–31	100	(1)	—
Wheat, winter	Belgium	250	EC	Foliar	BBCH 31–32	100–125	(1)	—

Crop	Country	Formulation		Application				PHI [days]
		g ai/L	Type	Method	Timing	Rate, g ai/ha	Season Max. (no.) or [g ai/ha/season]	
Wheat, winter	France	250	EC	Foliar	BBCH 25–39	125	(1)	—
Wheat, winter	Germany	250	EC	Foliar	BBCH 31–49	100	(1)	—
Wheat, winter, spring, durum	USA	249	EC	Foliar	Feekes 5–8	90–123	(1)	45
Wheat, winter, spring, durum	USA	249	EC	Foliar	Feekes 4–5 and Feekes 7	45	(2)	45
Wheat, winter, spring, durum	USA	120	EC	Foliar	Feekes 5–8	101–123	(1)	45
Wheat, winter, spring, durum	USA	120	EC	Foliar	Feekes 4–5 and Feekes 7	56	(2)	45
Grasses for sugar or syrup production								
Sugarcane (for ripening)	USA	249	EC	Foliar	28–60 days before harvest	202–347	(1)	28
Sugarcane (for internode shortening for seed piece production)	USA	249	EC	Foliar	When 6 fully developed full size leaves have formed then when 6 more fully developed full size leaves have formed (minimum of 2 applications)	78–224	[347 g/ha/ crop/season]	28
Sugarcane (for ripening)	USA	120	EC	Foliar	28–60 days before harvest	202–347	(1)	28
Sugarcane (for internode shortening for seed piece production)	USA	120	EC	Foliar	When 6 fully developed full size leaves have formed then when 6 more fully developed full size leaves have formed (minimum of 2 applications)	67–224	[347 g/ha/ crop/season]	—
Oilseeds								
Oilseed rape	Belgium	250	EC	Foliar	BBCH 55–57	300	(1)	—
Oilseed rape, winter	Germany	250	EC	Foliar	BBCH 39–55	375	(1)	—

^a Do not graze or feed forage 49 days after the last application

^b Other crops may be planted 30 days after the last application

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised trials for the uses of trinexapac on cereals (barley and wheat), oilseeds (oilseed rape) and grasses for sugar and syrup production (sugarcane).

Trials were well documented with laboratory and field reports. The former included method validation including recoveries with spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analyses or duration of sample storage were also provided. Trials were carried out in appropriately sized plots and sample sizes were within acceptable weights. Applications were generally made using backpack sprayers although occasionally tractor mounted sprayers were used. Samples were collected and stored frozen immediately or soon after sampling. Although trials included control plots, no control data are recorded in the Tables because no residues in control samples exceeded the LOQ. Residues are unadjusted for recoveries.

Residues, application rates and spray concentrations have generally been rounded to two significant figures. Residues from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels and dietary intake assessment. If a higher residue level was observed at a longer PHI than the GAP, the higher value has been used in MRL setting and dietary intake assessment. When residues were not detected they are shown as below the LOQ (e.g. < 0.01 mg/kg) and the LOQ value was utilised for maximum residue level estimation and dietary intake assessment.

For replicate samples (from the same plot), the mean value was used for maximum residue level estimation and dietary intake assessment. For two or more analyses of the same sample, the mean value was used for maximum residue level estimation and dietary intake assessment, with the individual results given in brackets. For multiple trials on a crop from the same location, the result from the trial yielding the highest residue was utilised for maximum residue level estimation and dietary intake assessment. In this case the trials are separated by a dotted line.

In some studies (barley, wheat, sugarcane) residues have been determined as total trinexapac (includes free trinexapac acid and conjugates of trinexapac acid) while in other studies (wheat, sugarcane and rape seed) residues have been determined as trinexapac (free trinexapac acid only). In both cases trinexapac means trinexapac acid. Residues of trinexapac-ethyl were considered to be 0 mg/kg in rape seed. Residues according to maximum GAP have been underlined.

Group	Commodity	Country	Table No.
GC Cereal Grains	Barley	USA	70
	Wheat	USA	71
	Wheat	USA	72
GS Grasses for sugar or syrup production	Sugarcane	USA	73
	Sugarcane	USA	74
SO Oilseeds	Rape seed	Germany	75
Animal Feeds	Barley hay and straw	USA	76
	Wheat forage	USA	77
	Wheat hay and straw	USA	78
	Wheat forage	USA	79
	Wheat hay and straw	USA	80
	Rape seed forage and straw	Germany	81

The results of these supervised trials are shown in the following tables:

Cereal Grains

Supervised trials were carried out on barley (12 trials—Table 70) in the USA during the 2008 and 2009 growing seasons (Mäyer 2010a, CGA163935_50026). A foliar application of a 250 g/L EC formulation was made at 127–134 g ai/ha at Feekes Growth Stage 7 (BBCH 32) or at 45 days before harvest, or (for generating processing samples) at 129 and 644 or 648 g ai/ha at 45 days before harvest. Applications were made to plots using spray volumes of 68–288 L/ha with ground equipment, except for one trial which simulated aerial application (Trial C08WI081703). Additional samples were collected at one site (Trial C30IA081702—Bagley, Iowa) to examine the residue decline. Residues of total trinexapac were quantitated as trinexapac acid by LC/MS/MS method GRM020.01A. Acceptable concurrent recovery data were obtained.

Residues in barley hay and straw are shown in Table 76. Processed fraction samples for analysis were generated from trials C13ND081704 and C13ND081705 (Table 82).

Table 70 Residues from the foliar application of trinexapac-ethyl to barley in the USA

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean *	
GAP, USA (barley)	1	123				45			
USA	1	132	288	BBCH 59/	Grain	45	1.3	<u>1.2</u>	Mäyer 2010a
(New Tripoli,				Feekes 10.5			1.1		CGA163935_50026
Pennsylvania)									E04PA081701
2009									
(Nomini)									
USA	1	132	68	BBCH 49	Grain	24	1.0		Mäyer 2010a
(Bagley, Iowa)					Grain	31	1.3		CGA163935_50026
2008					Grain	38	0.73		C30IA081702
(Robust)					Grain	45	0.90	0.95	
							1.0		
					Grain	52	<u>1.0</u>		
USA	1	133	19	BBCH 33	Grain	45	0.07	<u>0.08</u>	Mäyer 2010a
(Fitchburg,							0.09		CGA163935_50026
Wisconsin)									
2008									C08WI081703
(Kewaunee)									
USA	1	129	187	BBCH 51	Grain	45	0.65	<u>0.76</u>	Mäyer 2010a
(Northwood, North							0.86		CGA163935_50026
Dakota)									C13ND081704
2008									
(Tradition)									
USA	1	129	141	BBCH 73	Grain	45	0.75	<u>0.83</u>	Mäyer 2010a
(Carrington, North							0.90		CGA163935_50026
Dakota)									C13ND081705
2008									
(Tradition)									
USA	1	128	187	BBCH 73	Grain	45	0.53	<u>0.53</u>	Mäyer 2010a
(New Rockford,							0.52		CGA163935_50026
North									
Dakota)									C13ND081706
2008									
(Tradition)									
USA	1	134	146	BBCH 59	Grain	45	0.51	<u>0.52</u>	Mäyer 2010a
(Eldridge, North							0.53		CGA163935_50026
Dakota)									C12ND081707
2008									
(Tradition)									
USA	1	127	138	BBCH 59	Grain	45	0.56	<u>0.50</u>	Mäyer 2010a
(Adrian, North							0.44		CGA163935_50026
Dakota)									
2008									C12ND081708
(Drummond)									
USA	1	131	273	BBCH 45	Grain	45	0.05* (0.05,	<u>0.03</u>	Mäyer 2010a
(Monte Vista,							0.04, 0.05)		CGA163935_50026

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean ^a	
Colorado)							0.01 *		E13CO081709
2008									
(C-69)									
USA	1	128	282	BBCH 45	Grain	45	0.57	<u>0.60</u>	Mäyer 2010a
(Madera, California)							0.62		CGA163935_50026
2008									W29CA081710
(Recleaned whole barley)									
USA	1	130	194	BBCH 84	Grain	45	0.72	<u>0.72</u>	Mäyer 2010a
(Hermiston, Oregon)							0.71		CGA163935_50026
2008									W21OR081711
(Radiant)									
USA	1	130	97	BBCH 65	Grain	45	0.52	<u>0.44</u>	Mäyer 2010a
(Rupert, Idaho)							0.35		CGA163935_50026
2008									W15DO081712
(IDA Gold II)									

^a: residue values considered for estimation of STMR values

*Mean value of replicates

LOQ = 0.01 mg/kg

Supervised trials were carried out on wheat in the USA during the 2008 growing seasons (Mäyer 2010, CGA163935_50036) and the 2004 and 2005 growing seasons (Ediger 2006, 451534). The Mäyer study quantified total trinexapac residues.

Wheat (Total residues of trinexapac acid)

Supervised trials were carried out on wheat (20 trials—Table 71) in the USA during the 2008 growing season (Mäyer 2010, CGA163935_50026). A foliar application of a 250 g/L EC formulation was made at 127–134 g ai/ha at approximately Feekes Growth Stage 7 or at 45 days before harvest, or (for generating processing samples) at 129 or 130 and 646 or 649 g ai/ha at 45 days before harvest. Applications were made to plots using spray volumes of 97–252 L/ha with ground equipment, except for two trials which simulated aerial application (Trials C19KS078462 and C16SD078471). At three sites additional samples were collected to examine the residue decline. Residues of total trinexapac were quantitated as trinexapac acid by LC/MS/MS method GRM020.01A. Acceptable concurrent recovery data were obtained.

Residues in wheat forage are shown in Table 77 and in hay and straw in Table 78. Processed fraction samples for analysis were generated from trials C13ND078468 and W01TX078473 (Table 83).

Table 71 Residues from the foliar application of trinexapac-ethyl to wheat in the USA

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac ^a (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
GAP, USA (wheat)	1	123				45			
USA	1	130	120	BBCH 71	Grain	31	0.33		Mäyer 2010
(Suffolk, Virginia)					Grain	38	0.34		CGA163935_50036
2008					Grain	45	0.32	<u>0.32</u>	E07VA078460

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac ^a (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
(Winter wheat— R9184)							0.32		
					Grain	52	0.24		
USA	1	129	135	BBCH 65	Grain	45	4.03	<u>3.32</u>	Mäyer 2010
(Proctor, Arkansas)							2.61		CGA163935_50036
2008									C24AR078461
(Wheat—DK7710)									
USA	1	128	19	Boot	Grain	45	1.03	<u>1.01</u>	Mäyer 2010
(Minneapolis, Kansas)							0.98		CGA163935_50036
2008									C19KS078462
(Hard White Wheat – Danby)									
USA	1	129	188	BBCH 67	Grain	45	0.47	<u>0.47</u>	Mäyer 2010
(Northwood, North Dakota)							0.47		CGA163935_50036
2008									C13ND078463
(HRSW—Kelby)									
USA	1	134	183	BBCH 51	Grain	45	0.81	<u>0.77</u>	Mäyer 2010
(Perley, Minnesota)							0.73		CGA163935_50036
2008									C12MN078464
(Spring Wheat— Alsen)									
USA	1	130	158	Boot	Grain	45	0.30	<u>0.27</u>	Mäyer 2010
(St Joseph, Missouri)							0.24		CGA163935_50036
2008									C19MO078465
(Hard Red Winter Wheat—Kansas 2137)									
USA	1	132	134	BBCH 55	Grain	45	0.90	<u>0.99</u>	Mäyer 2010
(Kirklin, Indiana)							1.08		CGA163935_50036
2008									C05IN078466
(Wheat—Pioneer 25R78)									
USA	1	129	241	BBCH 53	Grain	45	0.07	<u>0.07</u>	Mäyer 2010
(Madill, Oklahoma)							0.07		CGA163935_50036
2008									W01OK078467
(Winter Wheat— Jagger)									
USA	1	129	188	BBCH 65	Grain	45	0.31	<u>0.31</u>	Mäyer 2010
(Carrington, North Dakota)							0.31		CGA163935_50036
2008									C13ND078468
(Durum—Divide)									
USA	1	129	187	BBCH 65	Grain	31	0.69		Mäyer 2010
(Carrington, North Dakota)					Grain	38	0.58		CGA163935_50036
					Grain	45	0.76	<u>0.82</u>	C13ND078469

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac ^a (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
2008							0.87		
(SWSW—WPB Nick)					Grain	52	0.61		
USA	1	130	144	BBCH 41	Grain	45	0.48	<u>0.53</u>	Mäyer 2010
(Velva, North Dakota)							0.57		CGA163935_50036
2008									C14ND078470
(Hard White Spring Wheat—Agawana)									
USA	1	130	19	BBCH 45	Grain	45	1.64	<u>1.64</u>	Mäyer 2010
(Lake Andes, South Dakota)							1.64		CGA163935_50036
2008									C16SD078471
(Spring Wheat— Briggs)									
USA	1	134	192	BBCH 51	Grain	31	0.49	0.42	Mäyer 2010
(Grand Island, Nebraska)					Grain	38	0.35		CGA163935_50036
2008					Grain	45	1.00 ^b (1.12, 0.89, 0.98)	<u>0.78</u>	
(Hard Red Winter Wheat—Com. Wesley)							0.56 ^b (0.23, 0.77, 0.67)		
					Grain	52	0.70		
USA	1	130	252	BBCH 52	Grain	45	0.10	0.10	Mäyer 2010
(Groom, Texas)							0.10		CGA163935_50036
2008									W01TX078473
(Winter Wheat— Cutter)									
USA	1	127	237	BBCH 52	Grain	45	0.41	<u>0.40</u>	Mäyer 2010
(Groom, Texas)							0.39		CGA163935_50036
2008									W01TX078476
(Winter Wheat— TAM 212)									
USA	1	128	239	BBCH 51	Grain	45	0.33	0.32	Mäyer 2010
(Groom, Texas)							0.30		CGA163935_50036
2008									W01TX078477
(Winter Wheat— Jagalene)									
USA	1	131	240	BBCH 52	Grain	45	0.14	<u>0.15</u>	Mäyer 2010
(Goodwell, Oklahoma)							0.15		CGA163935_50036
2008									W01OK078474
(Winter Wheat— Ogallalla)									
USA	1	134	126	BBCH 60	Grain	45	1.10	<u>1.14</u>	Mäyer 2010
(Frederick, Oklahoma)							1.18		CGA163935_50036

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac ^a (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
2008									C29OK078475
(Winter Wheat— Custer)									
USA	1	130	241	BBCH 51	Grain	45	0.44	<u>0.45</u>	Mäyer 2010
(Wellington, Texas)							0.45		CGA163935_50036
2008									W01TX078478
(Winter Wheat— TAM									
200)									
USA	1	127	97	BBCH 65	Grain	45	0.87	<u>0.85</u>	Mäyer 2010
(Rupert, Idaho)							0.82		CGA163935_50036
2008									W15ID078479
(Winter Wheat— Westbred 528)									

^a residue values considered for estimation of STMR values

^b Mean of three readings

^a Mean of three readings

LOQ = 0.01 mg/kg

Wheat (Free trinexapac acid)

Supervised trials were carried out on wheat (20 trials—Table 72) in the USA during the 2004 and 2005 growing seasons (Ediger 2006, 451534). A foliar application of a 250 g/L EC formulation was made at 123–130 g ai/ha (and at 384 or 391 and 643 g ai/ha at two sites) at approximately Feekes Growth Stage 7 or at 45 days before harvest, or (for generating processing samples) at 127 or 130 and 643 g ai/ha at 45 days before harvest. Applications were made to plots using spray volumes of 92–187 L/ha with ground equipment, except for three trials which simulated aerial application (Trials 4A-FR-04-5421, NN-FR-04-5424 and NM-FR-04-5429). At three sites additional samples were collected to examine the residue decline. Residues of trinexapac were quantitated as trinexapac acid using method 110-01. Acceptable concurrent recovery data were obtained.

Residues in wheat forage are shown in Table 79 and in hay and straw in Table 80. Processed fraction samples for analysis were generated from trials NN-FR-04-5418 and SC-FR-04-5430 (Table 84).

Table 72 Residues from the foliar application of trinexapac-ethyl to wheat in the USA

Country Year (Variety)	Application				Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
GAP, USA (wheat)	1	123				45			
USA	1	129	147	BBCH 43	Grain	50	0.50	<u>0.57</u>	Ediger 2006
(Pikeville, North Carolina)							0.64		451534
2005									SJ-FR-04-5415
(Winter Wheat—Coker 9184)									
USA	1	129	142	BBCH 55	Grain	45	1.0	<u>0.98</u>	Ediger 2006
(Lehi, Arkansas)							0.96		451534

[illegible]

Country Year (Variety)	Application				Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
Yuma)									
USA	1	127	140	BBCH 65	Grain	44	0.36	<u>0.32</u>	Ediger 2006
(Clovis, New Mexico)							0.27		451534
2005									SC-FR-04-5433
(Winter Wheat—TAM									
110)									
USA	1	129	139	BBCH 61	Grain	44	0.22	<u>0.25</u>	Ediger 2006
(Ephrata, Washington)							0.27		451534
2004									WF-FR-04-5435
(Winter Wheat—									
Stephens)									

LOQ = 0.05 mg/kg

Feekes 8 = Flag leaf (last leaf) visible but still rolled up, ear beginning to swell

Feekes 10.5 = Head emergence complete

Grasses for sugar or syrup production

Supervised trials were carried out on sugarcane in the USA during the 2008 and 2004 growing seasons (Mäyer 2010b, CGA163935_50038 and Ediger 2006a, 451598 respectively). The Mäyer study quantified total trinexapac residues.

Sugarcane (Total residues of trinexapac acid)

Supervised trials were carried out on sugarcane (eight trials—Table 73) in the USA during the 2008 growing season (Mäyer 2010b, CGA163935_50038). A foliar application of a 250 g/L EC formulation was made at 350–382 g ai/ha at 28 days before harvest, or (for generating processing samples) at 361 or 382 and 1779 or 1856 g ai/ha at 28 days before harvest. Applications were made to plots using spray volumes of 94–982 L/ha with ground equipment, except for one trial which simulated aerial application (Trial E19H1078497). At two sites (E19FL078491 and E18LA078494) additional samples were collected to examine the residue decline. Residues of total trinexapac were quantitated as trinexapac acid by LC/MS/MS method GRM020.01A. Acceptable concurrent recovery data were obtained.

Processed fraction samples for analysis were generated from trials E19FL078492 and E18LA078495 (Table 85).

Table 73 Residues from the foliar application of trinexapac-ethyl to sugar cane in the USA

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
GAP, USA	1	347				28			
USA	1	367	982	BBCH 49	Sugar cane	28	< 0.01	<u>< 0.01</u>	Mäyer 2010
(Bradenton, Florida)							< 0.01		CGA163935_50038
2008									E16FL078490
(CP88-1762)									
USA	1	356	94	BBCH 91	Sugar cane	0	< 0.01		Mäyer 2010
(Belle Glade, Florida)						7	0.02		CGA163935_50038

Country Year (Variety)	Application			Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.	
	No g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean		
2008					14	0.07		E19FL078491	
(CP96-1252)					28	0.04	<u>0.04</u>		
						0.04			
					35	0.03			
USA	1	382	105	BBCH 91	Sugar cane	28	0.06	<u>0.06</u>	Mäyer 2010
(Clewiston, Florida)						0.05		CGA163935_50038	
2008								E19FL078492	
(CL95-0776)									
USA	1	358	221	BBCH 70	Sugar cane	28	0.24	0.22	Mäyer 2010
(Washington, Louisiana)						0.20		CGA163935_50038	
2008								E18LA078493	
(85-384)									
USA	1	364	225	BBCH 70	Sugar cane	0	0.36		Mäyer 2010
(Washington, Louisiana)					7	0.34		CGA163935_50038	
2008					14	0.29		E18LA078494	
(85-384)					28	0.27	0.30		
						0.33			
					35	0.23			
USA	1	361	223	BBCH 70	Sugar cane	28	0.40	<u>0.42</u>	Mäyer, 2010
(Washington, Louisiana)						0.43		CGA163935_50038	
2008								E18LA078495	
(85-384)									
USA	1	350	234	BBCH 39	Sugar cane	28	0.05	<u>0.08</u>	Mäyer 2010
(Raymondsville, Texas)						0.10		CGA163935_50038	
2008								W08TX078496	
(1210)									
USA	1	358	19	BBCH 95	Sugar cane	28	0.13	<u>0.17</u>	Mäyer 2010
(Puunene, Hawaii)						0.21		CGA163935_50038	
2008								E19H1078497	
(H78-7750)									

LOQ = 0.01 mg/kg

Sugarcane (Free trinexapac acid)

Supervised trials were carried out on sugarcane (eight trials—Table 74) in the USA during the 2004 growing season (Ediger 2006a, 451598). A foliar application of a 250 g/L EC formulation was made at 345–365 g ai/ha (and at 1764 g ai/ha at one site) at 28 days before harvest of mature cane, or (for generating processing samples) at 345 and 1739 g ai/ha at 28 days before harvest of mature cane. Applications were made to plots using spray volumes of 102–948 L/ha with ground equipment, except

for one trial which simulated aerial application (Trial SD-FR-04-5505). At two sites additional samples were collected to examine the residue decline. Residues of trinexapac were quantitated as trinexapac acid using method 110-01. Acceptable concurrent recovery data were obtained.

Processed fraction samples for analysis were generated from trial VN-FR-04-5501 (Table 86).

Table 74 Residues from the foliar application of trinexapac-ethyl to sugar cane in the USA

Country Location Year (Variety)	Application			Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.	
	No	g ai/ha	Water (L/ha)			Growth Stage	Individual		Mean
GAP, USA	1	347				28			
USA	1	347	278	28 days to	Sugar cane	0	0.05	0.08	Ediger 2006a
(South Bay, Florida)				harvest			0.10		451598
2004						14	0.11	0.11	VN-FR-04-5500
(CP89-2143)							0.11		
						21	0.13	0.10	
							0.07		
						28	0.09	<u>0.09</u>	
							0.09		
						35	0.07	0.07	
							0.06		
USA	1	345	276	28 days to	Sugar cane	28	0.06	0.06	Ediger 2006a
(South Bay, Florida)				harvest			< 0.05		451598
2004									VN-FR-04-5501
(CP89-2143)									
USA	1	350	948	Mature	Sugar cane	28	0.06	<u>0.06</u>	Ediger 2006a
(Pahokee, Florida)				cane			< 0.05		451598
2004									VN-FR-04-5502
(CP88-1762)									
USA	1	365	102	BBCH 39	Sugar cane	0	0.09	0.07	Ediger 2006a
(Cheneyville, Louisiana)							< 0.05		451598
2004						14	0.22	0.16	SD-FR-04-5503
(LCP85-384)							0.09		
						21	0.50	0.48	
							0.46		
						28	0.11	0.14	
							0.17		
						35	0.20	<u>0.23</u>	
							0.25		
USA	1	365	152	28 days to	Sugar cane	28	< 0.05	<u>< 0.05</u>	Ediger 2006a
(Washington, Louisiana)				harvest			< 0.05		451598
2004	1	1764	147	28 days to	Sugar cane	28	1.7	0.93	SD-FR-04-5504
(LCP85-384)				harvest			0.16		
USA	1	359	21	BBCH 39	Sugar cane	28	0.17	<u>0.25</u>	Ediger 2006a

Country Year (Variety)	Application					Matrix PHI days	Trinexapac (mg/kg)	Trinexapac-ethyl (mg/kg)	Author, Study No., Trial No.
	No g ai/ha	Water (L/ha)	Growth Stage						
1991 (Ceres)									gr 40591
Germany (Achern-Gamshurst)	1	400	400	BBCB 55	Seed	103	<u>0.15</u>	< 0.02	Hauck 1993k CGA163935/0318
1991 (Libravo)									gr 60491
Germany (Burgwedel-Thönse)	1	448	224	BBCB 55	Seed	68	<u>1.0</u>	< 0.02	Hauck 1993h CGA163935/0329
1992 (Accord)									920EK101P
Germany (Braunschweig-Hondelage)	1	436	218	BBCB 55	Seed	77	<u>0.31</u>	< 0.02	Hauck 1993i CGA163935/0330
1992 (Lirajet 00)									920EK201P
Germany (Goch)	1	400	400	BBCB 55	Seed	72	<u>0.64</u>	< 0.02	Hauck 1993a CGA163935/0331
1992 (Lirajet)									AGR/RP-W92/CGD 01
Germany (Zülpich-Oberelvenich)	1	400	400	BBCB 53–55	Seed	83	<u>0.15</u>	< 0.02	Hauck 1993c CGA163935/0319
1992 (Lirajet)									gr 10492
Germany (Gnarrenburg)	1	400	400	BBCB 51–53	Seed	71	<u>0.26</u>	< 0.02	Hauck 1993 CGA163935/0322
1992 (Lirajet)									gr 21192
Germany (Rohlstorf)	1	400	400	BBCB 53–55	Seed	90	<u>0.29</u>	< 0.02	Hauck 1993d CGA163935/0323
1992 (Ceres)									gr 30392
Germany (Ursleben)	1	400	400	BBCB 53–55	Seed	82	<u>0.24</u>	< 0.02	Hauck 1993e CGA163935/0325
1992 (Lirajet)									gr 60592
Germany (Cunnersdorf)	1	400	300	BBCB 53–55	Seed	80	<u>0.90</u>	< 0.02	Hauck 1993g CGA163935/0328
1992 (Madora)									RF 04/92
Germany (Egeln)	1	400	300	BBCB 53–55	Seed	74	<u>0.64</u>	< 0.02	Hauck 1993f CGA163935/0327

Country Year (Variety)	Application				Matrix	PHI days	Trinexapac (mg/kg)	Trinexapac-ethyl (mg/kg)	Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage					
1992									RF 04/92
(Liberator)									
Germany	1	375	400	BBCH 39–51	Seed	108	<u>0.10</u>	–	Smith 2000
(Rohlsdorf)									CGA163935/0636
1999									Trial 1
(Lirajet)									
Germany	1	375	400	BBCH 33–51	Seed	113	<u>0.10</u>	–	Smith 2000a
(Ivenrode)									CGA163935/0637
1999									Trial 1
(Laser)									
Germany	1	375	400	BBCH 51–53	Seed	93	<u>0.16</u>	–	Smith 2000b
(See)									CGA163935/0638
1999									Trial 1
(Express)									
Germany	1	375	400	BBCH 50–51	Seed	104	<u>0.24</u>	–	Smith 2000c
(Kandel)									CGA163935/0639
1999									Trial 1
(Mohikan)									

LOQ = 0.02 mg/kg (trinexapac acid and trinexapac-ethyl)

^a The trinexapac-ethyl residues result for Lorsch is considered to be anomalous.

Animal Feeds

Note: Animal feed residues are expressed on a wet weight or 'as received' basis.

Table 76 Residues from the foliar application of trinexapac-ethyl to barley in the USA

Country Year (Variety)	Application			Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.	
	No g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean		
GAP, USA (barley, oat)	1	123			45				
USA	1	131	189	Feekes 7	Hay	30	0.23	<u>0.25</u>	Mäyer 2010a
(New Tripoli,							0.26		CGA163935_50026
Pennsylvania)	1	132	288	BBCH 59/	Straw	45	0.29	<u>0.24</u>	E04PA081701
2009				Feekes 10.5			0.19		
(Nomini)									
USA	1	134	121	BBCH 32	Hay	0	6.7		Mäyer 2010a
(Bagley, Iowa)					Hay	10	0.70		CGA163935_50026
2008					Hay	20	0.45		C30IA081702
(Robust)					Hay	30	0.54	<u>0.48</u>	
							0.41		
					Hay	37	0.32		
	1	132	68	BBCH 49	Straw	24	0.28		

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
					Straw	31	0.21		
					Straw	38	0.14		
					Straw	45	0.08	<u>0.14</u>	
							0.20		
					Straw	52	0.13		
USA	1	133	20	BBCH 33	Hay	30	0.34	<u>0.40</u>	Mäyer 2010a
(Fitchburg, Wisconsin)							0.46		CGA163935_50026
2008	1	133	19	BBCH 33	Straw	45	0.01	<u>0.02</u>	C08WI081703
(Kewaunee)							0.02		
USA	1	129	189	BBCH 32	Hay	30	0.13	<u>0.13</u>	Mäyer 2010a
(Northwood, North							0.13		CGA163935_50026
Dakota)	1	129	187	BBCH 51	Straw	45	0.08	<u>0.08</u>	C13ND081704
2008							0.07		
(Tradition)									
USA	1	129	187	BBCH 32	Hay	30	0.04	<u>0.05</u>	Mäyer 2010a
(Carrington, North							0.05		CGA163935_50026
Dakota)	1	129	141	BBCH 73	Straw	45	0.12	<u>0.12</u>	C13ND081705
2008							0.12		
(Tradition)									
USA	1	128	187	BBCH 32	Hay	30	0.03	<u>0.03</u>	Mäyer 2010a
(New Rockford, North							0.03		CGA163935_50026
Dakota)	1	128	187	BBCH 73	Straw	45	0.05	<u>0.07</u>	C13ND081706
2008							0.08		
(Tradition)									
USA	1	129	140	BBCH 32	Hay	30	0.10	<u>0.10</u>	Mäyer 2010a
(Eldridge, North							0.10		CGA163935_50026
Dakota)	1	134	146	BBCH 59	Straw	45	0.08	<u>0.09</u>	C12ND081707
2008							0.09		
(Tradition)									
USA	1	128	139	BBCH 32	Hay	30	0.13	<u>0.15</u>	Mäyer 2010a
(Adrian, North Dakota)							0.16		CGA163935_50026
2008	1	127	138	BBCH 59	Straw	45	0.11	<u>0.11</u>	C12ND081708
(Drummond)							0.10		
USA	1	129	271	BBCH 41	Hay	30	< 0.01	<u>≤ 0.01</u>	Mäyer 2010a
(Monte Vista,							< 0.01		CGA163935_50026
Colorado)	1	131	273	BBCH 45	Straw	45	< 0.01	<u>≤ 0.01</u>	E13CO081709
2008							< 0.01		
(C-69)									
USA	1	132	193	BBCH 32	Hay	30	0.34	<u>0.33</u>	Mäyer 2010a
(Madera, California)							0.31		CGA163935_50026
2008	1	128	282	BBCH 45	Straw	45	0.20	<u>0.20</u>	W29CA081710
(Re-cleaned whole							0.19		
barley)									
USA	1	129	192	BBCH 32	Hay	30	0.20	<u>0.18</u>	Mäyer 2010a

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
Cutter)									
USA	1	129	84	Feekes 7	Forage	30	0.01	0.01	Mäyer 2010
(Groom, Texas)							< 0.01		CGA163935_50036
2008									W01TX078476
(Winter Wheat— TAM									
212)									
USA	1	129	84	Feekes 7	Forage	30	< 0.01	0.02	Mäyer 2010
(Groom, Texas)							0.03		CGA163935_50036
2008									W01TX078477
(Winter Wheat— Jagalene)									
USA	1	130	84	BBCH 32	Forage	30	0.20	<u>0.17</u>	Mäyer 2010
(Goodwell, Oklahoma)							0.14		CGA163935_50036
2008									W01OK078474
(Winter Wheat— Ogallalla)									
USA	1	130	122	BBCH 32	Forage	30	0.40	<u>0.38</u>	Mäyer 2010
(Frederick, Oklahoma)							0.36		CGA163935_50036
2008									C29OK078475
(Winter Wheat— Custer)									
USA	1	129	84	Feekes 7	Forage	30	0.04	<u>0.08</u>	Mäyer 2010
(Wellington, Texas)							0.11		CGA163935_50036
2008									W01TX078478
(Winter Wheat— TAM									
200)									
USA	1	130	93	BBCH 32	Forage	30	0.08	<u>0.09</u>	Mäyer 2010
(Rupert, Idaho)							0.09		CGA163935_50036
2008									W15ID078479
(Winter Wheat— Westbred 528)									

LOQ = 0.01 mg/kg

Feekes 6 = First node detectable

Feekes 7 = Second node detectable

Table 78 Residues from the foliar application of trinexapac-ethyl to wheat in the USA

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
GAP, USA (wheat)	1	123				45			
USA	1	132	114	BBCH 32	Hay	0	2.47		Mäyer 2010
(Suffolk, Virginia)					Hay	7	0.54		CGA163935_50036

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
2008					Hay	14	0.27		E07VA078460
(Winter wheat— R9184)					Hay	30	0.17	<u>0.17</u>	
							0.17		
					Hay	37	0.15		
	1	130	120	BBCH 71	Straw	31	< 0.01		
					Straw	38	0.07		
					Straw	45	0.08	0.07	
							0.06		
					Straw	52	<u>0.11</u>		
USA	1	129	135	BBCH 32	Hay	30	0.54	<u>0.50</u>	Mäyer 2010
(Proctor, Arkansas)							0.45		CGA163935_50036
2008	1	129	135	BBCH 65	Straw	45	0.31	<u>0.20</u>	C24AR078461
(Wheat—DK7710)							0.08		
USA	1	130	19	BBCH 32	Hay	30	0.55	<u>0.59</u>	Mäyer 2010
(Minneapolis, Kansas)							0.62		CGA163935_50036
2008	1	128	19	Boot	Straw	45	0.22	<u>0.23</u>	C19KS078462
(Hard White Wheat – Danby)							0.24		
USA	1	130	188	BBCH 32	Hay	30	0.11	<u>0.11</u>	Mäyer 2010
(Northwood, North Dakota)							0.10		CGA163935_50036
	1	129	188	BBCH 67	Straw	45	0.06	<u>0.06</u>	C13ND078463
2008							0.06		
(HRSW—Kelby)									
USA	1	131	142	BBCH 33	Hay	30	0.08	<u>0.11</u>	Mäyer 2010
(Perley, Minnesota)							0.14		CGA163935_50036
2008	1	134	183	BBCH 51	Straw	45	0.08	<u>0.09</u>	C12MN078464
(Spring Wheat— Alsen)							0.10		
USA	1	127	155	Feekes 6-7	Hay	30	0.17	<u>0.19</u>	Mäyer 2010
(St Joseph, Missouri)							0.20		CGA163935_50036
2008	1	130	158	Boot	Straw	45	0.03	<u>0.03</u>	C19MO078465
(Hard Red Winter Wheat—Kansas 2137)							0.02		
USA	1	129	130	BBCH 32	Hay	30	0.31	<u>0.31</u>	Mäyer 2010
(Kirklin, Indiana)							0.30		CGA163935_50036
2008	1	132	134	BBCH 55	Straw	45	0.19	<u>0.17</u>	C05IN078466
(Wheat—Pioneer 25R78)							0.15		
USA	1	129	84	BBCH 32	Hay	30	0.02	<u>0.03</u>	Mäyer 2010
(Madill, Oklahoma)							0.03		CGA163935_50036
2008	1	129	241	BBCH 53	Straw	45	< 0.01	<u>0.01</u>	W01OK078467
(Winter Wheat— Jagger)							0.01		
USA	1	130	189	BBCH 32	Hay	30	0.04	<u>0.04</u>	Mäyer 2010

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
(Carrington, North Dakota)							0.03		CGA163935_50036
2008	1	129	188	BBCH 65	Straw	45	0.10	<u>0.11</u>	C13ND078468
(Durum—Divide)							0.11		
USA	1	129	187	BBCH 32	Hay	0	1.31		Mäyer 2010
(Carrington, North Dakota)					Hay	7	1.33		CGA163935_50036
2008					Hay	14	0.19		C13ND078469
(SWSW—WPB Nick)							0.09	0.08	
							0.07		
					Hay	37	<u>0.09</u>		
	1	129	187	BBCH 65	Straw	31	0.25		
					Straw	38	0.16		
					Straw	45	0.47	<u>0.46</u>	
							0.44		
					Straw	52	0.08		
USA	1	131	140	BBCH 31	Hay	30	0.05	<u>0.06</u>	Mäyer 2010
(Velva, North Dakota)							0.06		CGA163935_50036
2008	1	130	144	BBCH 41	Straw	45	0.14	<u>0.15</u>	C14ND078470
(Hard White Spring Wheat—Agawana)							0.16		
USA	1	129	20	BBCH 32	Hay	30	1.26	<u>1.18</u>	Mäyer 2010
(Lake Andes, South Dakota)							1.09		CGA163935_50036
2008	1	130	19	BBCH 45	Straw	45	0.64	<u>0.60</u>	C16SD078471
(Spring Wheat— Briggs)							0.56		
USA	1	134	192	BBCH 32	Hay	0	10.8		Mäyer 2010
(Grand Island, Nebraska)					Hay	7	0.46		CGA163935_50036
2008					Hay	14	0.42		C17NE078472
(Hard Red Winter Wheat —Com. Wesley)							< 0.01		
					Hay	37	<u>0.14</u>		
	1	134	192	BBCH 51	Straw	31	0.16		
					Straw	38	0.40		
					Straw	45	0.55	<u>0.59</u>	
							0.62		
					Straw	52	0.12		
USA	1	129	84	Feekes 7	Hay	30	0.31	<u>0.30</u>	Mäyer 2010
(Groom, Texas)							0.28		CGA163935_50036
2008	1	130	252	BBCH 52	Straw	45	0.16	<u>0.15</u>	W01TX078473
(Winter Wheat— Cutter)							0.13		
USA	1	129	84	Feekes 7	Hay	30	0.15	0.11	Mäyer 2010
(Groom, Texas)							0.07		CGA163935_50036

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
2008	1	127	237	BBCH 52	Straw	45	0.10	0.09	W01TX078476
(Winter Wheat— TAM 212)							0.07		
USA	1	129	84	Feekes 7	Hay	30	0.19	0.21	Mäyer 2010
(Groom, Texas)							0.22		CGA163935_50036
2008	1	128	239	BBCH 51	Straw	45	0.08	0.09	W01TX078477
(Winter Wheat— Jagalene)							0.10		
USA	1	130	84	BBCH 32	Hay	30	<u>0.41</u>		Mäyer 2010
(Goodwell, Oklahoma)	1	131	240	BBCH 52	Straw	45	0.04	<u>0.04</u>	CGA163935_50036
2008							0.04		W01OK078474
(Winter Wheat— Ogallalla)									
USA	1	130	122	BBCH 32	Hay	30	0.83	<u>0.78</u>	Mäyer 2010
(Frederick, Oklahoma)							0.72		CGA163935_50036
2008	1	134	126	BBCH 60	Straw	45	0.38	<u>0.28</u>	C29OK078475
(Winter Wheat— Custer)							0.18		
USA	1	129	84	Feekes 7	Hay	30	0.03	<u>0.04</u>	Mäyer 2010
(Wellington, Texas)							0.04		CGA163935_50036
2008	1	130	241	BBCH 51	Straw	45	0.03	<u>0.04</u>	W01TX078478
(Winter Wheat— TAM 200)							0.04		
USA	1	130	93	BBCH 32	Hay	30	0.24	<u>0.24</u>	Mäyer 2010
(Rupert, Idaho)							0.24		CGA163935_50036
2008	1	127	97	BBCH 65	Straw	45	0.39	<u>0.33</u>	W15ID078479
(Winter Wheat— Westbred 528)							0.26		

LOQ = 0.01 mg/kg

Feekes 6 = First node detectable

Feekes 7 = Second node detectable

Table 79 Residues in wheat forage from the foliar application of trinexapac-ethyl to wheat in the USA

Country Year (Variety)	Application			Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)			Individual	Mean	
GAP, USA (wheat)	1	123			45			
USA	1	130	156	BBCH 23	Forage	26	< 0.05	Ediger 2006
(Pikeville, North Carolina)				(Feekes 5– 7)			< 0.05	451534
2005								SJ-FR-04-5415
(Winter Wheat—								

Country Year (Variety)	Application			Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
Coker 9184)								
USA (Lehi, Arkansas)	1	129	90	Feekes 7	Forage	30	0.07	Ediger 2006
2005							0.10	451534
(Winter Wheat— DK9410)								SE-FR-04-5416
USA (Abilene, Kansas)	1	128	140	Feekes 8	Forage	31	0.07	Ediger 2006
2005							0.07	451534
(Winter Wheat— Burdett)								ND-FR-04-5417
USA (Northwood, North Dakota)	1	128	232	BBCH 32	Forage	30	< 0.05	Ediger 2006
2004							< 0.05	451534
(Spring Wheat— Briggs)								NN-FR-04-5418
USA (Campbell, Minnesota)	1	129	187	Feekes 7	Forage	30	< 0.05	Ediger 2006
2004							0.05	451534
(Spring Wheat— Oxen)								NF-FR-04-5419
USA (Kirksville, Missouri)	1	131	141	Feekes 5–7	Forage	27	< 0.05	Ediger 2006
2005							< 0.05	451534
(Winter Wheat— Ernie)								ND-FR-04-5420
USA (Champaign, Illinois)	1	129	39	BBCH 32	Forage	34	0.06	Ediger 2006
2005							0.06	451534
(Winter Wheat— Kaskaskia)								4A-FR-04-5421
USA (Hinton, Oklahoma)	1	129	128	BBCH 32	Forage	0	1.3	Ediger 2006
2005					Forage	7	1.3	451534
(Winter Wheat— Jagalene)							0.52	SC-FR-04-5422
					Forage	14	0.39	
							0.46	
					Forage	31	0.13	
							0.08	
					Forage	38	< 0.05	
							< 0.05	
USA (New Rockford, North Dakota)	1	129	189	Feekes 7	Forage	1	0.79	Ediger 2006
							0.98	451534
					Forage	7	0.17	NN-FR-04-5423

Country Year (Variety)	Application				Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No g ai/ha	Water (L/ha)	Growth Stage	Individual			Mean		
2004							0.15		
(Winter Wheat— Lebsock)					Forage	14	0.09	0.09	
							0.08		
					Forage	30	< 0.05	< 0.05	
							< 0.05		
					Forage	37	< 0.05	< 0.05	
							< 0.05		
USA	1	127	19	Feekes 6	Forage	33	0.13	0.12	Ediger 2006
(Froid, Montana)							0.10		451534
2004									NN-FR-04-5424
(Spring Wheat— Challis)									
USA	1	134	98	Feekes 6	Forage	33	< 0.05	< 0.05	Ediger 2006
(Froid, Montana)							< 0.05		451534
2004									NN-FR-04-5425
(Spring Wheat— Pristine)									
USA	1	128	172	BBCH 32	Forage	30	0.10	0.11	Ediger 2006
(Trail City, South Dakota)							0.12		451534
									NF-FR-04-5426
2004									
(Spring Wheat— Freyr)									
USA	1	129	186	BBCH 32	Forage	29	0.09	0.09	Ediger 2006
(Grand Island, Nebraska)							0.08		451534
									NB-FR-04-5427
2005									
(Winter Wheat— Arrowsmith HW)									
USA	1	123	129	Feekes 7	Forage	0	1.0	1.4	Ediger 2006
(Larned, Kansas)							1.7		451534
2005					Forage	7	0.06	0.07	NM-FR-04-5428
(Winter Wheat— Jagger)							0.08		
					Forage	14	< 0.05	< 0.05	
							< 0.05		
					Forage	30	< 0.05	< 0.05	
							< 0.05		
					Forage	37	< 0.05	< 0.05	
							< 0.05		
USA	1	129	20	Feekes 7	Forage	30	< 0.05	< 0.05	Ediger 2006
(Larned, Kansas)							< 0.05		451534
2005									NM-FR-04-5429
(Winter Wheat— Jagger)									
USA	1	128	144	BBCH 29	Forage	30	< 0.05	< 0.05	Ediger 2006
(Goodwell, Oklahoma)							< 0.05		451534

Country Year (Variety)	Application				Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No g ai/ha	Water (L/ha)	Growth Stage	Individual			Mean		
2005									SC-FR-04-5430
(Winter Wheat— Clark)									
USA	1	128	142	BBCH 32	Forage	30	0.08	0.08	Ediger 2006
(Levelland, Texas)							0.07		451534
2005									SC-FR-04-5431
(Winter Wheat— TAM									
200)									
USA	1	128	127	Feekes 7	Forage	30	0.34	0.31	Ediger 2006
(Ault, Colorado)							0.28		451534
2005									NM-FR-04-5432
(Winter Wheat— Yuma)									
USA	1	130	139	BBCH 32	Forage	30	0.14	0.15	Ediger 2006
(Clovis, New Mexico)							0.16		451534
2005									SC-FR-04-5433
(Winter Wheat— TAM									
110)									
USA	1	129	144	BBCH 32	Forage	29	< 0.05	< 0.05	Ediger 2006
(Ephrata, Washington)							< 0.05		451534
2004									WF-FR-04-5435
(Winter Wheat— Stephens)									

LOQ = 0.05 mg/kg

Feekes 5 = Pseudo stem (formed by sheaths of leaves) strongly erected

Feekes 6 = First node detectable

Feekes 7 = Second node detectable

Feekes 8 = Flag leaf (last leaf) visible but still rolled up, ear beginning to swell

Table 80 Residues from the foliar application of trinexapac-ethyl to wheat in the USA

Country Year (Variety)	Application				Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
GAP, USA (wheat)	1	123				45			
USA	1	130	156	BBCH 23	Hay	26	0.06	<u>0.07</u>	Ediger 2006
(Pikeville, North Carolina)				(Feekes 5– 7)			0.07		451534
2005							0.10		
(Winter Wheat— Coker 9184)									
USA	1	129	90	Feekes 7	Hay	30	0.19	<u>0.15</u>	Ediger 2006
(Lehi, Arkansas)							0.10		451534

Country Year (Variety)	Application			Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
2005	1	129	142	BBCH 55	Straw	45	< 0.05	SE-FR-04-5416
(Winter Wheat— DK9410)							0.06	
USA	1	128	140	Feekes 8	Hay	31	0.15	Ediger 2006
(Abilene, Kansas)							0.10	451534
2005	1	130	138	Feekes 10.5.2	Straw	45	< 0.05	ND-FR-04-5417
(Winter Wheat— Burdett)							< 0.05	
USA	1	128	232	BBCH 32	Hay	30	< 0.05	Ediger 2006
(Northwood, North Dakota)							< 0.05	451534
2004	1	127	92	BBCH 61	Straw	48	< 0.05	NN-FR-04-5418
(Spring Wheat— Briggs)							0.06	
	1	384	93	BBCH 61	Straw	48	0.26	0.21
							0.16	
	1	643	94	BBCH 61	Straw	48	0.51	0.63
							0.74	
USA	1	129	187	Feekes 7	Hay	30	0.06	Ediger 2006
(Campbell, Minnesota)							0.10	451534
2004	1	128	187	BBCH 65	Straw	44	0.11	NF-FR-04-5419
(Spring Wheat— Oxen)				Full			0.11	
				Flowering				
USA	1	131	141	Feekes 5–7	Hay	27	0.06	Ediger 2006
(Kirksville, Missouri)							0.06	451534
2005	1	130	151	BBCH 61	Straw	47	< 0.05	ND-FR-04-5420
(Winter Wheat— Ernie)							< 0.05	
USA	1	129	39	BBCH 32	Hay	34	0.09	Ediger 2006
(Champaign, Illinois)							0.09	451534
2005	1	127	31	BBCH 55	Straw	46	0.10	4A-FR-04-5421
(Winter Wheat— Kaskaskia)							0.09	
USA	1	129	128	BBCH 32	Hay	0	0.34	Ediger 2006
(Hinton, Oklahoma)							1.6	451534
2005					Hay	7	0.67	SC-FR-04-5422
(Winter Wheat— Jagalene)							0.58	
					Hay	14	0.46	0.46
							0.46	
					Hay	31	0.20	0.19
							0.18	
					Hay	38	0.13	0.17
							0.20	
	1	130	129	BBCH 71	Straw	42	0.07	0.08
							0.09	
					Straw	47	0.05	0.06

Country Year (Variety)	Application			Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
						0.06		
				Straw	51	0.05	<u>0.07</u>	
						0.08		
USA	1	129	189	Feekes 7	Hay	1	1.0	Ediger 2006
(New Rockford, North Dakota)						1.2		451534
2004				Hay	7	0.19	0.19	NN-FR-04-5423
(Winter Wheat— Lebsock)						0.19		
				Hay	14	0.09	0.10	
						0.10		
				Hay	30	< 0.05	<u>< 0.05</u>	
						< 0.05		
				Hay	37	< 0.05	< 0.05	
						< 0.05		
	1	128	187	BBCH 33	Straw	40	< 0.05	< 0.05
						< 0.05		
				Straw	50	< 0.05	<u>< 0.05</u>	
						< 0.05		
				Straw	56	< 0.05	< 0.05	
						< 0.05		
USA	1	127	19	Feekes 6	Hay	33	0.17	Ediger 2006
(Froid, Montana)						0.18		451534
2004	1	128	19	Feekes 10.5	Straw	42	0.08	NN-FR-04-5424
(Spring Wheat— Challis)						0.07		
USA	1	134	98	Feekes 6	Hay	33	< 0.05	Ediger 2006
(Froid, Montana)						< 0.05		451534
2004	1	129	93	Feekes 10.5	Straw	42	0.06	NN-FR-04-5425
(Spring Wheat— Pristine)						0.07		
USA	1	128	172	BBCH 32	Hay	30	0.11	Ediger 2006
(Trail City, South Dakota)						0.11		451534
2004	1	129	178	BBCH 65	Straw	45	< 0.05	NF-FR-04-5426
(Spring Wheat— Freyr)						< 0.05		
USA	1	129	186	BBCH 32	Hay	29	0.08	Ediger 2006
(Grand Island, Nebraska)						0.08		451534
2005	1	129	187	BBCH 61	Straw	44	< 0.05	NB-FR-04-5427
(Winter Wheat— Arrowsmith HW)						< 0.05		
USA	1	123	129	Feekes 7	Hay	0	2.6	Ediger 2006
(Larned, Kansas)						2.0		451534
2005				Hay	7	0.08	0.08	NM-FR-04-5428
(Winter Wheat— Jagger)						0.08		
				Hay	14	0.05	0.06	

Country Year (Variety)	Application				Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
							0.06		
					Hay	30	0.05	<u>0.05</u>	
							0.05		
					Hay	37	< 0.05	< 0.05	
							< 0.05		
	1	125	130	Flag leaf	Straw	31	0.05	0.05	
							< 0.05		
					Straw	38	< 0.05	< 0.05	
							< 0.05		
					Straw	45	< 0.05	<u>< 0.05</u>	
							< 0.05		
					Straw	52	< 0.05	< 0.05	
							< 0.05		
USA	1	129	20	Feekes 7	Hay	30	< 0.05	< 0.05	Ediger 2006
(Larned, Kansas)							< 0.05		451534
2005	1	129	21	Flag leaf	Straw	45	< 0.05	< 0.05	NM-FR-04-5429
(Winter Wheat— Jagger)							< 0.05		
USA	1	128	144	BBCH 29	Hay	30	< 0.05	<u>< 0.05</u>	Ediger 2006
(Goodwell, Oklahoma)							< 0.05		451534
2005	1	130	144	BBCH 45	Straw	45	0.08	<u>0.07</u>	SC-FR-04-5430
(Winter Wheat— Clark)							0.05		
	1	391	145	BBCH 45	Straw	45	0.12	0.09	
							0.06		
	1	643	143	BBCH 45	Straw	45	0.15	0.16	
							0.16		
USA	1	128	142	BBCH 32	Hay	30	0.11	<u>0.11</u>	Ediger 2006
(Levelland, Texas)							0.10		451534
2005	1	123	136	BBCH 67	Straw	44	< 0.05	<u>< 0.05</u>	SC-FR-04-5431
(Winter Wheat— TAM							< 0.05		
200)									
USA	1	128	127	Feekes 7	Hay	30	0.90	<u>0.75</u>	Ediger 2006
(Ault, Colorado)							0.60		451534
2005	1	130	126	Feekes 10.5	Straw	45	< 0.05	<u>< 0.05</u>	NM-FR-04-5432
(Winter Wheat— Yuma)							< 0.05		
USA	1	130	139	BBCH 32	Hay	30	0.19	<u>0.19</u>	Ediger 2006
(Clovis, New Mexico)							0.19		451534
2005	1	127	140	BBCH 65	Straw	44	< 0.05	<u>< 0.05</u>	SC-FR-04-5433
(Winter Wheat— TAM							< 0.05		
110)									
USA	1	129	144	BBCH 32	Hay	29	0.07	<u>0.07</u>	Ediger 2006
(Ephrata, Washington)							0.06		451534

Country Year (Variety)	Application				Matrix	PHI days	Trinexapac (mg/kg)		Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean	
2004	1	129	139	BBCH 61	Straw	44	< 0.05	< 0.05	WF-FR-04-5435
(Winter Wheat— Stephens)							< 0.05		

LOQ = 0.05 mg/kg

Feekes 5 = Pseudo stem (formed by sheaths of leaves) strongly erected

Feekes 6 = First node detectable

Feekes 7 = Second node detectable

Feekes 8 = Flag leaf (last leaf) visible but still rolled up, ear beginning to swell

Table 81 Residues from the foliar application of trinexapac-ethyl to winter rape in Germany

Country Year (Variety)	Application				Matrix	PHI days	Trinexapac (mg/kg)	Trinexapac- ethyl (mg/kg)	Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage					
GAP, Germany (oilseed rape, winter)	1	375							
Germany	1	375	400	BBCH 39– 51	Whole plant	0	4.5	3.7	Smith 2000
(Rohlsdorf)					Pods with seeds	56	0.28	—	CGA163935/0636
1999					Remaining Plant	56	< 0.04	—	Trial 1
(Lirajet)					type				
					Straw	108	0.11	—	
Germany	1	375	400	BBCH 33– 51	Whole plant	0	2.2	3.3	Smith 2000a
(Ivenrode)					Pods with seeds	68	0.22	—	CGA163935/0637
1999					Remaining Plant	68	< 0.04	—	Trial 1
(Laser)					type				
					Straw	113	0.07	—	
Germany	1	375	400	BBCH 51– 53	Whole plant	0	3.4	1.4	Smith 2000b
(See)					Pods with seeds	49	0.43	—	CGA163935/0638
1999					Remaining Plant	49	< 0.04	—	Trial 1
(Express)					type				
					Straw	93	0.07	—	
Germany	1	375	400	BBCH 50– 51	Whole plant	0	2.4	2.7	Smith 2000c
(Kandel)					Pods with seeds	57	0.33	—	CGA163935/0639
1999					Remaining Plant	57	0.04	—	Trial 1
(Mohikan)					type				
					Straw	104	0.05	—	

LOQ = 0.04 mg/kg (trinexapac acid in whole plant, remainder and straw and trinexapac-ethyl in whole plant)

LOQ = 0.02 mg/kg (trinexapac acid in pods with seeds)

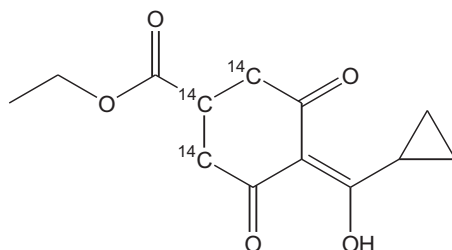
FATE OF RESIDUES IN STORAGE AND PROCESSING

Residues after processing

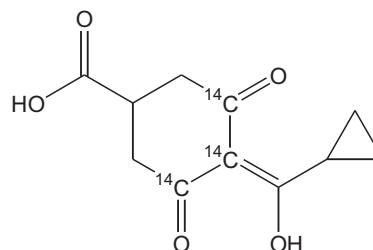
Processing studies are necessary according to the uses and the residues of trinexapac-ethyl on raw agricultural commodities. The fate of trinexapac-ethyl residues during processing of raw agricultural commodities was investigated in a number of major registered crops (barley, wheat, sugarcane and oilseed rape).

The high temperature hydrolysis of residues of trinexapac-ethyl and trinexapac acid under varying conditions were studied (CadAlbert and Buckel 2001, CGA163935/0733 and Mound and Clark 2004, CGA179500/0036 respectively). The labelled compounds used are depicted below.

[1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl



¹⁴C-cyclohexyl labelled trinexapac-acid



Trinexapac-ethyl

[1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was added to aqueous buffer solutions and subjected to hydrolysis at pH 4, 5 and 6 at high temperature at concentrations of 5 mg/L (0.01 M citrate, acetate and phosphate buffers respectively). The conditions were selected to simulate hydrolysis under processing conditions and included:

- The effect of pasteurisation (pH 4 and pasteurised at 90 °C for 20 minutes)
- The effect of baking, boiling and brewing (pH 5 and baked at 100 °C for 60 minutes)
- The effect of sterilisation (pH 6 and autoclaving at 120 °C for 20 minutes).

The pH ranged from 4.22 (beginning of the trial), 4.30 (end of the trial) for the pH 4 samples, 5.04 (beginning of the trial), 5.07 (end of the trial) for the pH 5 samples and from 6.15 (beginning of the trial), 6.25 (end of the trial) for the pH 6 samples. No major loss of radioactivity material occurred. For all three processing conditions, 99% (mean) of the applied radioactivity remained after the test. Subsamples of the test solutions were analysed by HPLC and TLC. The amount of radioactive material in the samples at the end of the test mainly corresponded to parent compound (93–94% of the applied radioactivity in all samples). Minor compounds were present up to 3.3% of the applied radioactivity, however as they were present at the start of the incubation, these were considered to be impurities.

In summary, the data show that trinexapac-ethyl was not degraded during the simulation of pasteurisation (pH 4, 90 °C, 20 minutes), baking, boiling and brewing (pH 5, 100 °C, 60 minutes) and sterilisation (pH 6, 120 °C, 20 minutes).

Trinexapac acid

¹⁴C-cyclohexyl labelled trinexapac acid was added to aqueous acetate buffer solutions and subjected to hydrolysis at pH 4, 5 and 6 at high temperature, at concentrations ranging from 4.30–4.87 mg/L.

The conditions were the same as described above except the pH 4 experiment, simulating the effects of pasteurisation, was run for 25 minutes.

The pH of the buffer solutions prior to the experiment were 4.01, 5.06 and 6.08. No major loss of radioactivity material occurred. For the pH 4 at 90 °C experiment, 104% (mean) of the applied radioactivity remained after the test while for the other two processing conditions, 102% (mean) of the applied radioactivity remained after the test.

The major component of the radioactive material in the samples at the end of the hydrolysis reactions corresponded to unchanged trinexapac acid; at pH 4 and 90 °C the mean value was 52.5%, at pH 5 and 100 °C the mean value was 58.5% and at pH 6 and 120 °C the mean value was 50.9%. The hydrolysis products were similar at each pH. At least two major and several minor degradates were observed. The two major components were identified as CGA313458 (at pH 4 and 90 °C the mean value was 19.7%, at pH 5 and 100 °C the mean value was 16.1% and at pH 6 and 120 °C the mean value was 21.0%) and CGA113745 (at pH 4 and 90 °C the mean value was 9.6%, at pH 5 and 100 °C the mean value was 10.5% and at pH 6 and 120 °C the mean value was 11.6%). The other degradates, comprising more than one component, represented < 11.6% in any of the hydrolysates with no individual unknown being more than 5%. Characterisation was by TLC co-chromatography and where possible by HPLC confirmation. Identification of CGA313458 was confirmed by NMR.

The proposed hydrolysis of trinexapac acid under processing conditions is as follows:

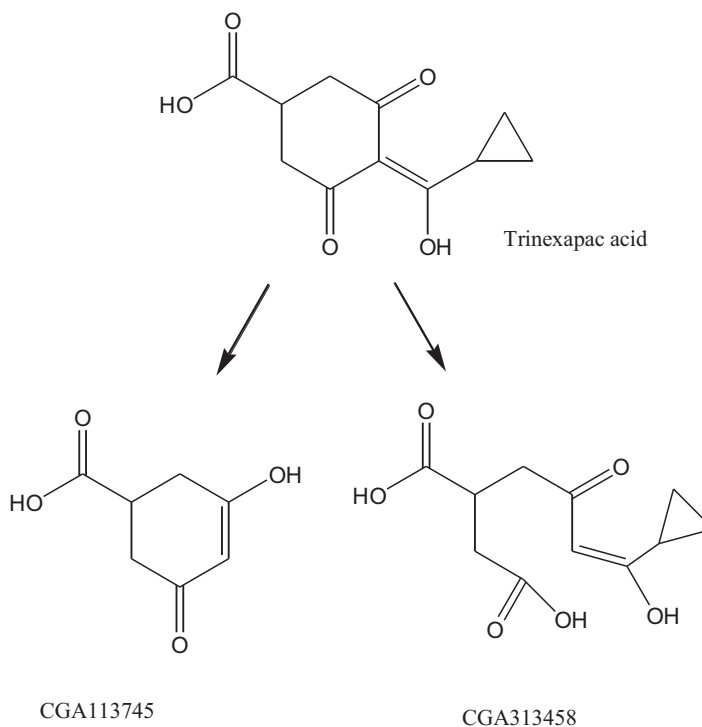


Figure 3 Hydrolysis of trinexapac acid under processing conditions

In summary, the data show that trinexapac acid undergoes limited degradation during the simulation of pasteurisation (pH 4, 90 °C, 25 minutes), during the simulation of baking, boiling and brewing (pH 5, 100 °C, 60 minutes) and during sterilisation (pH 6, 120 °C, 20 minutes).

Barley

The effect of processing (laboratory scale) on residues of trinexapac-ethyl in barley was investigated in two trials conducted in the USA in the 2008 growing season (Mayer 2010a, CGA163935_50026). Barley with incurred residues was obtained where plants were sprayed with a foliar spray at 0.129 and 648 k g ai/ha at BBCH 51 and at 0.129 and 0.644 k g ai/ha at BBCH 73. Applications were made in 141–188 L/ha using ground equipment. Barley bulk RAC samples were harvested 45 days after application.

Bulk barley grain samples were processed into processed barley commodity samples according to simulated commercial procedures into the following samples: pearled barley, flour and bran.

Barley was removed from storage and a representative RAC sample taken. Barley was oven-dried at 54–71 °C to a moisture content of 11–13.5%, then samples were cleaned by aspiration and screening. Light impurities were separated from the whole barley by aspiration. Large and small foreign particles were then separated from the barley. The cleaned barley was hulled, resulting in the fractions blocked (pearled) barley and husk. A sub-fraction of the pearled barley was then fed through a mill to break the grains. The broken grain was fed onto the sifter screens (0.14 and 0.80 mm) to obtain coarse bran, break flour and middlings. Coarse bran was sifted further to produce bran and shorts. Middlings were separated in a reduction mill to reduction flour and shorts. Break flour was combined with the reduction flour to produce barley flour. Shorts obtained after shifting bran and middlings were also combined.

Residues of total trinexapac in barley RAC and processed commodities were quantitated as trinexapac acid by LC/MS/MS using Method GRM 020.01A. Acceptable concurrent recovery data were obtained for all barley commodities.

Table 82 Residues of trinexapac in barley and processed commodities

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Processing Factor	Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean		
GAP, USA (barley)	1	123				45				
USA	1	129	187	BBCH 51	Grain	45	0.50, 0.55, 0.48	0.51	—	Mäyer 2010a
(Northwood, North Dakota)					Pearled		0.78, 0.72	0.75	1.5	CGA16393- 5_50026
2008					barley					C13ND081704p
(Tradition)					Flour		0.26, 0.31	0.29	0.57	
					Bran		0.95, 1.1	1.0	2.0	
	1	648	188	BBCH 51	Grain	45	9.1, 5.2, 5.9	6.7	—	
					Pearled		10.1, 8.6	9.4	1.4	
					barley					
					Flour		4.6, 3.7	4.2	0.63	
					Bran		10.8, 10.9	10.9	1.6	
USA	1	129	141	BBCH 73	Grain	45	0.65, 0.84, 0.76	0.75	—	Mäyer 2010a
(Carrington, North Dakota)					Pearled		0.82, 0.89	0.86	1.2	CGA16393- 5_50026
2008					barley					C13ND081705p
(Tradition)					Flour		0.24, 0.18	0.21	0.28	
					Bran		1.4, 1.3	1.4	1.9	
	1	644	141	BBCH 73	Grain	45	5.2, 5.4, 6.1	5.6	—	

Country Year (Variety)	Application			Matrix	PHI days	Total Trinexapac (mg/kg)		Processing Factor	Author, Study No., Trial No.
	No g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean		
				Pearled		5.5, 4.1	4.8	0.86	
				barley					
				Flour		1.4, 1.4	1.4	0.25	
				Bran		10.1, 9.6	9.9	1.8	

Wheat

The effect of processing (laboratory scale) on residues of trinexapac-ethyl in wheat was investigated in two trials conducted in the USA in the 2008 growing season (Mäyer 2010, CGA163935_50036). Wheat with incurred residues was obtained where plants were sprayed with a foliar spray at 0.129 and 646 kg ai/ha at BBCH 65 (durum wheat) and at 0.130 and 0.649 kg ai/ha at BBCH 52 (winter wheat). Applications were made in 188–252 L/ha using ground equipment. Wheat bulk RAC samples were harvested 45 days after application.

Bulk wheat grain samples were processed according to simulated commercial procedures into the following samples: aspirated grain fractions, bran, flour, middlings, shorts and germ.

Drying and aspiration was used to generate aspirated grain fractions. Light impurities were separated by aspiration and screened, removing foreign particles (screenings) from the wheat. For wheat germ recovery, the cleaned wheat was moisture adjusted to 16%, passed through a disc mill, and sieved to remove bran from the germ fraction. The germ (with endosperm) was then sifted to separate the germ from the endosperm and was aspirated again.

The moisture content of the cleaned wheat grain was adjusted to 17.5%. The sample was fed through a mill to break the grains. The broken grain was fed onto the sifter screens (0.14 and 0.80 mm) to obtain coarse bran, break flour and middlings. Coarse bran was sifted further to produce bran and shorts. Middlings were separated in a reduction mill to reduction flour and shorts. Break flour was combined with the reduction flour to produce wheat flour. Shorts obtained after shifting bran and middlings were also combined.

Residues of total trinexapac in wheat RAC and processed commodities were quantitated as trinexapac acid by LC/MS/MS using Method GRM 020.01A. Acceptable concurrent recovery data were obtained for all wheat commodities.

Table 83 Residues of trinexapac in wheat and processed commodities

Country Year (Variety)	Application			Matrix	PHI days	Total Trinexapac (mg/kg)		Processing Factor	Author, Study No., Trial No.
	No g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean		
GAP, USA (wheat)	1	123			45				
USA	1	129	188	BBCH 65	Grain	0.33, 0.31, 0.28	0.30	–	Mäyer 2010
(Carrington, North Dakota)				Wheat		0.24, 0.23	0.24	0.8	CGA163935_50036
				AGF					C13ND078468
2008				Bran		0.61, 0.71	0.66	2.2	
(Durum–Divide)				Flour		0.16, 0.11	0.13	0.4	
				Middlings		3.67, 3.29, 3.39	3.5	11.7	
				Shorts		0.15, 0.20, 0.20	0.18	0.6	
				Germ		0.60, 0.31, 0.35	0.42	1.4	

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Processing Factor	Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean		
	1	646	188	BBCH 65	Grain	45	5.57, 4.90, 5.73	5.4	—	
					Wheat		4.77, 4.03	4.4	0.8	
					AGF					
					Bran		7.85, 9.33	8.6	1.6	
					Flour		2.42, 2.88	2.7	0.5	
					Middlings		2.83, 2.45, 2.31	2.5	0.5	
					Shorts		0.12, 0.17, 0.17	0.15	0.03	
					Germ		5.88, 4.28, 5.11	5.1	0.9	
USA	1	130	252	BBCH 52	Grain	45	1.75, 1.66, 1.54	1.7	—	Mäyer 2010
(Groom, Texas)					Wheat		0.35, 0.34	0.35	0.2	CGA163935_50036
2008					AGF					W01TX078473
(Winter Wheat—					Bran		2.28, 4.63	3.5	2.1	
Cutter)					Flour		0.90, 0.58	0.74	0.4	
					Middlings		0.82, 0.42, 0.43	0.56	0.3	
					Shorts		0.93, 1.15, 0.95	1.0	0.6	
					Germ		1.62, 1.52, 1.34	1.5	0.9	
	1	649	251	BBCH 52	Grain	45	10.2, 9.55, 9.50	9.8	—	
					Wheat		3.50, 3.47	3.5	0.4	
					AGF					
					Bran		15.8, 104 ^a , 14.4, 13.8	14.7	1.5	
					Flour		3.67, 3.80	3.7	0.4	
					Middlings		5.73, 5.48, 4.93	5.4	0.6	
					Shorts		5.23, 6.25, 5.61	5.7	0.6	
					Germ		9.78, 11.1, 11.6	10.8	1.1	

^a Outlier, not used in calculations

In another study the effect of processing (laboratory scale) on residues of trinexapac-ethyl in wheat was investigated in two trials conducted in the USA in the 2004 or 2005 growing seasons (Ediger 2006, 451534). Wheat with incurred residues was obtained where plants were sprayed with a foliar spray at 0.127 and 0.643 k g ai/ha at BBCH 61 or 0.130 and 0.643 k g ai/ha at BBCH 45. Applications were made in 92–144 L/ha using ground equipment.

Bulk wheat grain samples were processed according to simulated commercial procedures into the following samples: aspirated grain fractions, bran, flour, middlings, shorts and germ (as described for Mäyer 2010, CGA163935_50036).

Residues of trinexapac in wheat RAC and processed commodities were quantitated as trinexapac acid using Method 110.01. Acceptable concurrent recovery data were obtained for all wheat commodities.

Table 84 Residues of trinexapac in wheat and processed commodities

Country Year (Variety)	Application				Matrix	PHI days	Trinexapac (mg/kg)	Processing Factor	Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage					
GAP, USA (wheat)	1	123				45			
USA	1	127	92	BBCH 61	Grain	48	1.0		Ediger 2006
(Northwood, North Dakota)					Wheat		0.35	0.35	451534
					AGF				NN-FR-04-5418
2004					Bran		2.2	2.2	
(Spring Wheat— Briggs)					Flour		0.32	0.32	
					Middlings		0.41	0.41	
					Shorts		0.45	0.45	
					Germ		0.29	0.29	
	1	643	94	BBCH 61	Grain	48	11		
					Wheat		3.3	0.30	
					AGF				
					Bran		23	2.1	
					Flour		3.4	0.31	
					Middlings		4.9	0.45	
					Shorts		7.5	0.68	
					Germ		9.4	0.85	
USA	1	130	144	BBCH 45	Grain	45	0.39		Ediger 2006
(Goodwell, Oklahoma)					Wheat		0.09	0.23	451534
					AGF				
2005					Bran		0.98	2.5	SC-FR-04-5430
(Winter Wheat— Clark)					Flour		0.12	0.31	
					Middlings		0.19	0.49	
					Shorts		0.56	1.4	
					Germ		0.40	1.0	
	1	643	143	BBCH 45	Grain	45	4.20		
					Wheat		0.68	0.16	
					AGF				
					Bran		10	2.4	
					Flour		1.0	0.24	
					Middlings		1.8	0.43	
					Shorts		4.6	1.1	
					Germ		4.5	1.1	

Sugarcane

The effect of processing (laboratory scale) on residues of trinexapac-ethyl in sugarcane was investigated in two trials conducted in the USA in the 2008 growing season (Mäyer 2010b, CGA163935_50038). Sugarcane with incurred residues was obtained where plants were sprayed with one foliar spray at 0.382 and 1.856 kg ai/ha at BBCH 91 and 0.361 and 1.779 k ai/ha at BBCH 70.

Application was made 28 days prior to the harvest of the mature cane. Applications were made in 102–223 L water /ha.

Bulk sugarcane samples were processed according to simulated commercial procedures into blackstrap molasses and refined sugar.

The sugarcane was cleaned by spraying the cane. Juice was pressed out using a cane crusher repeatedly until the majority of the juice was yielded. Juice of the first pressing was screened (sieve) to remove large particles prior to pH adjustment to 7.2–7.6 with a 20% w/w calcium-oxide solution. After pH adjustment, the juice was boiled (97–100 °C) for 3 minutes. The heated juice was then immediately centrifuged to separate mud and thin juice. Thin juice was evaporated under vacuum (rotary evaporator) until the juice contained 50–60% solids (thick juice) with the temperature maintained below 70 °C. After evaporation the thick juice was filtered using cotton. During laboratory evaporation a known amount of thick juice was evaporated to 70–80% solids and a small amount of sugar was added to “seed” crystallisation of sugar granules. The remaining thick juice was slowly added and continuously evaporated, and the solution was allowed to cool. Crystallised raw sugar and molasses were separated by centrifugation. Final black strap molasses was 60–65% solids. After molasses was removed, the remaining sugar was refined.

Equal parts of raw sugar and water were combined and mixed to dissolve the sugar. The pH of the mixture was adjusted to 5.2–5.8. After resting, mixing was resumed and the pH adjusted to 7.0–7.4. After heating to approximately 59–61 °C, filter aid was added and the solution was vacuum filtered. Upon obtaining a non-cloudy filtrate, the solution was evaporated and crystallised. Refined sugar was dried at 38–54 °C until the moisture content was approximately 3.0%.

Residues of total trinexapac in sugarcane RAC and processed commodities were quantitated as trinexapac acid by LC/MS/MS using Method GRM 020.01A. Acceptable concurrent recovery data were obtained for all sugarcane commodities.

Table 85 Residues of trinexapac in sugarcane and processed commodities

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)		Processing Factor	Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage			Individual	Mean		
GAP, USA (sugarcane)	1	347				28				
USA	1	382	105	BBCH 91	Sugarcane	28	0.04, 0.08, 0.05	0.06	–	Mäyer 2010b
(Clewiston, Florida)					Molasses		0.32, 0.32	0.32	5.3	CGA16393- 5_50038
2008					Refined		< 0.01, < 0.01	< 0.01	0.2	E19FL078492p
(CL95-0776)					sugar					
	1	1856	102	BBCH 91	Sugarcane	28	0.38, 0.23 0.24	0.28	–	
					Molasses		1.7, 1.8	1.8	6.4	
					Refined		< 0.01, < 0.01	< 0.01	0.03	
					sugar					
USA	1	361	223	BBCH 70	Sugarcane	28	0.31, 0.21, 0.11	0.21	–	Mäyer 2010b
(Washington, Louisiana)					Molasses		1.6, 1.3	1.5	7.1	CGA16393- 5_50038
2008					Refined		0.02, 0.03	0.03	0.1	E18LA078495p
(85–384)	1	1779	220	BBCH 70	Sugarcane	28	2.2, 3.0, 2.2	2.5	–	
					Molasses		12.6, 9.2	10.9	4.4	
					Refined		0.22, 0.24	0.23	0.1	

Country Year (Variety)	Application			Matrix	PHI days	Total Trinexapac (mg/kg)		Processing Factor	Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)			Individual	Mean		
				sugar					

In another study the effect of processing (laboratory scale) on residues of trinexapac-ethyl in sugarcane was investigated in one trial conducted in the USA in the 2004 growing season (Ediger 2006a, 451598). Sugarcane with incurred residues was obtained where plants were sprayed with a foliar spray at 0.345 or 1739 kg ai/ha at 28 days prior to harvest of the mature cane. Applications were made in 276–278 L/ha using ground equipment.

Bulk sugarcane samples were processed according to simulated commercial procedures into molasses and refined sugar (as described for Mäyer 2010b, CGA163935_50038, with very minor modifications).

Residues of trinexapac in sugarcane RAC and processed commodities were quantitated as trinexapac acid using Method 110.01. Acceptable concurrent recovery data were obtained for all sugarcane commodities.

Table 86 Residues of trinexapac in sugarcane and processed commodities

Country Year (Variety)	Application			Matrix	PHI days	Trinexapac (mg/kg)	Processing Factor	Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)					
GAP, USA (sugarcane)	1	347			28			
USA	1	345	276	28 days to	Sugarcane	28	0.06	Ediger 2006a
(South Bay, Florida)				harvest	Molasses		< 0.05	451598
2004					Refined		< 0.05	VN-FR-04- 5501
(CP89-2143)					sugar			
	1	1739	278	28 days to	Sugarcane	28	0.51	
				harvest	Molasses		1.4	2.7
					Refined		< 0.05	0.1
					sugar			

LOQ = 0.05 mg/kg

Rape seed

The effect of processing (laboratory scale) on residues of trinexapac-ethyl in rape seed was investigated in two trials carried out in Germany during the 1994 growing season (Sack 1995a, CGA163935/0416 and Sack 1995, CGA163935/0417). Rapeseed with incurred residues were obtained where plants were sprayed a foliar spray at 0.375 kg ai/ha. Application was made 84–85 days prior to the harvest of the mature rape seeds. Applications were made in 300 L water /ha.

Bulk rape seed samples were processed into processed rape seed commodity samples (crude oil, press cake and refined oil) according to simulated commercial procedures.

The harvested rape seed samples were processed into crude oil and press cake by cold pressing or hot extraction simulating industrial practice as closely as possible. Crude oil was processed further into refined oil.

Residues of trinexapac acid in rapeseed RAC and press cake were quantitated by LC/MS/MS using modified Method REM 137.02, while Method REM 137.11 was used for the quantification of

trinexapac acid residues in crude and refined oil. Acceptable concurrent recovery data for rape seed commodities were obtained for each analyte.

Table 87 Residues of trinexapac in rapeseed and processed commodities

Country Year (Variety)	Application				Matrix	PHI days	Total Trinexapac (mg/kg)	Processing Factor	Author, Study No., Trial No.
	No	g ai/ha	Water (L/ha)	Growth Stage					
GAP, Germany (oilseed rape, winter)	1	375							
Germany	1	375	300	BBCH 55	Rapeseed	85	0.64	—	Sack 1995a
(Kötschau) 1994					Crude oil (cold pressing)		< 0.02	0.03	CGA163935/0416 FR 31/94/40
(Lirajet)					Press cake (cold pressing)		0.56	0.9	
					Crude oil (hot extraction)		< 0.02	0.03	
					Press cake (hot extraction)		0.64	1.0	
					Refined oil		< 0.02	0.03	
Germany	1	375	300	BBCH 55–57	Rapeseed	84	0.33	—	Sack 1995
(Motterwitz) 1994					Crude oil (cold pressing)		< 0.02	0.06	CGA163935/0417 FR 31/94/70
(Lirajet)					Press cake (cold pressing)		0.49	1.5	
					Crude oil (hot extraction)		< 0.02	0.06	
					Press cake (hot extraction)		0.44	1.3	
					Refined oil		< 0.02	0.06	

LOQ = 0.02 mg/kg

The results of the processing factors are summarized in the table below:

Table 88 Summary of processing factors for trinexapac residues

Raw Agricultural Commodity (RAC)	Residues Determined	Processed Commodity	Application rate (g ai/ha)	Calculated Processing factors	PF Mean (<i>median</i>)
Barley	Total trinexapac	Pearled barley	129 644–648	1.5, 1.2 1.4, 0.86	1.2
		Flour	129 644–648	0.57, 0.28 0.63, 0.25	0.43
		Bran	129 644–648	2.2, 1.9 1.6, 1.8	1.9
Wheat	Total trinexapac	Aspirated grain fractions	129–130 646–649	0.8, 0.2 0.8, 0.4	0.55
		Bran	129–130 646–649	2.2, 2.1 1.6, 1.5	1.9
		Flour	129–130 646–649	0.4, 0.4 0.5, 0.4	0.43
		Middlings	129–130 646–649	11.7, 0.3 0.5, 0.6	(0.55)
		Shorts	129–130 646–649	0.6, 0.6 0.03, 0.6	0.46
		Germ	129–130	1.4, 0.9	1.1

Raw Agricultural Commodity (RAC)	Residues Determined	Processed Commodity	Application rate (g ai/ha)	Calculated Processing factors	PF Mean (median)
			646–649	0.9, 1.1	
Wheat	Trinexapac	Aspirated grain fractions	127–130 643	0.35, 0.23 0.30, 0.16	0.26
		Bran	127–130 643	2.2, 2.5 2.1, 2.4	2.3
		Flour	127–130 643	0.32, 0.31 0.31, 0.24	0.30
		Middlings	127–130 643	0.41, 0.49 0.45, 0.43	0.46
		Shorts	127–130 643	0.45, 1.4 0.68, 1.1	0.91
		Germ	127–130 643	0.29, 1.0 0.85, 1.1	0.81
Sugarcane	Total trinexapac	Molasses	361–382 1779–1856	5.3, 7.1 6.4, 4.4	5.8
		Refined sugar	361–382 1779–1856	0.2, 0.1 0.2, 0.1	0.15
Sugarcane	Trinexapac	Molasses	345 1739	0.8 2.7	1.8
		Refined sugar	345 1739	0.8 0.1	0.45
Rapeseed	Trinexapac	Crude oil (cold pressed)	375	0.03, 0.06	0.05
		Press cake (cold pressed)	375	0.9, 1.5	1.2
		Crude oil (hot extraction)	375	0.03, 0.06	0.05
		Press cake (hot extraction)	375	1.0, 1.3	1.2
		Refined oil	375	0.03, 0.06	0.05

RESIDUES IN ANIMAL COMMODITIES

Dairy cattle transfer study (Sack 2000, CGA179500/0030)

A feeding study with trinexapac acid was conducted in lactating cows (ten *Bos taurus Holstein* dairy cattle ranging from 2–6 years of age divided into three dose groups of three cows with one control animal, 514–720 kg during dosing).

The animals received nominal doses of trinexapac acid equivalent to 0, 2 (40 mg trinexapac acid, 1×), 6 (120 mg trinexapac acid, 3×) and 20 ppm in the feed (400 mg trinexapac acid, 10×) respectively (actual doses 40.4, 121.2 and 404.0 mg respectively). The doses were administered orally *via* gelatine capsules, for a period of 29–30 consecutive days.

Milk samples from each animal were collected twice daily, at approximately 6 am and pm, and combined as one pooled sample. Milk specimens were collected on day 0 (pre-dose) and days 1, 2, 3, 5, 8, 12, 15, 19, 22 and 28 of the feeding period. The cows were sacrificed within 20–24 hours after the final dosing (one cow from each treatment group on day 29 and two cows from each group, except the control group, on day 30). Besides blood, the following tissues were collected; liver, kidney, round muscle, tenderloin muscle, diaphragm, perirenal and omental fat.

Milk, tissues and blood samples were analysed for residues of trinexapac acid using Method REM 137.12.

The residues of trinexapac acid found in milk during the treatment periods are summarized in Table 89.

Table 89 Residues of trinexapac acid in milk

Study day	Group mean (and maximum individual) residues of trinexapac acid (mg/kg)			
	0 ppm	2 ppm	6 ppm	20 ppm
0	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	< 0.005 (< 0.005)
1	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	0.005 (0.005)
2	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	0.006 (0.006)
3	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	0.005 (0.005)
5	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	0.007 (0.011 ^a)
8	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	0.005 (0.005)
12	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	0.005 (0.005)
15	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	0.005 (0.006)
19	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	0.005 (0.006 ^b)
22	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	0.005 (0.005)
28	< 0.005	< 0.005 (< 0.005)	< 0.005 (< 0.005)	0.005 (0.005)

< 0.005 denotes less than the LOQ

^a Average of three analyses (0.010, 0.011, 0.011 mg/kg)

^b Average of two analyses (0.0061 and 0.005 mg/kg)

No quantifiable residues of trinexapac acid were found in the milk of the 0, 2 and 6 ppm dose groups. Residues in the 20 ppm dose group ranged from < 0.005–0.011 mg/kg. Residues reached a plateau after one day.

Results of the tissue and blood analysis are summarized in Table 90.

Table 90 Residues of trinexapac acid in tissues

Treatment Group	Group mean (and maximum individual) residues in tissue for trinexapac acid (mg/kg)							
	Muscle Tenderloin	Muscle Round	Diaphragm	Liver	Kidney	Perirenal Fat	Omental Fat	Blood
0 ppm	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.010
2 ppm	< 0.02 (< 0.02)	< 0.02 (< 0.02)	< 0.02 (< 0.02)	< 0.02 (< 0.02)	0.03 (0.03)	< 0.02 (< 0.02)	< 0.02 (< 0.02)	0.018 (0.023)
6 ppm	< 0.02 (< 0.02)	< 0.02 (< 0.02)	< 0.02 (< 0.02)	< 0.02 (< 0.02)	0.04 (0.05)	< 0.02 (< 0.02)	< 0.02 (< 0.02)	0.031 (0.036)
20 ppm	< 0.02 (< 0.02)	< 0.02 (< 0.02)	< 0.02 (0.02)	0.03 (0.03)	0.17 (0.29)	< 0.02 (0.02)	< 0.02 (0.02)	0.13 (0.17)

< 0.02 denotes less than the LOQ

No quantifiable residues of trinexapac acid were found in the tissues of the control cow. In the lowest and mid-range dose groups (2 and 6 ppm), no quantifiable residues were detected in muscle, liver and fat, although residues slightly above LOQ were observed in kidney (means 0.03 and 0.04 mg/kg respectively).

In the highest dose group (20 ppm), quantifiable residues were detected in one diaphragm sample (0.02 mg/kg), two liver samples (both 0.03 mg/kg) and one perirenal fat sample (0.02 mg/kg). Quantifiable residues were observed in all kidney samples (mean 0.17 mg/kg).

Quantifiable residues were observed in all blood samples from all dose groups (means 0.018, 0.031 and 0.13 mg/kg respectively).

Laying hen transfer study (Simmons 2010, CGA179500_50008)

A feeding study with trinexapac acid was conducted in laying hens (forty *Hyline Browns*, approximately 37 weeks old upon arrival, divided into 3 dose groups and a control group each of ten hens, 1.80–1.92 kg from 7 days before dosing until the end of dosing). The target doses of trinexapac acid were equivalent to 3.3, 9.9 and 33.0 ppm in the feed. Mean doses in the feed were determined to be 3.7, 10 and 37 ppm.

The doses were administered orally *via* gelatine capsules, for a period of 28 days. Ten animals were allocated per dose group divided into three subgroups of 3–4 birds. Eggs from each hen were collected on day 0 (pre-dose) and days 1, 3, 7, 10, 14, 17, 21, 24 and 28 of the feeding period. Egg production by group was at or above 89% with two exceptions (the control group on week 4 at 74% and the high dose group on week 4 at 75%). The animals were sacrificed within 6 hours after the last administration of the treated feed. Tissues collected were skin plus attached fat and peritoneal fat, liver, kidney and breast and thigh muscle.

Liver, kidney, breast and thigh muscle, skin with attached fat and peritoneal fat and eggs were analysed for residues of trinexapac acid using Method REM 137.14 with some modifications.

Residues of trinexapac acid found in eggs during the treatment period are summarized in Table 91. Residues in control samples were all < LOQ (< 0.01 mg/kg).

Table 91 Residues of trinexapac acid in eggs

Study day	Group mean (and maximum individual) residues of trinexapac acid (mg/kg)			
	0 ppm	3.7 ppm	10 ppm	37 ppm
0	< 0.01	NA	< 0.01 (< 0.01)	< 0.01 (< 0.01)
1	–	NA	< 0.01 (< 0.01)	< 0.01 (< 0.01)
3	–	NA	< 0.01 (< 0.01)	< 0.01 (< 0.01)
7	–	NA	< 0.01 (< 0.01)	< 0.01 (< 0.01)
10	–	NA	< 0.01 (< 0.01)	< 0.01 (< 0.01)
14	–	NA	< 0.01 (< 0.01)	< 0.01 (< 0.01)
17	–	NA	< 0.01 (< 0.01)	< 0.01 (< 0.01)
21	–	NA	< 0.01 (< 0.01)	< 0.01 (< 0.01)
24	–	NA	< 0.01 (< 0.01)	< 0.01 (< 0.01)
28	–	NA	< 0.01 (< 0.01)	0.013 (0.013)

< 0.01 denotes less than the LOQ

NA = Samples were not analysed, because residues of higher dose groups are < LOQ

No quantifiable residues were detected in any dose group apart from in the 37 ppm dose group at day 28 (mean residues in groups A (three hens), B (three hens) and C (four hens) were all 0.013 mg/kg).

Residues of trinexapac acid in tissues are summarized below in Table 92. Residues in control samples were all < LOQ.

Table 92 Residues of trinexapac acid in tissues

Treatment Group	Group mean (and maximum individual) residues in tissue for trinexapac acid (mg/kg)			
	Fat	Liver	Kidney	Muscle
0 ppm	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)	< 0.01 (< 0.01)
3.7 ppm	NA	NA	0.06 (0.08)	NA
10 ppm	< 0.01 (< 0.01)	< 0.01 (< 0.01)	0.04 (0.05)	NA
37 ppm	0.03 (0.03)	0.02 (0.02)	0.45 (0.54)	< 0.01 (< 0.01)

< 0.01 denotes less than the LOQ

NA = Samples were not analysed, because residues of higher dose groups are < LOQ

No residues of trinexapac acid above LOQ (0.01 mg/kg) were detected in any muscle (breast and thigh muscle) sample from any treatment group. No residues of trinexapac acid above LOQ (0.01 mg/kg) were detected in any liver sample from any treatment group apart from the highest dose group (mean 0.02 mg/kg). No residues of trinexapac acid above LOQ (0.01 mg/kg) were detected in any fat sample from any treatment group apart from the highest dose group (mean 0.03 mg/kg). Mean residues of trinexapac acid in kidney were 0.06, 0.04 and 0.45 mg/kg in the lowest to highest dose groups respectively.

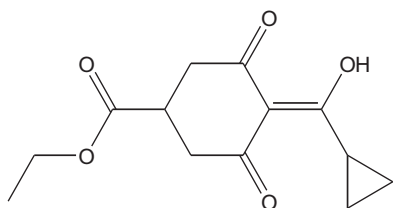
APPRAISAL

At the Forty-fourth Session of the CCPR (2012), trinexapac-ethyl was scheduled for evaluation as a new compound by 2013 JMPR.

Trinexapac-ethyl is a synthetic plant growth regulator that is derived from cyclohexanecarboxylate. It is applied as a foliar spray, post-emergence and is approved for use on cereal crops such as barley, durum wheat, oats, rye, triticale and wheat, oilseed rape and sugarcane as well as on grassland pastures.

The manufacturer supplied information on identity, metabolism, methods of residue analysis, freezer storage stability, registered use patterns, supervised residue trials, fates of residues in processing and farm animal feeding studies.

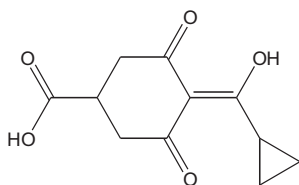
The IUPAC name is 4-(cyclopropyl-hydroxy-methylene)-3,5-dioxo-cyclohexanecarboxylic acid ethyl ester.



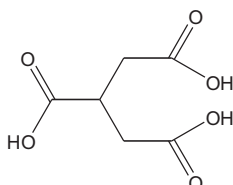
Trinexapac-ethyl

The 2013 JMPR established an ADI for trinexapac-ethyl of 0–0.3 mg/kg bw trinexapac acid equivalents.

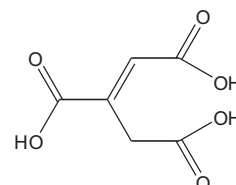
The structures of the key metabolites discussed are shown below:



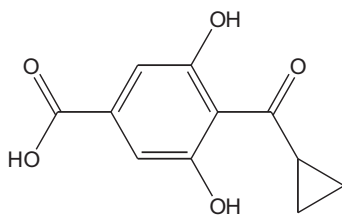
CGA 179500
Trinexapac acid



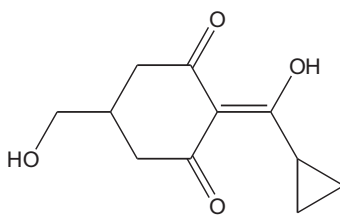
CGA 275537
Tricarballic acid



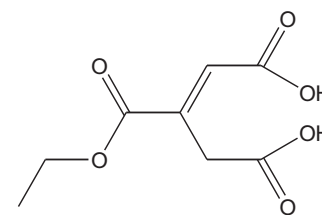
CGA 312753
Trans aconitic acid



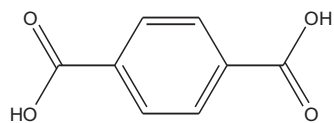
CGA 329773



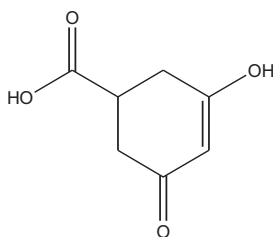
CGA 351210



CGA 312753 mono-ethyl ester



Terephthalic acid



CGA113745

Animal metabolism

The Meeting received animal metabolism studies with trinexapac-ethyl in rats, hens and goats.

Rats

Evaluation of the metabolism studies in rats was carried out by the WHO Core Assessment Group.

Trinexapac-ethyl undergoes limited metabolism in the rat, involving predominantly ester hydrolysis of trinexapac-ethyl to trinexapac acid. The predominant urinary metabolite was trinexapac acid (up to 100% of total urinary radioactivity), with low levels of a conjugated derivative of trinexapac acid detected only in the urine of bile-duct cannulated rats (6.3% of the administered dose). In faeces, the parent compound accounted for 5–22% of total faecal radioactivity (1–2.5% of the administered dose), with the balance comprising trinexapac acid. Bile contained mainly a conjugated derivative of trinexapac acid (2.9% of the administered dose), with low levels of the parent compound also detected (0.2% of the administered dose).

Goats

[1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl was orally administered via capsule to lactating goats at 7.2 ppm or 694 ppm in the feed (or 0.20 or 19.9 mg/kg bw/day respectively) for 4 consecutive days. Milk was sampled twice daily, in the morning and afternoon. Animals were sacrificed approximately 4 hours after the last dose.

The low dose goat eliminated 16% and 50% via faeces and urine of the total administered dose respectively at 76 hours in the study, while the corresponding values of the high dosed goat were 19% and 62%. In milk, 0.02% of the administered dose was recovered at both dose levels. A plateau was reached after 2 days (low dose-0.002 mg/kg equiv (am) and 0.007 mg/kg equiv. (pm)) or 3 days (high dose-0.22 mg/kg equiv (am) and 0.83 mg/kg equiv. (pm)) after administration.

The tissue residues of the low dosed goat were 0.035–0.043 mg/kg equiv. in muscles, 0.017–0.094 mg/kg equiv. in fat, 0.25 mg/kg equiv. in liver and 0.50 mg/kg equiv. in kidney. In the high dosed goat the residues were correspondingly higher, i.e., 1.90–2.49 mg/kg equiv. in muscles, 1.20–1.55 mg/kg equiv. in fat, 12.1 mg/kg equiv. in liver and 41.9 mg/kg equiv. in kidney.

Residues in muscle and kidney were mostly trinexapac acid (81–90% TRR). In milk, trinexapac acid accounted for 46–76% TRR. In liver and fat trinexapac acid was 31–67% TRR, although for fat this represented 87–96% of the extracted radioactivity. For liver this represented only 34–47% of the extracted radioactivity.

In another study [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was orally administered by gelatine capsule to two lactating goats at 100 ppm in the feed (or 3.1 mg/kg bw/day) for 4 consecutive days. Milk was sampled twice daily. Animals were sacrificed approximately 6 hours after the last dose.

The goats had eliminated 3% and 81% via faeces and urine of the total administered dose respectively at 78 hours in the study while 0.05% of the administered dose was recovered in milk. Residues in the Day 2 pm sample of milk were 0.076 mg/kg equiv.

The tissue residues were 0.28 mg/kg equiv. in muscles, 0.11 mg/kg equiv. in fat, 0.80 mg/kg equiv. in liver and 5.90 mg/kg equiv. in kidney.

No parent was observed in tissues or milk. Residues in liver, kidney, muscle and fat were mostly trinexapac acid (CGA179500) (66–97% TRR). In milk, trinexapac acid accounted for 85% TRR. In liver, kidney and fat the metabolite CGA113745 accounted for 6–16% TRR. This metabolite was not detected in either muscle or milk.

Hens

[1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl was orally administered daily to laying hens using gelatine capsules at a low dose level (2 hens, 0.4 mg/kg body weight equivalent to 3.8 ppm in feed) or a high dose level (4 hens, 20.3 mg/kg body weight equivalent to 180 ppm in feed) for 4 consecutive days. Eggs were collected throughout the day and in the morning before subsequent administration. Animals were sacrificed approximately 4 hours after the last dose.

Over the period of the experiment (76 hours), 85–89% (high and low doses respectively) of the total administered dose was eliminated in excreta. Transfer of radioactivity into eggs accounted for only 0.01% and 0.02% of the total administered dose for the low and high dosed hens, respectively. A plateau was reached at Day 2 of the dosing period. Concentrations of radioactivity in egg yolk were generally less than in egg whites. Concentrations of radioactivity in egg white and egg yolk in the low-dosed hens did not exceed 0.007 and 0.002 mg/kg equiv., respectively. In the high dosed hens the corresponding values were 0.33 and 0.055 mg/kg equiv.

Mean radioactive residues in tissues of the low-dosed hens were 0.002 mg/kg equiv. in lean meat (0.12 mg/kg equiv. high dose), 0.011 mg/kg equiv. in skin (including attached fat) (0.37 mg/kg equiv.), 0.003 mg/kg equiv. in peritoneal fat (0.18 mg/kg equiv.), 0.013 mg/kg equiv. in liver (0.60 mg/kg equiv.) and 0.043 mg/kg equiv. in kidney (1.77 mg/kg equiv.).

Radioactive residues in muscle (lean meat), liver, kidney and fat samples of low and high-dosed hens were predominantly trinexapac acid (44–84% TRR). In skin including attached fat in which the extractability was low, trinexapac acid was again the major metabolite accounting for 64–80% of the extracted radioactivity.

In the yolk the major metabolite was trinexapac acid accounting for 57–76% of the extracted radioactivity (0.0003–0.011 mg/kg equiv.), while parent trinexapac-ethyl was present at only 10–25% (< 0.0001–0.005 mg/kg equiv.). In egg white the major residue was parent accounting for 64–78% of the extractable TRR (0.0017–0.124 mg/kg equiv.). Trinexapac acid was either not detected (high dose) or accounted for only 13% (0.0003 mg/kg equiv.) of the extractable TRR (low dose).

In another hen metabolism study [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was orally administered daily to 5 laying hens by gelatine capsule at 8.1–10.4 ppm in feed for 10 consecutive days. Eggs were collected at 24 hour intervals throughout the morning before subsequent administration. Animals were sacrificed approximately 22 hours after the last dose.

Of the administered dose 89% was recovered in the excreta. Residue levels in the various tissue samples were all < 0.01 mg/kg equiv. Residue levels in egg yolk were very low, ranging from < 0.003–0.009 mg/kg equiv. Egg white residues ranged from 0.005–0.031 mg/kg equiv. The maximum residue levels of 0.009 and 0.031 mg/kg equiv. were reached by Day 8 of the dosing period. Overall retention of the radioactivity in eggs was < 0.1% of the administered dose.

TRR values for edible tissues and egg yolks were below 0.01 mg/kg equiv., so no further analysis was undertaken. The major metabolites identified in the organosoluble residue of the composite egg white sample were parent trinexapac-ethyl and trinexapac acid which accounted for 31% TRR and 20% TRR respectively.

Summary of animal metabolism

The metabolic pathways of trinexapac-ethyl observed in rats, goats and poultry are similar. Animal metabolism studies showed that parent was rapidly absorbed and almost completely hydrolysed to

trinexapac acid before excretion. No accumulation of residues was observed in any organ, tissue or animal commodity.

Plant metabolism

Paddy rice, spring wheat, spring rape and grass (foliar treatment) metabolism studies were carried out with [1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl or [1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl.

[1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was applied by foliar methods to rice at rates of 40 and 160 g ai/ha. TRRs in samples taken at maturity (60 days after treatment at 160 g ai/ha) were 1.58 mg/kg equiv. for straw, 2.22 mg/kg equiv. for husks and 1.07 mg/kg equiv. for grain. Trinexapac acid was the only identified compound present in rice grain at greater than 10% TRR (36% TRR) and was the major identified component of rice husks (30% TRR). It was present in rice straw at 9% TRR. Tricarballic acid (CGA 275537) was present at 14% TRR in straw. Some parent compound was observed in grain, husks and straw (all < 10% TRR). Metabolite CGA 329773 was a minor metabolite in grain, husks and straw (< 3% TRR).

[1, 2-¹⁴C-cyclohexyl] trinexapac-ethyl was applied to spring wheat by foliar spraying at a rate of 150 g ai/ha. Trinexapac acid was the only identified component in wheat grain (24% TRR) and was the only identified component of both wheat husks and wheat straw observed at > 10% of the TRR (15 and 21% TRR respectively).

A stem-injection experiment was conducted on six week old wheat plants grown under greenhouse conditions. Trinexapac acid was the major identified component of wheat grain (27.9% TRR, 0.129 mg/kg equiv.) and was the only identified component of both wheat husks and wheat straw observed at > 10% of the TRR (17% (0.073 mg/kg equiv.) and 13% TRR (0.069 mg/kg equiv.) respectively). Metabolites CGA329773 and CGA275537 were present in grain at 11% (0.050 mg/kg equiv.) and 3% TRR (0.014 mg/kg equiv.) respectively and in straw at 3 and 2% TRR respectively.

[1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was applied to spring rape under greenhouse conditions in plastic containers filled with soil. Trinexapac acid (free and conjugated) was the major metabolite observed in rape meal (31% TRR, 0.647 mg/kg equiv.), rape whole seeds (30% TRR, 0.431 mg/kg equiv.), pods (19% TRR, 1.06 mg/kg equiv.) and stalks (10% TRR, 0.304 mg/kg equiv.) and was also observed in oil (4% TRR, 0.004 mg/kg equiv.). Metabolite CGA 351210 was observed in oil at 16% TRR but at only 0.02 mg/kg equiv. This metabolite, only observed in rape, accounted for 16–28% TRR in pods and stalks (0.918 mg/kg equiv. and 0.869 mg/kg equiv. respectively).

[1, 2, 6-¹⁴C-cyclohexyl] trinexapac-ethyl was applied by foliar methods to tall fescue grass at 560 g ai/ha. TRRs of 5.45 mg/kg equiv., 7.13 mg/kg equiv. and 4.78 mg/kg equiv. were observed for seeds, seed screenings and for straw respectively. TRRs of 2.03 mg/kg equiv. and 0.054 mg/kg equiv. were observed for 22 day forage and 105 day forage respectively. In grass, trinexapac acid was the major identified component of 22 day forage (16% TRR), straw (22% TRR) and regrowth forage (10% TRR) and was also a major component of seeds (15% TRR) and seed screenings (13% TRR). Also observed in all matrices were CGA 275537 (9-17% TRR) and terephthalic acid (7–12% TRR) the latter metabolite only observed in grass.

Summary of plant metabolism

Parent compound was completely degraded and was not detectable (< 0.001/< 0.002 mg/kg) in any plant part of wheat, rapeseed and grass at harvest time. In rice only traces (0.001 and 0.003 mg/kg) were observed in straw and husks respectively.

Trinexapac acid was therefore the major metabolite which was present in all species and all plant parts at harvest. Sugar conjugates of trinexapac acid were hydrolysed in some crop parts to yield free acid which, in some cases, significantly increased the levels of trinexapac acid recovered. Trinexapac acid sugar conjugates accounted for an increase in trinexapac acid of 11.6% TRR in rice grain and 10% and 14% TRR in grass forage and straw, respectively.

Rotational Crops

Studies of residues in confined rotational crops have been submitted in which soil was treated at 350 g ai/ha, followed by soil aging at 30, 120 and 270 days. Representative succeeding crops of lettuce (leafy vegetable), radish (root vegetable) and wheat (cereal grain) were planted at the above intervals to determine whether trinexapac-ethyl residues or degradates appear in follow crops.

The uptake of residues by the rotational crops lettuce, radish and wheat planted or sown after several intervals after application of trinexapac-ethyl to bare ground was very low. No accumulation was observed. Residues of trinexapac-ethyl in the rotational crop RACs were below the LOQ (< 0.001 mg/kg). The residues of trinexapac acid and CGA 312753 (trans aconitic acid) were very close to or below the LOQ (< 0.001 – 0.002 mg/kg). The very limited uptake of radioactive material in succeeding crops clearly indicates the lack of systemic behaviour of trinexapac-ethyl. It was concluded that residues in rotational crops are negligible.

The Meeting received information on field rotational crop studies for trinexapac-ethyl which were conducted in both the USA and Switzerland.

In a study conducted in the USA in the 2004–2005 growing season, a 250 g/L EC formulation of trinexapac-ethyl was applied once as a broadcast spray to wheat at 203 g ai/ha. Radish, wheat and spinach were planted after three different plant back intervals (14, 30 and 45 days). The results showed that rotational crops sown 14, 30 and 45 days after application of trinexapac-ethyl to the target crop, are very unlikely to contain residues of trinexapac-ethyl as its main metabolite trinexapac acid, above the LOQ of 0.05 mg/kg.

A trial was conducted in Switzerland during 1989 to investigate residues of trinexapac-ethyl in succeeding crops, grown in soil previously treated with [^{14}C]cyclohexyl trinexapac-ethyl. A 250 g/L EC formulation of trinexapac-ethyl was applied once to bare soil at a rate of 150 g ai/ha. Treated plots were planted after four different time intervals (69, 119, 299 and 338 days after treatment). The crops investigated were lettuce, winter wheat, sugar beet and maize (corn).

The uptake of residues by the rotational crops lettuce, winter wheat, sugar beet and maize planted or sown after several intervals after application of trinexapac-ethyl to bare ground was therefore very low. No accumulation was observed. Residues of trinexapac-ethyl in the rotational crop RACs were below the LOQ (< 0.001 mg/kg) so no characterization was possible. The very limited uptake of radioactive material in succeeding crops clearly indicates the lack of systemic behaviour of trinexapac-ethyl. It was concluded that the residues situation in rotational crops is negligible.

The confined and field rotational crop studies suggest that residues of trinexapac acid are unlikely to occur in succeeding crops.

Methods of analysis

The Meeting received information on analytical methods suitable for the determination of residues of trinexapac acid in plant matrices and animal matrices. The methodology involves quantification of free trinexapac acid (plant and animal matrices) or quantification of both free and conjugated trinexapac acid with the inclusion of an acid hydrolysis step (plant matrices). The methods used are based on HPLC-MS/MS (LOQs of 0.01 or 0.05 mg/kg for trinexapac acid in plant matrices and 0.02 mg/kg for animal matrices (0.01 mg/kg for milk)) and HPLC-UV (LOQs of 0.02 mg/kg for trinexapac acid in plant matrices or 0.01 mg/kg in animal matrices (0.005 mg/kg for milk)).

Details of HPLC-UV methods for determining residues of parent trinexapac-ethyl have also been submitted (LOQs of 0.02 or 0.04 mg/kg).

Stability of pesticide residues in stored analytical samples

The Meeting received information on the freezer storage stability of trinexapac acid in plant and animal commodities.

Freezer storage stability studies indicate that trinexapac acid is stable for at least 24 months in wheat grain and rapeseed and up to 24 months in wheat straw and for at least 12 months in wheat

processed fractions. The stability of trinexapac acid in extracts of animal matrices was tested in the dairy cattle and laying hen feeding studies. No significant degradation of residues of trinexapac acid was observed in cattle matrices (83–121 days) or in poultry matrices (31–82 days).

The periods of storage stability studies cover the sample storage intervals of residue trials.

Definition of the residue

Animals

In the goat metabolism studies, no parent was observed in tissues and milk. Trinexapac acid accounted for 81–97% of the total residues in muscle and kidney, 31–84% of the TRRs in liver and fat and 46–85% of the TRRs in milk. In one study the metabolite CGA 113745 accounted for 6–16% TRR in liver, kidney and fat, but was not detected in either muscle or milk.

In the hen metabolism studies residues in muscle (lean meat), liver, kidney and fat samples of low and high-dosed hens were dominated by trinexapac acid (44–84% of TRR). Only in the skin (with subcutaneous fat) was the major portion of the total radioactivity (70–86%) not extractable. However trinexapac acid was the dominant metabolite in the extract (64–80% of the extractable radioactivity). The major metabolites identified in the organosoluble residue of egg whites were parent trinexapac-ethyl and trinexapac acid which accounted for 31% TRR and 20% TRR respectively.

The observed metabolic pathway of trinexapac-ethyl in livestock is comparable to that observed for the rat in which trinexapac acid is the major and only residue component of significance.

The ratio of trinexapac acid residues in muscle and fat observed in the livestock metabolism and feeding studies support the conclusion that trinexapac is not fat soluble. There is no evidence to suggest that there is significant potential for bioaccumulation in fat tissues.

It is considered that a residue definition of “Trinexapac (acid)” is appropriate for commodities of animal origin for compliance with MRLs (enforcement) and for risk assessment.

Plants

In the rice study trinexapac acid was the major identified component in rice grain (36% TRR) and rice husks (30% TRR). In the spring wheat study, trinexapac acid was the major identified component of wheat grain (28% TRR) and was the only identified component of both wheat husks and wheat straw observed at > 10% of the TRR. It was the major metabolite observed in rape meal, rape whole seeds and pods (19–31% TRR) and was also observed in oil and stalks (4–10% TRR). In grass, trinexapac acid was the major identified component of 22 day forage, straw, straw and regrowth forage (10–22% TRR) and was also a major component of seed screenings and seeds (13–15% TRR). Sugar conjugates of trinexapac acid were hydrolysed in some crop parts to yield free acid.

Trinexapac acid was present in all species and all plants parts at harvest and was generally the main component of the TRR. A definition of trinexapac acid is therefore considered suitable as the residue definition for compliance. Since conjugates of trinexapac acid were sometimes significant in edible commodities and are supposed to be of similar toxicity, the Meeting decided to include conjugates of trinexapac acid in the residue definition for risk to the acid assessment. A suitable method is available for determining residues of free and conjugated trinexapac acid.

It is therefore considered that a residue definition of “Trinexapac (acid)” is appropriate for plant commodities for compliance with MRLs (enforcement). It is considered that a residue definition of “Trinexapac and its conjugates, expressed as trinexapac acid” is appropriate for plant commodities for risk assessment.

Definition of the residue (for compliance with the MRL for plant and animal commodities and for estimation of dietary intake for animal commodities): Trinexapac (acid)

Definition of the residue (for estimation of dietary intake for plant commodities): Trinexapac and its conjugates, expressed as trinexapac acid

The residue is considered not fat soluble.

Results of supervised residue trials on crops

Supervised trials were available for the use of trinexapac on barley, wheat, oilseed rape and sugarcane.

In some studies (barley, wheat and sugarcane) residues have been determined as total trinexapac (includes free trinexapac acid and conjugates of trinexapac acid) while in other studies (wheat, sugarcane and rape seed) residues have been determined as trinexapac (free trinexapac acid only). In both cases trinexapac means trinexapac acid. For dietary intake assessment (risk assessment) residues expressed as total trinexapac acid, where available, have been considered. For maximum residue level estimation (compliance) residues expressed as trinexapac acid, where available, have been considered.

Product labels were available from Belgium, France, Germany and the United States of America.

Cereals - wheat (free trinexapac acid)

Residue trials were conducted in wheat in the USA according to the critical GAP in the USA (1 application at 0.123 kg ai/ha, 45-day PHI).

For the estimation of maximum residue levels the ranked order of residues of trinexapac acid in wheat grain from supervised trials according to the GAP in the USA was 0.10, 0.25, 0.32, 0.34, 0.35, 0.46, 0.49, 0.55, 0.55, 0.57, 0.77, 0.88, 0.91, 0.98, 0.99, 1.05, 1.35 and 1.95 mg/kg.

The Meeting estimated a maximum residue level for trinexapac acid in wheat of 3 mg/kg.

The Meeting recognized that wheat (spring wheat, winter wheat and durum wheat) and triticale, barley and oats have similar GAPs and normally show comparable residues after early treatment. As application was before flowering, the Meeting decided to extrapolate the MRL estimated for wheat grain to barley, oats and triticale.

Cereals - barley

Residue trials were conducted in barley in the USA according to the GAP in the USA (1 application at 0.123 kg ai/ha, 45-day PHI).

For dietary intake purposes the ranked order of total residues of trinexapac acid in barley grain from supervised trials according to the GAP in the USA was 0.03, 0.08, 0.44, 0.50, 0.52, 0.53, 0.60, 0.72, 0.76, 0.83, 1.0 and 1.2 mg/kg.

Cereals - wheat (total residues of trinexapac acid)

Residue trials were conducted in wheat in the USA according to the GAP in the USA (1 application at 0.123 kg ai/ha, 45-day PHI).

For dietary intake purposes the ranked order of total residues of trinexapac acid in wheat grain from supervised trials according to the GAP in the USA was 0.07, 0.15, 0.27, 0.31, 0.32, 0.40, 0.45, 0.47, 0.53, 0.77, 0.78, 0.82, 0.85, 0.99, 1.01, 1.14, 1.64 and 3.32 mg/kg.

The Meeting noted that the USA GAP is the same for barley and wheat. The Meeting noted that the populations of residues data for barley and wheat matching USA GAP resulted in similar distributions of residues for barley and wheat (e.g. medians do not differ by more than 5×). Given the similarity of the datasets (confirmed by the Mann-Whitney U test), the Meeting decided to combine the datasets for barley and wheat to give a larger dataset for estimation of dietary parameters for the purposes of determining an STMR residue level for barley grain and wheat grain.

For dietary intake purposes residues were 0.03, 0.07, 0.08, 0.15, 0.27, 0.31, 0.32, 0.40, 0.44, 0.45, 0.47, 0.50, 0.52, 0.53, 0.53, 0.60, 0.72, 0.76, 0.77, 0.78, 0.82, 0.83, 0.85, 0.99, 1.0, 1.01, 1.14, 1.2, 1.64 and 3.32 mg/kg.

The Meeting estimated an STMR of 0.57 mg/kg.

The Meeting recognized that wheat (spring wheat, winter wheat and durum wheat), triticale, barley and oats have similar GAPs and normally show comparable residues after early treatment. As application was before flowering, the Meeting decided to extrapolate the STMR estimated for barley grain and wheat grain to oats and triticale.

Grasses for sugar or syrup production - sugarcane (free trinexapac acid)

Residue trials were conducted in sugarcane in the USA according to the critical GAP in the USA (1 application at 0.347 kg ai/ha, 28-day PHI).

For the estimation of maximum residue levels the ranked order of residues of trinexapac acid in sugar cane from supervised trials according to the GAP in the USA was < 0.05, 0.06, 0.09, 0.12, 0.22, 0.23 and 0.25 mg/kg.

The Meeting estimated a maximum residue level for trinexapac acid in sugarcane of 0.5 mg/kg.

Grasses for sugar or syrup production—sugarcane (total residues of trinexapac acid)

Residue trials were conducted in sugarcane in the USA according to the critical GAP in the USA (1 application at 0.347 kg ai/ha, 28-day PHI).

For dietary intake purposes the ranked order of total residues of trinexapac acid in sugar cane from supervised trials according to the GAP in the USA was < 0.01, 0.04, 0.06, 0.08, 0.17 and 0.42 mg/kg.

The Meeting estimated an STMR value for trinexapac acid in sugarcane of 0.07 mg/kg.

Oilseeds - Rape

As conjugates of trinexapac acid were not significant in the submitted rape metabolism studies, residue levels from the submitted rape seed studies, which were determined as trinexapac only, have been considered suitable for estimation of a maximum residue level and also for estimation of dietary intake parameters.

Residue trials were conducted in winter rape (canola) in Germany according to the critical GAP in Germany for winter rape (1 application at 0.375 kg ai/ha).

For the estimation of maximum residue levels and for dietary purposes the ranked order of residues of trinexapac acid in winter rape seed from supervised trials according to GAP was 0.04, 0.10, 0.10, 0.13, 0.15, 0.15, 0.16, 0.24, 0.24, 0.26, 0.29, 0.31, 0.64, 0.64, 0.90 and 1.0 mg/kg.

The Meeting estimated maximum residue level and STMR values for trinexapac acid in rape seed of 1.5 and 0.24 mg/kg respectively.

Animal feeds

The Meeting received supervised trials data for barley hay and straw, wheat forage, hay and straw and rape seed forage.

Moisture content percentages for animal feeds have not been determined. The values from the FAO Manual on the Submission and Evaluation of Pesticides Residues Data for the feeds, have been used to convert wet weight or 'as received' residues values to dry weight residues values.

Forage - Wheat (residues of free and conjugated trinexapac acid)

Wheat forage was collected in the trials carried out in the USA according to GAP in the USA (1 application at 0.123 kg ai/ha).

For the calculation of the livestock animal dietary burden the ranked order of total residues in wheat forage samples collected 30 days after application (wet weight) at the GAP application rate was

0.02, 0.03, 0.04, 0.06, 0.07, 0.08, 0.08, 0.09, 0.10, 0.10, 0.12, 0.17, 0.17, 0.22, 0.23, 0.33, 0.38 and 0.94 mg/kg.

For the calculation of the livestock animal dietary burden the ranked order of total residues in wheat forage samples collected 30 days after application (dry weight) at the GAP application rate was 0.08, 0.12, 0.16, 0.24, 0.28, 0.32, 0.32, 0.36, 0.40, 0.40, 0.48, 0.68, 0.68, 0.88, 0.92, 1.32, 1.52 and 3.76 mg/kg.

The Meeting estimated median and highest residue values for trinexapac acid in wheat forage (dry weight) of 0.40 and 3.76 mg/kg respectively.

The Meeting recognized that wheat (spring wheat, winter wheat and durum wheat) and triticale, barley and oats have similar GAPs and normally show comparable residues after early treatment. The Meeting decided to extrapolate the dietary parameters estimated for wheat forage to barley, oats and triticale.

Hay and Straw - Barley and Wheat

Data for wheat hay and straw were collected in the trials carried out in the USA which approximate USA GAP (1 application at 0.123 kg ai/ha).

For the estimation of maximum residue levels the ranked order of residues in wheat hay samples collected 30 days after application (wet weight) at the GAP application rate was < 0.05, < 0.05, < 0.05, 0.05, 0.06, 0.07, 0.07, 0.08, 0.08, 0.09, 0.11, 0.11, 0.13, 0.15, 0.18, 0.19, 0.19 and 0.75 mg/kg.

The ranked order of residues in wheat hay samples converted to dry weight basis at the GAP application rate was < 0.06, < 0.06, < 0.06, 0.06, 0.07, 0.08, 0.08, 0.09, 0.09, 0.10, 0.13, 0.13, 0.15, 0.17, 0.20, 0.22, 0.22 and 0.85 mg/kg.

For the estimation of maximum residue levels the ranked order of residues in wheat straw samples collected 45 days after application (wet weight) at the GAP application rate was < 0.05, < 0.05, < 0.05, < 0.05, < 0.05, < 0.05, < 0.05, < 0.05, < 0.05, 0.06, 0.06, 0.07, 0.07, 0.08, 0.10, 0.11 and 0.12 mg/kg.

The ranked order of residues in wheat straw samples (dry weight) at the GAP application rate was < 0.06, < 0.06, < 0.06, < 0.06, < 0.06, < 0.06, < 0.06, < 0.06, < 0.06, < 0.06, 0.07, 0.07, 0.08, 0.08, 0.09, 0.11, 0.13 and 0.14 mg/kg.

The Meeting used the wheat hay data for the free trinexapac acid to estimate a maximum residue level in wheat straw and fodder (dry) of 0.9 mg/kg. The Meeting recognized that wheat (spring wheat, winter wheat and durum wheat), triticale, barley and oats have similar GAPs and normally show comparable residues after early treatment. It was therefore decided to apply the maximum residue level recommended for trinexapac acid on wheat straw and fodder (dry) to barley, oats and triticale.

For the calculation of the livestock animal dietary burden the ranked order of total residues in barley hay samples collected 30 days after application (wet weight) at the GAP application rate was < 0.01, 0.03, 0.05, 0.10, 0.13, 0.15, 0.17, 0.18, 0.25, 0.33, 0.40 and 0.48 mg/kg.

The ranked order of total residues in barley hay samples converted to a dry weight basis at the GAP application rate was < 0.011, 0.03, 0.06, 0.11, 0.15, 0.17, 0.19, 0.20, 0.28, 0.38, 0.45 and 0.55 mg/kg.

For the calculation of the livestock animal dietary burden the ranked order of total residues in barley straw samples collected 45 days after application (wet weight) at the GAP application rate was < 0.01, 0.02, 0.07, 0.08, 0.08, 0.09, 0.11, 0.12, 0.14, 0.17, 0.20 and 0.24 mg/kg.

The ranked order of total residues in barley straw samples converted to a dry weight basis at the GAP application rate was 0.01, 0.02, 0.08, 0.09, 0.09, 0.10, 0.12, 0.13, 0.16, 0.19, 0.22 and 0.27 mg/kg.

For the calculation of the livestock animal dietary burden the ranked order of total residues in wheat hay samples collected 30 days after application (wet weight) at the GAP application rate was 0.03, 0.04, 0.04, 0.06, 0.09, 0.11, 0.11, 0.14, 0.17, 0.19, 0.24, 0.30, 0.31, 0.41, 0.50, 0.59, 0.78 and 1.18 mg/kg.

The ranked order of total residues in wheat hay samples collected 30 days after application (dry weight) at the GAP application rate was 0.03, 0.05, 0.05, 0.07, 0.10, 0.13, 0.13, 0.16, 0.19, 0.22, 0.27, 0.34, 0.35, 0.47, 0.57, 0.67, 0.89 and 1.34 mg/kg.

For the calculation of the livestock animal dietary burden the ranked order of total residues in wheat straw samples collected 45 days after application (wet weight) at the GAP application rate was 0.01, 0.03, 0.04, 0.04, 0.06, 0.09, 0.11, 0.11, 0.15, 0.15, 0.17, 0.20, 0.23, 0.28, 0.33, 0.46, 0.59 and 0.60 mg/kg.

The ranked order of total residues in wheat straw samples collected 45 days after application (dry weight) at the GAP application rate was 0.01, 0.03, 0.05, 0.05, 0.07, 0.10, 0.13, 0.13, 0.17, 0.17, 0.19, 0.23, 0.26, 0.32, 0.38, 0.52, 0.67 and 0.68 mg/kg.

The Meeting noted that the USA GAP is the same for barley and wheat. The Meeting also noted that the populations of residues data for barley and wheat hay matching USA GAP gave higher residues than the straw and resulted in similar distributions of residues (e.g., medians do not differ by more than 5×). Given the similarity of the datasets (confirmed by the Mann-Whitney U test), the Meeting decided to combine the datasets for barley and wheat hay (dry weight) to give a larger dataset for estimation of dietary parameters for the purposes of determining median and highest residue levels for barley straw and fodder (dry) and wheat straw and fodder (dry).

For the calculation of the livestock animal dietary burden the ranked order of total residues of trinexapac acid in barley and wheat hay (dry weight) collected 30 days after application (dry weight) from supervised trials according to the GAP in the USA was < 0.011, 0.03, 0.03, 0.05, 0.05, 0.06, 0.07, 0.10, 0.11, 0.13, 0.13, 0.15, 0.16, 0.17, 0.19, 0.19, 0.20, 0.22, 0.27, 0.28, 0.34, 0.35, 0.38, 0.45, 0.47, 0.55, 0.57, 0.67, 0.89 and 1.34 mg/kg.

The Meeting used the barley and wheat hay data to estimate median and highest residue values for trinexapac acid in barley straw and fodder (dry) and wheat straw and fodder (dry) of 0.19 and 1.34 mg/kg respectively, based on the combined dataset for barley and wheat hay.

The Meeting recognized that wheat (spring wheat, winter wheat and durum wheat) and barley have similar GAPs to oats and triticale and normally show comparable residues after early treatment. The Meeting decided to extrapolate the dietary parameters estimated for wheat and barley to oats and triticale.

Rape seed forage

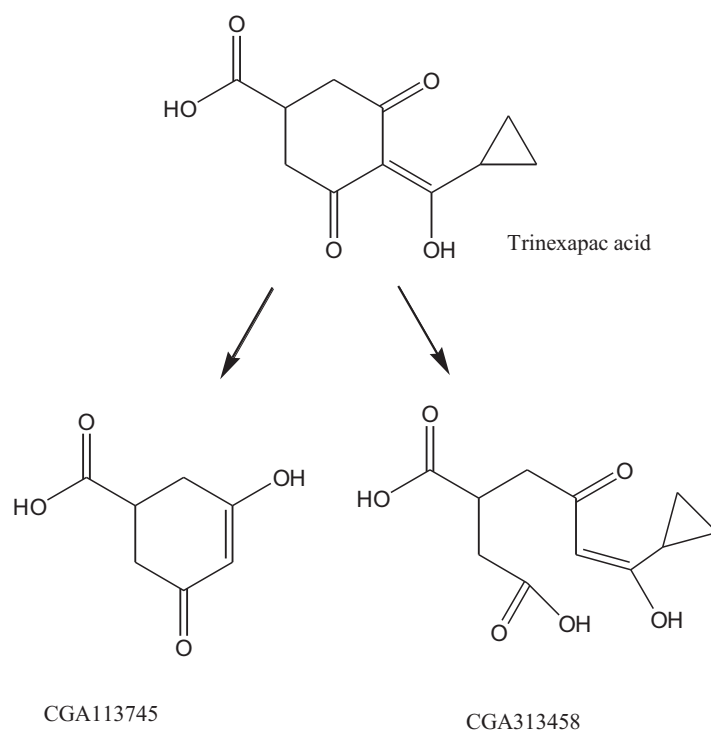
In four trials conducted according to GAP in Germany, residues in rape remaining plant type (forage) at PHIs from 49–68 days were < 0.04, < 0.04, < 0.04 and 0.04 mg/kg.

The Meeting agreed that four trials according to GAP were not sufficient to estimate a highest residue for trinexapac in rape forage.

Fate of residues during processing

High temperature hydrolysis of residues of trinexapac-ethyl and trinexapac acid under varying conditions have been reported. The [¹⁴C]-labelled compounds were dissolved in aqueous buffer; at pH 4 and heated for 20 or 25 minutes at 90 °C to simulate pasteurisation, at pH 5 and refluxed at 100 °C for 60 minutes to simulate baking, brewing and boiling and at pH 6 at about 120 °C in an autoclave for 20 minutes to simulate sterilisation. Trinexapac-ethyl was not degraded. Trinexapac acid underwent limited degradation and was the major component of the radioactive material at the end of the hydrolysis reactions (51–59%). It degraded into the compounds CGA113745 (10–12%) and CGA313458 (16–21%).

CGA113745 was observed as a goat metabolite in one metabolism study, while CGA313458 was observed as a rapeseed and rice metabolite. Based on a structural assessment of CGA 113745 and CGA 313458 and the estimated levels of chronic dietary intake, the Meeting concluded that these metabolites are unlikely to pose a dietary risk.



Hydrolysis of trinexapac acid under processing conditions

The Meeting also received processing studies for barley, wheat, sugarcane and rape seed. The table below summarizes STMR-P values calculated on the determined processing factors. In addition the following maximum residue levels were estimated.

Barley

Based on the total trinexapac processing factor of 1.9 for barley bran (in the absence of a trinexapac processing factor) and the barley grain MRL of 3 mg/kg, the calculated expected highest residues in barley bran are 5.7 mg/kg. The Meeting estimated an MRL for trinexapac in barley bran of 6 mg/kg.

Wheat

Based on the trinexapac processing factor of 2.3 for wheat bran and the wheat grain MRL of 3 mg/kg the calculated expected highest residues in wheat bran are 6.9 mg/kg. The Meeting estimated an MRL for trinexapac in wheat bran of 8 mg/kg.

The processing factors derived from the processing studies and the resulting recommendations for STMR-Ps (and maximum residue levels) are summarized in the table below.

Processing Factors from the Processing of Raw Agricultural Commodities (RACs) with Field-Incurred Residues from Foliar Treatment with Trinexapac-ethyl

RAC	Processed Commodity	Best Estimate Processing Factor	RAC MRL	RAC STMR	Processed Commodity STMR-P
Barley	Pearled barley	1.2	3	0.57	0.68
	Bran	1.9			1.08
	Flour	0.43			0.25
Wheat	Aspirated Grain Fractions	0.55	3	0.57	0.31

RAC	Processed Commodity	Best Estimate Processing Factor	RAC MRL	RAC STMR	Processed Commodity STMR-P
	Bran	1.9			1.08
	Flour	0.43			0.25
	Middlings	0.55			0.31
	Shorts	0.46			0.26
	Germ	1.1			0.63
Sugarcane	Molasses	5.8	0.5	0.07	0.40
	Refined sugar	0.15			0.01
Rapeseed	Press cake	1.2	1.5	0.24	0.32
	Refined oil	0.05			0.01

Except for the rapeseed study (in which processing factors were determined based on residues of trinexapac), processed commodity STMR-Ps were calculated on the basis of the total trinexapac acid processing factors.

Residues in animal commodities

Estimated maximum and mean dietary burdens of farm animals

Dietary burden calculations for beef cattle and dairy cattle and poultry are provided below. The dietary burdens were estimated using the OECD diets listed in Appendix IX of the 2009 edition of the FAO Manual.

Potential cattle feed items include: wheat, barley, oat and triticale grain, straw, forage, hay and silage, wheat milled by-products (bran), wheat aspirated grain fractions, barley bran fractions, sugarcane molasses and bagasse and rape forage and rape seed meal.

Summary of livestock dietary burden for trinexapac (ppm of dry matter diet)

	US-Canada		EU		Australia		Japan	
	max	mean	max	mean	max	mean	max	mean
Beef cattle	0.98	0.87	1.76	0.82	3.76 ^a	0.88	0.97	0.97 ^c
Dairy cattle	1.76	0.77	1.76	0.76	3.76 ^b	0.86 ^d	1.00	0.83

^a Highest maximum beef or dairy cattle dietary burden suitable for HR and MRL estimates for mammalian meat

^b Highest maximum dairy cattle dietary burden suitable for HR and MRL estimates for mammalian milk

^c Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat

^d Highest mean dairy cattle dietary burden suitable for STMR estimates for mammalian milk

Potential poultry feed items include: wheat, barley, oat and triticale grain, straw, forage, hay and silage, wheat milled by-products (bran), wheat aspirated grain fractions, barley bran fractions, sugarcane molasses and bagasse and rape forage and rape seed meal.

Summary of poultry dietary burden for trinexapac (ppm of dry matter diet)

	US-Canada		EU		Australia		Japan	
	max	mean	max	mean	max	mean	max	mean
Poultry Broiler	0.94	0.94	0.70	0.70	0.34	0.34	0.13	0.13
Poultry Layer	0.94	0.94 ^b	1.08 ^a	0.76	0.34	0.34	0.37	0.37

^a Highest maximum poultry dietary burden suitable for HR and MRL estimates for poultry meat and eggs

^b Highest maximum poultry dietary burden suitable for STMR estimates for poultry meat and eggs

Farm Animal Dietary Burden

The Meeting received a lactating dairy cow feeding study which provided information on residues of trinexapac acid arising in tissues and milk when dairy cows were dosed for 29–30 days, at target feeding levels equivalent to 0, 2, 6 and 20 ppm trinexapac acid in the diet.

No quantifiable residues of trinexapac acid were observed in milk at the 0, 2 and 6 ppm dose groups. Residues in the 20 ppm dose group ranged from < 0.005–0.011 mg/kg. Residues reached a plateau after one day.

No quantifiable residues of trinexapac acid were observed in the tissues of the control cow. In the lowest and mid-range dose groups (2 and 6 ppm), no quantifiable residues were detected in muscle, liver and fat, although residues slightly above LOQ (0.02 mg/kg) were observed in kidney (highest (mean in brackets) were 0.03 (0.03) and 0.05 (0.04) mg/kg respectively). No quantifiable residues were detected in muscle in the 20 ppm dose group while the highest residues (mean in brackets) observed in liver, kidney and fat in the 20 ppm dose group were 0.03 (0.03), 0.29 (0.17) and 0.02 (< 0.02) mg/kg respectively.

The Meeting also received information on the residue levels arising in tissues and eggs when laying hens were dosed with trinexapac acid for 28 days, at feeding levels equivalent to 3.7, 10 and 37 ppm in the diet.

No quantifiable residues of trinexapac acid were observed in eggs at any feeding level except in the 37 ppm dose group at 28 days (highest and mean residues were 0.01 mg/kg).

No residues of trinexapac acid above LOQ (0.01 mg/kg) were detected in any muscle (breast and thigh muscle) sample from any treatment group. No residues of trinexapac acid above LOQ were detected in any liver sample from any treatment group apart from the highest dose group (highest and mean residues were 0.02 mg/kg). No residues of trinexapac acid above LOQ were detected in any fat sample from any treatment group apart from the highest dose group (highest and mean residues were 0.03 mg/kg). Highest (mean) residues of trinexapac acid in kidney were 0.08 (0.06), 0.05 (0.04) and 0.54 (0.45) mg/kg in the lowest to highest dose groups respectively.

*Animal commodity maximum residue levels**Cattle- STMR, HR and MRLs*

For highest residue level estimation, the high residues in the cattle tissues were calculated by interpolating the maximum dietary burden for beef cattle (3.76 ppm) between the relevant feeding levels (2 and 6 ppm) in the dairy cow feeding study and using the highest tissue concentrations from individual animals within those feeding groups. For highest residue level estimation, the high residues in the cattle milk were calculated by interpolating the maximum dietary burden for dairy cattle (3.76 ppm) with the lowest feeding level (2 and 6 ppm) in the dairy cow feeding study and using the highest mean milk concentrations from those feeding groups.

The STMR values for the tissues were calculated by extrapolating the mean dietary burden for beef cattle (0.97 ppm) with the 2 ppm feeding level from the dairy cow feeding study and using the mean tissue concentrations from that feeding group. The STMR values for the milk were calculated by extrapolating the mean dietary burden for dairy cattle (0.86 ppm) with the 2 ppm feeding level from the dairy cow feeding study and using the mean milk concentrations from that feeding group.

Trinexapac Feeding Study	Feed Level (ppm) for milk residues	Residues (mg/kg) in milk	Feed Level (ppm) for tissue residues	Residues (mg/kg)			
				Muscle	Liver	Kidney	Fat
HR Determination (beef or dairy cattle)							
Feeding Study	2	< 0.005	2	< 0.02	< 0.02	0.03	< 0.02
	6	< 0.005	6	< 0.02	< 0.02	0.05	< 0.02
Dietary burden and estimate of highest	3.76	< 0.005	3.76	< 0.02	< 0.02	0.04	< 0.02

residue							
STMR Determination (beef or dairy cattle)							
Feeding Study	2	< 0.005	2	< 0.02	< 0.02	0.03	< 0.02
Dietary burden and estimate of highest residue	0.86	< 0.0022	0.97	< 0.010	< 0.010	0.015	< 0.010

The Meeting estimated the following STMR values: milk 0 mg/kg; muscle 0 mg/kg; edible offal (based on kidney) 0.015 mg/kg and fat 0 mg/kg.

The Meeting estimated the following maximum residue levels: milk 0.005(*) mg/kg; meat (mammalian except marine mammals) 0.01(*) mg/kg, edible offal (based on kidney) 0.1 mg/kg and mammalian fats (except milk fats) 0.01(*) mg/kg.

Poultry - STMR, HR and MRLs

For highest residue level estimation, the high residues in the hen tissues and eggs were calculated by extrapolating the maximum dietary burden (1.08 ppm) with the lowest feeding level (3.7 ppm) in the laying hen feeding study and using the highest tissue concentrations from individual animals within that feeding group and using the highest mean egg concentration from that feeding group.

The STMR values for the tissues and eggs were calculated by extrapolating the mean dietary burden (0.94 ppm) with the lowest feeding level (3.7 ppm) from the poultry feeding study and using the mean tissue and egg concentrations from that feeding group.

Trinexapac Feeding Study	Feed Level (ppm) for egg residues	Residues (mg/kg) in egg	Feed Level (ppm) for tissue residues	Residues (mg/kg)			
				Muscle	Liver	Kidney	Fat
HR Determination (poultry broiler or layer)							
Feeding Study	3.7	< 0.01	3.7	< 0.01	< 0.01	0.08	< 0.01
Dietary burden and estimate of highest residue	1.08	< 0.003	1.08	< 0.003	< 0.003	0.023	< 0.003
STMR Determination (poultry broiler or layer)							
Feeding Study	3.7	< 0.01	3.7	< 0.01	< 0.01	0.06	< 0.01
Dietary burden and estimate of highest residue	0.94	< 0.0025	0.94	< 0.0025	< 0.0025	0.015	< 0.0025

The Meeting estimated the following STMR values: egg 0 mg/kg; muscle 0 mg/kg; edible offal (based on kidney) 0.015 mg/kg and fat 0 mg/kg.

The Meeting estimated the following maximum residue levels: eggs 0.01(*) mg/kg; poultry meat 0.01(*) mg/kg, poultry edible offal (based on kidney) 0.05 mg/kg and poultry fats 0.01(*) mg/kg.

RECOMMENDATIONS

Definition of the residue (for compliance with the MRL for plant and animal commodities and for estimation of dietary intake for animal commodities): Trinexapac (acid)

Definition of the residue (for estimation of dietary intake for plant commodities): *Trinexapac and its conjugates, expressed as trinexapac acid*.

The Meeting estimated the maximum residue levels and STMR values shown below.

Commodity		MRL, mg/kg	STMR or STMR-P, mg/kg	HR or HR-P, mg/kg
CCN	Name			
GC 0640	Barley	3	0.57	
	Barley bran	6	1.08	
AS 0640	Barley straw and fodder, dry (dry weight)	0.9	0.19	1.34
MO 0105	Edible offal (mammalian)	0.1	0.015	
PE 0112	Eggs	0.01 (*)	0	
MF 0100	Mammalian fats (except milk fats)	0.01 (*)	0	
MM 0095	Meat (from mammals other than marine mammals)	0.01 (*)	0	
ML 0106	Milks	0.005 (*)	0	
GC 0647	Oats	3	0.57	
AS 0647	Oat straw and fodder, dry (dry weight)	0.9	0.19	1.34
PF 0111	Poultry fats	0.01 (*)	0	
PM 0110	Poultry meat	0.01 (*)	0	
PO 0111	Poultry, edible offal of	0.05	0.015	
SO 0495	Rape seed	1.5	0.24	
GS 0659	Sugar cane	0.5	0.07	
GC 0653	Triticale	3	0.57	
AS 0653	Triticale straw and fodder, dry (dry weight)	0.9	0.19	1.34
GC 0654	Wheat	3	0.57	
CM 0654	Wheat bran	8	1.08	
AS 0654	Wheat straw and fodder, dry (dry weight)	0.9	0.19	1.34
	Barley flour		0.25	
	Barley forage (dry weight)		0.40	3.76
AF 0647	Oat forage (green) (dry weight)		0.40	3.76
	Pearled barley		0.68	
	Rape seed refined oil		0.01	
DM 0659	Sugar cane molasses		0.40	
	Triticale forage (dry weight)		0.40	3.76

Commodity		MRL, mg/kg	STMR or STMR-P, mg/kg	HR or HR-P, mg/kg
CCN	Name			
	Wheat aspirated grain fractions		0.31	
CF 1211	Wheat flour		0.25	
	Wheat forage (dry weight)		0.40	3.76
CF 1210	Wheat germ		0.63	

DIETARY RISK ASSESSMENT

Long-term intake

The evaluation of trinexapac has resulted in recommendations for MRLs and STMRs for raw and processed commodities. Consumption data were available for 36 food commodities and were used in the dietary intake calculation. The results are shown in Annex 3. The International Estimated Daily Intakes for the 13 GEMS/Food regional diets, based on estimated STMRs were in the range 0–1% of the maximum ADI of 0.3 mg/kg bw (Annex 3).

The Meeting concluded that the long-term intake of residues of trinexapac from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The International Estimated Short-term Intake (IESTI) for trinexapac was not calculated, as it was not considered necessary to establish an ARfD.

The Meeting concluded that the short-term intake of residues of trinexapac from uses that have been considered by the JMPR is unlikely to present a public health concern.

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CGA163935_50036	Mayer, T	2010	Trinexapac-ethyl—Magnitude of the residues in or on wheat Final report. Syngenta Crop Protection, Inc., Greensboro, USA. Report Number T003605-07. Syngenta File No CGA163935_50036. Unpublished.

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CGA163935_50024	Quistad, G and Kovatchev, A	2010	[¹⁴ C] Trinexapac-ethyl—Uptake and metabolism in confined rotational crops Final report. Syngenta Crop Protection, Inc., Greensboro, USA PTRL West, Inc., Hercules, USA. Report Number 1802W. Syngenta File No CGA163935_50024. Unpublished.
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Annex I. Reports and other documents resulting from previous Joint Meetings of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO CORE ASSESSMENT GROUP on Pesticide Residues

1. Principles governing consumer safety in relation to pesticide residues. Report of a meeting of a WHO Expert Committee on Pesticide Residues held jointly with the FAO Panel of Experts on the Use of Pesticides in Agriculture. FAO Plant Production and Protection Division Report, No. PL/1961/11; WHO Technical Report Series, No. 240, 1962.
2. Evaluation of the toxicity of pesticide residues in food. Report of a Joint Meeting of the FAO Committee on Pesticides in Agriculture and the WHO Expert Committee on Pesticide Residues. FAO Meeting Report, No. PL/1963/13; WHO/Food Add./23, 1964.
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4. Evaluation of the toxicity of pesticide residues in food. FAO Meeting Report, No. PL/1965/10/1; WHO/Food Add./27.65, 1965.
5. Evaluation of the hazards to consumers resulting from the use of fumigants in the protection of food. FAO Meeting Report, No. PL/1965/10/2; WHO/Food Add./28.65, 1965.
6. Pesticide residues in food. Joint report of the FAO Working Party on Pesticide Residues and the WHO Expert Committee on Pesticide Residues. FAO Agricultural Studies, No. 73; WHO Technical Report Series, No. 370, 1967.
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The annual Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group on Pesticide Residues was held in Geneva, Switzerland, from 17 to 26 September 2013. The FAO Panel of Experts had met in preparatory sessions from 6 to 10 September. The Meeting was held in pursuance of recommendations made by previous Meetings and accepted by the governing bodies of FAO and WHO that studies should be undertaken jointly by experts to evaluate possible hazards to humans arising from the occurrence of pesticide residues in foods. During the meeting the FAO Panel of Experts was responsible for reviewing pesticide use patterns (use of good agricultural practices), data on the chemistry and composition of the pesticides and methods of analysis for pesticide residues and for estimating the maximum residue levels that might occur as a result of the use of the pesticides according to good agricultural use practices. The WHO Core Assessment Group was responsible for reviewing toxicological and related data and for estimating, where possible and appropriate, acceptable daily intakes (ADIs) and acute reference doses (ARfDs) of the pesticides for humans. This report contains information on ADIs, ARfDs, maximum residue levels, and general principles for the evaluation of pesticides. The recommendations of the Joint Meeting, including further research and information, are proposed for use by Member governments of the respective agencies and other interested parties.

E-ISBN 978-92-5-108245-4 ISSN 0259-2517



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I3689E/1/03.14