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Pesticide residues in food 1998

Joint FAO/WHO Meeting on Pesticide Residues

EVALUATIONS

1998

PART I - RESIDUES

Rome, 1999

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* First evaluation

As a result of the size of the Residue Evaluations of the 1998 JMPR it was necessary to print the monographs in two separate volumes

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ABBREVIATIONS WHICH MAY BE USED

(Well-known abbreviations in general use are not included)

Ache	acetylcholinesterase
ADI	acceptable daily intake
AFI(D)	alkali flame-ionization (detector)
ai	active ingredient
ALAT	alanine aminotransferase
AR	applied radioactivity
ASAT	aspartate aminotransferase
BBA	Biologische Bundesanstalt für Land- und Forstwirtschaft
Bw	body weight
BOD	biological oxygen demand
CA	Chemical Abstracts
CAS	Chemical Abstracts Services
CCN	Codex Classification Number (this may refer to classification numbers for compounds or for commodities).
CCPR	Codex Committee on Pesticide Residues
CCRVDF	Codex Committee on Residue of Veterinary Drugs in Food
ChE	cholinesterase
CI	chemical ionization
CNS	central nervous system
cv	coefficient of variation
CXL	Codex Maximum Residue Limit (Codex MRL). See MRL.
DFG	Deutsche Forschungsgemeinschaft
DL	racemic (optical configuration, a mixture of dextro- and laevo-)
DP	dustable powder
DS	powder for dry seed treatment
DT-50	time for 50% decomposition (i.e. half-life)
DT-90	time for 90% decomposition
EBDC	ethylenebis(dithiocarbamate)
EC	(1) emulsifiable concentrate (2) electron-capture [chromatographic detector]
ECD	electron-capture detector
EI	electron-impact
EMDI	estimated maximum daily intake
EPA	Environmental Protection Agency
ERL	extraneous residue limit
ETU	ethylenethiourea
F_1	filial generation, first
F_2	filial generation, second
f.p.	freezing point
FAO	Food and Agriculture Organization of the United Nations
FDA	Food and Drug Administration
FI(D)	flame-ionization (detector)
FP(D)	flame-photometric (detector)
g (not gm)	gram
µg	microgram

GAP	good agricultural practice(s)
GC-MS	gas chromatography - mass spectrometry
GC-MSD	gas chromatography with mass-selective detection
G.I.	gastrointestinal
GL	guideline level
GLC	gas-liquid chromatography
GLP	good laboratory practice
GPC	gel-permeation chromatograph or chromatography
GSH	glutathione
h (not hr)	hour(s)
ha	hectare
Hb	haemoglobin
hl	hectolitre
HPLC	high-performance liquid chromatography
HPLC-MS	high-performance liquid chromatography - mass spectrometry
IEDI	International Estimated Daily Intake
i.d.	internal diameter
i.m.	intramuscular
i.p.	intraperitoneal
IPCS	International Programme on Chemical Safety
IR	infrared
IRDC	International Research and Development Corporation (Mattawan, Michigan, USA)
i.v.	intravenous
JMPR	Joint FAO/WHO Meeting on Pesticide Residues (Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group
LC	liquid chromatography
LC_{50}	lethal concentration, 50%
LC-MS	liquid chromatography - mass spectrometry
LD_{50}	lethal dose, median
LOAEL	lowest observed adverse effect level
LOD	limit of determination (see also "*" at the end of the Table)
LSC	liquid scintillation counting or counter
M	molar
µm	micrometre (micron)
MFO	mixed function oxidase
min (no stop)	minute(s)
MLD	minimum lethal dose
mo (not mth.)	month(s)
MRL	Maximum Residue Limit. MRLs include draft MRLs and Codex MRLs (CXLs). The MRLs recommended by the JMPR on the basis of its estimates of maximum residue levels enter the Codex procedure as draft MRLs. They become Codex MRLs when they have passed through the procedure and have been adopted by the Codex Alimentarius Commission.
MRLM	Maximum Residue Limit for Monitoring (*See* explanation in preamble to Annex I).
MS	mass spectrometry
MSD	mass-selective detection or detector
MTD	maximum tolerated dose
n (not *n*)	normal (defining isomeric configuration)
NCI	National Cancer Institute (USA)
NEDI	National Estimate of Dietary Intake
NMR	nuclear magnetic resonance

NOAEL	no-observed-adverse-effect level
NOEL	no-observed-effect level
NP(D)	nitrogen-phosphorus (detector)
NTE	neuropathy target esterase
OECD	Organization for Economic Co-operation and Development
OP	organophosphorus pesticide
PHI	pre-harvest interval
ppm	parts per million. (Used only with reference to the concentration of a pesticide in an experimental diet. In all other contexts the terms mg/kg or mg/l are used).
PT	prothrombin time
PTDI	provisional tolerable daily intake. (See 1994 report, Section 2.3, for explanation)
PTT	partial thromboplastin time
PTU	propylenethiourea
RAC	raw agricultural commodity
RBC	red blood cell
r.d.	relative density. (Formerly called specific gravity)
Rfd	acute reference dose
RSD	relative standard deviation
s.c.	subcutaneous
SC	suspension concentrate (= flowable concentrate)
SD	standard deviation
SE	standard error
SG	water-soluble granule
SL	soluble concentrate
SP	water-soluble powder
sp./spp.	species (only after a generic name)
SPE	solid-phase extraction
STMR	supervised trials median residue
t	tonne (metric ton)
T_3	tri-iodothyronine
T_4	thyroxine
TADI	Temporary Acceptable Daily Intake
tert	tertiary (in a chemical name)
TLC	thin-layer chromatography
TMDI	Theoretical Maximum Daily Intake
TMRL	Temporary Maximum Residue Limit
TRR	total radioactive residue
TSH	thyroid-stimulating hormone (thyrotropin)
UDMH	1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine)
USEPA	United States Environmental Protection Agency
USFDA	United States Food and Drug Administration
UV	ultraviolet
WG	water-dispersible granule
WHO	World Health Organization
WP	wettable powder
<	less than
≤	less than or equal to

$>$	greater than
$\geq$	greater than or equal to

USE OF JMPR REPORTS AND EVALUATIONS BY REGISTRATION AUTHORITIES{TC "OF JMPR REPORTS AND EVALUATIONS BY REGISTRATION AUTHORITIES"}

The summaries and evaluations contained in this book are, in most cases, based on unpublished proprietary data submitted for the purpose of the JMPR assessment. 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 who submitted the data for 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.

INTRODUCTION

The report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group (JMPR), held in Rome, 21-30 September 1998, contains a summary of the evaluations of residues in foods of the various pesticides considered as well as information on the general principles followed by the Meeting. The present document contains summaries of the residues data considered, together with the recommendations made.

The Evaluations are issued in two parts:

Part I: Residues (by FAO)
Part II: Toxicology (by WHO)

For those interested in both aspects of pesticide evaluation, not only both parts but also the reports containing summaries of residue and toxicological considerations will be available. Special attention is drawn to Annex I containing updated ADIs, recommendations for MRLs, and STMR levels which also appears in full as part of the report of the Meeting.

Some o the compounds considered at the Meeting have been previously evaluated and reported on in earlier publications. In general only new information is summarized in the relevant monographs and reference is made to previously published evaluations, which should also be consulted. In the case of older compounds which are re-evaluated as part of the Periodic Review Programme of the CCPR a review of all available data, including data which may have previously been submitted, is carried out. Compounds evaluated for the first time are indicated by single asterisks and those evaluated in the CCPR Periodic Review Programme by double asterisks in the Table of Contents.

The name of the compound appearing as the title of each monograph is followed by its Codex Classification Number in parentheses.

References to previous Reports and Evaluations of Joint Meetings are listed in Annex II.

Acknowledgements

The monographs in these Evaluations were prepared by the following participants in the 1998 JMPR for the FAO Panel of Experts on Pesticide Residues in Food and the Environment:
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Note: Any comment on residues in food and their evaluation should be addressed to the:
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00100 Rome, Italy

AMITROLE (079)

EXPLANATION

Amitrole was first considered by the JMPR in 1974. It was re-evaluated in 1993 within the CCPR Periodic Review Programme, and a temporary ADI was allocated. A full ADI was allocated in 1997. No MRLs have been established, but it is stated that uses of amitrole should be restricted to those where residues in food would not be expected to occur. The 1993 Meeting recommended a further note that "A realistic limit of determination for the general monitoring of amitrole would be 0.05 mg/kg". This evaluation is within the CCPR Periodic Review Programme. New data on metabolism in rats and environmental fate, in addition to residue trials on apples, pears, peaches and grapes were reported by the manufacturer. The governments of The Netherlands and Poland provided information on analytical methods and national MRLs.

IDENTITY

ISO common name: amitrole

Chemical names:

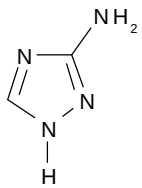
IUPAC: 1*H*-1,2,4-triazol-3-ylamine
CA: 1*H*-1,2,4-triazol-3-amine

CAS Registry. No.: 61-82-5

CIPAC No.: 90

Synonyms: aminotriazole (common name in France and Spain)

Structural formula



Molecular formula: $C_2H_4N_4$

Molecular weight: 84.08

Physical and chemical properties

<u>Pure active ingredient</u>

Appearance: white to yellowish crystalline powder
Vapour pressure: 3.3×10^{-5} Pa at 20°C.

Melting point: 155°C

Octanol/water partition coefficient: log P_{ow} = -0.93 at pH 4.5, -0.77 at pH 7.1, -0.80 at pH 9.9

Solubility: in water at 20°C: >1384 g/l at pH 4.0 (amitrole chlorohydrate)

	264 g/l at pH 7.0 261 g/l at pH 10.0
Specific gravity:	1.54 g/cm^3 at 20°C
Hydrolysis:	indefinitely stable in sterile water.
Photolysis:	photolytically stable.
Dissociation constant:	pK_a = 4.0; other values (for pH <2 and pH >9) are still under evaluation.
Thermal stability:	stable up to 269°C

Technical material

Minimum purity:	90%
Main impurities:	7 impurities (6 identified), typically amounting 0.2 to 1.9%. The most abundant impurities are formyl-amitrole (maximum 1.9%) and 3,4-diamino-amitrole (maximum 1.1%). All other impurities are <1%.

Solubility in organic solvents at 20°C:

acetone:	2.9-3.3 g/l
1,2-dichloroethane:	<0.1 g/l
ethyl acetate:	1 g/l
n-heptane:	<<0.1 g/l
p-xylene:	<<0.1 g/l
methanol:	133-160 g/l

Melting range: 150 - 153°C

Stability: stable under storage conditions (≥2 years)

Formulations

As of February 1990, two types of product were commercialized: soluble concentrates (SL) containing 200 g/l to 500 g/l amitrole and water-soluble powders (SP) containing 50% to 90% amitrole. A water-soluble granule (SG) containing 86% amitrole is presently under registration in many countries world-wide.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Four studies of the metabolism of [5-^{14}C]amitrole in rats were carried out. In all cases, amitrole was the main elimination product in the urine, and its metabolism dose-related. Up to three metabolites were detected. The proportion of metabolites in the urine after 24 hours was higher in rats dosed at low than at high levels (Fang *et al*. 1966). Within 23 hours of dosing the amount and proportion of amitrole excreted in the urine had declined markedly (Table 1).

Table 1. Radioactivity in the urine of rats after oral doses of [5-^{14}C]amitrole.

Time after dose (hours)	Amitrole		Metabolite 1		Metabolite 2	
	cpm	% of TRR	cpm	% of TRR	cpm	% of TRR
0 - 3	183 800	95	9 680	5	0	0
3 - 7	487 430	79	129 570	21	0	0
7-11	220 460	73	75 500	25	6 040	2
11-23	86 400	60	53 280	37	4 320	3

Amitrole is quickly metabolised in the liver. Fang *et al*. (1964) showed that the proportion of amitrole declined to 50% of the radioactivity in the liver by 3 hours after dosing (Table 2).

Table 2. Distribution of radioactivity extracted with alcohol from the liver of rats killed at different times after dosing with [^{14}C]amitrole.

Time (hours)	Amitrole, %	Metabolites, %
0.5	100.0	0
1	95.4	4.6
2	80.4	19.6
3	46.2	53.0
4	36.4	63.6
6	45.5	54.5
12	42.3	57.7
18	34.5	65.5
24	0	100.0

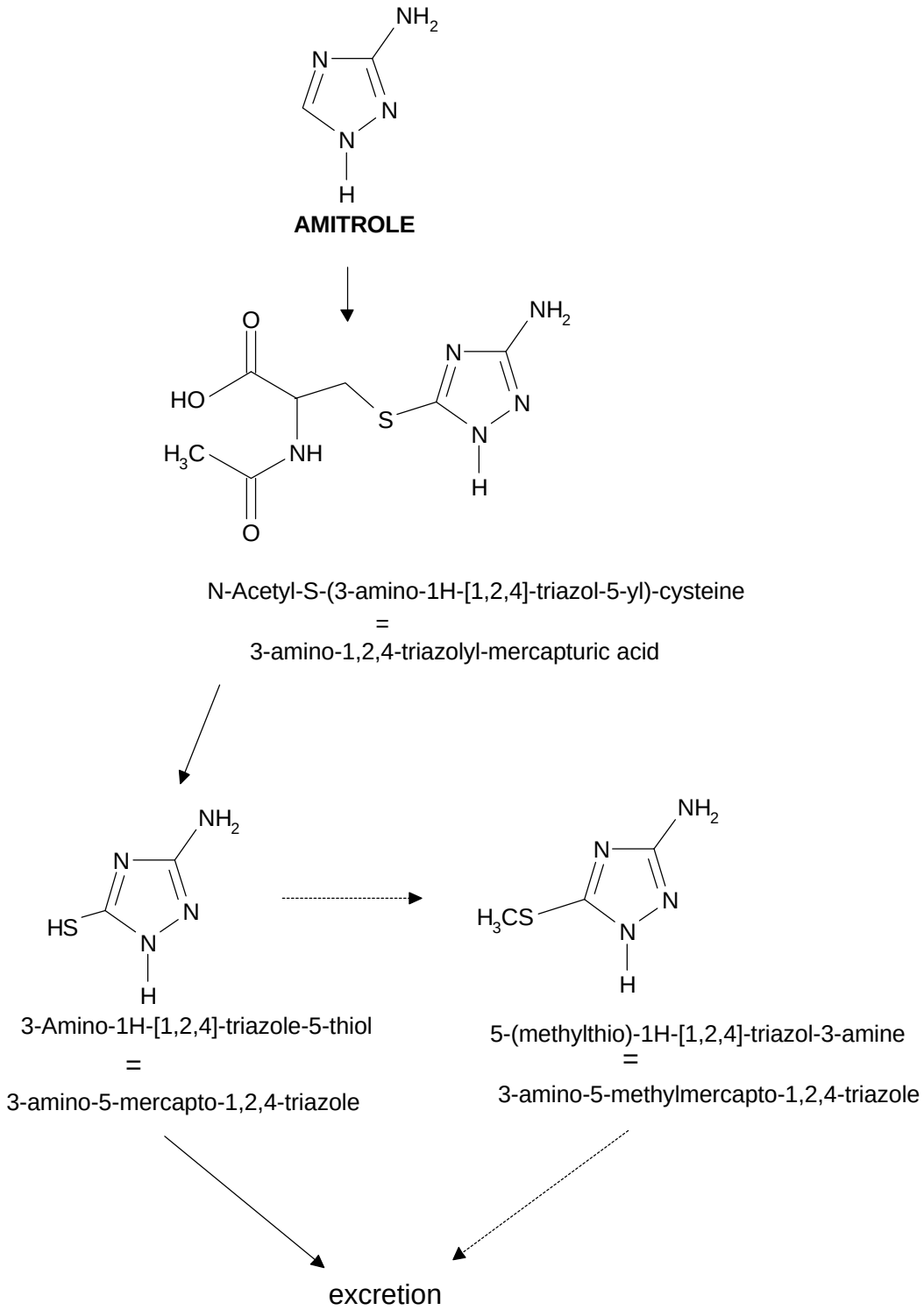
In an experiment with the ^{14}C and ^{3}H-labelled compounds, amitrole was metabolised in rats mainly at the 5-position (Table 3). The average ratio of ^{3}H to ^{14}C for the active ingredient fraction isolated from the urine was 8.6, and for the metabolite fraction 1.1 (Fang *et al.*, 1966).

Table 3. Ratio of ^{3}H to ^{14}C in amitrole and metabolite fractions from the urine of rats treated with ^{3}H- and 5-^{14}C-labelled amitrole (ratio 11/1).

Dose	Ratio ^{3}H/^{14}C											
	Rat n° 68 F		Rat n° 69 M		Rat n° 70 F		Rat n° 71 M		Rat n° 72 F		n°73 M	
	Amitr	Metab	Amitr	Metab	Amitr	Metab	Amitr	Metab	Amitr	Metab	Amitr	Metab
1	9.0	1.7	7.7	0.6	9.1	1.7	8.7	1.2	9.4	1.3	9.1	0.6
2	9.1	2.2	7.3	0.7	8.4	0.9	8.2	1.0	-	-	-	-
3	8.7	1.3	7.8	0.5	8.1	0.6	7.3	0.6	-	-	-	-
4	9.2	1.7	8.6	0.9	9.1	0.9	8.5	0.8	-	-	-	-
5	9.0	1.8	9.7	0.9	-	-	-	-	-	-	-	-
^{3}H/^{14}C amitrole for male rats: 8.30 ± 0.7												
^{3}H/^{14}C amitrole for female rats: 8.90 ± 0.3												
^{3}H/^{14}C metabolites for male rats: 0.78 ± 0.20												
^{3}H/^{14}C metabolites for female rats: 1.42 ± 0.46												

The proposed degradation pathway is shown in Figure 1.

Figure 1. Metabolism of amitrole in rats.



Grunow *et al.* (1975) confirmed that amitrole is metabolised in rats by substitution at the 5-carbon atom. The urine of rats 24 hours after a 50 mg/kg bw dose contained unchanged amitrole and small amounts of 3-amino-5-methylthio-1,2,4-triazole, 3-amino-5-mercapto-1,2,4-triazole and 3-amino-1,2,4-triazolyl-5-mercapturic acid, identified by comparative paper and/or thin-layer chromatography in several mobile solvent systems as well as comparative IR and mass spectrometry. The alanine conjugate postulated by Franco and Municio (1975) could not be detected by Grunow *et al.*

In another more recent study (Anderson and Brauner, 1995) [5-^{14}C]amitrole was administered orally or intravenously to four groups of 5 rats to study the dependence of kinetic parameters on the route of administration (oral or i.v.), dose (1 or 500 mg/kg), pre-treatment and sex.

Absorption from the gastrointestinal tract started immediately after administration and the peak plasma level was reached after 40 to 60 minutes in all groups. The test compound was distributed extensively into peripheral compartments. Under steady state conditions the radioactivity permeated readily into the tissues and, with a very low mean residence time, back into the plasma before elimination. In rats killed after short times increased concentrations of radioactivity (whole-body autoradiography) were recognisable in all organs and tissues except bone marrow, brain, eye and brown fat. Owing to the fast excretion, radioactivity in all organs and tissues was depleted quickly. In rats killed 48 hours after administration of the compound, radioactivity was detected mainly in the liver and to a small extent in the kidney cortex and nasal mucosa. Recoveries of radioactivity were on average higher than 93.8% of the dose.

Biotransformation to volatile metabolites including carbon dioxide was negligible (0.1% of the administered dose). More than 97% of the recovered radioactivity was excreted within 48 or 72 hours after oral administration. The major elimination route was renal, with the high-dose animals excreting 97 to 98% and the low-dose 91 to 95% in the urine, irrespective of the administration route. Repeated oral doses resulted in urinary excretion in the same range. Faecal elimination accounted for 1.6 to 6.3%. The residues in the rat bodies excluding the gastrointestinal tract were significantly lower after a single high dose than after single or repeated low doses. Radioactivity after a single intravenous dose was slightly lower than after a single oral dose and slightly lower in female than in male rats after single and repeated oral doses. The half-life of elimination was shorter after intravenous administration than after oral dosing.

Analysis of the urine by chromatography established that a very high percentage of amitrole passed through unchanged, accounting for more than 86% of the identified radioactivity and for two thirds or more of the administered dose. Small amounts of 7 different metabolites were detected, one of which was identified by mass spectrometry. Two other biotransformation products were identified by chromatography with the authentic reference compounds on thin-layer plates and by HPLC. The proportion of identified compounds was high and independent of the route of administration or sex, ranging from about 76 to 93% of the recovered radioactivity.

In a further study (Iatropoulos *et al.*, 1996), amitrole was administered in the NIH-07 diet *ad libitum* to F344 rats and C57BL/6N mice at concentrations of 0, 1, 10, 100 or 1000 mg/kg in the diet. Animals were killed after 4 or 21 days of exposure. Three days before being killed at 21 days, four of the ten animals in each group were given bromodeoxyuridine (BrdU) which was incorporated into proliferating cells. In both rats and mice the blood levels of radioactivity were proportional to the dose but lower in mice, indicating probably more effective liver enzyme induction and systemic elimination. After 21 days serum levels were identical to those after 4 days in rats, but lower in mice. In rats amitrole at 100 and 1000 ppm caused significant time- and dose-related decreases in body weight. Liver weights were decreased, although hepatocellular BrdU labelling indices were increased, reaching a maximum of a 3-fold increase compared to controls. Hepatic glutathione peroxidase activity was inhibited at 1000 ppm. Thyroid follicular cell hyperplasia was induced at 10 ppm and above. In mice amitrole at the same dose levels did not cause body weight changes. Liver weights were increased by day 21, increases in hepatocellular BrdU labelling indices were evident, and hepatic glutathione peroxidase activity was inhibited at 100 and 1000 ppm. At those levels, thyroid hyperplasia was induced, reaching a maximum of 8-fold.

Plant metabolism

The metabolism of amitrole was studied after application of [3,5-^{14}C]amitrole (8 kg/ha) to the soil under apple trees under outdoor conditions and in tubs, to excised apple tree sprouts, and to cell suspension cultures (Schneider *et al*., 1991). Mature fruit from outdoor experiments contained a maximum of 0.05 mg/kg total radioactive residues of which about 75% was soluble and 25% bound to insoluble material, but amitrole itself was not detected. The main metabolite ([0.012 mg/kg, 22-24% of the ^{14}C) was 2-amino-3-(1,2,4-triazol-l-yl)propionic acid (triazolylalanine) which occurred in the free form and as conjugates. More than 50% of the radioactivity was incorporated into natural plant constituents, some of which were insoluble and characterized after treatment with cellulase/pectinase. In the tub experiments, one apple tree absorbed 1.1% of the radioactivity applied to the soil, 0.07% was found in the mature fruit and about 42% remained in the soil after 5 months.

In contrast to the results of outdoor experiments, the main metabolite in model experiments with excised apple sprouts and most cell suspension cultures was 3-(3-amino-1,2,4-triazol-l-yl)-2-aminopropionic acid (aminotriazolylalanine), but only small amounts were present. In cell suspension cultures at high concentrations of amitrole 3,5-dihydroxy-1,2,4-triazole was the main product. The distribution of radioactivity and the proposed metabolic pathways are shown in Tables 4 and 5 and Figure 2.

Table 4. Nature of residues in harvested apples following application of [3,5-^{14}C]amitrole.

Sample	1985[1]			1986[2]		
	Radioactivity		mg/kg, as amitrole	Radioactivity		Residue,
	Bq/g FW[3]	%		Bq/g FW[3]	%	mg/kg
Total radioactivity	16.4	100.0	0.0456	19.4	100.0	0.0322
Soluble radioactivity	11.2	68.3	0.0311	14.7	75.8	0.0244
Incorporated radioactivity	6.0	36.6	0.0167	7.8	40.2	0.0130
Basic metabolites	0.7	4.3	0.0019	1.5	7.8	0.0025
Triazolylalanine and conjugate	3.6	21.9	0.0100	4.7	24.2	0.0078
Not determined	0.9	5.5	0.0025	0.7	3.6	0.0012
Radioactivity in cell wall components	5.2	31.7	0.0145	4.7	24.2	0.0078
Re-assimilated radioactivity	3.4	20.7	0.0095	3.0	15.5	0.0050
Bound metabolites	1.5	9.2	0.0042	1.6	8.2	0.0027
Not determined	0.3	1.8	0.0008	0.1	0.5	0.0002

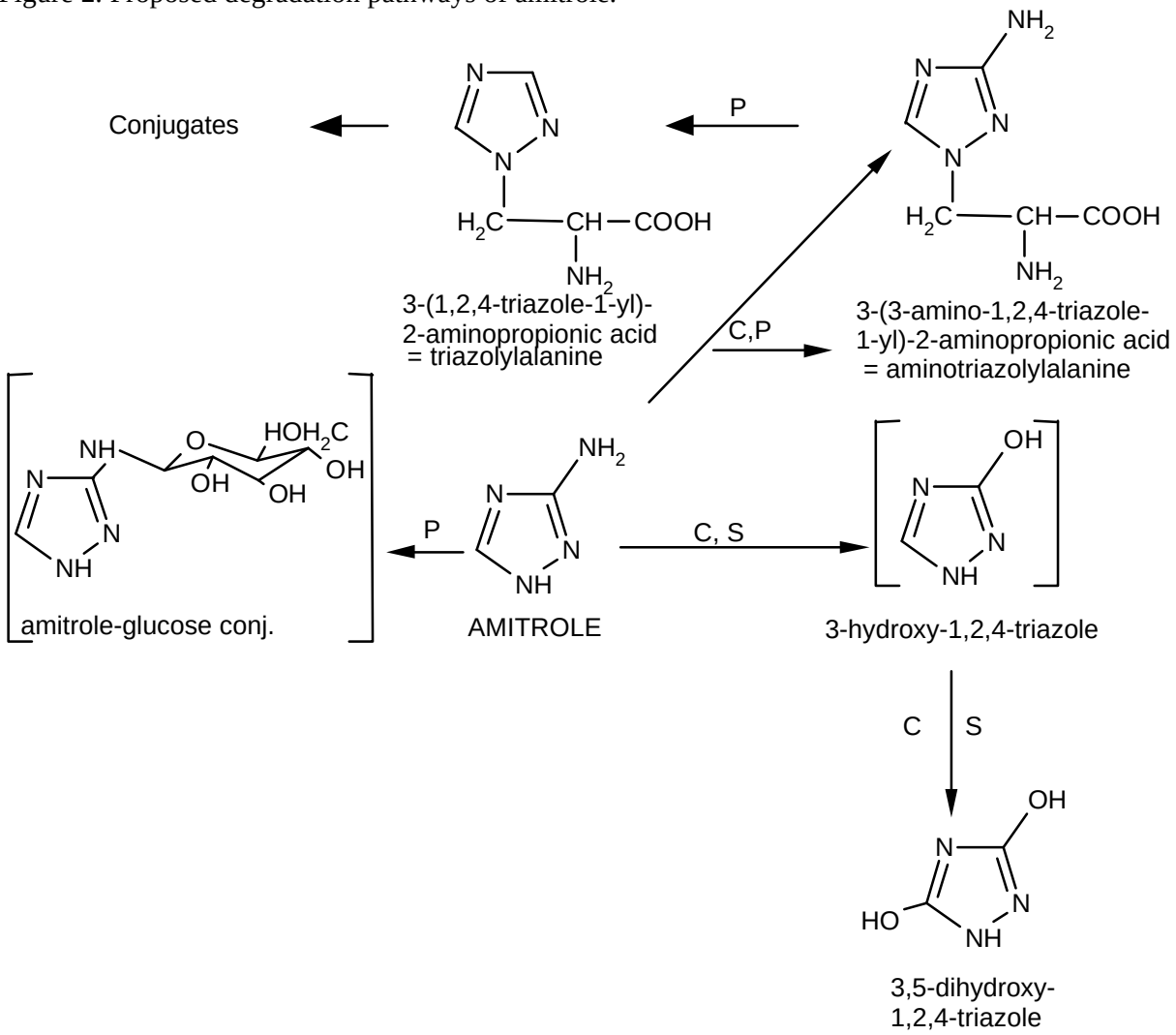
[1]Specific radioactivity 0.359 MBq/mg
[2]Specific radioactivity 0.602 MBq/mg
[3]FW: Fresh weight of harvested fruit

Table 5. Radioactivity balance at harvest (14/10/1986) following application of 400 mg [3,[5-^{14}C]amitrole (61.3 MBq/mmol) in 2 doses of 200 mg on 14/05 and 9/07/1986 to one apple tree of cultivar "Gelber Köstlicher" in a tub.

Applied radioactivity	292.000 (kBq)	100.00 (%)
Radioactivity in tree	3 240.2	1.11
Fruit	204.7	0.07
Leaves	83.9	0.03
Trunk and roots	2 951.6	1.01
One year old branches	405.4	0.14
Two year old branches	51.5	0.02
Branches older than two year	210.7	0.07
Trunk	1 312.0	0.45

Applied radioactivity	292.000 (kBq)	100.00 (%)
Rootstock	503.0	0.17
Roots	469.0	0.16
Radioactivity in soil	122 768.3	42.04
Radioactivity found(soil + tree)	126 008.5	43.15
Radioactivity lost (atmosphere)	165 991.5	56.85

Figure 2. Proposed degradation pathways of amitrole.



P = Plant, S = Soil, C = Cell culture

Environmental fate in soil

Amitrole has been extensively investigated with respect to its route and rate of degradation, adsorption/desorption, and leaching potential.

Routes of degradation

Degradation was studied in the laboratory in German standard soil 2.2 and an English loam. Amitrole was labelled with ^{14}C in the 3 and 5 positions, and the soil was kept in the dark. Under aerobic conditions after 28 days the production of $^{14}CO_2$ in the German standard soil 2.2 was 70% of the applied radioactivity, and in the English loam soil 40-50%, but in strictly anaerobic soil no

volatile radioactivity was produced. In the aerobic soil most of the involatile radioactivity was unextractable and the main extractable radioactive compound was unchanged amitrole. No intermediates in the degradation to $^{14}CO_2$, including urea and cyanamide observed in other experiments, were detected in the soil extracts. In anaerobic soil the total unbound radioactivity decreased to 60% after 28 days and to 25% after one year.

When soil under aerobic conditions was sterilized there was no significant loss of radioactivity, indicating that degradation to CO_2 is strongly influenced by micro-organisms and oxygen. Similar results were obtained with [3-^{14}C]- and [5-^{14}C]amitrole (Hawkins *et al.,* 1982).

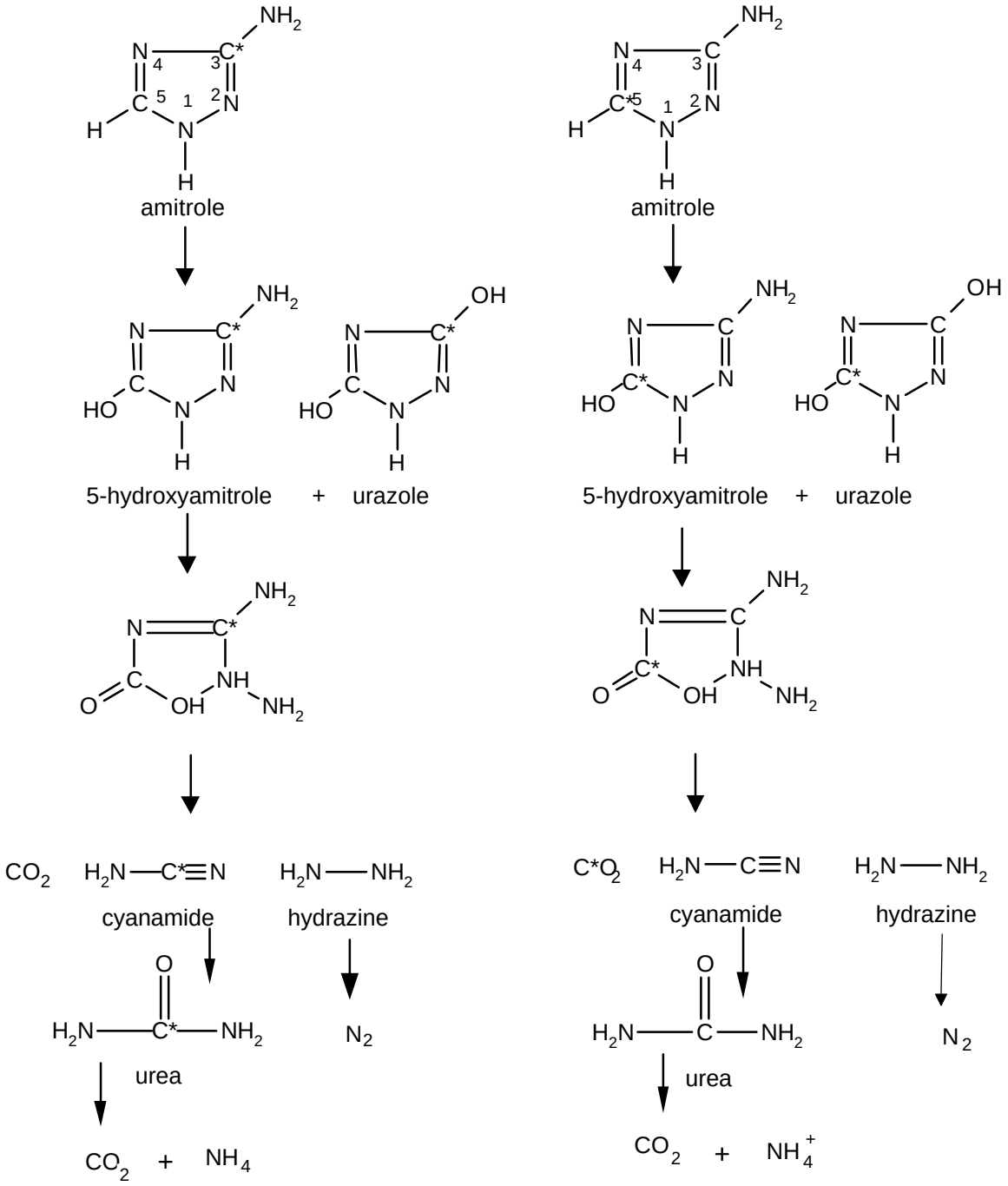
An additional laboratory experiment (Scholz, *et al*., 1988) was carried out with amitrole labelled at the 3 or 5 positions with the aim of identifying the intermediate compounds involved. A clayish silt soil was treated with 0.1 and 1.0 mg [^{14}C]amitrole/100 g soil and incubated from 1 to 20 days. Amitrole (both labelled forms) was rapidly degraded to CO_2. The residue in the soil extract consisted mainly of the parent compound, with <2.5% as metabolites. The primary metabolite was 5-hydroxy-amitrole but it was degraded very rapidly. Cyanamide and urea were also found as degradation products. Urazole (3,5-dihydroxy-1,2,4-triazole) presumably represents a secondary pathway in the metabolism. In the proposed degradation scheme, the ring is opened between positions 1 and 5 of 5-hydroxy-amitrole, CO_2 is eliminated at position 5 and hydrazine at positions 1 and 2, leaving cyanamide which is hydrolysed *via* urea to CO_2 and ammonia (Figure 3).

This degradation to simple organic compounds was confirmed in a more recent study (Hall, 1994) which showed CO_2 as the most abundant product, with urazole and aminoguanidine putatively identified at levels of ≤2%. Finally the presence of cyanamid at a very low concentration (≤0.02 mg/kg maximum at day 1) was confirmed in a recent field study (Biever, 1995).

The photodegradation of [3,5-^{14}C]amitrole has been studied by means of TLC plates of California sandy loam either developed immediately, stored in the dark, or exposed to natural sunlight or Chroma 50 lamps. Amitrole was degraded in dry soil in the dark with a half-life of approximately 330 hours. When exposed to light the half-life was approximately 10 to 20 hours of equivalent solar exposure. The products formed by exposure did not migrate from the soil in methanol or methanol/ethyl acetate/ammonium hydroxide, but when water/ammonium hydroxide was used as the solvent the products of photodegradation were shown to comprise at least two components. The smaller fraction was bound to the soil but the larger fraction migrated in the water. Although not clearly identified, these products were presumed to be cyanamide and urea (Huhtanen, 1985a).

In an investigation of the photodegradation of [^{14}C]amitrole on soil under artificial sunlight the parent concentrations without irradiation varied from 86.6% to 91.1% without any cleasr decline pattern. Under irradiated conditions however the parent concentrations decreased from 91.1% to 66.4% by 30 days. There was only one degradation product under both conditions, identified as 1,2,4-triazole. This reached a maximum concentration of 4.1% by day 21 without irradiation and 9.9% by day 30 when irradiated. The calculated photolytic half-life of amitrole was 73 days, each day consisting of 12 hours irradiation and 12 hours darkness (Das, 1990).

Figure 3. Degradation scheme for [3-^{14}C]amitrole and [5-^{14}C]amitrole in soil.



Rate of degradation

Laboratory studies. Technical amitrole was incubated in 3 German standard soils at 22°C for 17 days after treatment at 0.2 mg ai/kg soil. Amitrole was determined after extraction with acetone/water and purification on cation exchange and aluminium oxide columns by HPLC with ion pairing and electrochemical detection (limit of determination 0.02 mg/kg). The calculated half-lives were 2.4, 2.4 and 4.6 days (Jarczyk, 1982 b-d).

More recently (Hall, 1994,1995) the rate of degradation of amitrole was studied on a very light soil, a loamy sand originating from the USA. The study was conducted according to US-EPA

and Canadian requirements, at 7°C and 22°C. A half-life of 87 days was calculated at 7°C, decreasing to 26 days at 22°C.

Field studies. A terrestrial dissipation study (Biever, 1995) was conducted during 1993 in Hillsboro, Oregon and Moses Lake, Washington (close to the Canadian border) to determine the persistence of amitrole and one of its degradation products, cyanamide, in soil. At both locations the surface soil was a loam with 1.3 to 1.8% organic matter. Amitrole, formulated as Amizol®, was applied to 0.1 ha plots of bare soil at an average rate of 8.7 kg ai/ha, 97% of the maximum labelled application rate for non-crop use in the USA. The amitrole concentrations in the soil were highest on day 0 at both sites, 1.77 mg/kg at Oregon and 2.50 mg/kg at Washington. The decrease after 7 days was rapid with concentrations at the limit of quantification (LOQ) by 124 days at Oregon and 131 days at Washington. Mean monthly temperatures ranged from 13°C to 19°C at Oregon and 10°C to 21°C at Washington. The theoretical half-life of amitrole in soil was 17 days (r = 0.98) in Oregon and 21.0 days (r = 0.96) in Washington.

Adsorption and desorption

One g portions of soil were equilibrated with 10 ml of solutions containing 0.51 to 10.1 mg/l of [3,5-^{14}C]amitrole for 2 hours at 25°C, the samples were centrifuged and the supernatants analysed. A similar procedure was followed for desorption. The results are summarized in Table 6. Amitrole was adsorbed to some extent by all the soils studied. Adsorption followed a Freundlich isotherm. Freundlich constant (K_d) values ranged from 0.685 to 3.79. Desorption of adsorbed amitrole ranged from 0.7 to 52%, from 20 to 50% in most cases. From the results, amitrole can be classified as "highly mobile" (Huhtanen, 1985b).

Table 6. Soil characteristics and Freundlich constants.

Soil	Freundlich constants K_d	l/n	Organic content (%)	Correlation coefficient	K_{oc}	pH	CEC
California sandy loam	3.52	0.6487	3.0	0.9969	117	6.1	6
Plano silt loam	3.79	0.7739	5.9	0.9923	64.2	6.8	13
Kewaunee silty clay loam	1.57	0.8563	5.0	0.9990	31.4	7.0	17
Plainfield sand	0.685	0.7975	0.8	0.7525	85.6	5.6	1

In the same way, adsorption/desorption was investigated in four soils by equilibrating 12.5 g of soil with 10 ml of [3,5-^{14}C]amitrole solution at concentrations of 2 to 20 mg/l (Tables 7 and 8; Anderson and Hellpointner, 1989).

Table 7. Freundlich adsorption constants for soils at natural pH (5.3 to 7.4).

Soil	Constants 1/n	K_d	% organic carbon[1]	Correlation coefficient of the linear regression	K_{oc}	pH	CEC
Silty clay	0.7671	0.7141	0.64	0.9999	111.6	7.4	21.1
Sandy loam	0.8549	0.2231	0.75	0.9980	29.7	6.8	10
Sand	0.8722	0.1515	0.75	0.9993	20.2	5.6	4
Silt	0.8590	0.9215	1.8	0.9999	51.2	5.3	10.5

[1]Organic matter x 0.58

Table 8. Freundlich desorption constants for soils at natural pH (5.3 to 7.4).

	Constants	% organic carbon[1]	Correlation coefficient			

Soil	1/n	K_d		of the linear regression	K_{oc}	pH	CEC
Silty clay	0.9140	1.8078	0.64	0.9939	282.4	7.4	21.1
Sandy loam	0.9170	0.7839	0.75	0.9976	104.5	6.8	10
Sand	0.9321	0.7398	0.75	0.9982	98.6	5.6	4
Silt	0.8533	1.1986	1.80	0.9829	66.6	5.3	10.5

[1] Organic matter x 0.58

The investigation showed that 10.3 to 53.4% of the applied amitrole was adsorbed at equilibrium. There was no linear relationship between adsorption and the content of organic carbon or clay in the soils. The values for 1/n were <1 in all cases which corresponds to a decrease of adsorption with increasing concentration. Higher values were found for desorption than adsorption constants, with K_d values from 0.740 to 1.808 and K_{oc} from 66.6 to 282.4, and 24.8 to 72.3% of the adsorbed amitrole desorbed after single-stage desorption.

At a concentration of 20 mg adsorption to all the soils varied from pH 4.5 to pH 8, with differences in the amount adsorbed up to 46.5%. Increased adsorption was seen under acid conditions, where adsorption K_d values ranged from 0.575 to 2.279 and K_{oc} values from 76.7 to 356.2. The authors concluded that amitrole would be expected to show a high to very high mobility in soil at pH 5.3 to 7.4, and a medium to high mobility at pH 4.5 .

Mobility

The mobility of amitrole was compared with that of four reference compounds (refs) in selected soils by soil thin-layer chromatography (Table 9).

Table 9. Mobility of amitrole and four reference compounds in various soils.

Soil	% organic matter	Mobility class*				
		amitrole	Ref. 1	Ref. 2	Ref. 3	Ref. 4
Plainfield sand	0.8	5	5	5	5	1
California sandy loam	3.2	2	5	4	3	1
Dubuque silt loam	2.9	4	5	4	3	1
Hagerstown silty clay loam	2.5	3	4	3	3	1

* As defined by US EPA Pesticide Assessment Guidelines, Subdivision N, Page 67 (1982). 1 = Immobile (R_f = 0.0-0.09); 2 = Low mobility (R_f = 0.1-0.34); 3 = Intermediate mobility (R_f = 0.35-0.64); 4 = Mobile (R_f = 0.65-0.89); 5 = Very mobile (R_f = 0.90-1.0)

Amitrole and refs 2 and 4 were more mobile in Plainfield sand than in the other soils, while amitrole was generally less mobile than the standards (Huhtanen, 1985c).

In the above-mentioned field study (Biever, 1995), amitrole was rarely detected or quantified at any soil depth below 15 cm. It was quantified in one sample on day 89 in the 15 to 30 cm depth in Oregon and in two samples on day 61 at 15 to 30 cm in Washington.

Mobility of aged residues. [3, 5-^{14}C]amitrole was applied at 3.37 mg/kg dry soil to California sandy loam and incubated for 5 days at 25 ± 1°C. The aged soil was placed at the bottom of soil TLC plates which were developed in water. Amitrole is rapidly converted to carbon dioxide by wet, active soil. Aged amitrole residues are less mobile than unaged, probably because the carbon has been incorporated into soil or soil micro-organisms (Huhtanen, 1985d ; Table 10).

Table 10. Mobility of aged and unaged amitrole and standards in California sandy loam soil.

	Aged amitrole	Unaged amitrole	Ref. 1	Ref. 2
Rf	0.10	0.18	0.57	0.80
Mobility class	2	2	3	4

The mobility of amitrole and its degradation products was examined in two European soils. German standard soil 2.1 containing 0.6% organic carbon and 6.8% of the fraction <0.02 mm, and "Höfchen" soil containing 2.9% organic carbon and 32% of the fraction <0.02 mm. ^{14}C-labelled amitrole was used at an exaggerated concentration of 10 kg ai/ha, and duplicate tests were carried out after the soil had been incubated with amitrole for 0-30 and 92 days. The incubated soil was placed on top of 27 cm of untreated soil in glass columns and eluted with about 400 ml deionized water over 2 days.

More than 1% of the initially applied ^{14}C was leached from the German standard soil 2.1, 24-31% from the unaged soil, 1.5-1.9% from the 30-day and 0.7-1.6% from the 92-day soil. Most of the radioactivity in the 0-day leachate was from the parent compound (20-27%) but less than 0.1% of the residue after 30 days ageing. In the Höfchen soil, which had a higher content of organic matter, the radioactivity in the leachate decreased from 0.8% from the unaged soil to 0.1% from that aged for 92 days. Again, there was little leaching of fresh amitrole, and the aged residue was even less mobile (Weller, 1987).

Finally, in the field study by Biever (1995) cyanamide concentrations between 0.01 mg/kg and 0.02 mg/kg were measured in the 0 to 15 cm soil depth during the first 3 days at the Oregon site and were just detected from 0 to 21 days at the Washington site. Quantifiable concentrations of cyanamide were never found below 15 cm.

Lysimeter studies. In a lysimeter study conducted by Bayer A.G. with a grey-brown podzolic soil from loess, Ustinex KR (40% amitrole) was applied at 10 kg/ha (4 000 g/ha amitrole), twice a year from 1979 to 1983 and once a year from 1984 to 1986. Amitrole was not detected in the leachate at the limit of detection of 10 µg/l. Analyses were continued during 1988 and 1989 and no amitrole was detected at a limit of 0.05 µg/l (Bachlechner, 1988).

Environmental fate in water/sediment systems

Scholz (1995) investigated the aerobic degradation of amitrole in two water-sediment systems freshly sampled from fields in The Netherlands. Sediments were sieved to 2 mm and pre-incubated for 14 days in the ambient laboratory conditions. [3-^{14}C]amitrole was applied to the surface water at a rate equivalent to 5,000 g ai/ha. Both systems were analysed after 0, 3, 7, 14, 30, 60 and 91 days.

In both systems the recovery of ^{14}C exceeded 95% at all sampling times. The extent of mineralization was about 19% in one sediment and 10% in the other after 91 days. Radioactivity decreased continuously in water to 50% in one system and 36% in the other. The elimination half-lives in the total systems were 95 days and 76 days. Triazole and urea, both <3%, were the only identified products at day 7 in one system and at day 14 in the other. At least 4 other polar products (at the TLC origin) were observed, at a fairly constant total level of about 4-5%. Unextractable residues increased with time, reaching 27% and 40% of the applied radioactivity in the two sediments; but it was shown by vigorous hydrolysis that about 50% of this unextractable fraction was combined amitrole.

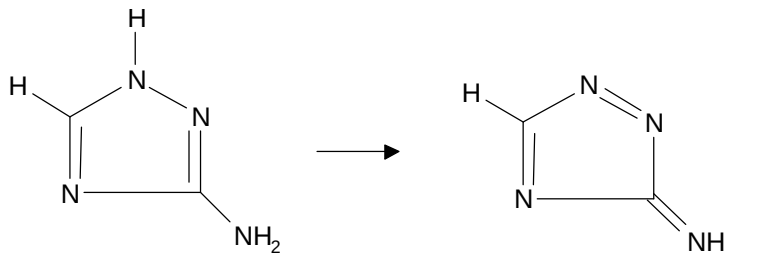
This study confirms the path followed by amitrole in biological media, the main difference being due to the continuous equilibrium between the aqueous phase where amitrole is mainly stable

and the sediment where it undergoes biological breakdown, and a reduced rate compared with aerobic soil degradation owing to the lower level of oxygen in the sediment.

These results were confirmed in another recent study (McCowan, 1995a) conducted for 52 weeks according to the US-EPA guideline. Analyses of surface waters and sediment extracts by thin-layer chromatography indicated that [^{14}C]amitrole was degraded over the incubation period, and accounted for about 5% of the applied radioactivity in raw samples and about 60% in sterile samples at the end of the study. A minor polar degradation product, with negligible mobility on the TLC plate, accounted for about 3% of the applied activity in non-sterile and about 7% in sterile samples. HPLC analysis indicated that this product probably consisted of 4 separate components, suggesting that this degradation pathway was partly abiotic. The half-life of amitrole at 22°C was in the same range as in the Scholz study at about 73-82 days, but was shorter (44 days) at 7°C.

The same aquatic system was used by McCowan *et al*. (1995b) to measure the rate of degradation of [^{14}C]amitrole over 52 weeks under anaerobic conditions at 22°C under sterile and non-sterile conditions and 7°C (non-sterile). The mean overall recoveries of applied radioactivity ranged from 96% to 105%. The volatile radioactivity, as $^{14}CO_2$ and organic volatiles, was very low throughout the incubation period in both experiments, accounting for less than 1% of the applied radioactivity. The radioactivity associated with the surface water at both temperatures decreased as the incubation progressed, accounting for about 74% of the applied radioactivity at 52 weeks. Extractable radioactivity in the sediment remained relatively constant throughout the incubation period, accounting for up to about 20% at 52 weeks. Bound residues were low (about 5% at 52 weeks) under both sterile and non-sterile conditions

Analysis by thin-layer chromatography indicated that [^{14}C]amitrole was the major radioactive component in surface waters and sediment extracts, accounting for about 84-87% of the applied radioactivity at 52 weeks in non-sterile samples and about 71% in sterile samples. A minor polar degradation product with negligible mobility on the TLC plate was detected in both sediment and water from 26 weeks onwards, accounting for about 4% of the ^{14}C at the end of the study. This was later postulated to be dehydrogenated amitrole (Williams and McGuire, 1997).



Amitrole 3-Imino-1,2,4-triazole

In conclusion, [^{14}C]amitrole is degraded very slowly under anaerobic conditions, irrespective of temperature and biological activity. The half-life could not be calculated because of the limited degradation, but is more than one year.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Crops and soil. A GLC method of analysis for the determination of amitrole residues in various plants and plant products was developed by Jarczyk and Möllhoff (1991). Fruits are extracted cold with ethanol/water (2:1). Grape must and wine are rotary-evaporated. The aqueous extract or

concentrate is purified by shaking with dichloromethane. Amitrole is acetylated with acetic anhydride and the derivative is partitioned into dichloromethane and cleaned up by gel permeation chromatography and column chromatography on silica gel before GLC determination with a thermionic nitrogen-phosphorus detector (NPD). The method has a routine limit of determination of 0.01 mg/kg with mean recovery levels of 82, 79, 98, 83, 77 and 76% for apples, pears, cherries, grapes, grape must and wine respectively.

Several important features are given special attention. (1) The analysis can only be interrupted after the acetylation of the extracts or standards. The final determination should be performed without delay because acetylated amitrole in solution is stable only for a short time even in a refrigerator. (2) Aqueous phases must not be evaporated to dryness and the water bath temperature must not exceed that specified. (3) Depending on the column and temperature programme used, GLC analyses may require 20-30 minutes between injections to allow time for interfering peaks from the previous samples to elute. (4) The peak areas of monoacetyl-amitrole on the capillary columns used are dependent on the sample matrix, so the derivative standard solution should be added to the cleaned-up extract from a control sample to yield a reference standard suitable for quantification.

An analytical method for blackberries was submitted by The Netherlands, in which amitrole is extracted with a mixture of ethanol and water, the extract is treated with hydrogen peroxide and interfering substances are removed by ion-exchange on both strongly and weakly acidic cation exchangers. Amitrole is converted to a complex with fluorescamine and determined by HPLC with fluorescence detector. The limit of determination is 0.02 mg/kg.

The GLC method of Jarczyk and Möllhoff (1991) for soil is essentially identical to their method for crops. The method has a routine limit of determination of 0.01 mg/kg with recoveries of 82-91%.

In addition to the points given special attention in the analysis of crops, the water content and the maximum water capacity of soil samples must be determined before the soil is extracted.

The HPLC method of Weber (1988) is applicable to crops, soil and water. It is described below.

More recently, the HPLC method was also adapted for determining residues of amitrole in grapes, wine and vine leaves (Clemson, 1995a,b,1966). Owing to difficulties encountered, a new method was developed for determining residues in plant material, which has been validated for use on grapes (McGuire, 1997) over the range 0.005-0.5 mg/kg. It involves extraction into acetone/water and dichloromethane partitioning. After acidification, the aqueous extract is cleaned up by solid-phase extraction and the eluate evaporated to dryness, resuspended in pyridine and derivatized with bis(trimethylsilyl)trifluoracetamide/trimethylchlorosilane (BSTFA/TMCS) before determination by GC-MS. GC-MS of amitrole standards over the range 0.01 to 5 µg/ml produced a linear calibration with a correlation coefficient of 0.997. The overall mean recovery of amitrole from fortified control grapes was 83.44%. This method is now being validated for must and wine, barley, wheat, peas and canola seeds.

Water. The HPLC method was developed by Weber (1988). Water samples are applied directly onto a cation exchange column, eluted with ammonia solution and further cleaned up by column chromatography on aluminium oxide. The HPLC determination is with ion pairing and electrochemical detection. The routine limit of determination is 0.1 µg/l with recoveries of 86-102%.

Products of animal origin. An HPLC method was validated by Weber (1997) is related to his 1998 method for crops, soil and water. Samples are extracted with water/acetone (3 :1), partitioned with dichloromethane and cleaned up on cation exchange and aluminium oxide columns. Amitrole is determined by HPLC with ion pairing and electrochemical detection. Mean recoveries at fortification levels of 0.01 mg/kg to 0.1 mg/kg were 74% for milk, 82% for eggs and 87% for muscle. The limit of detection was 0.005 mg/kg and the LOD 0.01 mg/kg. At this level the recovery was 81% from muscle.

GLC methods have been adapted from those used for fruit, soil and water (Jarczyk, 1981, 1982a, 1984). They involve extraction with ethanol/water (2/1), clean-up by partition with organic solvents such as carbon tetrachloride or chloroform, derivatization with acetic anhydride, and further clean-up by column chromatography on silica gel. Amitrole is determined as the monoacetyl derivative by GLC with a thermionic nitrogen-phophorus detector (NPD).

These methods have been validated at various fortification levels over a long period by many analysts. The recoveries are usually between 70 and 110% with a relative standard deviation below 20% and blank values below 30% of the limit of quantification. The limits of quantificaton differ between methods and samples, but are in the range 0.01-0.025 mg/kg.

Stability of residues in stored analytical samples

In a frozen storage stability study on grapes (Clemson, 1997) untreated grapes were dipped into a solution of amitrole at 0.28 mg/kg. After two years at -20°C, the residues were about 60% of the initial level. A study on apples by Biever is in progress. Residues after 16 months were about 75% of the initial levels.

USE PATTERN

Besides uses on industrial land, roadsides, railways, ditches etc. amitrole is used world-wide as a herbicide in vineyards and orchards against all kinds of weeds (grasses and dicotyledons, annual, biannual and perennial), and also as a total weed killer after harvest and before the next annual sowing. Table 11 shows the recommended uses of amitrole on apples, pears, peaches and grapes.

Table 11. Use patterns of amitrole.

Crop	Country	Formulation	Application			PHI, days
			Number	kg ai/ha	kg ai/hl	
Fruit trees	Australia	SL	2	1.4-2.8	0.14-0.28	56
	Belgium	SL		3.6-4.8	0.9-1.2	
	France	SL		2.4-4.8		
	Germany	WG	1	3	0.3-0.75	60
	Morocco	SL	1-2	2.4-7.2	0.24-1.4	
	Spain	SL		1.92-3.84	0.48	45
Vines	Australia	SL	2	1.2-2.4	0.14-0.28	56
	Germany	WG	1	3	0.3-0.75	60
	France	SL		2.4-4.8		
	Morocco	SL	1-2	2.4-7.2	0.24-1.4	
	Spain	Sl		0.192-0.384	0.048	45

RESIDUES RESULTING FROM SUPERVISED TRIALS

Apples. Thirty four trials were conducted in Europe. In the eighteen trials in France according to GAP the residues from day 5 to day 171 were <0.01 mg/kg. In fourteen trials in Germany above the GAP rate the residues after 4 to 120 days were <0.02 mg/kg. In two trials in Portugal above reported European GAP rates the residues after 111 days were <0.01 mg/kg. The samples were stored at -20ºC for 56 to 483 days before analysis.

Table 12. Results from residue trials with amitrole on apples.

COUNTRY Report No Year	Formulation	Application			PHI	Residues,	Reference
		No.	kg ai/ha	kg ai/hl	days	mg/kg	
FRANCE[1] 95-08-6065 1993	SL	2-4	2.88	0.576	62 116 151 172	<0.01 <0.01 <0.01 <0.01	
	SL	2-4	4.80	0.960	62 116 151 172	<0.01 <0.01 <0.01 <0.01	
	SL	2-4	2.88	0.576	31 85 120 141	<0.01 <0.01 <0.01 <0.01	
	SL	2-4	4.80	0.960	31 85 120 141	<0.01 <0.01 <0.01 <0.01	
	SL	2-4	2.88	0.576	54 89 110	<0.01 <0.01 <0.01	
	SL	2-4	4.80	0.960	54 89 110	<0.01 <0.01 <0.01	
	SL	2-4	2.88	0.576	5 56	<0.01 <0.01	
	SL	2-4	4.80	0.960	35 56	<0.01 <0.01	

COUNTRY Report No Year	Formulation	Application No.	kg ai/ha	kg ai/hl	PHI days	Residues, mg/kg	Reference
	SL	2-4	2.88	0.576	61 101 150 171	<0.01 <0.01 <0.01 <0.01	
	SL	2-4	4.80	0.960	61 101 150 171	<0.01 <0.01 <0.01 <0.01	
	SL	2-4	2.88	0.576	40 89 110	<0.01 <0.01 <0.01	
	SL	2-4	4.80	0.960	40 89 110	<0.01 <0.01 <0.01	
	SL	2-4	2.88	0.576	49 70	<0.01 <0.01	
	SL	2-4	4.80	0.960	49 70	<0.01 <0.01	
	SL	2-4	2.88	0.576	58 92 119	<0.01 <0.01 <0.01	
	SL	2-4	4.80	0.960	58 92 119	<0.01 <0.01 <0.01	
	SL	2-4	2.88	0.576	34 61	<0.01 <0.01	
	SL	2-4	4.80	0.960	34 61	<0.01 <0.01	
GERMANY 0625-79 1979	WP	2	4	0.666	50 70 90	<0.02 <0.02 <0.02	
0626-79	WP	2	4	0.666	50 70 90	<0.02 <0.02 <0.02	
0627-79	WP	2	4	0.4	50 70 90	<0.02 <0.02 <0.02	
0637-79	WP	2	4	0.666	55 79 98	<0.02 <0.02 <0.02	
0600-82 1982	WP	2	4	0.666	6 36 56 96	<0.02 <0.02 <0.02 <0.02	
0601-82 1982	WP	2	4	0.666	4 34 64 93	<0.02 <0.02 <0.02 <0.02	
0726-90 1990	WP	1	4	1	42	<0.01	
0727-90	WP	1	4	1	42	<0.01	
0600-83 1983	WP	1	15	3.75	60 90 120	<0.02 <0.02 <0.02	
0601-83	WP	1	15	3.75	60 90 120	<0.02 <0.02 <0.02	
0602-83	WP	1	15	3.75	60 90 120	<0.02 <0.02 <0.02	

COUNTRY Report No Year	Formulation	Application No.	kg ai/ha	kg ai/hl	PHI days	Residues, mg/kg	Reference
RA-200391	WP	2	5	0.833	11	<0.01	0514-91
	WP	2	5	0.833	50	<0.01	0515-91
	WP	2	5	0.833	26	<0.01	0516-91
PORTUGAL RA-2004	WP	1	6	0.6	111	<0.01	0229-92
1991	WP	1	6	0.6	111	<0.01	0230-92

[1]The number of applications varied from 2 to 4, but the number of applications in each trial was not clear

Pears. In one trial in Portugal and three trials in Germany, at higher rates than German and other European GAP, residues after 60 to 120 days were below the LOD (0.01 or 0.02 mg/kg).

Table 13. Results from trials with amitrole on pears after 1 application of a WP formulation.

COUNTRY Report No Year	Application N°	kg ai/ha	kg ai/hl	PHI, Days	Residues, mg/kg
PORTUGAL 0231-92 1992	1	6	0.6	81	<0.01
GERMANY 0603-83 1983	1	15	3.75	60 90 108	<0.02 <0.02 <0.02
0604-83	1	15	3.75	60 90 120	<0.02 <0.02 <0.02
0605-83	1	15	3.75	60 90 120	<0.02 <0.02 <0.02

Peaches. In four trials with amitrole in Spain with 1 application of 6 kg ai/ha (0.6 kg ai/hl) of WP formulation which corresponds to nearly twice the GAP rate, residues in the fruit without stone were <0.01 mg/kg at PHIs of 42 to 105 days. The GAP PHI is 45 days.

Grapes. In twenty four trials in France and sixteen in Germany at GAP rates or higher, the residues in all but one trial were below the LOD (0.02 mg/kg).

Table 14. Results from trials on grapes in France and Germany with SL and WG formulations.

COUNTRY Report No Year	Application N°	kg ai/ha	kg ai/hl	PHI days	Residues mg/kg
FRANCE 94/CPF017/0450 1992	1	2.8	0.576	102 137 165 179	0.087[1] <0.02 <0.02 <0.02
	1	4.8	0.960	102 137 165 179	<0.02 <0.02 <0.02 <0.02
	1	2.8	0.576	20 55 83 97	<0.02 <0.02 <0.02 <0.02
	1	4.8	0.960	20 55	<0.02 <0.02

COUNTRY Report No Year	Application			PHI	Residues
	N°	kg ai/ha	kg ai/hl	days	mg/kg
				83 97	<0.02 <0.02
	1	2.8	0.576	35 63 77	<0.02 <0.02 <0.02
	1	4.8	0.960	35 63 77	<0.02 <0.02 <0.02
	1	2.88	0.576	98 129 158 178	<0.02 <0.02 <0.02 <0.02
	1	4.80	0.960	98 129 158 178	<0.02 <0.02 <0.02 <0.02
	1	2.8	0.576	29 60 89 109	<0.02 <0.02 <0.02 <0.02
	1	4.80	0.960	29 60 89 109	<0.02 <0.02 <0.02 <0.02
	1	2.8	0.576	31 60 80	<0.02 <0.02 <0.02
	1	4.80	0.960	31 60 80	<0.02 <0.02 <0.02
	1	2.8	0.576	94 126 146 175	<0.02 0.03 <0.02 <0.02
	1	4.80	0.960	94 126 146 175	<0.02 <0.02 <0.02 <0.02
	1	2.8	0.576	41 73 93 122	<0.02 <0.02 <0.02 <0.02
	1	4.80	0.960	41 73 93 122	<0.02 0.03 <0.02 <0.02
	1	2.8	0.576	18 50 70 99	<0.02 <0.02 <0.02 <0.02
	1	4.80	0.960	18 50 70 99	<0.02 <0.02 <0.02 <0.02
	1	2.8	0.576	113 147 168 189	0.03 <0.02 <0.02 <0.02
	1	4.80	0.960	113 147 168	<0.02 <0.02 <0.02

COUNTRY Report No Year	Application			PHI days	Residues mg/kg
	N°	kg ai/ha	kg ai/hl		
				189	<0.02
	1	2.8	0.576	43 77 98 119	<0.02 <0.02 <0.02 <0.02
	1	4.80	0.960	43 77 98 119	<0.02 <0.02 <0.02 <0.02
	1	2.8	0.576	15 49 70 91	<0.02 <0.02 <0.02 <0.02
	1	4.8	0.960	15 49 70 91	<0.02 <0.02 <0.02 <0.02
GERMANY 0634-79 1979	2	4	0.666	60 80 100 120	<0.02 <0.02 <0.02 <0.02
0635-79	2	4	0.666	60 80 100 120	<0.02 <0.02 <0.02 <0.02
0636-79	2	4	0.666	60 78 100 120	<0.02 <0.02 <0.02 <0.02
0606-83	2	4	1	80	<0.02
0607-83	2	4	1	80	<0.02
0600-85	2	4	1	28 35 42 49	<0.02 <0.02 <0.02 <0.02
0601-85	2	4	1	28 35 42 49	<0.02 <0.02 <0.02 <0.02
0602-85	1	4	40	28 35 42 49	<0.02 <0.02 <0.02 <0.02
0603-85	1	4	1	28 35 42 49	<0.02 <0.02 <0.02 <0.02
0604-85	2	4	1	28 42 56 63	<0.02 <0.02 <0.02 <0.02
0605-85	2	4	1	28 42 56 63	<0.02 <0.02 <0.02 <0.02
0724-90 1990	1	4	1	42	<0.01
0725-90	1	4	1	43	<0.01
0252-91 1991	1	4	1	75	<0.01
0253-91	1	4	1	75	<0.01

COUNTRY Report No Year	Application			PHI days	Residues mg/kg
	N°	kg ai/ha	kg ai/hl		
0254-91	1	4	1	56	<0.01

[1]High residue was found to be a result of cross contamination between trials

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country	Commodity	MRL, mg/kg
Australia	Citrus fruits, pome fruits, grapes	0.01
	Stone fruits	0.02
	Cereal grains	0.01
	Potato	0.05
	Pecan nut	0.01
	Sugar cane	0.01
Canada	Maize, soya beans, white beans, apples	no MRL (no residue > 0.1 mg/kg)

APPRAISAL

Amitrole was first considered by the JMPR in 1974. It was re-evaluated in 1993 within the CCPR Periodic Review Programme, and a temporary ADI was allocated. A full ADI was allocated in 1997. No MRLs have been established, but it is stated that uses of amitrole should be restricted to those where residues in food would not be expected to occur. The 1993 Meeting recommended a further note that "A realistic limit of determination for the general monitoring of amitrole would be 0.05 mg/kg". This evaluation is within the CCPR Periodic Review Programme. New data on metabolism in rats and environmental fate, in addition to residue trials on apples, pears, peaches and grapes were reported by the manufacturer. The governments of The Netherlands and Poland provided information on analytical methods and national MRLs.

In addition to studies submitted previously to the JMPR, two recent studies (1995 and 1996) on metabolism in mice and rats were submitted. When [5-^{14}C]amitrole was administered orally to rats, absorption from the gastrointestinal tract was rapid and the peak plasma level was reached after 40 to 60 minutes in both dose groups (1 and 500 mg/kg bw). When the animals were killed 48 hours after administration, radioactivity was detected mainly in the liver and to a small extent in the kidney cortex and nasal mucosa. Biotransformation to volatile metabolites including carbon dioxide was negligible. More than 97% of the recovered radioactivity was excreted within 48 or 72 hours after oral administration. The major route of elimination (91 to 98%) was renal. The half-life of elimination was shorter after intravenous than after oral administration. Amitrole accounted for more than 86% of the identified radioactivity and for about 66% or more of the administered dose. Small amounts of 7 metabolites were detected. The proposed pathway of biotransformation, mainly in the liver, is *via* substitution at C-5 by *N*-acetylcysteine to form 3-amino-1,2,4-triazolyl-5-mercapturic acid, which is hydrolysed to 3-amino-5-mercapto-1,2,4-triazole and excreted either directly or after methylation to 3-amino-5-methylthio-1,2,4-triazole.

Amitrole is a fast-acting herbicide which is taken up predominantly through the leaves. The only significant difference between the metabolism of amitrole in rats and in plants is the production of triazolylalanine (3-(1,2,4-triazol-l-yl)-2-aminopropionic acid) in plants. In a study on apples, triazolylalanine was the major metabolite (22-24%), occurring in the free form and as conjugates. This compound is also produced by the metabolism of other triazole pesticides and was therefore reviewed by the 1989 JMPR, which concluded that residues of triazolylalanine do not

present a toxicological hazard. The ^{14}C balance at harvest after 5 months showed 1.11% in the tree, 0.07% in the harvested fruit, 0.16% in the roots and 42% remaining in the soil.

No metabolism studies were reported on farm animals.

In addition to studies which have been evaluated previously by the JMPR, new studies on the environmental fate in soil, water and sediment were reported. In soils, amitrole is rapidly degraded to NH_3 and CO_2, in addition to cyanamide and urea. In laboratory studies, the half-life of amitrole ranged from 2 to 26 days at ambient temperature in different soils. Adsorption-desorption studies showed significant adsorption and desorption, with K_{OC} values varying with the soil type from 20 to 120. It therefore appears that amitrole would readily be leached, but in leaching studies of soil with fresh or aged residues, as well in the lysimeter studies, leaching was not observed. This can be attributed to adsorption to the soil which, although reversible, gives time for breakdown to occur and prevents the compound from being leached to groundwater. This was confirmed by a field study in which amitrole was rarely detected below 15 cm. Therefore under practical conditions there is little risk that amitrole would reach the groundwater level.

The aerobic degradation of amitrole was investigated in 2 water-sediment systems, freshly sampled from fields in The Netherlands. mineralization amounted to 19 and 10% after 91 days and the half-lives were 95 and 76 days. Triazole and urea, both <3%, were the only identified products and at least 4 other polar compounds were observed at levels of about 4-5%. Unextractable residues increased with time, but it was shown by reverse isotope dilution analysis that approximately 50% of the unextractable fraction was still unchanged amitrole. In another study under anaerobic conditions at 22°C amitrole was also the major component present, accounting for about 71-87% of the applied radioactivity, after 52 weeks.

In a method of analysis for the determination of amitrole residues in various plants and plant products cold extraction with ethanol/water is followed by partition with dichloromethane and acetylation of the amitrole. The derivative is cleaned up by gel permeation and silica gel chromatography. The limit of determination is 0.01 mg/kg and recoveries ranged from 76 to 98%. The same method can be applied to soil, with a limit of determination of 0.01 mg/kg and recoveries of 82-91%. A method for blackberries using HPLC with fluorescence detection after conversion to a complex with fluorescamine was reported by the government of The Netherlands. The LOD is 0.02 mg/kg and recoveries range from 103 to 127%.

In an HPLC method with EC detection for the determination of amitrole residues in water, the sample is applied directly to a cation exchange column which is eluted with ammonia solution, and the eluate is further cleaned up on an aluminium oxide column. The limit of determination is 0.1 µg/l with recoveries in the range 86-102%. HPLC with electrochemical detection can also be used for samples of animal origin, after extraction with water/acetone, partition with dichloromethane and clean-up on ion-exchange and aluminium oxide columns. Mean recoveries at fortification levels of 0.01 to 0.1 mg/kg varied from 74% for milk to 87% for muscle.

A method in which extraction with acetone/water is followed by partitioning with dichloromethane was validated for grapes over the range 0.005-0.5 mg/kg. After acidification, a portion of the aqueous extract is cleaned up by solid-phase extraction, the eluate is evaporated to dryness, the residue is re-suspended in pyridine and the amitrole is derivatized with bis(trimethylsilyl)trifluor-oacetamide/trimethylchlorosilane (BSTFA/TMCS) before determination by GC-MS. The overall mean recovery was 83%.

The stability of residues in stored analytical samples was determined in grapes and apples at -20°C, after spiking with amitrole at levels from 0.05 to 1 mg/kg. The residues after 16 to 24 months were 60 to 75% of the initial levels.

On the basis of the animal and plant metabolism studies, the definition of the residue for both enforcement and the estimation of dietary intake should be amitrole.

Residues resulting from supervised trials

In eighteen trials on apples at the GAP rate (no specified PHI) in France, fourteen trials above the GAP rate (60 days PHI) in Germany, and two trials in Portugal where there is no GAP, the residues in the fruit from day 4 to day 171 were below the LOD (0.01 or 0.02 mg/kg). In one trial with pears in Portugal (no GAP) and three in Germany at a higher rate than recommended GAP, the residues after 60 to 120 days were similar. In four trials with peaches in Spain at twice the GAP rate (no PHI), the residues in the fruit without stones were <0.01 mg/kg at PHIs from 42 to 105 days.

As the reported GAP covers stone and pome fruits and the residues were determined over a wide range of PHIs, the Meeting estimated a maximum residue level at a practical limit of determination of 0.05 mg/kg and an STMR of 0 for amitrole in pome fruits and stone fruits. The residues of amitrole in fruit below the LOD are consistent with the results of the metabolism studies on apples.

In twenty four trials on grapes in France according to GAP (no PHI) the residues were <0.02 (20), 0.03 (3) and 0.087 mg/kg. The high value of 0.087 mg/kg was reported to be due to contamination from an adjacent trial and was ignored. Sixteen trials in Germany at a higher rate than the recommended GAP (60 days PHI) yielded residues in fruit after 15-189 days below the LOD (0.02 mg/kg).

The Meeting estimated a maximum residue level of 0.05 mg/kg and an STMR of 0.02 mg/kg for amitrole in grapes.

DIETARY RISK ASSESSMENT

STMRs were estimated for amitrole in pome fruits, stone fruits and grapes. As no other MRLs or STMRs have been previously established for amitrole these were the only ones used in the estimates of dietary intake. The International Estimated Daily Intakes for the five GEMS/Food regional diets were 0% of the ADI. The Meeting concluded that the intake of residues of amitrole resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

RECOMMENDATIONS

The Meeting estimated the maximum residue levels and STMR levels shown below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for enforcement and estimation of dietary intake: amitrole.

CCN	Commodity	MRL, mg/kg	STMR, mg/kg
FS 0009	Pome Fruit	0.05*	0
FS 0012	Stone Fruit	0.05*	0
FB 0269	Grapes	0.05	0.02

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BENOMYL (069)

[See also CARBENDAZIM (072)]

EXPLANATION

Benomyl was first evaluated in 1973, and the last evaluations were in 1994 (residues) and 1995 (toxicology and environmental). The present review is a re-evaluation under the Periodic Review Programme of the CCPR. Data on supervised trials with apricots, citrus fruits, pineapple, rice and tomatoes were to be provided for the 1998 JMPR The three main manufacturers compiled a joint submission to the present Meeting. As benomyl is metabolized in plants to carbendazim, much of the information on benomyl is reviewed in the monograph on carbendazim.

IDENTITY

ISO common name: benomyl

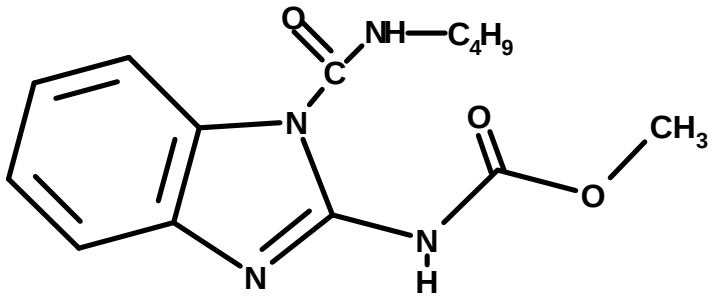
Chemical name

IUPAC: methyl 1-(butylcarbamoyl)benzimidazol-2-ylcarbamate

CA: methyl [1-[(butylamino)carbonyl]-1*H*-benzimidazol-2-yl]carbamate

CAS number: 17804-35-2

Structural formula



Molecular formula: $C_{14}H_{18}N_4O_3$
Molecular weight: 290.3

Physical and chemical properties

Pure active ingredient

Hydrolysis. Benomyl is degraded both by hydrolysis and elimination in aqueous solution, with faster degradation under alkaline conditions. The half-lives of benomyl in pH 5, 7 and 9 buffered solutions were approximately 3.5 hours, 1.5 hours and <1 hour, respectively (Wheeler, 1985). Benomyl is mainly hydrolysed to carbendazim at pH 5, while at pH 9 3-butyl-1,3,5-triazino[1,2a]benzimidazole-2,4(1*H*,3*H*)-dione (STB) is the main transformation product (Wheeler, 1985). At pH 7 the ratio of carbendazim to STB was about 3:1.

Photolysis was not a significant degradation pathway for benomyl in either buffered or natural water. In pH 5 buffered water the dark control solution showed similar degradation kinetics to the irradiated solution, so the degradation was due to hydrolysis rather than photolysis. Degradation was rapid, with a half-life of 4 hours. Carbendazim was the only significant degradation product, accounting for 99% of the initial radioactivity, with STB contributing the remaining 1% in both irradiated and control solutions. In natural river water benomyl was readily degraded to carbendazim which was not degraded further under the conditions of the study.

Technical material

Purity: Not reported

Melting point: Differential scanning calorimetry (DSC) analysis indicates that decomposition of benomyl technical occurs at about 100°C, but thermogravimetric analysis (TGA) indicates a temperature of about 80°C. TGA was with a relatively fast increase of temperature so the actual temperature at which decomposition starts to occur may be lower.

Relative density: The absolute density of technical benomyl was not reported. The bulk density is 449 kg/m^3.

Vapour pressure: $<5.0 \times 10^{-6}$ Pa at 25°C.

Colour: white
Physical state: crystalline solid
Odour: negligible

Spectra: benomyl technical, 98.3 or 95% pure, was used for the NMR, IR and mass spectra, and a benomyl analytical standard (unspecified purity) for the ultraviolet/visible spectrum.
NMR spectrum, chemical shifts, in ppm: 11.44 (a); 10.18 (b); 8.36-8.47 (c); 7.20-7.34 (d, e or f); 3.84(g); 3.48 (h); 1.69 (i); 1.49 (j) and 1.01(k).
Mass spectrum (CI): m/z 331, 319, 291, 259, 192 and 100.
IR spectrum: wave numbers, cm^{-1}: 1649.1 (urea carbonyl); 1724.4 (methyl carbamate carbonyl); 1462.0 (urea N-C-N asymmetric stretch); 1278.8 (methyl carbamate C-O-C stretch); 1620.2 and 1595.1 (imidazole C = N and C = C).
UV spectrum: maximum absorbance at 294 nm in acetonitrile.

Solubility at 25°C
water: 3.6, 2.9 and 1.9 µg/ml at pH 5, 7 and 9 respectively.
chloroform: 9.4 g/100g
dimethyl formamide: 5.3 g/100g
acetone: 1.8 g/100g
xylene: 1.0 g/100g
ethanol: 0.4 g/100g
heptane: 0.04 g/100g

Partition coefficient (n-octanol/water): 23.4 (not concentration-dependent)

Stability in air/photochemical degradation: not applicable owing to the low vapour pressure of benomyl.

Flammability: flammable solid (average time of combustion <45 seconds).

Auto-flammability: not applicable as the melting point of benomyl is >40°C.

Explosive properties: not impact-explodable.

Oxidising properties: on structural evidence, technical benomyl is not an oxidizer.

Stability: stable under normal, dry storage conditions. Subject to decomposition in the presence of moisture.

Formulations

The formulations registered for use internationally are Benlate (50 g benomyl/kg) for foliar and soil application and Benlate T (200 g /kg benomyl + 200 g/kg thiram) for seed treatment. Both are wettable powders.

[For information on the following see the monograph on carbendazim:

METABOLISM AND ENVIRONMENTAL FATE

METHOD OF RESIDUE ANALYSIS

STABILITY OF RESIDUES IN STORED ANALYTICAL SAMPLES]

USE PATTERN

Table 1 shows the registered uses of benomyl on the crops for which data were provided, as of February 1998.

Table 1. Registered uses of WP formulations of benomyl. Unless otherwise indicated, application is by foliar spray, from the ground and in the field. NA = not applicable (post-harvest use or seed treatment).

Crop	Country	Application			Mode of application	PHI. days
		Number	kg ai/ha	kg ai/hl		
Citrus fruit	Argentina	2	0.750-1.5			15
	Australia	1-3	1.5	0.025		NA
	Bolivia	1-3	1-1.5	0.05-0.07		15
	Brazil	2-3	-	0.025-0.050	8-10l/plant	1
	Chile	2	1.5-3.0			0
	Colombia	1-2/year		12.5		
	Ecuador	2	0.25	0.125		2
	France	1-3	0.9 - 1.12	0.03-0.042		2
	Indonesia	6	0.4	0.03-0.05		-
	Japan	1-4	0.51-1.25	0.017-0.025		7
	Mexico		1.0-2.0	0.001-0.0025		1
	New Zealand	1-2	0.5	0.0125		7
	Spain	3		0.03		14
	Thailand	-		0.187-0.562		NA
	Turkey			0.03		0

Crop	Country	Application			Mode of application	PHI. days
		Number	kg ai/ha	kg ai/hl		
	Uruguay	1-3	0.44-1.20	0.022-0.030		14
	USA	1-2	0.84-1.68	0.6-1.8		2
	Venezuela	1-2	-	0.5		-
	Korea	1-4	2.22-3.25	0.065		7
Orange	Japan	1-4	0.24-1.25	0.008-0.025		1
	Peru	2	0.05			-
Pome fruit	Argentina	-	0.250-.0.50	0.007-0.010		30
	Argentina	1	0.75	0.025		30
	Australia	1-3	1.5	0.025		
	Bolivia	1-3	0.2	0.01 -0.030		30
	Chile	1-4	0.9	15-25		0
	Germany	3	0.15	0.03		7
	Italy		0.03-0.05	0.03-0.05		15
	New Zealand	1-2	0.25	12.5		7
Apple	Brazil	4-8*	*	0.03		1
	Bulgaria	1-2	2.0	0.32		20
	Canada	every 7-14 days	0.275-0.55	0.025		1
	Cyprus	1-2	1.0-2.0	0.05		7
	France	1-4	0.15-0.45	0.03		7
	Greece			0.03-0.05		14
	Indonesia	3	0.6	0.2		-
	Japan	-		0.05	dipping	-
	Japan	1-6	0.51-1.75	0.017-0.025		7
	Korea	1-6	2.22-3.25	0.065		7
	Mexico		-	0.05-0.07		14
	Netherlands	1-2		0.025-0.03		14
	Portugal	2-6	0.20-0.30	0.020-0.030		7
	Turkey			0.03		14
	Uruguay	1-2	0.120-0.375	0.020-0.025		14
	Uruguay	1-3	0.21-0.75	0.035-0.050		14
	USA	6 -13	0.42	0.45		14
	Venezuela	1-2	-	0.075		-
	Yugoslavia	3	0.45	0.002-0.03		14
Pear	Bulgaria	1-3	4.5	1.5		20
	Canada	every 7-14	0.275	0.025		1
	Cyprus	1-2	1.0-2.0	0.05		7
	France	1-4	0.15-0.45	0.03		7
	Greece			0.03-0.05		14
	Japan	1-6	0.51-1.25	0.017-0.025		7
	Korea	1-6	1.75-3.25	0.05-0.065		7
	Mexico			0.05-0.07		14
	Netherlands	1-2		0.025-0.03		14
	Portugal	2-6	0.20-0.30	0.020-0.030		
	Turkey			0.03		14
	Uruguay	1-2	0.120-0.375	0.020-0.025		14
	Uruguay	1-3	0.21-0.75	0.035-0.050		14
	USA	3 - 6	0.42-0.84	0.9		14
	USA	NA	0.56	2.4	aerial	NA
	Yugoslavia	3	0.45	0.002-0.03		14
Stone fruit	Argentina	3	0.75-0.9			30
	Australia	1-2	2.0	0.025		NA
	Bolivia	1-3	0.7 - 0.9	0.06 -0.07		30
	Chile	3-4	1.5-2.25			0
	Cyprus	1-2	1.0-1.5	0.05		7
	Greece	2-4		0.01-0.03		14
	Italy	-	0.03-0.05	0.03-0.05		15
Apricot	Canada	2	0.425	0.025		2
	France	1-4	0.15-0.45	0.03		7

Crop	Country	Application			Mode of application	PHI. days
		Number	kg ai/ha	kg ai/hl		
	Portugal	2-6	0.30-0.50	0.030-0.050		7
	Turkey			0.03		14
	USA	2-4	0.60-1.12	1.2		3
	USA	2-6	1.12	2.4	aerial	3
Cherries	Canada	1-2	0.425-0.875	0.025		1, 2, 5
	France	2-6	0.15-0.45	0.03		7
	Japan		0.51-1.19	0.017		14
	Netherlands	1-3		0..25		-
	Portugal	6	0.30-0.50	0.030-0.050		7
	Turkey	1-2		0.03		0
	USA	3-6	0.60-1.12	0.6-1.2		3
	USA	3 - 6	0.60-1.12	2.4	aerial	3
	Yugoslavia	3 - 6	0.45	0.03		42
Nectarine	Canada	2	0.425	0.025		2
	USA	2-4	0.60-1.12	1.2		3
	USA	2-6	1.12	2.4	aerial	3
Peach	Bulgaria	1-2	-	0.032		20
	Canada	2	0.425	0.025		2
	France	1-4	0.15-0.45	0.03		7
	Japan		0.51-1.25	0.017-0.025		3
	Mexico	1-2	0.0035-0.05	0.07-0.10		3
	Peru	1-3	0.05			-
	Portugal	2-6	0.30-0.50	0.030-0.050		7
	New Zealand	1-3	2.0	0.025		NA
	Turkey	1-2		0.03		14
	USA	2-4	0.60-1.12	1.2		3
	USA	2-6	1.12	2.4	aerial	3
	Venezuela		0.035	0.025		-
	Yugoslavia	2	0.45	0.03		21
Plum	Canada	2	0.425	0.025		2
	France	1-4	0.15-0.45	0.03		7
	Japan	1-3	0.51-1.25	0.017-0.025		60
	Mexico		0.0035-0.05	0.07-0.10		3
	Portugal	2-6	0.30-0.50	0.030-0.050		7
	USA	2 - 6	0.84-1.12	1.2-2.4	ground/aerial	3
Prunes	USA	2-4	0.60-1.12	1.2		3
	USA	2-6	1.12	2.4	aerial	3
Berries	Bolivia	1-3	0.25	0.02 -0.03		15
Blackberry	Canada	every 7 days	0.55	0.025		2
	USA	1-5	0.42			3
Blueberry	USA	1-3	0.56	0.6		21
	USA	1-3	0.56	2.4	aerial	21
Boysenberry	USA	1-5	0.42			3
Grapes	Argentina	2	1.8	0.06		15
	Australia	1-4	3.0	0.05		3
	Brazil	2-8	*	0.03	aerial	18
	Bulgaria	1-3	1.5	0.5		20
	Canada	3	0.75	0.025		7
	Chile	4	1.0-1.5			7
	Colombia	1-2/year		12.5		
	Cyprus	2	0.35-0.5	0.05		14
	France	1-4	0.25-0.50	0.05		14
	Greece	5		0.03-0.04		14
	Italy	5-6	0.045	0.03		15
	Japan	1-3	0.51-1.25	0.017-0.025		60
	Japan	-	2-7.5	0.1-0.25		
	Korea	NA	0.65-0.98	0.065		7
	Mexico			0.050-0.070		7 days
	New Zealand	1	0.500	0.025		7

Crop	Country	Application			Mode of application	PHI. days
		Number	kg ai/ha	kg ai/hl		
	Portugal	4	0.60	0.060		7
	Spain	-	0.03-1.0	-		14
	Thailand	-		0.187-0.562		7
	Uruguay	1-3	0.15-0.30	0.03		14
	USA	4-8	0.42-0.84	0.9		50
	USA	4-8	0.42-0.84	1.2	aerial	50
	Venezuela	2	0.025	0.0125		-
	Vietnam		0.5			
Raspberry	Australia	1-4	1.0	0.025		4
	Canada	every 7 days	0.55	0.025		2
	Chile	3-4	0.9			3
	New Zealand	1	0.250	0.025		1
	USA	5	0.42			3
Strawberry	Argentina	-	0.050-0.060	0.025-0.030		15
	Australia	1-4	2.0	0.025		4
	Brazil	2-4*	*	0.03		3
	Bulgaria	1-3	1.5	0.5		20
	Canada	every 7 days	0.875	0.025		2
	Chile	2-3	1			0
	Colombia	1-2/year		0.065		
	Ecuador	3	0.25	0.125		1
	Greece	3-4		0.06-0.12		14
	Japan	1-3		0.1	dipping	-
	Japan	1-3	30	0.1	drench	-
	Mexico		0.350-0.50	0.050-0.07		0
	Netherlands	every 10-14 days		0.03-0.0375		14
	New Zealand	1	0.250	-		1
	Portugal	4	0.30-0.50	0.03-0.05		7
	Spain	-	-	0.03		14
	Uruguay	1-3	0.066-0.210	0.022-0.030		14
	USA	5-10	0.28-0.56	0.6		1
	USA	1-10	0.56	1.2	aerial	1
	Venezuela	1-2	-	0.075		-
Avocado	Mexico			0.04-0.06		30
	New Zealand	1-3	1.5	0.025		14
	USA	3 - 6	0.56-1.12	1.2-2.4	ground/aerial	30
	Venezuela	1-2	-	0.075		-
Banana	Australia	2-6	0.150	-		NA
	Brazil**	4-8*	0.125-0.15	0.3-1.5		3
	Central America	-	0.125-0.15	-		-
	Colombia	4-6		0.125	aerial	
	Ecuador	4-6	-	0.14	aerial	-
	France	6	125	-		0
	Portugal	1	0.30-0.50	0.03-0.05		1
	Venezuela	4-6	-	0.125-0.75	aerial	7-15
Mango	Mexico			0.040-0.060		14
	Peru	1-2	0.05			-
	Thailand	-		0.187-0.562		14
	USA	3 - 6	0.56-1.12	0.56-1.12		14
Pineapple	Brazil**	2-4*	*	0.25		1
	Central America	1		2-4lb/100gl	dipping	-
	Central America	1		1.25lb/100gl	seed dressing	
	Colombia	1-2/year		0.0125		
	Mexico			0.25-0.50		-
	USA	1	NA	NA	dipping	NA

Crop	Country	Application			Mode of application	PHI. days
		Number	kg ai/ha	kg ai/hl		
	Venezuela	2	0.025	0.0125		-
Brussels sprouts	Australia	1-4	2.0	0.05		5
	New Zealand	1-4	0.250			7
	UK	2	0.55			21
	USA	1-3	1.12	4.8	aerial	NA
	USA	1-3	1.12	1.2		7
	USA	1-3	1.12	8	aerial	7
Cucurbits	Australia	1-3	0.750	0.025		5
	Chile	3-4	0.25-0.5	-		0-7
	Colombia	1-2	12.5			
	France	1-3	0.15-0.45	0.03		7
	Greece	1		0.03		14
	Mexico		0.3-0.35			14
	New Zealand	1-3	0.250			7
	Spain	-	-	0.03		14
Cucumber	Argentina	3-4	0.030-0.120	0.015-0.060		30
	Brazil	3-6*	*	0.035		1
	Canada	3	0.425	.04-.09		14
	Canada	1-2	0.425	.04-.09	Greenhouse	14
	France	1-3	0.15-0.45	0.03		7
	Japan	1-3	0.17-0.5	0.017-0.025		1
	Mexico		0.30-0.35			14
	Netherlands	every 10-14 days		0.05		3
	Romania	1-2	0.95	0.035	1 l/plant	14
	Thailand	-		0.062-0.187		NA
	Turkey			0.03		14
	Venezuela	1-2	0.25	0.175		-
	Vietnam		0.5			
	USA	4 - 8	0.14-0.28	0.12		1
	USA	4	0.28	1.2	aerial	1
Melon	Brazil**	3-6*	*	0.035		1
	Canada	3	0.425	0.04-0.09		14
	Netherlands	every 10-14 days		0.05		3
	Romania	1-2	0.84	0.035	1 l/ plant	14
	USA	4 - 8	0.28	0.12		1
	USA	4	0.28	1.2	aerial	1
	Venezuela	1-2	0.25	0.175		-
Squash , Summer	Mexico		0.30-0.38			14
	USA	4-8	0.12-0.28	0.12		1
	USA	4	0.28	1.2	aerial	1
Watermelon	Brazil	3-6*	*	0.035		1
	Japan	1-5	0.17-0.5	0.017-0.025		1
	Korea	1-5	0.5-0.98	0.05-0.065		2
	Venezuela	1-2	0.25	0.175		-
	Turkey			0.03		14
Tomato	Argentina	-	0.060-0.120	0.030-0.060		20
	Australia	1-3	0.75	0.25-0.50		5
	Bolivia	1-3	0.20 - 0.30	0.03 - 0.06		20
	Brazil	2-6*	*	0.05		1
	Bulgaria	1-3	0.75	0.25		20
	Canada	2	0.42-0.55	0.025		7
	Canada	1- 2	0.55	0.025	greenhouse	7
	Chile	3-4	0.25-0.5	-		0-7
	Ecuador	4	0.25	0.125		7
	France	1-3	0.15 - 0.3	0.03		14
	Greece	1		0.03		14

Crop	Country	Application			Mode of application	PHI. days
		Number	kg ai/ha	kg ai/hl		
	Indonesia	2	0.25	0.05	drench	20
	Japan	1-3		0.05	drench	
	Japan	1-5	0.17-0.5	0.017-0.025		1
	Japan	1		0.1	soaking	-
	Mexico		0.4-0.5			0
	Netherlands	-	-	0.04		3
	New Zealand	1-3	3.0	1.0		3
	New Zealand	1-2	0.500	0.025	Individual plant	3
	Portugal	-	0.15-0.30	0.015-0.03		4
	Romania	1-2	0.22	0.025		14
	Thailand	-		0.062-0.187		NA
	Uruguay	1-3	0.066-0.210	0.022-0.030		14
	USA	5-10	0.28-0.56	0.24		1
	USA	5-10	0.28-0.56	2.4	aerial	1
	Vietnam		0.5			
Bean, broad	Argentina	2	0.375-0.500			28
Bean	Australia	1-2	1			5
	Bolivia	2	0.25-0.80	0.05-0.1		30
	Brazil	2-6*	*	0.25		17
	Canada	1	1.13	0.025		14
	Chile	2	1.5-2.0			14
	Colombia	2		12.5		
	Greece	1		0.03		14
	Mexico		0.35-0.50			14
	Netherlands	1-2	1.0-2.0	-		14
	New Zealand	1-2	1.0			14
	Japan	1-4	0.33-0.5	0.033-0.05		7
	Peru	2	0.05			-
	Thailand	-		0.187-0.375		14
	UK	2	0.55			21
	USA	1-2	0.84-1.12	0.96		28
	USA	2	0.84-1.12	8	aerial	28
	Venezuela	2	0.25	0.175		-
	Vietnam		0.6			
Beans, dry, snap	Argentina	-	0.04	0.02		28
	USA	1-2	0.84-1.12	0.96		14
Beans, Snap	USA	1	0.56	0.8		NA
Pea	Greece	1		0.03		14
	Japan	1-4	0.25-1	0.025-0.05		7
	UK	2	0.55			21
Soya bean	Argentina	2	0.125			35
	Bolivia	1	0.25 - 0.30	0.05		35
	Brazil	2-3	*	0.25	ground/aerial	12
	Colombia	2		0.25	aerial	
	Ecuador	1-3	0.25	0.125	aerial	35
	Japan	1-4	0.25-0.5	0.025-0.05		14
	Japan	1			dressing	-
	Mexico		0.350-0.500			35
	Thailand	-	0.187-0.375			NA
	USA	1 - 2	0.28-0.56	0.6		35
	USA	1 - 2	0.28-0.56	2.4	aerial	35
	Venezuela	2	0.25	0.175		-
	Vietnam		0.6			
Carrot	Ecuador	4	0.25	0.125		7
	Colombia	2				
	Australia	1-4	2.0	0.050		5
	Canada	3	0.55	0.055		15
	USA	3 - 12	0.14-0.56	0.6		4

Crop	Country	Application			Mode of application	PHI. days
		Number	kg ai/ha	kg ai/hl		
	USA	3 - 12	0.14-0.56	2.4	aerial	4
Sugar beet	Bulgaria	1-3	2.4	1.2		20
	Chile	3	0.5-1.0	-		21
	Japan	1-4	0.125-0.25	0.0125-0.025		21
	Portugal	-	0.30-0.50	0.03-0.05		21
	Romania	1-2	0.15	0.035		14
	Spain	-	-	0.03		14
	Turkey			0.02		0
	Yugoslavia	2	0.1-0.2	0.033-0.060		42
Cereals	Chile	2	0.525			26
	Germany	1	0.25	0.06		56
	Spain	1-2	0.250	-		14
Rice	Argentina	2	0.250-0.50			21
	Bolivia	2	0.25 - 0.50	0.05		21
	Brazil	1-3	*	0.25		36
	Colombia	1-2		0.125	aerial	
	Ecuador	2	0.25	0.125		21
	France	2	1.125	-		21
	Indonesia	3	0.40	0.03-0.05		20
	Korea	NA	0.65-1.5	0.065-0.1		21
	Mexico	2-3	0.05			21
	Peru	2	0.05			-
	Thailand	-		0.375		21
	Turkey			0.03		21
	Uruguay	1-2	0.500	-	aerial	14
	USA	1-2	0.56-1.12	1.2		21
	USA	1-2	0.56-1.12	8	aerial	21
	Venezuela	2	0.175	0.125		-
	Vietnam		0.6			-
Wheat	Argentina	2	0.125			35
	Australia	1	0.25			126
	Brazil	1-2	*	0.25		14
	Colombia	1-2	0.25	0.125		21
	Japan	1	0.17-0.25	0.017-0.025		-
	Netherlands	1	0.25	-		35
	New Zealand	1	0.25	0.15-0.25		60
	Italy	2	0.20-0.250	0.02-0.04		30
	Uruguay	1	0.25	-		14
	USA	1-2	0.28-1.12	0.2-1.6	ground/aerial	21
	Yugoslavia	1	0.3	-	seed dressing	42
Winter wheat	Bulgaria	1	4	4 / ROW	seed dressing	-
	UK	1	0.250	0.125		***
	Yugoslavia	2	0.2-0.3	0.060-0.075		42
Almonds	USA	2 -3	0.56-0.84	1.8	ground/aerial	50
	Italy	2-4	0.05	0.05		15
Macadamia Nuts	USA	3	0.98	1.05		NA

Crop	Country	Application			Mode of application	PHI, days
		Number	kg ai/ha	kg ai/hl		
Peanut	Argentina	2	0.07			14
	Australia	1	0.150	0.150		21
	Bolivia	2	0.15 - 0.25	0.04	aerial	14
	Brazil	2-4*	*	0.125		2
	Indonesia	5	0.4	0.03-0.05		20
	Japan	1-4	0.17-0.5	0.017-0.025		7
	Korea	1-4	0.65-0.98	0.065		7
	Mexico		0.25-0.35			14
	Thailand	-		0.187-0.375		N/A
	USA	12	0.14	0.15		14
	USA	12	0.14	0.6	aerial	14
	Vietnam		0.6			

* Not specified on the current label; will be included after re-evaluation by regulatory authorities expected by end of 1998 (typical agricultural practice indicated)
** Recommended on the current labels, but subject to withdrawal because of request for additional data by regulatory authorities.
*** Apply before detectable 1st node

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of residue trials are shown in Tables 2-31. In some trials separate sub-plots were treated, separated from each other by sufficient distance to avoid contamination by spray drift. Residues from sub-plots treated by exactly the same application regime are regarded as being from one trial. Unless otherwise indicated, all trials were conducted outdoors with foliar sprays. Underlined and double underlined residues were from treatments within the range covered by GAP (± 30%) and from those at the maximum GAP rate respectively. The latter were considered for estimating maximum residue levels and STMRs. All residues are expressed as carbendazim.

Grapefruit and limes. Seven trials were carried out in the USA, of which two on grapefruit were according to GAP for citrus fruit (1-2 x 0.56-1.68 kg ai/ha), giving residues at a PHI of 2 days of 0.08 and 0.09 mg/kg (Table 2).

Table 2. Results of residue trials with benomyl on grapefruit and limes in Florida, USA.

Report No. Commodity Year	Application			PHI, days	Residues, mg/kg	Reference
	No	kg ai/ha	kg ai/hl			
Beno/Res16	3	0.56-1.12	-	53	0.20	Trial 2
grapefruit	4	0.56-1.12	0.015-0.048	24	0.11	Trial 3
1972	3	0.56-1.12	0.024-0.05	17	0.24	Trial 4
1973	1	0.070	-	28	<0.05, <0.05	Trial 5
1974	1	0.561	-	2	0.08, <0.05	Trial 6
	1	1.12	-	2	0.08, 0.09	
1972 lime	4	0.56-1.12	0.024-0.048	0	0.79	

Oranges. Of twelve trials on oranges in the USA, 2 were according to GAP for citrus fruit, yielding residues in the fruit of 0.29 and 0.43 mg/kg at a PHI of 2 days. In Brazil, four trials with single applications, instead of the specified 2 or 3, at the recommended rate (0.025-0.05

kg ai/hl) gave residues in the fruit at the GAP PHI of 1 day of 0.13-0.36 mg/kg. Two trials with 1 application at a double rate gave much higher residues (Table 3). The results in Brazil show that residue levels decrease significantly from 1 to 7 days, although one trial in the USA did not show a significant decrease in residues from 0 to 10 days (0.22 and 0.19 mg/kg respectively).

Table 3. Residues from trials with benomyl on oranges.

Country Report N° Year, Location	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	days	mg/kg	Reference
USA Beno/Res 16 1968 Florida 1969	3	0.28	0.01	10 20	<0.02 <0.02	Test 1
	1	0.417	0.05	8	0.42	Test 2
	1	0.28	0.024	0 10 30	0.22 0.19 <0.02	Test 3
	1	-	0.10	24	0.28	Test 4
1970	1	0.417	0.05	8 15	0.79 0.86	Test 6
1971	4	1.12-1.68	-	15	0.38	Test 7
	4	1.12-3.38	-	15	0.48	Test 8
	4	1.12-3.36	-	20	0.92	Test 9
1972	4	0.561	-	17	0.32	Test 11
	4	0.56-1.12	0.018-0.0682	22	0.45	Test 13
	4	0.561-1.12	0.015-0.048	24	0.26	Test 15
1974	1	0.841	-	2	0.29; 0.23	Test 16
		1.12	-	2	0.43	
Brazil BRG92-027 1992 São Paulo	1	0.025	0.025	0 1 7 14 21	0.13 0.13 0.05 <0.01 <0.01	
	1	0.05	0.05	1 7	0.36 0.23	
	1	0.1	0.1	1 7	0.82 0.38	
BRG.92-028 1992 São Paulo	1	0.025	0.025	1 7	0.14 0.02	
	1	0.05	0.05	1 7	0.24 0.03	
	1	0.1	0.1	1 7	0.63 0.17	

Pome fruit

Apples. Fourteen trials in France were at the GAP recommended rate (1-4 x 0.15-0.45 kg ai/ha) but only in eleven were samples harvested at the recommended PHI of 7 days, giving residues ranging from <0.05 to 1.75 mg/kg (Table 6). In three trials in Germany and in 9 in the UK at higher rates (up to 15 applications of 8.4 kg ai/ha) than the German GAP for pome fruit (1-3 x 0.15 kg ai/ha) the residues on the day of application varied from 0.18 to 1.2 mg/kg, and after 7 days from 0.09 to 0.74 mg/kg.

In a total of 39 trials in the USA from 1972 to 1996, 23 according to GAP (6-13 x 0.12-0.42 kg ai/ha) gave residues at a PHI of 14 days ranging from <0.1 to 1.6 mg/kg. Four trials at twice the GAP rate at the same PHI and twelve other trials within the GAP range at with PHIs

from 9 to 64 days yielded residues within the same range. Decline studies showed that the decrease of residues from 0 to 21 days varied over a wide range up to about 90% (Table 4).

Table 4. Results from trials with benomyl on apples.

Country Report No. year location	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	days	mg/kg	Reference
France BEA118910BG 1971 Bouches du Rhone	1	0.3	0.03	1 8 13	0.12 <0.05 <0.05	Test 6
1988 Bouches du Rhone	1	0.3	0.03	1 8 15	0.85 0.60 0.31	Test 7 control=0.13 mg/kg
	1	0.3	0.03	1 8 15	1.98 1.8 1.49	Test 8 control=0.09 mg/kg
Gironde	1	0.30	0.030	4	<0.05	
	3	0.22-0.342	0.030	5	0.81	control=0.07 mg/kg
BEA119122BG 1990	2	0.32	0.083	8	<0.05	Trial1
Lafrancaise	2	0.33	0.083	2	<0.05	Trial 2
Cordes	2	0.345	0.045	7	0.15	Trial 1
Tolosannes	2	0.345	0.045	1	0.12	Trial 2
Trizay	4	0.21	0.030	7	0.16; 0.19	Trial 1/2
BEA119213BG 1991 Tarn et Garonne	2	0.45	0.124	6	0.49	
Cordes Tolosannes	2	0.27	0.036	7	0.11	
A119412 Balma 1993	1	0.6	0.096	3 7 15 21 30	0.30 0.19 0.16 0.12 0.07	
	2	0.6	0.096	7 15	0.28 0.17	
Germany BENO/RESO 10 1968 Weinstraße	7	1.0	0.050	4 8 11 15 21 29	0.82 0.22 0.27 0.66 0.16 <0.1	
Heidelberg	10	0.5	0.025	3 7 11 14 21 28	1.5 0.53 0.66 0.34 0.43 0.34	
Neustadt 1969	7	0.36	0.015-0.025	0 1 3 7 14 21	0.92 0.79 0.66 0.59 0.39 <0.1	
UK BENORES/10 Nottingham 1969	1	0.56	0.060	0 3 7 14	0.18 0.24 0.09 <0.05	

Country Report No. year location	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	days	mg/kg	Reference
Nottingham 1970	2	2.24	1.120	0	0.48	
Suffolk 1969	1	0.56	0.060	0 3 7 14	0.49 0.38 0.29 0.09	
	12	6.72	0.060	0 7	0.91 0.74	
Thurgarton 1969	8	0.56	0.060	0 7	0.80 0.38	
	9	5.04	0.060	0 7	1.2 0.25	
Norton 1969	9	5.04	0.060	0 7	0.90 0.28	
Ipswich 1969	7	3.92	0.060	0 7	0.54 0.13	
Faversham, 1969	15	8.4	0.060	0 7	0.99 0.32	
USA BENO/RES 10 1972	14	0.420	0.015-	13	<0.1	Trial 1
	12	0.420	0.015	13	0.28	trial 2
NY	9	0.560	0.030	14	<0.1; 0.36	Trial 1/2
PA	6	0.210	0.0075	28	0.15; 0.16	Trial 1/3
	6	0.420	0.015	28	0.31; 0.17	Trial 2/4
Ohio	9	0.63	0.067	9	0.27	Trial 1
	9	0.630	0.067	9	0.40	Trial 2
	9	0.630- 0.113	0.030-0.067	9	0.79; 0.43	Trial 3/4[1]
MO	12	0.735	0.022	23	0.11; 0.26	Trial 1/2
VA	12	0.420	0.015	56	0.14	Trial 1
	12	0.210	0.0075	56	0.17	Trial 2
	9	0.420	0.015	64	<0.1; <0.1	Trial 1/2
MI	11	0.210	0.022	41	0.14; 0.14	Trial 1/3
	11	0.140	0.015	41	0.12	Trial 2
ME	12	0.350	0.015	22	0.28; 0.39	Trial1/2
AMR 1594-90[2] 1990 PA	7	0.28-0.42	0.048-0.072	0 3 7 10 14 21	0.92 0.60 0.54 0.78 0.54 0.48	Test 1
	7	0.56-0.84	0.097-0.14	0 3 7 10 14 21	2.2 1.1 1.6 1.1 1.2 1.0	
MD	6	0.28-0.42	0.031-0.046	0 3 7 10 14 21	0.28 0.31 0.35 0.31 0.18 0.24	Test 2
IL	7	0.28-0.42	0.020-0.030	0 3 7 10 14 21	0.92 0.55 0.59 0.58 0.78 0.51	Test 3

Country Report No. year location	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	days	mg/kg	Reference
NY	7	0.28-0.42	0.030-0.045	0 3 7 10 14 21	0.72 0.49 0.60 0.61 0.27 0.21	Test 4
	7	0.56-0.84	0.060-0.090	0 3 7 10 14 21	1.7 1.2 0.98 1.4 0.92 0.50	
MI	7	0.28-0.42	0.024-0.036	0 3 7 10 14 21	1.7 2.0 1.8 1.4 1.6 0.98	Test 5
	7	0.28-0.42	0.020-0.030	0 3 7 10 14 21	0.32 0.16 0.23 0.16 0.20 0.14	Test 6
CA	7	0.28-0.42	0.023-0.030	0 3 7 10 14 21	0.50 0.35 0.19 0.09 0.16 0.11	Test 7
	7	0.56-0.84	0.047-0.07	0 3 7 10 14 21	1.5 1.0 1.4 0.20 0.20 0.17	
WA	7	0.28-0.42	0.030-0.045	0 3 7 10 14 21	0.72 0.61 0.53 0.58 0.60 0.48	Test 8
	7	0.56-0.84	0.060-0.090	0 3 7 10 14 21	1.4 1.4 1.3 0.98 1.2 1.0	
AMR3742-96[2] 1996 NY	7	0.28-0.42	0.030-0.045	14	0.48; 0.51	Trial1/2
PA	7	0.28-0.42	0.026-0.040	14	0.37; 0.25	Trial 1/2
	7	0.28-0.42	0.058-0.086	14	0.38; 0.34	Trial 1/2
MD	7	0.28-0.42	0.027-0.040	14	0.78; 0.48	Trial 1/2
MI	7	0.28-0.42	0.030-0.045	14	1.2; 1.4	Trial 1/2

Country Report No. year location	Application			PHI, days	Residues, mg/kg	Reference
	No	kg ai/ha	kg ai/hl			
	7	0.28-0.42	0.058-0.091	14	1.0; 0.98	Trial 1/2
UT	7	0.28-0.42	0.029-0.043	14	1.2; 1.04	Trial 1/2
CA	7	0.28-0.42	0.014-0.021	14	0.98; 1.6	Trial 1/2
WA	7	0.28-0.42	0.020-0.030	14	0.72; 0.72	Trial 1/2
	7	0.28-0.42	0.030-0.045	14	0.72; 0.98	Trial 1/2
	7	0.28-0.42	0.029-0.039	14	0.59; 0.65	Trial 1/2
OR	7	0.28-0.42	0.038-0.051	14	1.0; 0.50	Trial 1/2

[1] Orchard spray + post harvest dip
[2] One application at lowest and 6 at highest rate

Pears. In three trials in the UK with 1 or 6 applications 0.06 kg ai/hl, residues from 0 to 11 days varied from 0.16 to 1.5 mg/kg. No GAP was reported to evaluate the trials. In eight trials in the USA according to GAP (3-6 x 0.42-0.84 kg ai/ha) the residues at the recommended PHI of 14 days varied from 0.50 to 2.4 mg/kg. One trial at a higher rate gave residues of 1.7 mg/kg after 14 days. One decline study showed that the residues did not change significantly from day 0 to day 21 (1.4 and 1.3 mg/kg respectively) (Table 5).

Table 5. Residues from trials with benomyl on pears.

Country Report No. Year location	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	days	mg/kg	Reference
UK BENO/RES 8 1969 Thurgarton	6	0.56	0.060	0 7	0.51 0.22	
Ipswich	6	0.56	0.060	0 7	1.5 0.16	
Essex	1	-	0.060	11	0.59	
USA AMR1595-90 1990 CA	4	0.56-0.84	0.043-0.074	0 3 7 10 14 21	1.4 1.11 0.92 0.92 1.3 1.3	Test 1
MI,	4	0.82-1.23	0.058-0.088	14	1.7	Test 1
OR	4	0.56-0.84	0.030-0.045	14	0.65	Test 3
AMR3742-96 1996 NY	4	0.56-0.84	0.060-0.090	14	0.50; 0.52	Trial 1/2
CA	4	0.56-0.84	0.039-0.057	14	0.78; 1.1	Trial 1/2
	4	0.56-0.84	0.060-0.090	14	0.72; 0.59	Trial 1/2
WA	4	0.56-0.84	0.060-0.090	14	0.59; 0.72	Trial 1/2
	4	0.56-0.84	0.040-0.060	14	2.4; 2.2	Trial 1/2
OR	4	0.56-0.84	0.063-0.091	14	0.85; 0.85	Trial 1/2

Stone fruit

Apricots and nectarines. In one trial on apricots in Switzerland the application was according to French GAP (1-4 x 0.03 kg ai/hl) but the sample was taken much later than the recommended PHI of 7 days. In two trials in the USA on apricots and four on nectarines at a lower application rate than the recommended GAP (2-4 x 0.60-1.2 kg ai/hl) the residues ranged from <0.06 to 1.4 mg/kg after 0 to 19 days (Table 6). In a decline study the residues increased slightly from day 1 to day 19 (0.65 and 0.72 mg/kg respectively).

Table 6. Residues from trials with benomyl on apricots and nectarines .

Country Report No. year	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	days	mg/kg*	Reference
Apricots						
Switzerland BENO/RES 14 1971	4	-	0.030	30	0.45	
USA BENO/RES 14 1967 California	1	-	0.030	4	<0.06	
1969	3	-	0.030	8	1.7	
Nectarines						
USA	1	-	0.030	1	0.65	

Country Report No. year	Application			PHI, days	Residues, mg/kg*	Reference
	No	kg ai/ha	kg ai/hl			
BENO/RES 17 1967 California				3 5 7 12 19	0.72 1.3 0.92 0.98 0.72	
1969	3	-	0.03	1	1.4	
	2	-	0.030	0	1.0	
	3	-	0.03	13	1.1	

* Results were corrected for blanks and recovery

Cherries. Two trials in Italy in 1996 according to French GAP (2-6 x 0.15-0.45 kg ai/ha) gave residues at 7 days of 0.24 and 0.65 mg/kg. In a decline study residues were similar 0 and 7 days after the application.

Forty one trials in the USA from 1967 to 1976 were at rates above and below the recommended GAP (3-6 x 0.60-1.12 kg ai/ha, PHI 3 days). Residues from 0 to 26 days after application varied from <0.03 to 8.2 mg/kg (Table 7).

Table 7. Residues from trials with benomyl on cherries.

Country Report No. year	Application			PHI, Days	Residues, mg/kg	Reference
	No	kg ai/ha	kg ai/hl			
Italy AMR 3830-96 1996 Vignola	4	0.312-0.615	0.03-0.05	0 1 3 5 7	0.53, 0.54 0.58, 0.67 0.19, 0.44 0.84, 0.19 0.50, 0.65	Test 2
AMR 3831-96	4	0.312-0.615	0.03-0.05	7	0.24, 0.23	Test 5
USA BENO/RESO 15* 1967 CA	3	-	0.030	1	1.6	Trial 1N
	2	-	0.030	1	1.2	Trial 2N
	2	-	0.030	21	0.47	Trial 3N
	2	-	0.030	1	0.78	Trial 1S
	2	-	0.030	21	<0.06	Trial 2S
DE	4	-	0.007	7 19	0.36 0.10	Trial 1
	4	-	0.022	7	0.99	Trial 2
1968 CA	3	-	0.030	13	0.78	Trial 1
	2	-	0.030	26	0.34	Trial 2
1969 CA	2	-	0.060	2	8.2	
	2	-	0.030	0	0.12	
TAS-000-005 1967 CA	3	0.28	0.030	1	1.6	STCA67L1
	2	0.28	0.030	1	1.2	STCA67L2
	2	0.28	0.030	21	0.47	STCA67L3
	2	0.28	0.030	1	0.78	STA67RA1
	2	0.28	0.030	21	<0.06	STA67RA2
DE	4	0.07	0.030	7 19	0.34 0.10	NEDE67M1 NEDE67M2
	4	0.21	0.030	7	0.98	NEDE67M3

Country Report No. year	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	Days	mg/kg	Reference
1968	2	0.28	0.030	13	0.78	STCA68L1
CA	2	0.28	0.030	26	0.34	STCA68L2
1969	2	0.56	-	2	8.23	
CA	2	0.28	-	0	0.12	LICA69RA
	2	0.28	0.030	0	0.12	LICA69RA1
1971 CA	1	1.12	0.12	1	0.18	
1972	3	0.63	0.067	10	0.14	ELMI72M1
MI	3	0.35	0.037	10	0.22	ELMI72M2
	3	0.35	0.037	10	0.78	ELMI72M3
1973	5	0.56	0.060	0	1.2	
WI	5	0.56	0.060	0	1.4	
1974	4	0.42	0.045	0	0.65	
MI	5	0.42	0.045	0	1.3	
1975	5	0.56	0.024	0	0.61	
MI	5	0.56	0.020	0 7	0.93 0.57	
	5	0.56	0.020	0 7	0.33 0.31	
	4	0.56	0.060	14	1.2	
1976 MI	1	1.68	0.18	0 3 7	0.65 0.21 0.12	
	7	2.24	0.240	0	3.53	
CA	3	6.72	0.18	14 25	0.09 <0.03	
	3	8.96	0.24	14 25	0.16 <0.03	
	3	8.96	0.24	7	<0.03	
	3	6.72	0.18	7	<0.03	

Peaches. A total of 9 trials were in Europe from 1988 to 1996 and 21 in the USA from 1967 to 1990 (Table 8). Four of five trials in France were according to GAP (1-4 x 0.15-0.45 kg ai/ha, 7 days PHI) giving residues in the fruit from 0.07 to 0.15 mg/kg. Two trials in Portugal and two in Spain according to Portuguese GAP (2-6 x 0.3-0.5 kg ai/ha) gave residues at 7 days - from 0.08 to 0.56 mg/kg.

Seven trials in the USA according to GAP (2-4 x 0.60-1.12 kg ai/ha) gave residues at 3 days from 0.21 to 1.0 mg/kg. Residues from 3 trials at twice the GAP rate ranged from 0.59 to 1.7 mg/kg 3 days after application.

Table 8. Residues from trials with benomyl on peaches.

Country Report No. Year, Location	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	days	mg/kg*	Reference
France BEA118910-BG 1988 Bouches du Rhone	1	0.3	0.03	1 5 10	0.23 0.12 <0.05	

Country Report No. Year, Location	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	days	mg/kg*	Reference
Gard	1	0.3	0.03	1 4 11	1.2 0.54 0.24	
1988 Trizay	2	-	0.03	7	0.07	
AMR3425-95 1995 Les Valance	4	0.294-0.298	0.03-0.04	0 1 3 5 7	0.44 0.39 0.21 0.18 0.09	
AMR 3426-95	4	0.294-0.298	0.03-0.04	7	0.15	
Portugal AMR 3426-95 1995	4	0.288-0.383	0.03	7	0.56	
AMR3831	4	0.295-0.457	0.03	7	0.09	
Spain AMR3426-95 1995 Binefar	4	0.298-0.603	0.03-0.04	7	0.26	
AMR3831-96 1995 Huesca	4	0.301-0.456	0.03	7	0.08	
USA BENO/RES 18* 1967	2	-	0.030	0	0.14	
CA	2		0.030	9	0.16	
1968 SC	4		0.022	6	<0.06	
GA	6		0.022	2 9	0.44 0.09	
FL	7	-	0.022	12	0.20	
1969	2	-	0.030	14	0.51	Trial 1
CA	2	-	0.060	14	1.4	Trial 3
	3	-	0.030	6	4.1	
	4	-	0.030	0	5.4	
	2	-	0.030	0	3.1	
NC	9	-	0.30	1 7 14	3.6 2.1 1.7	
AMR1599-90 1990 SC	2	1.12	0.060	0 3 7 10 14	0.37 0.21 0.25 0.02 0.19	Trial 3
	2	2.24	0.120	0 3 7 10 14	0.98 0.59 0.52 0.31 0.28	Trial 4
MI	2	1.12	0.060	0 3 7	1.2 1.0 1.1	

Country Report No. Year, Location	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	days	mg/kg*	Reference
				10	2.0	
				14	1.0	
	2	2.24	0.120	0	1.4	
				3	1.4	
				7	0.20	
				10	1.2	
				14	0.85	
CA	2	1.12	0.085-0.093	0	0.05	
				3	0.61	
				7	0.72	
				10	0.92	
				14	0.64	
	2	2.24	0.170-0.186	0	0.92	
				3	1.7	
				7	1.3	
				10	2.6	
				14	1.2	
AMR 1691-90 1990 CA	2	1.12	0.116	3	0.30	PS
SC	2	1.12	0.096	3	0.51	PS
AMR 1692-90 1990 CA	2	1.12	0.120	3	0.72	PS
SC	2	1.12	0.120	3	1.0	PS

*Results were corrected for blanks and recoveries

Plums. In seven trials in France and Italy according to French GAP (1-4 x 0.15-0.45 kg ai/ha) the residues at 7 days ranged from <0.05 to 0.34 mg/kg. In two decline studies, residues at day 0 either did not change or increased slightly after 7 days. In two trials in Spain according to Portuguese GAP (2-6 x 0.3-0.5 kg ai/ha) the residues were 0.07 and 0.05 mg/kg after 7 days.

In four trials in the USA according to GAP (2-4 x 0.60-1.12 kg ai/ha) the residues at 3 days ranged from 0.02 to 0.24 mg/kg in the fruit. In eight other trials at lower (0.03 kg ai/hl) or higher rates (4 x 1.96 kg ai/ha) the residues in the fruit ranged from 0.23 to 4.0 mg/kg after 0 to 7 days. In 6 of the US trials residues were measured in the fresh fruit and after processing to prunes.

In eleven decline studies in Europe and the USA residues either increased or did not change significantly from day 0 to day 7 or 14. The results are shown in Table 9.

Table 9. Residues from trials with benomyl on plums.

Country Report No. year location	Application			PHI,	Sample	Residues,
	No	kg ai/ha	kg ai/hl	days		mg/kg*
France AMR 3830-96 1996 Armon	4	0.298-0.303	0.04	0	fresh fruit	<0.05
				1		<0.05
				3		<0.05
				5		<0.05

Country Report No. year location	Application			PHI,	Sample	Residues,
	No	kg ai/ha	kg ai/hl	days		mg/kg*
				7		<0.05
AMR 3831-96 Fronton	4	0.281-0.326	0.03-0.04	7	fresh fruit	0.34
Italy AMR 3425-95 1995 Trentino, TN	4	0.283-0.365	0.02-0.03	0	fresh fruit	<0.05
				1		<0.05
				3		<0.05
				5		<0.05
				7		<0.05
AMR 3426-95 Trentino, TN	4	0.283-0.365	0.02-0.03	7	fresh fruit	0.05
AMR 3830-96 1996	4	0.294-0.506	0.03	0	fresh fruit	0.06
				1		0.06
				3		0.06
				5		0.05
				7		0.08
AMR 3831-96 Collebeato, Bs	4	0.294-0.506	0.03	7	fresh fruit	0.06
Bordano	4	0.294-0.506	0.03	7	fresh fruit	0.10
Spain AMR 3426-95 1995 Binefar, Huesca	4	0.303-0.459	0.03-0.04	7	fresh fruit	0.07
AMR 3831-96	4	-	0.03	7	fresh fruit	0.05
USA BENO/RES 19* 1969	4	-	0.030	1	fresh fruit	0.92
	2	-	0.030	0	fresh fruit	0.42
				5		0.44
TAS-000-005 1985 CA	3	1.12	-	7	fresh fruit/prunes	0.65/0.54
	4	0.985	-	0	fresh fruit/prunes	0.23/0.13
				1		1.4/0.13
				3		0.65/0.65
				7		3.0/0.078
				14		0.92/0.078
	4	1.96	-	0	fresh fruit/prunes	2.8/0.05
				1		3.3/0.61
				3		4.0/0.61
				7		3.1/0.40
				14		3.1/0.32
AMR 1418 1988 CA	3	1.12	-	7	fresh fruit/prunes	0.65/0.54
	4	0.988	-	0	fresh fruit/prunes	0.23/0.13
				1		1.4/0.14
				3		0.66/0.16
				7		3.0/0.08
				14		0.92/0.08
	4	1.96	-	0	fresh fruit/prunes	2.8/0.50
				1		3.3/0.63
				3		4.0/0.60
				7		3.1/0.40
				14		3.1/0.32
AMR 1613-90	2	0.60	-	0	fresh fruit	0.01

Country Report No. year location	Application			PHI,	Sample	Residues,
	No	kg ai/ha	kg ai/hl	days		mg/kg*
1990 CA				3		0.02
				7		0.01
				10		0.01
				14		0.02
	2	1.12	-	0	fresh fruit	0.07
				3		0.06
				7		0.11
				10		0.06
				14		0.05
	2	0.60	-	0	fresh fruit	0.09
				3		0.24
				7		0.17
				10		0.20
				14		0.22
	2	1.12	-	0	fresh fruit	0.10
				3		0.21
				7		0.17
				10		0.20
				14		0.07

* Results were corrected for blanks and recovery

Berries

Cane berries. Thirteen trials were conducted on berries in the USA and Canada in 1967 and 1971 (Table 10). In three trials on blackberries and blueberries in the USA according to GAP (1-5 x 0.42 kg ai/ha, PHI 3 days 1-3 x 0.56 kg ai/ha, PHI 21 days) the residues at the GAP PHI were 0.42 to 1.7 mg/kg.

Table 10. Residues from trials with benomyl on cane berries.

Country/Report No. Berry Location	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	Mg/kg
USA/ TAS000-005/1969 Blackberries					
OR	3	0.56	0.060	2	2.0
	5	0.45	0.013	6	3.3
	3	0.45	0.013	0	3.9
				3	1.7
				7	1.6
				14	1.0
	4	0.45	0.013	0	2.0
				3	1.6
				7	1.2
				14	0.49
Boysenberries					
CA	2	1.12	0.06	1	1.8
	3	0.56	0.06	2	2.1
Blueberries					

Country/Report No. Berry Location	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	Mg/kg
WA	4	0.84	-	50	1.3
	5	0.70	-	39	<0.03
	1	0.84	-	31	0.91
MI	5	0.56	-	21	0.42
Canada/TAS000-005/1971 Raspberries					
Ontario	4	0.28	0.030	1	3.7
	4	0.28	0.030	7	0.98
	3	0.28	0.030	12	0.98

Grapes. Twenty two trials were conducted in Europe (Table 11). In two trials in Greece according to GAP (0.03-0.04 kg ai/hl) and four in France and Italy according to French GAP (1-4 x 0.25-0.50 kg ai/ha) the residues were 0.30 to 1.0 mg/kg at the GAP PHI of 14 days. In two trials in Germany at higher than usual rates in Europe the residues were 0.24 and 0.94 mg/kg after 14 days. One trial in Portugal and two in Spain according to Spanish GAP (0.03-1.0 kg ai/ha, 14-day PHI) gave residues of 0.46 to 0.86 mg/kg.

Decline studies showed that residues either decreased by 23-42%, remained unchanged or increased by 53% within periods of 14 to 35 days.

Table 11. Residues from trials with benomyl on grapes.

Country Report No. Year location	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	mg/kg
France AMR 3449-95 1995 Nambsheim	4	0.270-0.526	0.05-0.07	0 1 3 7 14	0.78 0.84 1.1 0.72 0.45
AMR3938-96 1996	4	0.50	0.06	14	1.0
Germany BENO/RES 20 1968 Weinstrasse	3	0.9-1.8	0.15-0.30	14 21 28 35 52	0.24 <0.06 0.24 0.24 0.35
	4	0.9	0.15	4 8 14 22 28	0.47 0.47 0.94 0.53 0.72
Greece 1995	4	0.320-0.417	0.05	14	1.0
AMR3938-96 1996	4	0.258-0.499	0.05	14	0.30
Italy AMR 3450-95 1995 Puglia	4	0.49	0.05	14	0.36
AMR3938-96	4	0.349-0.507	0.05	0	1.3

Country Report No. Year location	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	mg/kg
Puegnago del Garda				1 3 7 14	0.73 0.96 0.67 1.0
Portugal AMR3938-96 1996	4	0.288-0.510	0.05	14	0.84
Spain 1995 Barcelona	4	0.274-0.341	0.05	14	0.86
AMR3938-96 1996 Sevilla	4	0.500-0510	0.05	14	0.46

Strawberries. The application in a Canadian trial approximated the GAP rate (0.875 kg ai/ha) but no samples were taken at the GAP PHI of 2 days. Residues after 1 and 4 days were 0.91 and 0.72 mg/kg. Eighteen trials in the USA were at lower or higher rates, or longer or shorter PHIs, than GAP (5-10 x 0.28-0.56 kg ai/ha, 1-day PHI). The residues at 0 to 14 days varied from 0.13 to 2.4 mg/kg. Residues decreased or increased irregularly during the 6-7 days after the last application. The results are shown in Table 12.

Table 12. Residues from trials with benomyl on strawberries.

Country Report No. year	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	mg/kg
Canada TAS000-005 1975 Vineland	5	1.12	0.12	1 4 7	0.91 0.72 0.60
USA TAS000-005 1969 OR	4	0.56	0.060	8	0.42
	4	1.12	0.120	8	0.72
	4	0.84	0.090	2	0.98
	5	0.84	0.090	1	0.58
	5	0.84	0.090	1 3 4 7	0.58 0.98 0.65 1.1
	4	1.68	0.180	2	1.3
	5	1.68	0.180	1 3 4 7	1.3 1.8 1.5 2.1
CA	3	0.56	0.040	0	1.1
	5	0.56	0.040	0 7	0.98 0.10
	5	0.56	0.030	3	1.1

Country Report No. year	Application			PHI, days	Residues, mg/kg
	No	kg ai/ha	kg ai/hl		
	1	0.56	0.030	0	0.59
				2	0.92
				4	0.84
				6	0.42
	1	1.12	0.060	0	0.92
				2	1.9
				4	2.4
				6	0.50
WA	5	0.28	0.03	3	1.1
1974	5	1.12	-	0	0.32
WA	5	2.24	-	0	0.74
	5	3.36	-	0	0.92
1976	7	0.28	0.015	7	0.24, 0.13
NY	8	0.28	0.015	14	0.21, 0.24

Tropical fruits

Avocados. In two trials in the USA according to GAP (3-6 x 0.56-1.12 kg ai/ha, 30 days PHI) the residues in the fruit were 0.11 and <0.06 mg/kg after 22-30 days. In eight other trials at shorter PHIs residues in samples harvested after 11 to 21 days varied from 0.09 to 1.1 mg/kg (Table 13).

Report No. year	Application			PHI, days	Residues, mg/kg
	No	kg ai/ha	kg ai/hl		
TAS000-005 1968 TX	3	1.12	0.024	22	0.11
1971 FL	6	0.56	0.006	30	<0.06
1973 FL	4	1.12	0.030	1	1.0
				3	0.91
				12	0.78
	8	0.56-1.12	0.015-0.030	1	0.84
				4	0.43
				11	0.54
1974 FL	6	1.12	0.12	10	0.39
				14	0.36
				21	0.23
	7	1.12	0.12	10	1.4
				14	1.5
				21	1.1
	4	1.12	0.059	10	0.48
				14	0.22
				21	0.25
	4	1.12	0.059	14	0.07
				21	0.16
	6	1.12	0.059	14	0.28
				21	0.18

Report No. year	Application			PHI, days	Residues, mg/kg
	No	kg ai/ha	kg ai/hl		
	6	1.12	0.059	14 21	0.18 0.09
	6	1.12	0.059	14 21	0.35 0.36

Bananas. Twenty three trials were conducted in Central America where the GAP rate is 0.125-0.15 kg ai/ha with no specification of the number of applications or PHI. Residues in the whole fruit and pulp in 14 trials with 4 to 14 applications of 0.14 kg ai/ha ranged from <0.03 to 0.11 mg/kg at PHIs of 0 or 1 day. Eight trials at twice this rate and one at a lower rate gave similar results. One trial in Brazil according to GAP (0.125-0.130 kg ai/ha) and one at a double rate gave residues in the pulp of 0.44 and 0.07 mg/kg respectively. One trial in Jamaica according to Central American GAP and one at a double rate gave residues at day 0 of <0.03 and 0.04 mg/kg in the fruit and <0.03 mg/kg in the pulp respectively (Table 14).

Table 14. Residues from trials with benomyl on bananas.

Country Report No. year	Application			PHI, days	Portion analysed	Residues, mg/kg
	No	kg ai/ha	kg ai/hl			
COSTA RICA BENO/RES 21 1969[1]	6	0.14	0.5	0	fruit peel pulp	<0.06 <0.06 <0.06
1970[1]	7	0.14	0.5	0	fruit peel pulp	<0.06 <0.06 <0.06
1977[2]	6	0.14	0.75	1	fruit pulp	0.06, <0.03 <0.03, <0.03
	6	0.28	1.5	1	fruit pulp	0.07, 0.08 <0.03, <0.03
	6	0.14	0.75	1	fruit pulp	<0.03, 0.11 <0.03, <0.03
	6	0.28	1.5	1	fruit pulp	<0.03, 0.07 <0.03, <0.03
	6	0.14	0.75	1	fruit pulp	0.03, 0.05 <0.03, <0.03
	6	0.28	1.5	1	fruit pulp	0.06, 0.12 <0.03, <0.03
	7	0.14	0.75	1	fruit pulp	<0.03, <0.03 <0.03, <0.03
	7	0.28	1.5	1	fruit pulp	<0.03, 0.09 0.06, <0.03
	7	0.14	0.75	1	fruit pulp	<0.03 <0.03
	7	0.28	1.5	1	fruit pulp	<0.03 <0.03
	7	0.14	0.75	1	fruit pulp	<0.03 <0.03
	7	0.28	1.5	1	fruit pulp	<0.03 <0.03

Country Report No. year	Application			PHI,	Portion	Residues,
	No	kg ai/ha	kg ai/hl	days	analysed	mg/kg
	7	0.14	0.75	1	fruit pulp	<0.03 <0.03
	7	0.28	1.5	1	fruit pulp	<0.03 <0.03
	7	0.14	0.75	1	fruit pulp	<0.03 <0.03
	7	0.28	1.5	1	fruit pulp	<0.03 <0.03
HONDURAS 1970[1]	6	0.146	-	1	pulp	0.10
1971[1]	4	0.140	1.5	29	fruit pulp	<0.06 <0.06
	4	0.140	0.601	29	fruit pulp	<0.06 <0.06
1977-1978[2]	14	0.140	0.03	1	fruit pulp	<0.03 <0.03, <0.03
	14	0.07	0.015	1	fruit pulp	<0.03 <0.03
JAMAICA 1977[2]	5	0.140	-	0	fruit pulp	<0.03, <0.03 <0.03, <0.03
	5	0.280	-	0	fruit pulp	0.04, 0.04 <0.03, <0.03
BRAZIL 1985[2]	8	0.15	0.05	3	peel pulp	0.06 0.44
São Paulo	8	0.30	0.1	3	peel pulp	0.65 0.07

[1] Aerial spray
[2] Ground spray

Mangoes. Of nineteen trials in the USA 9 were at a lower rate (0.28 kg ai/ha) and 4 at higher rates (up to 3.92 kg ai/ha) than the recommended GAP (3-6 x 0.56-1.12 kg ai/ha, 14 days PHI). Of 6 trials at rates within the GAP range, 3 were with too many applications. The residues in all the trials ranged from <0.06 to 3.0 mg/kg in samples taken 2 to 29 days after the last application (Table 15).

Table 15. Residues from trials with benomyl on mangoes in the USA (FL).

Report No. year	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	mg/kg
TAS000-005 1968	12	1.96	0.030	9	0.17
	17	1.96	0.030	9	3.0
	5	3.92	0.060	21	0.91
	11	3.92	0.06	19	2.0
1969	11	1.12	0.030	22	0.43
1970	6	0.28	0.015	15	<0.06
	6	0.28	0.015	15	<0.06
	6	0.6	0.018	6	0.72

Report No. year	Application			PHI, days	Residues, mg/kg
	No	kg ai/ha	kg ai/hl		
	6	0.6	0.018	6	0.85
1971	5	1.12	0.03	14	0.09
	12	1.12	0.030	14	0.14
	7	1.12	0.030	2	0.28
	8	0.28	0.03	29	<0.06
	8	0.28	0.03	29	<0.06
	6	0.28	0.030	12	0.10
	5	0.28	0.030	17	0.15
	7	0.28	0.030	2	0.28
	6	0.28	0.030	12	<0.06
	5	0.28	0.030	17	0.08

Pineapples. Eight trials in Costa Rica according to Mexican GAP (0.25-0.50 kg ai/hl) gave residues at day 0 from 1.9 to 3.3 mg/kg in the fruit and <0.03 mg/kg in the pulp (Table 16).

Table 16. Residues from trials with benomyl on pineapples in Costa Rica.

Report No. year	Application			PHI, days	Sample	Residues, mg/kg	Reference
	No	kg ai/ha	kg ai/hl				
AMR 3300-95 1995	1	5.11	0.25	0	fruit* pulp	2.0 <0.03	Test 1
	1	4.94	0.25	0	fruit pulp	2.1 <0.03	Test 2
	1	5.26	0.25	0	fruit pulp	2.5 <0.03	Test 3
	1	5.13	0.25	0	fruit pulp	3.3 <0.03	Test 4
1996	1	4.74	0.25	0	fruit pulp	2.9 <0.03	Test 5
	1	5.04	0.25	0	fruit pulp	2.7 <0.03	Test 6
	1	5.21	0.25	0	fruit pulp	1.9 <0.03	Test 7
	1	5.29	0.25	0	fruit pulp	2.3 <0.03	Test 8

* Residues in the whole fruit were calculated from the residues in the pulp and peel

Vegetables

Brussels sprouts. Six trials in the UK according to GAP (2 x 0.55 kg ai/ha, 21-day PHI) gave residues from <0.05 to 0.27 mg/kg at 21 days, and two in the USA at the GAP rate (1-3 x 1.12 kg ai/ha) gave residues at the GAP PHI of 7 days of 2.4 and 2.9 mg/kg (Table 17).

Table 17. Residues from trials with benomyl on Brussels sprouts.

Country Report No. Year Location	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	Days	mg/kg	Reference
UK AMR 4050-96 1995 Derbyshire	2	0.56	0.03	21	0.04	
North Yorkshire	2	0.56	0.03	21	<0.05	
Lincolnshire	2	0.56	0.03	21	0.08	
AMR 4015-96 Derbyshire	2	0.55	0.3	21	0.27	
N. Yorks	2	0.55	0.3	21	0.05	
Lincolnshire	2	0.55	0.3	21	0.16	
USA[1] TAS 000-005 1976 NY	1	0.56	-	0 7 14 21	3.0 2.3 1.1 0.45	
	1	1.12	-	0 7 14 21	5.57 2.9 1.4 2.1	
-	3	1.12	-	0 7 14	5.6 2.4 2.0	IR-4 NPRP

[1] Residues corrected for blanks

Cucumbers. In two greenhouse trials in Canada above and below the rate required by GAP (1-2 x 0.425 kg ai/ha, 14 days PHI), two trials in Greece above the recommended rate (1 x 0.03 kg ai/hl) and six in the USA at lower or higher rates and/or longer PHIs than GAP (4-8 x 0.14-0.28 kg ai/ha, PHI 1 day) the residues after 0 to 17 days ranged from <0.03 to 0.36 mg/kg. One trial in the USA according to GAP gave residues of <0.06 mg/kg at 1 day PHI.

Two trials in Germany with a soil drench and three indoor trials in the UK could not be evaluated in the absence of information on GAP.

In six trials in Portugal and Spain at the Spanish GAP rate (0.03 kg ai/hl) the residues after 7 days were <0.03 mg/kg. Although the recommended PHI is 14 days it is unlikely that the residues after 7 days would increase so these residues could be used in estimating maximum residue levels (Table 18).

Table 18. Residues from trials with benomyl on cucumbers.

Country Report No. year	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	mg/kg
Canada[1,3] TAS000-005 1969	4	0.28	0.03	0 7 14	0.34 0.17 0.08
	4	0.56	0.06	0	0.36

Country Report No. year	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	mg/kg
				7	0.24
Germany [1, 2] BENO/RES 22	3	3.75-7.5	-	3 17	0.07 0.05
1969 Veitshochheim	2	3.75-7.5	-	3	0.10
Greece AMR 3427-95 1995 Attica	3	0.156-0.232	0.03	0 1 3 5 7	0.06 <0.03 <0.03 <0.03 <0.03
AMR 3889-96 1996	3	0.265-0.298	0.03	7	<0.03
Portugal AMR 3427-95 Lisbon, 1995	3	0.192-0.204	0.03	0 1 3 5 7	0.03 <0.03 <0.03 <0.03 <0.03
AMR 3889-96 1996	3	0.215-0.247	0.03	7	0.05
Spain AMR 3427-95 1995 Huesca	3	0.228-0.239	0.03	0 1 3 5 7	<0.03 <0.03 <0.03 0.03 <0.03
	3	0.231-0.240	0.03	0 1 3 5 7	<0.03 0.05 <0.03 0.04 <0.03
AMR 3889-96 1996 Sevilla	3	0.190	0.03	0 1 3 5 7	<0.03 <0.03 <0.03 <0.03 <0.03
	3	0.179-0.185	0.03	0 1 3 5 7	<0.03 <0.03 <0.03 <0.03 <0.03
UK BENO/RES 22 1969[1, 2, 3] Suffolk	1	0.22	0.022	15	0.28
1970[3]	2	0.30	0.03	0	0.42
1972[1, 2, 3] Essex	9	0.22	0.022	7	0.33
USA[3] TAS000-005 1967 CA	4	0.42	-	0 9	0.23 <0.03
1968	2	0.28	-	3	<0.03
TX	2	0.44	-	3	0.08

Country Report No. year	Application			PHI, days	Residues, mg/kg
	No	kg ai/ha	kg ai/hl		
				7	<0.03
SC	6	0.21	-	15 17	<0.06 <0.06
	2	0.21	-	1	<0.06
	3	0.21	-	1	<0.06
CA	3	0.28	-	11	<0.06

[1]Indoor
[2] Soil drench
[3]Residues were corrected for blanks

Melons and watermelons. In two trials on melons in Canada at lower rates but shorter PHIs than GAP (3 x 0.425 kg ai/ha, 14 days PHI) the residues were 0.18 and <0.06 mg/kg after 0 and 6 days. In two trials in France according to GAP for cucurbits (1-3 x 0.15-0.45 kg ai/ha) the residues at the GAP PHI of 7 days were <0.05 and 0.19 mg/kg. In five trials on melons in the USA the rates and/or PHIs did not comply with GAP (4-8 x 0.28 kg ai/ha, 1-day PHI). The residues were <0.03 to 0.21 mg/kg.

Four trials were conducted in the USA on watermelons, but no information on GAP was provided. The results are shown in Table 19.

Table 19. Residues from trials with benomyl on melons and watermelons.

Country Report No. year	Application			PHI, days	Residues, mg/kg
	No	kg ai/ha	kg ai/hl		
Melons					
Canada TAS 000-005[1] 1968	7	0.14	-	0	0.18
	6	0.21	-	6	<0.06
France BEA118908-BG Tarn 1988	4	0.37	0.03	3 7 14	0.10 <0.05 <0.05
	4	0.39	0.03	3 7 14	0.33 0.19 0.08
USA TAS 000-005[1] 1967 CA	4	0.28	-	0 7	0.08 <0.03
AZ 1968	7	0.28	-	3	<0.03
TX	2	0.28	-	3	<0.03
	2	0.45	-	3 7	0.07 0.05
	5	0.22	-	13	0.21
Watermelons					
USA	7	0.42	-	1	0.18

Country Report No. year	Application			PHI, days	Residues, mg/kg
	No	kg ai/ha	kg ai/hl		
TAS 000-005[1] SC				7	<0.06
	7	0.21		1 7	<0.06 <0.06
	7	0.42		1 7	0.09 0.12
	4	0.42		1 7	0.09 0.09

[1]Residues corrected for blanks

Summer squash. Four trials in the USA were at higher rates than GAP (4-8 x 0.12-0.28 kg ai/ha, 1-day PHI). The residues after 0 to 3 days varied from 0.06 to 0.36 mg/kg (Table 20).

Table 20. Residues from trials with benomyl on summer squash in the USA.

Report No. year	Application			PHI, days	Residues, mg/kg[1]
	No	kg ai/ha	kg ai/hl		
TAS000-005 1967 CA	4	0.42	-	0 7	0.36 <0.03
FL	5	0.84	-	1 5	0.32 0.11
TX	2	0.70	-	3	0.11
TX	3	0.70	-	3	0.06

[1] Corrected for blanks

Tomatoes. Thirteen trials were conducted on tomatoes in Europe from 1970 to 1996 (Table 21). Two trials in Greece were with three applications instead of one, but at the GAP concentration (0.03 kg ai/hl). The residues at the GAP PHI of 14 days were 0.04 and 0.08 mg/kg. Five trials in the UK with 1-7 applications of 0.28 or 0.56 kg ai/ha gave residues of 0.24 to 0.96 mg/kg after 0 to 16 days, but no information on GAP was provided.

In six trials in Portugal and Spain which approximated Portuguese GAP (0.15-0.30 kg ai/ha, 4-day PHI) the residues after 3 days were <0.03 to 0.12 mg/kg.

In three trials in the USA according to GAP (5-10 x 0.28-0.56 kg ai/ha) the residues at the GAP PHI of 1 day were 0.15-0.98 mg/kg. Sixteen other trials which did not conform to GAP gave residues of <0.06 to 2.9 mg/kg after 0 to 14 days.

Table 21. Residues from trials with benomyl on tomatoes in Europe and the USA.

Country Report No. year	Application			PHI, days	Residues, mg/kg
	No	kg ai/ha	kg ai/hl		
Greece AMR 3449-95 1995	3	0.279-0.309	0.03	0 1 3 7 14	0.16 0.08 0.13 0.08 0.08
AMR 3939-96	3	0.149-0.233	0.03	0	0.03

Country Report No. year	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	mg/kg
1996				1 3 7 14	0.06 0.04 0.05 0.04
Portugal AMR 3449-95 1995	3	0.172-0.180	0.03	0 1 3 7 14	<0.03 <0.03 <0.03 <0.03 <0.03
AMR 3939-96 1996	3	0.197-0.281	0.03	0 1 3 7 14	0.14 0.08 0.12 0.08 0.08
Spain AMR 3449-95 1995 Barcelona	3	0.334-0.352	0.02-0.03	0 1 3 7 14	0.15 0.09 0.08 0.06 <0.03
Sevilla	3	0.211-0.219	0.03	0 1 3 7	<0.03, <0.03 0.03 0.03 <0.03
AMR 3939-96 1996 Sevilla	3	0.171-0.181	0.03	0 1 3 8 14	0.07 0.07 0.03 0.03 0.03
	3	0.177-0.182	0.03	0 1 3 8 14	0.09 0.10 0.06 0.08 0.07
UK BENO/RES 24 1970 Suffolk	1	0.56	0.56	0	0.96
Lincs[1] 1971-72	6	0.28	0.03	14	0.30
	7	0.28	0.03	16	0.24
	6	0.28	0.03	0	0.76
Essex[1]	6	0.28	0.03	7	0.33
USA [2] TAS000-005 1968 AR[1]	8	0.56	0.060	7	<0.06
TX	9	0.14	-	3 6	<0.06 <0.06
OH[1] 1969	2	0.56	0.060	2	0.72
1971 FL	3	0.28	-	0 6	0.06 0.10
	3	0.42	-	0	<0.06

Country Report No. year	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	mg/kg
				6	0.08
	3	0.28	-	0 6	<0.06 <0.06
	3	0.42	-	0 6	<0.06 <0.06
1972 CA	3	0.28	-	0 1 4	0.92 0.59 0.46
	3	0.56	-	0 1 4	1.2 0.98 0.59
	4	0.28	-	0 1 4	0.27 0.15 0.36
	4	0.56	-	0 1 4	0.50 0.56 0.52
FL	3	0.28	-	3 6	0.19 0.06
	3	0.28-0.56	-	3 6	0.20 0.14
	3	0.28	-	8	0.13
	1	0.41	-	7 14	0.08 <0.06
	2	0.56	-	7	0.32
IN[1]	3	0.56	0.030	10	<0.06
	3	0.56	0.060	10	<0.06
AMR 1352-89 1989 NY[3]	2	2.8	2.4	5	2.9

[1]Indoor
[2] Residues were corrected for blanks
[3] Also analysed for 2-AB

Legume vegetables

Beans. One trial in France with 2 applications of 0.96 kg ai/ha gave residues of 0.14 and <0.05 mg/kg after 11 and 25 days respectively. No GAP was reported.

Four of twelve trials in the USA on green beans (lima beans) were according to GAP (1-2 x 0.84-1.12 kg ai/ha). The residues in the whole commodity (bean plus pod) ranged from <0.06 to 0.14 mg/kg at PHIs of 20-33 days (Tables 22).

Table 22. Residues in beans plus pods from trials with benomyl on beans.

Country Report No. year	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	Days	mg/kg
France BEA118908-BG 1988 Bouches du Rhone	2	0.96	0.04	11 25	0.14 <0.05
USA TAS000-005 1970	1	0.56	-	14	0.38
OR	1	1.12	-	14	0.91
1971	1	1.12	-	16	0.31
CA	2	1.12	-	19	<0.03
	2	1.12	-	20	0.14
WA	2	1.12	-	27	<0.06
ID	2	1.12	-	33	<0.06
	2	1.12	-	33	0.03
NY	2	1.12	-	38	0.09
	3	1.12	-	31	0.10
1975	2	1.12	-	14	0.10
NY	2	1.12	-	14	0.58

Dry and snap beans. In seven trials in Canada and the UK samples were taken much later than the recommended PHI (14 and 21 days).

Thirty two trials were carried out in the USA from 1968 to 1972. In six trials according to GAP (1-2 x 0.84-1.12 kg ai/ha, PHI 14 days) the residues in the whole commodity (beans plus pods) ranged from <0.06 to 0.47 mg/kg at PHIs of about 14 days. Residues in the pods from trials carried out at or above the GAP rate varied from <0.06 to 1.2 mg/kg after 2 to 45 days (Table 23).

Table 23. Residues from trials with benomyl on dry and snap beans.

Country Report No. year	Application			PHI,	Sample	Residues,
	No	kg ai/ha	kg ai/hl	days		mg/kg
Canada TAS000-005 1968 Ontario	1	1.68	-	27	pods and beans	<0.06
UK AMR 4014-96	2	0.55	0.30	44	Bean	0.73
1995	2	0.55	0.30	48	Bean	0.75
AMR 3994-96	2	0.563-0.583	0.03	67	Bean	<0.03
1996	2	0.559-0.577	0.03	54	Bean	<0.03
	2	0.575-0.583	0.03	51	Bean	<0.03
	2	0.577	0.03	56	Bean	<0.03

Country Report No. year	Application			PHI, days	Sample	Residues, mg/kg
	No	kg ai/ha	kg ai/hl			
USA TAS000-005	1	2.24	-	26	Pods Vines	0.46 3.28
1968	1	2.24	-	19	Pods	0.11
OR	1	1.12	-	17	Pods Vines	<0.06 2.7
NY	1	1.12	-	10	Pods	0.14
	1	1.12	-	32	Pods	<0.06
	1	1.12	-	27	Pods	0.12
	2	0.84	-	20	Pods	0.07
	1	1.68	-	13	Pods	0.07
	2	1.68	-	7	Pods	0.12
WA	1	1.12	-	23	Pods	0.06
	1	2.24	-	2	Pods	0.33
	1	1.12	-	22	Pods Vines	0.07 2.5
	1	2.24	-	22	Pods Vines	0.07 5.8
	2	1.12	-	15	Pods Vines	0.28 1.6
	2	2.24	-	15	Pods Vines	0.28 3.3
OR	2	1.12	-	15	Pods	0.61
	2	2.24	-	15	Pods	1.2
1969 FL	1	1.12	-	45	Pods	<0.06
1970	1	1.12	-	22	pods and beans	0.07
WA	1	1.12	-	22	pod s and beans	0.06
	2	0.56[1]	-	15	pods and beans	<0.06
	2	0.56[1]	-	15	pods and beans	<0.06
1971	1	0.56	-	14	pods and beans	0.06
OR	1	0.56	-	14	pods and beans	0.06
	1	1.12	-	14	pods and beans	0.27
	1	1.12	-	26	pods and beans	<0.06
1972	2	1.12	-	15	pods and beans	0.10
OR	2	1.12	-	14	pods and beans	<0.06
	2	1.12	-	16	pods and beans	<0.06
1972	2	1.12[1]	-	19	pods and beans	<0.06
ID	2	1.12	-	42	pods and beans	<0.06
CO	2	0.84	-	15	pods and beans	0.47

[1] Aerial application

Peas. In two trials in the UK at the recommended rate (2 x 0.55 kg ai/ha) the residues were 0.11 and 0.04 mg/kg after 12 and 10 days. No samples were taken at the GAP PHI of 21 days (Table 24).

Table 24. Residues from trials with benomyl on peas in the UK.

Report No. year location	Application			PHI,	Residues,
	No	kg ai/ha	kg ai/hl	days	mg/kg[1]
AMR 4013-96 1995	2	0.550	0.30	12	0.11
South Humberside	2	0.550	0.30	10	0.04

[1]In peas without pod

Soya beans. In four trials in the USA according to GAP (1-2 x 0.28-0.56 kg ai/ha, PHI 35 days) the residues in the grain at 35-43 days were <0.03 to 0.04 mg/kg. Three other trials at higher rates and one at the GAP rate but a longer PHI yielded residues from <0.03 to 0.23 mg/kg (Table 25).

Table 25. Residues from trials with benomyl on soya beans in the USA.

Report No. year location	Application			PHI,	Residues in seed,
	No	kg ai/ha	kg ai/hl	days	mg/kg
AMR 1378-89 1989 IL	2	4.48	-	30	0.22
AMR 2564-93 1993	2	4.48	2.1	35	0.23
AMR 2894-94 1994	1	0.56	0.12	43	<0.03
MD	1	1.12	0.24	43	0.04
MS	1	0.56	0.62	47	<0.03
IN	1	0.56	0.24	35	0.04
IL	1	0.56	0.27	36	0.03
MN	1	0.56	0.32	35	<0.03

Root vegetables

Carrots. Twenty one trials in the USA on carrots according to GAP (3-12 x 0.14-0.56 kg ai/ha) gave residues of <0.01 to 0.14 mg/kg at the GAP PHI of 4 days. Eight other trials at higher rates or longer PHIs gave similar results (Table 26).

Table 26. Residues from trials with benomyl on carrots in the USA.

Report No. Year Location	Application			PHI,	Residues,	
	No	kg ai/ha	kg ai/hl	days	mg/kg	Reference
TAS000-005 1974 FL	6	0.14-0.28	0.49	4	<0.03	
	9	0.14-0.28	0.49	4	<0.03	
	10	0.56	0.49	5	<0.03	
	11	0.56	0.49	5	<0.03	
1975 FL	8	0.14	0.49	5	<0.03	
	10	0.56	0.49	10	<0.03	

Report No. Year Location	Application			PHI, days	Residues, mg/kg	Reference
	No	kg ai/ha	kg ai/hl			
AMR 2287-92 1992 CA	3	0.56	1.19	4	0.12	Test 4
	3	0.56	0.0055	4	0.05	Test 5
	3	0.56	0.24	4	<0.01	Test 6
	3	0.56	0.19	4	0.10	Test 7
	3	0.56	0.19	4	0.13	Test 8
	3	0.56	0.0073	4	0.11	Test 9
	3	0.56	0.0041	4	0.06	Test 10
	3	0.56	0.0042	4	0.04	Test 11
	3	0.56	0.24	4	0.01	Test 18
	3	1.12	0.48	4	0.01	
FL	3	0.56	0.12	4	0.02	Test 1
	3	1.12	0.24	4	0.04	
MI	3	0.56	0.25	4	0.04	Test 16
	3	1.12	0.50	4	0.13	
TX	3	0.56	0.24	4	0.14	Test 12
	3	0.56	0.46	4	0.05	Test 13
	3	0.56	1.19	4	0.02	Test 14
	3	0.56	0.30	4	0.04	Test 15
	3	1.12	0.60	4	0.14	
WI	3	0.56	0.22-0.21	4	0.05	Test 3
1993 FL	3	0.56	0.20	4	0.05	Test 2
	3	0.56	0.12	4	0.02	Test 15
	3	1.12	0.24	4	0.07	

Sugar beet. In one trial on sugar beet in France and twelve in the USA at rates from 1 x 0.16 to 6 x 0.42 kg ai/ha, residues in the roots were <0.05 or <0.06 mg/kg and in the tops 0.10 to 11 mg/kg after 21 to 53 days (Table 27). No information on GAP was reported.

Table 27. Residues from trials with benomyl on sugar beet.

Country Report No. year	Application			PHI, days	Sample	Residues, mg/kg
	No	kg ai/ha	kg ai/hl			
France BEA118909-BG Cote d'Or 1988	1	0.16	0.16	21	roots	<0.05
USA TAS000-005 1967 OH	5	0.21	0.022	23	roots tops	<0.06 0.22
IA	3	0.21	0.037	36	roots tops	<0.06 0.20
MN	4	0.21	0.045	23	roots tops	<0.06 11
1968 MN	4	0.28	0.037	31	roots tops	<0.06 0.15
CA	5	0.42	0.045	24	roots tops	<0.06 1.1

Country Report No. year	Application			PHI,	Sample	Residues,
	No	kg ai/ha	kg ai/hl	days		mg/kg
MI	6	0.21	0.022	16	roots tops	<0.06 0.27
OH	3	0.42	0.045	53	roots tops	<0.06 0.65
MO	4	0.42	0.045	39	roots tops	<0.06 0.16
IO	3	0.28	0.16	34	roots tops	<0.06 0.10
	3	0.28	0.075	34	tops	0.11
TX	6	0.21	0.049	46	roots tops	<0.06 0.65
	6	0.42	0.049	46	roots tops	<0.06 0.44

Cereal grains

Rice. Of twenty nine trials on rice in the USA from 1969 to 1989, 21 were according to GAP (1-2 x 0.56-1.12 kg ai/ha, 21-day PHI). The residues ranged from <0.03 to 1.6 mg/kg in the husked grain and from 0.25 to 11 mg/kg in the straw (Table 28).

Table 28. Residues in husked grain and straw from trials with benomyl on rice in the USA.

Report No. year location	Application			PHI,	Portion	Residues,	
	No	kg ai/ha	kg ai/hl	days	analysed	mg/kg	Reference
BENO/RES 23 1969	2	0.56	0.2	32	grain straw	<0.07 1.6	
LA	2	2.24	0.86	32	grain straw	0.12 4.8	
1970	2	0.672	0.748	25	grain	0.08	
TX	2	0.672	0.748	20	grain	0.36	
1972	2	1.12	1.12	29	grain straw	0.07 2.5	
TX	2	0.672	0.187	23	grain straw	0.26 8.5	
	2	1.12	-	24	grain straw	<0.03 0.25	
	2	1.12	1.03	26	grain straw	0.20 5.9	
	2	1.12	1.03	29	grain straw	<0.03 1.4	
1973	3	0.56	0.28	40	grain straw	0.07 0.29	
LA	2	0.56	0.28	21	grain straw	<0.03 0.65	

Report No. year location	Application			PHI, days	Portion analysed	Residues, mg/kg	Reference
	No	kg ai/ha	kg ai/hl				
	2	0.56	0.28	15	grain	0.70	
					straw	2.5	
TX	2	0.28	0.17	24	grain	<0.05	
	2	0.56	0.17	24	grain	0.05	
	2	0.56	0.448	21	grain	<0.03	
	2	0.56	0.448	21	grain	<0.03	
	2	0.56	0.448	21	grain	<0.03	
1974	2	0.56	0.093	7	grain	<0.03	
				14	grain	<0.03	
				14	straw	2.5	
				21	grain	<0.03	
				21	straw	0.41	
				30	grain	<0.03	
LA	2	0.56	0.280	7	grain	1.8	
				14	grain	1.8	
				14	straw	3.7	
				21	grain	1.6	
				21	straw	5.9	
				33	grain	<0.03	
				33	straw	2.4	
	2	0.56	0.093	7	grain	0.5	
				14	grain	0.11	
				14	straw	1.3	
				21	grain	0.04	
				21	straw	0.98	
				30	grain	<0.03	
AR	2	0.56	0.093	10	grain	0.67	
				10	straw	1.5	
				19	grain	0.16	
				19	straw	0.65	
				33	grain	<0.03	
				33	straw	<0.03	
AMR 1433-89	2	1.12	1.3	21	straw	11	Test 1
MS	2	2.24	2.5	21	straw	29	
AK	2	1.12	1.2	21	straw	4.3	Test 2
	2	2.24	2.4	21	straw	14	
	2	1.12	1.2	21	straw	4.3	Test 3
	2	2.24	2.4	21	straw	12	
LA	2	1.12	0.7	21	straw	1.3	Test 4
	2	2.24	1.4	21	straw	7.5	

Wheat. Two trials in the Netherlands according to GAP (1 x 0.25 kg ai/ha, 35 days PHI) gave residues of <0.04 mg/kg in the grain and 0.05 and 0.18 mg/kg in the straw at 34 or 35 days. In two other trials at twice this rate, the residues were <0.07 mg/kg in the grain and 0.50 and 0.44 mg/kg in the straw after 63 or 64 days (Table 29).

In four trials in the USA according to GAP (1-2 x 0.28-1.12 kg ai/ha) the residues at PHIs close to GAP (21 days) were <0.03 mg/kg in the grain and <0.1 and 0.72 mg/kg in the straw. In three trials at shorter PHIs they were 0.09 to 0.15 mg/kg in the grain and 1.6 to 2.7 mg/kg in the straw.

Table29. Residues from trials with benomyl on wheat.

Country Report No. year	Application			PHI,	Sample	Residues,	
	No	kg ai/ha	kg ai/hl	days		mg/kg	Reference
Netherlands R4278 1973	1	0.25	0.050	35	grain straw	<0.04 0.05	
	1	0.25	0.050	34	grain grain	<0.04 0.18	
1972	1	0.50	-	63	grain straw	<0.07 0.50	
	1	0.50	-	64	grain straw	<0.07 0.44	
USA TAS000-005 1974/1975 MD	2	0.28	0.067	28	grain straw	<0.03 <0.1	
	2	0.56	0.133	28	grain straw	<0.03 <0.1	
DE	2	0.28	-	19	grain straw	<0.03 0.72	
IL	2	0.28	0.15	26	grain	<0.03	
	2	0.28	0.15	30	grain	<0.03	
	8	0.56	0.05	9	grain straw	0.09 2.2	
	4	0.56	0.05	9	grain straw	0.15 2.7	
	2	0.56	0.05	9	grain straw	0.10 1.6	

Nuts

Fourteen trials in the USA on almonds at or above the GAP rate (2-3 x 0.56-0.84 kg ai/ha) gave residues of <0.06-0.08 mg/kg in the kernels, but all the samples were taken much later than the recommended PHI of 50 days.

Seven trials on macadamia nuts, five of them above the recommended rate (3 x 0.98 kg ai/ha), gave residues of <0.06 mg/kg in the kernels after 95-151 days.

Six trials on pecans gave the same residues but no GAP was reported to evaluate the results (Table 30).

Table 30. Residues from trials with benomyl on tree nuts in the USA (Report No. TAS 000-005).

Commodity, location year	Application No	kg ai/ha	kg ai/hl	PHI, days	Sample	Residues, mg/kg	Reference
Almonds, California							
1969	2	0.448	0.019	162	kernels hulls	<0.06 <0.13	
	2	0.896	0.038	162	kernels hulls	<0.06 <0.13	
	2	0.448	0.03	204	kernels hulls	<0.06 <0.13	
	2	0.896	0.03	204	kernels hulls	<0.06 <0.13	
	2	0.448	0.03	204	kernels hulls	<0.06 <0.13	
	2	0.896	0.03	204	kernels hulls	<0.06 <0.13	
1970	1	1.4	0.030	233	kernels hulls	<0.06 0.27	
1971	1	1.4	0.12	204	kernels hulls	<0.06 <0.06	
	1	1.4	0.03	201	kernels hulls	<0.06 <0.06	
	1	1.12	0.17	177	kernels hulls	0.06 0.08	
	1	0.56	0.023	175	kernels hulls	<0.06 <0.06	
	1	1.12	0.046	175	kernels hulls	0.08 0.48	
	1	1.12	0.046	175	kernels hulls	<0.06 <0.06	
	3	0.784	0.0335	175	kernels hulls	<0.06 0.06	
Macadamia nuts, Hawaii, 1970							
	5	1.4	0.30	102	kernels	<0.06	
	10	1.4	0.30	95	kernels	<0.06	
	10	2.8	0.60	95	kernels	<0.06	
	4	1.0	0.31	144	kernels	<0.06	
	7	1.0	0.31	144	kernels	<0.06	
	7	2.0	0.62	144	kernels	<0.06	
	4	1.4	0.30	151	kernels	<0.06	
Pecans, 1967/1968							
GA	6	0.84	0.029	69	kernels	<0.06	
	6	0.56	0.019	86	kernels	<0.06	
FL	6	0.56	0.039	70	kernels	<0.06	
MS	4	0.56	0.029	64	kernels	<0.06	
	5	0.84	0.029	64	kernels	<0.06	
AR	3	0.56	0.059	98	kernels	<0.06	

Peanuts. Ten trials in the USA above the GAP rate (12 x 0.14 kg ai/ha) gave residues in the kernels of <0.06 mg/kg after 11 to 86 days. The recommended PHI is 14 days (Table 31).

Table 31. Residues from trials with benomyl on peanuts in the USA (Report No. TAS 000-005).

Location	Application			PHI, days	Residues in kernels, mg/kg
	No	kg ai/ha	kg ai/hl		
GA	7	0.21	-	20	<0.06
FL	6	0.21	-	25	<0.06
AL	13	0.21	-	11	<0.06
TX	4	0.21	-	18	<0.06
	3	0.44	-	14	<0.06
	4	0.33	-	32	<0.06
	6	0.33	-	33	<0.06
OK	4	0.44	-	37	<0.06
NC	1	4.48	-	86	<0.06
	2	0.56	-	14	<0.06

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

Oranges. In a study in the USA (McNally and Hay, 1991a) a WG formulation of benomyl was applied at more than seven times the GAP rate. On the day of the last application the harvested oranges were dipped in a water solution of 240 g ai/hl of benomyl. In two studies in Brazil (Galhiane, 1994a,b) 0.025-0.1 kg ai/ha of a WP formulation of benomyl was applied 3 or 4 times. The oranges and the processed fractions were analysed for benomyl, carbendazim and 2-aminobenzimidazole (2-AB). The results are shown in Table 32. In all the studies the processing procedures simulated commercial practice.

In the US study the residues increased only in orange oil (by a factor of 1.36). The other processing factors varied from 0.012 in finisher pulp to 0.88 in dried peel. The processing factors for juice were 0.016 in the USA and 0.23-0.83 in Brazil.

Table 32. Effects of processing on residues in oranges.

Sample	PHI, days	Residues as carbendazim, mg/kg	Processing factor
USA			
Unwashed fruit	0	6.0	1.0
Washed fruit	0	0.74	0.12
Juice	0	0.10	0.016
Finisher pulp	0	0.07	0.012
Oil emulsion water	0	0.93	0.15
Press liquor	0	1.0	0.16
Peel frits	0	2.6	0.43
Orange oil	0	8.2	1.36
Chopped peel	0	1.5	0.25
Dried peel	0	5.3	0.88
Molasses	0	3.6	0.60

Sample	PHI, days	Residues as carbendazim, mg/kg	Processing factor
BRAZIL			
Fruit Juice	1	0.13; 0.14 0.03; 0.05	0.23; 0.36
Fruit Juice	1	0.36; 0.24 0.10; 0.20	0.28; 0.83

Apples. In simulated household and industrial processing studies in the USA a benomyl WG formulation was applied to apple trees according to US GAP (6 x 0.0238-0.09 kg ai/hl). In the household preparation study, in New York and Ohio (Sharp, 1993a), freshly harvested apples were washed and packed at commercial packing facilities to produce fruit for supermarket shelves and samples were collected throughout the packing line process. Typical household preparation was used to produce consumer-prepared washed, peeled and cooked apples. In the industrial study (North Carolina and Pennsylvania, Sharp, 1993b) apples were conventionally harvested and commercially processed at industrial food processing facilities to produce puréed apples, canned apple slices, apple sauce and apple juice using state-of-the-art food processing technology. The results are shown in Table 33.

Table 33. Effects of household and industrial processing on residues in apples, USA.

Sample	PHI, days	Residue, mg/kg as carbendazim	Processing factors	
			From line start	From raw fruit
New York Trial				
Unwashed fruit	14	0.20		1.0
Packing line start apples	64	0.18	1.0	0.9
Washed & brushed	64	0.14	0.81	0.73
Consumer washed	92	0.14	0.74	0.66
Consumer cooked with peel	92	0.16	0.89	0.80
Consumer peeled and cooked	92	0.05	0.27	0.24
Ohio Trial				
Unwashed fruit	14	0.16	--- 1.0	1.0
Early pack-out				
Packing line start apples	33	0.07	1.0[b]	0.46
Washed & brushed	33	0.05	0.71	0.33
Consumer washed	40	0.05	0.68	0.31
Consumer cored and sliced	40	0.05	0.74	0.34
Late pack-out				
Packing line start apples	194	0.06	1.0	0.42
Washed & brushed	194	0.06	1.0	0.42
Consumer washed	229	0.05	0.70	0.29
Consumer cored and sliced	229	0.06	0.92	0.38
Consumer peeled and sliced	229	0.03	0.49	0.20
North Carolina Trial				
Unwashed fruit	14	0.19	---	
Processing lines 1, 2, 3				
RAC line start apples	62/6	0.22, 0.17, 0.18	1.0, 1.0, 1.0	
(mean of sample means)	4	(0.19 ± 0.03)*		
Water-washed apples	62/6	0.18, 0.20, 0.17	0.82, 1.2, 0.93	
(mean of sample means)	4	(0.18 ± 0.02)*	(0.98 ± 0.20)*	
Final puréed apple (H_2O)	62/6	0.12, 0.11, 0.14	0.58, 0.65, 0.75	
(mean of sample means)	4	(0.12 ± 0.02)*	(0.66 ± 0.08)*	
Lye-washed apples	62	0.13	0.61	
Final puréed apple (lye)	62	0.12	0.58	
Pennsylvania Trial				
Unwashed fruit	14	0.27	---	1.0
Canned slice line				

Sample	PHI, days	Residue, mg/kg as carbendazim	Processing factors	
			From line start	From raw fruit
Packing line start apples	31	0.17	1.0	0.62
Washed apples	31	0.12	0.69	0.43
Peeled & cored slices	31	0.06	0.38	0.23
Canned apple slices	31	0.04	0.23	0.14
Apple sauce line				
Packing line start apples	73	0.10	1.0	0.36
Washed apples	73	0.07	0.73	0.26
Peeled & cored apples	73	0.04	0.41	0.15
Applesauce	73	0.04	0.37	0.13
Apple juice line				
Packing line start apples	73	0.10	1.0	0.36
Gradeout fruit	73	0.16	1.6	0.57
Pressed raw juice	73	0.07	0.73	0.26
Clarified & filtered juice	74	0.07	0.67	0.23

* Mean of two or more values

Washing and packing generally decreased the residues in the apples: the factors ranged from 0.26 to 1.2 (0.55 ± 0.28) and from 0.36 to 1.0 (0.68 ± 0.29) respectively. Residues in cooked peeled and unpeeled apples were 0.80 and 0.24 times those in the raw fruit respectively, while the processing factors for peeled and cored apple slices were 0.23-0.38 (0.24 ± 0.10). The factors for canned apple slices, apple sauce and gradeout fruit were 0.14, 0.13 and 0.57 respectively, and apple purée showed an average factor of 0.47 (0.58-0.75). Residues in the juice were decreased by factors of 0.26 and 0.23.

Peaches and plums. Two studies were conducted on peaches in the USA with 2 applications of 0.096 to 0.12 kg ai/hl (Sharp 1992, 1993c). Washing decreased the residues by factors of 0.18 and 0.37, and washing and peeling by factors of 0.02 and 0.12. Sliced and puréed peaches showed processing factors of <0.01 and 0.06 respectively (Table 34).

Plums treated with 4 applications of 0.99 or 1.96 kg ai/ha were processed into prunes in California (Goldberg, 1989a) with processing factors of 0.12 and 0.48. Plums from some of the residue trials in California were processed to prunes. The residues in the prunes are shown in Table 9 and the processing factors are listed in Table 34. The processing factors for prunes from all the trials ranged from 0.08 to 0.83, with an average of 0.24 ± 0.27 (n = 24)

Table 34. Effects of processing on residues in peaches and plums.

Peaches			Plums		
Sample	mg/kg as carbendazim	Processing factor	Sample	mg/kg as carbendazim	Processing factor
Whole	1.0		plum	1.2; 3.3	
Rinsed	0.37	0.37	prune	0.12; 0.48	0.1, 0.14
Peeled	0.12	0.12	Results from Table 9		0.83, 0.56, 0.09, 1.0,
Purée	0.06	0.06	6 trials, PHIs 0-14 days		0.026, 0.08, 0.018,
Whole	0.71				0.18, 0.15, 0.13, 0.10,
Flume washed	0.18	0.13			0.83, 0.56, 0.10, 0.24,
Lye peeled	0.02	0.01			0.027, 0.087, 0.18, 0.19,
Halves	<0.01	<0.01			0.15, 0.13, 0.10
Slices	0.01	<0.01	Average ± SD		0.24 ± 0.27

Grapes. The results of four processing studies on grapes in Switzerland (1971) after 3 to 6 applications of 0.6-3.0 kg ai/ha and PHIs from 15 to 56 days (Hornshuh, 1994c) and two in the USA

in 1986 after 2 applications of 0.84 kg ai/ha and a PHI of 7 days (Goldberg, 1989b) are shown in Table 35. Processing factors for grapes to wine averaged 0.53, to raisins 1.3 and to raisin waste 4.1.

Table 35. Effects of processing on residues in grapes.

Country	Commodity	mg/kg as carbendazim	Processing factor
Switzerland	Grapes	2.3; 1.2 ; 5.3; 1.8	
	Wine	1.7; 0.40; 3.6; 0.65	0.74; 0.33; 0.68; 0.36
USA	Grapes	3.1; 1.2	
	Raisins	3.1; 1.9	1.0; 1.6
	Raisin waste	11; 5.6	3.5; 4.7

Tomatoes. A single processing study was conducted in the USA (Vincent and Tomic, 1989) after two applications of benomyl WG formulation at 5.6 kg ai/ha and a PHI of 5 days (GAP is 0.90 kg ai/ha with a PHI of 14 days). The pilot-scale plant differed from normal commercial practice only in having shorter start-up and shut-down intervals, leading to lower yields than would be expected in a commercial process. Processing factors varied from 0.27 for juice to 0.66 for purée (Table 36).

Table 36. Effects of processing on residues in tomatoes.

Commodity	mg/kg carbendazim	Processing factor
Whole fruit	2.9	
Wet tomato pomace	0.85	0.29
Dry tomato pomace	1.4	0.48
Juice	0.78	0.27
Purée	1.9	0.66
Ketchup	1.8	0.62

Soya beans. Two processing trials were conducted in the USA. In the first (McNally and Tomic, 1992) application was at 8 times the recommended rate and the processing closely simulated commercial procedures. The second (Adams, 1994), with four times the maximum label rate, was designed to determine the residues in aspirated grain fractions, comprising an assortment of seeds, stems, leaves, straw, hay, hulls, millings, sand and dirt. The results of both trials are shown in Table 37.

Table 37. The effects of processing on residues in tomatoes.

Sample	Benomyl as carbendazim, mg/kg	Processing factor
Whole soya beans	0.33	
Meal	0.24	0.71
Hulls	0.65	1.9
Refined oil	<0.03	<0.1
Crude oil	0.08	0.23
Soap stock	1.1	3.3
Whole soya beans	0.59	
Aspirated fractions	11	19.2

Rice. In two processing studies in the USA (McNally and Hay, 1991b) two applications of a WG benomyl formulation were made at 2.24 kg ai/ha (twice the GAP rate) with PHIs of 22 and 30 days. The pilot-scale plant differed from normal commercial practice only in having

shorter start-up and shut-down intervals, giving lower yields. The results are shown in Table 38.

Table 38. The effect of processing on residues in rice.

Commodity	mg/kg as carbendazim	Processing factor
Whole grain	4.0	
Processed white rice	0.04	0.01
Whole grain	5.3	
Bran	1.6	0.31
Hulls	12	2.3

Milk. Benomyl was added to whole milk at a level of 1 mg/kg, and the treated milk was processed into common milk fractions (Chin *et al*., 1986). Although benomyl was lost in the production of sterile evaporated canned milk (processing factors of 0.64 and 0.43 for whole and skimmed milk respectively) pasteurisation did not affect the residue levels. The residues tended to concentrate in cream and other high-fat fractions (Table39).

Table39. The effect of processing on residues in milk.

Sample	mg/kg as carbendazim	Processing factor
Whole milk	0.47	
Heated at 140 °F	0.03	0.06
Skimmed milk	0.32	0.68
Pasteurized skimmed milk	0.32	0.68
Standardized whole milk	0.31	0.67
Canned evaporated whole milk	0.30	0.64
Canned evaporated skimmed milk	0.20	0.43
Spray-dried lactose	0.72	1.5
Anhydrous butter oil	0.72	1.5
Casein	0.54	1.1
Crude lactose	0.24	0.45
Whey	0.21	0.44
Mother liquor	2.5	5.2
Cream	0.78	1.7
Pasteurized cream	0.72	1.5
Residual cream solids	1.6	3.5

APPRAISAL

Benomyl, carbendazim and thiophanate-methyl are benzimidazole fungicides with extensive use on fruit, vegetables and cereals in many countries. Carbendazim and benomyl were first evaluated in 1973 and most recently in 1994 (residues) and 1995 (toxicology). They were proposed for re-evaluation within the Periodic Review Programme in 1998 by the 1995 CCPR. The 1996 CCPR postponed discussion on individual MRLs not recommended for deletion, awaiting the evaluation by the 1998 JMPR. It noted that the residue definition would be reconsidered on the basis of information provided by the UK and that a risk assessment would be required in relation to any new definition (ALINORM 97/24, para 51). Information on use patterns, national MRLs and analytical methods was provided by the main manufacturers and the governments of The Netherlands, Poland and Australia. This section discusses data on metabolism, environmental fate and analytical methods for benomyl and carbendazim, and residue trials on all three compounds. The metabolism, environmental fate and

methods of determination thiophanate-methyl are dealt with in the separate item on that compound (4.25).

The metabolism of benomyl and carbendazim was studied in rats, mice, ruminants, hens and plants. In rats, benomyl and carbendazim are rapidly absorbed after oral administration; the bioavailability is up to 85% and is dependent to a great extent on the route of administration (less after incorporation in the diet than after administration by gavage). Excretion is rapid and takes place almost entirely in the urine. After the oral administration of 3 mg/kg bw of labelled carbendazim, the maximum blood level of 1.0 µg/ml was reached after 15 to 40 minutes, and up to 63% of the administered radioactivity was found in the urine after 6 hours. Excretion in the faeces accounted for a maximum of 1%. At higher doses (300 mg/kg bw) peak blood levels were less than proportionately higher and were reached later (after 0.4 to 4 hours). Repeated doses showed no indications of a cumulative effect. Minor amounts of the labelled substance or its metabolites were found for a short time in the excretory organs, liver and kidney, but with no accumulation.

The metabolic conversion of carbendazim in rats and mice occurs mainly by hydroxylation and hydrolysis. The main metabolite in rats is methyl 5-hydroxybenzimidazol-2-ylcarbamate (5-HBC), and other hydroxylated metabolites are also found to a minor extent. They are usually excreted as sulfates or glucuronides. Metabolites may also be present in the faeces after higher doses.

Benomyl and carbendazim are metabolized in a similar manner in both ruminants (cows and goats) and laying hens. Reported data indicate that the initial metabolism of benomyl occurs by loss of the butylcarbamoyl group to form carbendazim. It is hyphothesized that carbendazim is oxidized to an epoxide, which can undergo a number of transformations to the identified compounds. These include hydrolysis to a dihydrodiol, reduction to methyl 4-hydroxybenzimidazol-2-ylcarbamate (4-HBC) and 5-HBC, and sulfide conjugation. Sulfide conjugation is proposed as the source of the unextractable residues in the livers of goats, cows, and poultry, which can only be released by reductive cleavage using Raney nickel as a catalyst. In two cow and two goat metabolism studies, with either [2-^{14}C]benomyl or [2-^{14}C]carbendazim, the majority of the dosed ^{14}C was excreted in the urine (57-85%) and faeces (14-18%), with only a small fraction in the tissues (0.09 to 0.45% in the kidneys and 2.6 to 4.1% in the liver) or milk (0.37 to 2.2%). In the carbendazim-dosed cows 4,5-DDBC (methyl 4,5-dihydro-4,5-dihydroxybenzimidazol-2-ylcarbamate), ADDB (2-amino-4,5-dihydro-4,5-dihydroxy-benzimidazole), DHBC-G (the monoglucuronide of 5,6-dihydroxy-cabenazim), 4-HBC and 5-HBC occurred in urine, while 4-HBC (3%), 5-HBC (41%), 4,5-DDBC, and DHBC-G were the major residues in the kidneys. In the liver, 4,5-DHHBC-G (*S*-[4,5-dihydro-5-hydroxy-2-(methoxycarbonylamino)-1*H*-benzimidazol-4-yl]glutathione) and other sulfur-linked dihydrohydroxy-carbendazim conjugates (15.2%) predominated, with smaller amounts of 4,5-DDBC and ADDB (0.8%), and 5-HBC (2.7%). 4,5-DDBC (<0.06 mg/kg, <25%) was found in the milk in addition to 4-HBC (0.05 mg/kg, 21%) and 5-HBC (0.11 mg/kg, 42%). The metabolites seen in benomyl-treated cows were similar, indicating the loss of the butylcarbamoyl group before further metabolism occurs.

Benomyl is metabolized in plants mainly to carbendazim. Benomyl itself accounted for 48, 60, 77, 53 and 62% of the total benomyl plus carbendazim residue on the leaves of apple, cucumber, banana, orange and grape plants respectively, 21-23 days after treatment. In orange and apple peel the proportions of benomyl were 61 and 34% respectively after 15-16 days, and in rice and peaches 19.8 and 33% respectively. To determine the amount of benomyl remaining in or on plant tissues, the sample was subjected to reflux under caustic conditions to convert any remaining benomyl to the stable derivative BUB (*N*-(1*H*-benzimidazol-2-yl)-*N*'-butylurea); carbendazim under these conditions is converted to 2-aminobenzimidazole (2-AB).

In soya beans treated with benomyl, 2-AB was found to be a major metabolite in addition to carbendazim. After the plants were treated twice at the early pod stage, the major residues in the mature beans after 35 days were 2-AB (0.42 mg/kg), benomyl (0.05 mg/kg) and carbendazim (0.14 mg/kg). Unextractable residues accounted for 13% of the total radioactivity. In all the other plants tested, 2-AB was always below 10%.

Crop rotation studies with lettuce, radishes, beet, cabbage, barley, beans, maize, carrots, tomatoes, alfalfa and ryegrass showed little or no uptake of benomyl or its major soil degradation product carbendazim into succeeding crops. The residues in plants grown in soil treated with carbendazim or benomyl at 1 to 3.4 kg ai/ha and aged for 30 to 224 days were <0.1 mg/kg.

Studies of environmental fate with carbendazim and benomyl were conducted in soil, water and air. Benomyl is rapidly converted to carbendazim in the environment, with half-lives of 2 and 19 hours in water and soil respectively. Carbendazim decomposes in the environment with half-lives of 6 to 12 months on bare soil, 3 to 6 months on turf, and 2 and 25 months in water under aerobic and anaerobic conditions respectively. In degradation studies with [*phenyl*-^{14}C]benomyl, [2-^{14}C]benomyl or [2-^{14}C]carbendazim, incubated with soil or sediment under aerobic or anaerobic conditions, carbendazim was the major compound (34 to 57% of the applied radioactivity), followed by STB (3-butyl-1,3,5-perhydrotriazino[1,2-*a*]benzimidazole-2-4-dione) or BUB (up to 7.6%) and 2-AB (up to 1.5%). No formation of CO_2 (<0.1%) from benomyl was observed in sterilized aerobic soil or under strictly anaerobic conditions, but, 9.2% of the applied ^{14}C was evolved as CO_2 after 1 year of incubation under non-sterile aerobic conditions.

Adsorption/desorption experiments showed carbendazim desorption coefficients higher than adsorption coefficients (9 to 51 and 1.6 to 6.6 respectively), and a K_{oc} between 200 and 246. Column and container leaching studies showed that the leachate contained <2% of the applied radioactivity. In leaching experiments with benomyl in water-saturated silty clay loam soils, 94% of the applied radioactivity was found in the top soil segment (0-0.5 cm). Benomyl was well adsorbed to soils (K_a 6.1-90) but desorption occurred slowly (K_d 2.4-2.5), and the compound did not move significantly from the site of application (0.1-0.7% of the TRR was detected in the run-off water).

The hydrolytic, photochemical and biological degradation of carbendazim in aquatic systems at pH 5 to 9, under aerobic or anaerobic conditions and temperatures of 20-70°C, showed that 2-AB was the main degradation product, accounting for <3 to 30% of the total radioactivity. The half-life ranged from <0.125 days (aerobic, 20°C) to 457 days (pH 5, 22°C). There is little or no photolysis of benomyl. In an aerobic degradation study of [*phenyl*-^{14}C]benomyl in pond water and sediment the carbendazim formed had a half-life of 61 days under non-sterile conditions. After 30 days, 22% of the applied radioactivity was bound to the sediments and <1% was evolved as carbon dioxide.

The volatilization of carbendazim from bare soil and bean leaves was tested under outdoor conditions. After 6 hours from 76 to 117% of the applied compound remained in the soil and 83-100% on the leaves.

In the residue analysis for benomyl and carbendazim in plants, soil and water, the samples are homogenized with ethyl acetate or acetone under acidic condition to convert any benomyl present to carbendazim. The extracts are cleaned up by liquid-liquid partition and/or solid-phase extraction and carbendazim is determined by HPLC with UV, fluorescence or mass spectrometric detection, or by GLC with an ECD. In one study on pineapples, recoveries were 67-120% for benomyl (as carbendazim), 68-114% for carbendazim and 73-124% for 2-AB. The limit of determination ranged from 0.01 to 0.1 mg/kg. An ELISA immunoassay was developed for benomyl, as carbendazim, in water, with a linear range from 0.1 to 5 µg/l, a recovery of 100% and limit of determination of 0.65 µg/l.

Carbendazim and the metabolites 5-HBC and 4-HBC can be determined in animal products after hydrolysis and liquid-liquid extraction by HPLC with UV detection, with limits of determination of 0.01- 0.02 mg/kg in milk, 0.05-0.1 mg/kg in tissues and faeces, 0.1 mg/kg in urine and 0.05 mg/kg in eggs. Recoveries ranged from 50 to 100%.

Carbendazim residues in analytical samples were shown to be stable at -20°C for 18 months in apples and processed fractions, 26 months in peaches and processed fractions, 30 months in tomatoes and green beans, 24 months in wheat grain, wheat straw and soya beans and 9 months in soil, with the remaining residue ranging from 79 to 107% of the initial residue. 2-AB was shown to be stable for 24 months in tomatoes and for 9 months in soya beans.

Definition of the residue

The current residue definition to be used for enforcement for benomyl, carbendazim and thiophanate-methyl is "carbendazim". The Meeting noted however that an appreciable proportion of the residue in crops arising from the use of benomyl was likely to be benomyl (which would be determined as carbendazim), and concluded that the definition of residues of benomyl for compliance with MRLs should be “the sum of benomyl and carbendazim expressed as carbendazim”. Since the ADI of benomyl is five times that of carbendazim, the same definition would avoid under-estimating the dietary risk from benomyl and would therefore be appropriate for the estimation of STMRS.

The definition of residues arising from the use of carbendazim should continue to be “carbendazim” (both for compliance with MRLs and for the estimation of dietary intake), with the addition of a note that maximum residue levels and STMRs cover carbendazim residues arising as a result of the use of benomyl or thiophanate-methyl (occurring as a metabolite and/or hydrolysis product during analysis) or from the direct use of carbendazim.

Residues resulting from supervised trials

All the residues are expressed as carbendazim. Trials with benomyl, carbendazim and thiophanate-methyl are evaluated together for each crop. STMRs for benomyl, carbendazim or thiophanate-methyl have been estimated when there were enough trials according to GAP with each compound.

Citrus fruit, Oranges. Two trials with benomyl in the USA according to GAP yielded residues in the fruit, as carbendazim, of 0.29 and 0.43 mg/kg at a PHI of 2 days. Eleven other trials were at higher rates and/or longer PHIs. Four trials in Brazil at the GAP rate gave residues of 0.13, 0.14, 0.36 and 0.63 mg/kg at a 1-day PHI. Two other trials were at twice the GAP rate. The residues from treatments according to GAP were, in rank order, 0.13, 0.14, 0.29, 0.36, 0.43 and 0.63 mg/kg.

Two post-harvest trials were conducted with carbendazim in France, where no GAP was reported. One pre-harvest trial in South Africa at the GAP rate gave residues of 0.07 and 1.6 mg/kg in the pulp and fruit respectively, at 15 days. Another trial was at twice the GAP rate.

Two trials with thiophanate-methyl in Japan were according to GAP, giving residues in the pulp of 0.11 and 0.16 mg/kg at a 1-day PHI. The residues in the fruit, calculated from the peel/pulp ratio, were 0.16 and 0.23 mg/kg.

On the basis of the benomyl data the Meeting estimated a maximum residue level of 1 mg/kg, as carbendazim, in oranges. As there were not enough data on residues in the pulp from trials according to GAP, the Meeting estimated an STMR from the residues in the fruit of 0.325 mg/kg for benomyl, as carbendazim.

Other citrus fruit. Two trials were conducted with benomyl on grapefruit in the USA, according to GAP for citrus, giving residues in the fruit at a PHI of 2 days of 0.08 and 0.09 mg/kg. Four other trials on grapefruit and one trial on limes were at higher or lower rates or PHIs.

Two trials with thiophanate-methyl on Chinese citron were at a higher rate than the recommended GAP.

There were insufficient data from trials according to GAP to estimate a maximum residue level for grapefruit, Chinese citron or limes.

Pome fruit, Apples. Eleven trials with benomyl in France according to GAP gave residues in the fruit, as carbendazim, at PHIs of about 7 days of <0.05 (2), 0.11, 0.15, 0.19 (2), 0.28, 0.49, 0.60, 0.81 and 1.75 mg/kg. Three other trials were carried out in France at shorter PHIs and three in Germany at a higher rate than the recommended GAP. Nine trials in the UK (where there is no GAP) did not comply with any GAP in the northern part of Europe. Of 39 trials carried out in the USA 23 were according to GAP, giving residues at 14 days PHI of <0.01, 0.16, 0.18, 0.20, 0.27, 0.28, 0.36, 0.37, 0.38, 0.51, 0.54, 0.60, 0.65, 0.72, 0.78 (2), 0.98, 1.0 (2), 1.2, 1.4 and 1.6 (2) mg/kg.

Eight trials with carbendazim in Germany according to UK GAP gave residues at 7 days PHI of 0.30, 0.35, 0.36, 0.42, 0.49, 0.70, 0.84 and 0.90 mg/kg.

Two trials with thiophanate-methyl in France according to GAP gave residues as carbendazim at a 1-day PHI of 0.57 and 0.31 mg/kg. Sixteen post-harvest trials could not be evaluated as there was no GAP. Two trials in Japan at the GAP rate gave residues at a 1-day PHI of 0.25 and 1.0 mg/kg. Sixteen other trials in the UK and one in Denmark were at higher rates or longer or shorter PHIs than the recommended GAP.

Pears. Three trials with benomyl in the UK did not match any reported GAP. In eight trials in the USA according to GAP the residues at a PHI of 14 days were 0.52, 0.65, 0.72 (2), 0.85, 1.1, 1.3 and 2.4 mg/kg. Another trial was at a higher rate.

Two trials with thiophanate-methyl in Japan at the GAP rate gave residues at a 1-day PHI of 0.54 and 0.94 mg/kg. Four trials in the UK were at longer or shorter PHIs than the recommended GAP.

As the residue populations and the recommended uses on apples and pears are similar, the Meeting agreed to combine the residues in the two commodities and estimate a maximum residue level for pome fruits. The combined results are listed below.

Benomyl (as carbendazim): <0.01, <0.05 (2), 0.11, 0.15, 0.16, 0.18, 0.19 (2), 0.20, 0.27, 0.28 (2), 0.36, 0.37, 0.38, 0.46, 0.51, 0.52, 0.54, 0.60 (2), 0.65 (2), 0.72 (3), 0.78 (2), 0.81, 0.85, 0.98, 1.0 (2), 1.1, 1.2, 1.3, 1.4, 1.6 (2) 1.8 and 2.4 mg/kg.

Carbendazim: 0.30, 0.35, 0.36, 0.42, 0.49, 0.70, 0.84 and 0.90 mg/kg.

Thiophanate-methyl (as carbendazim): 0.31, 0.54, 0.57 and 0.94 mg/kg.

On the basis of the benomyl data the Meeting estimated a maximum residue level of 3 mg/kg as carbendazim in pome fruit, and STMRs for benomyl, carbendazim and thiophanate-methyl of 0.60, 0.455 and 0.555 mg/kg respectively.

Apricots and nectarines. One trial was conducted with benomyl on apricots in Switzerland, but no GAP was reported. Two trials in the USA on apricots and four on nectarines were at lower rates than the recommended GAP.

Eight trials were conducted with thiophanate-methyl on apricots in Italy, but the spray concentration was not reported.

As there were no data which could be related to approved GAP the Meeting could not estimate maximum residue levels and recommended the withdrawal of the existing draft MRLs for apricot and nectarine.

Cherries. Two trials with benomyl in Italy according to French GAP gave residues, as carbendazim, at a PHI of 7 days of 0.24 and 0.65 mg/kg. Forty one trials in the USA were at lower or higher rates than the recommended GAP.

Six residue trials with carbendazim in Germany did not match any reported GAP.

The treatment in one trial with thiophanate-methyl in France was below the recommended rate. One trial in the UK according to French GAP and another in France according to Belgian GAP gave residues, as carbendazim, of 0.17 mg/kg at day 0 and 0.22 mg/kg at 13 days respectively.

The Meeting concluded that there were insufficient data from trials according to GAP to estimate a maximum residue level for cherries, and recommended the withdrawal of the draft MRL.

Peaches. Four trials with benomyl in France according to GAP gave residues in fruit, as carbendazim, of 0.07, 0.09, 0.12 and 0.15 mg/kg at a PHI of 7 days. Trials in Portugal and Spain according to Portuguese GAP gave residues at a PHI of 7 days of 0.08, 0.09 and 0.56 mg/kg. Seven trials in the USA according to GAP gave residues at a PHI of 3 days of 0.21, 0.30, 0.51, 0.61, 0.72, 1.0 (2) mg/kg. Three other trials in the USA were at twice the GAP rate. The trials according to GAP gave residues, in rank order, of 0.07, 0.08, 0.09 (2), 0.12, 0.15, 0.21, 0.30, 0.51, 0.56, 0.61, 0.72 and 1.0 (2) mg/kg.

In 12 trials with carbendazim in Europe, where recommended PHIs are 14-15 days, the samples were harvested after 40 days or more.

In three trials with thiophanate-methyl in France at the GAP rate (no PHI specified) samples were harvested after 12 or 19 days. Two other trials were at a lower rate. Thirteen trials in Italy did not match GAP in Italy or a neighbouring country. In two trials in Japan at the GAP rate the residues in the pulp, as carbendazim, at a PHI of 1 day were 0.41 and 0.22 mg/kg.

On the basis of the benomyl data, the Meeting confirmed the draft MRL of 2 mg/kg for peach and estimated an STMR of 0.255 mg/kg for benomyl, as carbendazim.

Plums. In seven trials in France and Italy with benomyl according to French GAP, the residues in the fruit at a PHI of 7 days were <0.05(2), 0.05, 0.06, 0.08, 0.10 and 0.34 mg/kg. Two trials in Spain according to Portuguese GAP gave residues of 0.07 and 0.05 mg/kg after 7 days. In four trials in the USA according to GAP the residues at a PHI of 3 days were 0.02, 0.06, 0.21 and 0.24 mg/kg in the fruit. Another eight trials in the USA were at lower or higher rates. In rank order, the trials according to GAP gave residue of <0.05(2), 0.02, 0.05 (2), 0.06 (2), 0.07, 0.08, 0.10, 0.21, 0.24 and 0.34 mg/kg.

In three trials with thiophanate-methyl in France according to GAP (no PHI specified) none of the samples were taken at day 0. Four other trials were at a lower rate. In five trials in Italy the application concentration was not reported.

The Meeting confirmed the draft MRL of 0.5 mg/kg for plums and estimated an STMR of 0.06 mg/kg for benomyl as carbendazim.

Berries and small fruits, Grapes. In four trials with benomyl in France and Italy according to French GAP and two in Greece, one in Portugal and two in Spain according to the national GAP, the residues as carbendazim were 0.30, 0.36, 0.45, 0.46, 0.84, 0.86 and 1.0 (3) mg/kg at a PHI of 14 days. Two trials in Germany (no GAP) were at higher rates than reported European GAP.

Ten trials carried out with carbendazim on grapes in France and two in Spain did not match any reported GAP. Nine trials in Germany and two in Italy were at higher rates than the recommended GAP.

Of twenty trials with thiophanate-methyl in Italy, five which complied with Portuguese or Spanish GAP gave residues as carbendazim after 22 or 28 days of 0.21, 0.36, 0.56, 0.87 and 1.9 mg/kg. Two trials in Portugal according to GAP gave residues of 1.1 and 1.3 mg/kg at the GAP PHI of 28 days. Two trials in Japan were at the GAP rate, but at a longer PHI. The trials according to GAP gave residues of 0.21, 0.36, 0.56, 0.87, 1.1, 1.3 and 1.9 mg/kg.

On the basis of the trials with benomyl and thiophanate-methyl the Meeting estimated a maximum residue level of 3 mg/kg as carbendazim, and STMRs for benomyl and thiophanate-methyl, as carbendazim, of 0.84 and 0.87 mg/kg respectively.

Strawberries. One trial with benomyl in Canada and eighteen in the USA were at lower or higher rates or PHIs than the recommended GAP.

Two trials with carbendazim in the UK and one in Finland according to GAP in The Netherlands gave residues at a PHI of 15 days of 0.30, 1.2 and 2.0 mg/kg. Six other trials in Germany and one in Italy could not be evaluated because no GAP was reported.

One trial with thiophanate-methyl in Denmark was at a higher rate than the recommended GAP and two trials in The Netherlands and 7 in the UK did not comply with any reported GAP.

The Meeting concluded that there were insufficient data from trials according to GAP to recommend an MRL or estimate an STMR for strawberries.

Other berries. Three trials with benomyl on blackberries and blueberries in the USA according to GAP gave residues at PHIs of 3 days (blackberries) or 21 days (blueberries) of 0.42, 1.6 and 1.7 mg/kg. Ten other trials were at lower or higher rates.

Twenty one trials in the UK with thiophanate-methyl did not match any reported GAP.

The Meeting concluded that there were insufficient data from trials according to GAP and recommended the withdrawal of the draft MRL for berries and other small fruits.

Avocados. In two trials with benomyl in the USA according to GAP, the residues were 0.22 and <0.06 mg/kg at 30 days PHI. Eight other trials were carried out at higher rates.

There were too few trials according to GAP. The Meeting recommended the withdrawal of the CXL for avocado.

Bananas. Fourteen trials were conducted with benomyl in Central America (no PHI) and Brazil (3 days PHI) according to GAP, with residues of <0.03 (7), 0.05, 0.06 (3) and 0.11 mg/kg in whole fruit and <0.03 (10), <0.06 (2), 0.10 and 0.44 mg/kg in the pulp.

The Meeting estimated a maximum residue level of 0.2 mg/kg to replace the existing CXL of 1 mg/kg. On the basis of the residues in pulp the Meeting estimated an STMR of 0.03 mg/kg for benomyl, as carbendazim.

Kiwifruit. Two trials in Japan with thiophanate-methyl according to GAP gave residues of 0.20 and 0.61 mg/kg in the pulp.

There were too few trials to estimate a maximum residue level.

Mangoes. Nineteen trials with benomyl in the USA were at lower or higher rates than the recommended GAP. The Meeting recommended the withdrawal of the CXL for mango.

Persimmons. One trial was conducted with thiophanate-methyl in Italy, but no GAP was reported. The Meeting could not estimate a maximum residue level.

Pineapples. Eight trials with benomyl in Costa Rica complied with Mexican GAP, giving residues at a 0-day PHI of 1.9, 2.0, 2.1, 2.3, 2.5, 2.7, 2.9 and 3.3 mg/kg in the whole fruit and <0.03 mg/kg in all trials in the pulp.

The Meeting estimated a maximum residue level of 5 mg/kg for pineapple and an STMR of 0.03 mg/kg for benomyl, as carbendazim, in pineapples.

Onions. Two trials with thiophanate-methyl in Japan at the GAP rate gave residues of <0.02 and 0.04 mg/kg at a PHI of 1 day. One trial in The Netherlands and 7 trials in the UK with a seed dressing and/or foliar treatment could not be evaluated as there was no information on GAP.

The Meeting concluded that there were insufficient data from trials according to GAP and recommended the withdrawal of the CXL for bulb onion.

Brussels sprouts. Six trials with benomyl in the UK which complied with GAP (21 days PHI) gave residues, as carbendazim, of 0.04, <0.05, 0.05, 0.08, 0.16 and 0.27 mg/kg, and two in the USA according to GAP gave residues of 2.4 and 2.9 mg/kg (7 days PHI).

Two trials with thiophanate-methyl in The Netherlands could not be evaluated as there was no reported GAP.

The Meeting concluded that the benomyl residues were from two different populations and on the basis of the UK data confirmed the CXL of 0.5 mg/kg for Brussels sprouts. It estimated an STMR of 0.065 mg/kg for benomyl as carbendazim.

Fruiting vegetables, Cucumbers and gherkins. Two trials with benomyl in Canada and six in the USA were at a lower or higher rate than the recommended GAP. Two trials in Germany with a soil drench and three indoor trials in the UK could not be evaluated in the absence of information on GAP. One trial in the USA in 1967 according to GAP gave a residue, as carbendazim, of <0.06 mg/kg. In two trials in Portugal, two in Greece and four in Spain, according to the recommended rate in Spain, where the PHI is 14 days, the residues after 7 days were <0.03 (7) and 0.05 mg/kg.

In four trials with carbendazim in Belgium and The Netherlands above the GAP rate only the peel and washed commodities were analysed. In ten trials on gherkins in Germany according to GAP in Belgium or The Netherlands the residues were <0.05 mg/kg at 3 days.

In one trial with thiophanate-methyl in Denmark and 3 trials in The Netherlands the treatments were below or above recommended rate in The Netherlands. Five trials in the UK were below the GAP rate or with drench treatments for which no GAP was reported.

On the basis of the carbendazim trials with support from the benomyl trials at 7 days PHI, the Meeting estimated maximum residue levels at the limit of determination of 0.05* mg/kg for cucumbers and gherkins to replace the previous recommendations of 0.5 mg/kg for cucumber and 2 mg/kg for gherkins. The Meeting estimated STMRs of 0.03 and 0.05 mg/kg for benomyl and carbendazim respectively in both cucumbers and gherkins.

Melons. Two trials with benomyl in Canada were at shorter PHIs than the recommended GAP. In two trials in France according to GAP for cucurbits, the residues at a PHI of 7 days were <0.05 and 0.19 mg/kg.

One trial with thiophanate-methyl in Italy according to Spanish GAP gave a residue of 0.11 mg/kg at a PHI of 21 days.

The Meeting concluded that there were insufficient data from trials according to GAP and recommended the withdrawal of the CXL for melons, except watermelon.

Tomatoes. Two trials with benomyl in Greece were at a higher rate than the recommended GAP, and five in the UK did not match any reported GAP. In six trials in Portugal and Spain according to Portuguese GAP the residues at 3 days PHI were <0.03, 0.03(2), 0.06, 0.08 and 0.12 mg/kg. In three trials in the USA according to GAP the residues at 1 day were 0.15, 0.56 and 0.98 mg/kg. Sixteen other trials in the USA were at lower or higher rates. The European and US trials represent two different populations and the results cannot be combined.

A total of ten trials were carried out with carbendazim in Finland, France, Italy and Spain, but no relevant GAP was reported. Seven of 10 trials in The Netherlands were according to GAP and yielded residues at a PHI of 3 days of <0.1 mg/kg in the pulp and of 0.08, 0.11, 0.12, 0.16, 0.17, 0.18 and 0.22 mg/kg in the whole fruit. The other trials at higher rates gave similar results.

Two trials with thiophanate-methyl in Italy and eight trials with drench or foliar treatments in the UK could not be evaluated because no relevant GAP was reported. Two trials in Japan according to GAP gave residues at 1 day of 0.59 and 0.73 mg/kg. Two other trials at a higher spray concentration gave residues of 0.69 and 0.31 mg/kg.

On the basis of the carbendazim data, the Meeting estimated a maximum residue level of 0.5 mg/kg for tomato to replace the draft MRL of 0.1 mg/kg, and an STMR of 0.16 mg/kg for carbendazim. The Meeting estimated an STMR of 0.045 mg/kg for benomyl, as carbendazim, on the basis of the European trials with benomyl.

Other fruiting vegetables. In the USA, four trials were conducted with benomyl on watermelons (no GAP reported) and four trials on summer squash at a higher rate than the recommended GAP.

One trial with thiophanate-methyl on egg plants and two on peppers in Italy, and ten trials on mushrooms in The Netherlands, could not be evaluated because information was incomplete or no GAP was reported.

As there were no data from trials according to GAP, the Meeting could not estimate a maximum residue level for watermelon and recommended the withdrawal of the draft MRLs for carbendazim in mushrooms and peppers, and the CXLs for egg plant and summer squash. No trials on winter squash were reported so the Meeting recommended the withdrawal of the CXL.

Lettuce. Seven trials were conducted with thiophanate-methyl in the UK in the field and in glasshouses, but no relevant GAP was reported. The Meeting recommended the withdrawal of the draft MRL for carbendazim in head lettuce.

Common beans. One trial was conducted with benomyl in France, but no GAP was reported. In four trials on green beans in the USA according to GAP, residues in the whole commodity were <0.06 (2), 0.03 and 0.14 mg/kg at a PHI of 28 days.

In three trials with carbendazim on dwarf beans in the UK according to GAP, residues at 22 days were all <0.1 mg/kg. Another three trials were at higher or lower rates or PHIs.

In one trial on dwarf beans and one on runner beans with thiophanate-methyl in the UK according to GAP and seven other trials on dwarf, broad and French beans at higher rates or PHIs, only the beans were analysed.

The Meeting concluded that there were insufficient data from trials according to GAP and recommended the withdrawal of the CXLs for common bean and broad bean.

Dry beans. Seven trials with benomyl in Canada and the UK and 32 trials in the USA did not comply with GAP.

Seven trials with carbendazim on field beans in the UK were at the GAP rate or higher, but there was not enough information to decide whether the trials were according to GAP.

Two trials with thiophanate-methyl in Japan on kidney beans according to the GAP rate for adzuki beans gave residues of 0.09 and 0.39 mg/kg in the beans. Four other trials on adzuki and kidney beans were at higher rates. In six trials with field beans in the UK at the GAP rate, the residues in the beans were 0.06, 0.09, 0.13, <0.2 (2) and 0.21 mg/kg after 6 to 19 days. The eight trials according to GAP gave residues in the beans of 0.06, 0.09 (2), 0.13, <0.2 (2), 0.21 and 0.39 mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg in dry beans, on the basis of the thiophanate-methyl data, to replace the CXL of 2 mg/kg, and an STMR of 0.165 mg/kg for thiophanate-methyl.

Peas. Two trials were conducted with benomyl in the UK at the recommended rate but with a shorter PHI.

Two trials with thiophanate-methyl in Japan were at a longer PHI, and nine in France were at a lower rate than recommended GAP. In four trials in the UK at GAP rates the residues in shelled peas, as carbendazim, were <0.01 (2) and 0.01 (2) mg/kg at 21 days PHI. Two other trials at shorter PHIs and two at longer PHIs gave similar results.

On the basis of the thiophanate-methyl trials according to GAP supported by two other trials at a shorter PHI, the Meeting estimated a maximum residue level of 0.02 mg/kg and an STMR of 0.01 mg/kg for thiophanate-methyl, as carbendazim, in garden pea, shelled.

Soya beans. In four trials with benomyl in the USA according to GAP, residues in the beans at a PHI of 35 days were <0.03 (2), 0.03 and 0.04 mg/kg. Four other trials were at higher rates or longer PHIs.

The Meeting concluded that there were insufficient data from trials according to GAP and recommended the withdrawal of the existing CXLs for soya bean (dry) and soya bean fodder.

Carrots. Twenty one trials with benomyl on carrots in the USA according to GAP yielded residues of <0.01, 0.01, 0.02 (3), <0.03 (3), 0.04 (3), 0.05 (4), 0.06, 0.10, 0.11, 0.12, 0.13 and 0.14 mg/kg at a PHI of 4 days. Eight other trials carried out at higher rates or a longer PHI gave similar results.

The Meeting estimated a maximum residue level of 0.2 mg/kg for carrot and an STMR of 0.05 mg/kg for benomyl, as carbendazim, in carrots.

Sugar beet. No GAP was reported to evaluate one trial in France and twelve in the USA with benomyl or six trials in France and nine in Germany with carbendazim. In one trial in Germany according to Belgian GAP, the residue at a PHI of 28 days was <0.05 mg/kg. Residues were similar in five other trials at higher or lower rates, and in all but one trial at a 0-day PHI.

Two trials with thiophanate-methyl in Japan according to GAP gave residues of <0.04 mg/kg at a PHI of 7 days.

The Meeting concluded that there were insufficient data from trials according to GAP to estimate a maximum residue level for sugar beet or sugar beet leaves or tops, and recommended the withdrawal of the existing CXL and draft MRL.

Celery. Two trials were conducted with thiophanate-methyl in The Netherlands, but no GAP was reported.

As no data from trials according to approved GAP were submitted, the Meeting recommended the withdrawal of the CXL.

Cereals, Barley grain. In three trials with carbendazim in Germany according to GAP, residues in the grain at a PHI of 56 days were <0.02, 0.03 and 0.05 mg/kg. In five other trials at higher rates and/or shorter PHIs the residues were in the same range. Fourteen other trials in Germany, France, Italy and Spain were at lower rates or longer PHIs than the recommended GAP. In the UK, two trials according to GAP (the PHI is “up to and including grain watery ripe”) yielded residues at 42-45 days PHI of <0.05 and 0.29 mg/kg. In rank order, the residues in the grain were <0.02, 0.03, <0.05, 0.05 and 0.29 mg/kg.

In fourteen trials with thiophanate-methyl in the UK (1973-1974) at up to 3 times the GAP rate (no PHI specified), the residues in the grain were <0.1 (13) and <0.2 mg/kg after 72 to 121 days. Fourteen trials with a seed dressing treatment (no GAP reported) gave similar results.

On the basis of the carbendazim trials complying with GAP (5 results), supported by the trials at a higher rate and/or shorter PHI (5 results), the Meeting estimated a maximum residue level of 0.5 mg/kg and an STMR of 0.05 mg/kg for carbendazim in barley grain.

Barley straw. In six trials with carbendazim in Germany and two in the UK according to GAP, the residues in rank order were <0.05, 0.20 (2), 0.49, 0.77 and 0.98 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg (the existing CXL) and an STMR of 0.345 mg/kg for carbendazim in barley straw and fodder, dry.

Maize. In three trials with carbendazim in France in 1988 at the GAP rate and three at a lower rate the residues in the kernels after 10-31 days were <0.05 mg/kg.

The Meeting concluded that the data from trials according to GAP were insufficient to estimate a maximum residue level for maize.

Rice, grain. In seventeen trials with benomyl in the USA according to GAP, residues at 21 days, as carbendazim, were <0.03 (7), 0.04, 0.05, <0.07, <0.08, 0.16, 0.20, 0.26, 0.36, 0.70 and 1.6 mg/kg in the grain.

Three trials with thiophanate-methyl in Japan were at a higher rate than the recommended GAP.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR of 0.05 mg/kg for benomyl as carbendazim in rice, husked

Straw. In fifteen trials with benomyl in the USA according to GAP the residues, as carbendazim, were 0.25, 0.41, 0.65 (2), 0.98, 1.3, 1.4, 2.5 (2), 4.3 (2), 5.9 (2), 8.5 and 11 mg/kg in straw at a 21-day PHI.

The Meeting confirmed the CXL of 15 mg/kg for rice straw and fodder, dry, and estimated an STMR of 2.5 mg/kg for benomyl as carbendazim.

Wheat, grain. In two trials with benomyl in The Netherlands according to GAP the residues, as carbendazim, were <0.04 mg/kg at a PHI of 34/35 days. Two other trials at twice the rate and PHI gave similar results. In four trials in the USA according to GAP the residues at a PHI of 21 days were <0.03 mg/kg. Three other trials were at shorter PHIs than the recommended GAP. The residues in rank order from the trials according to GAP were <0.03 (4) and <0.04 (2) mg/kg.

In 30 trials with carbendazim in Germany the rates were higher than the recommended GAP and/or samples were not taken at the recommended PHI. In the UK, one trial according to GAP showed residues at a PHI of 42 days of <0.05 mg/kg. Seven trials in France, three in Italy, one in Spain and one in the UK were at higher or lower rates than allowed by GAP.

In two trials with thiophanate-methyl in Japan at the GAP rate the residues in husked grain after 14 or 30 days were <0.02 or 0.03 mg/kg. Seven trials in the UK which complied with GAP gave residues in the grain after 46 to 83 days of <0.01 (3), 0.01 and <0.03 (3) mg/kg. Another 15 trials at higher rates gave similar results. Four trials in The Netherlands with treatments up to four times the German GAP rate showed similar residues in the grain.

On the basis of the trials with thiophanate-methyl supported by those with benomyl, the Meeting estimated a maximum residue level in wheat grain 0.05* mg/kg as a practical limit of determination, and estimated STMRs of 0.03 and 0.01 mg/kg for benomyl and thiophanate-methyl, as carbendazim respectively.

Straw. In two trials with benomyl in The Netherlands and three in the USA according to GAP, residues, as carbendazim, were 0.05, <0.1 (2), 0.18 and 0.72 mg/kg.

In six trials with carbendazim in Germany and one in the UK according to GAP the residues were <0.03 (4), <0.05, 0.2 and 0.66 mg/kg, at PHIs of 42 or 56 days.

On the basis of the benomyl and carbendazim data, the Meeting estimated a maximum residue level of 1 mg/kg to replace the CXL of 5 mg/kg and STMRs of 0.1 mg/kg for benomyl as carbendazim and 0.03 mg/kg for carbendazim in wheat straw and fodder, dry.

Rye. Six trials with carbendazim in Germany at the GAP rate or higher gave residues in the grain below the LOD (0.01 or 0.05 mg/kg) at a longer PHI than the recommended GAP (56 days). In two trials the residues in stalks at 56 days were 0.33 and <0.05 mg/kg.

In the UK there is no GAP for the use of thiophanate-methyl on rye, so the estimated maximum residue level for wheat cannot be extended to rye.

As there were no data from trials according to GAP were submitted, the Meeting could not estimate a maximum residue level for rye, and recommended the withdrawal of the existing draft MRL.

Tree nuts. Fourteen trials with benomyl in the USA in almonds or macadamia nuts were at the GAP rate or higher, but the samples were taken much later than the recommended PHI. Six trials were conducted on pecans, but no GAP was reported.

As there were no data from trials according to GAP, the Meeting could not estimate a maximum residue level in tree nuts and recommended the withdrawal of the existing CXL.

Rape seed. Residues in ten trials with carbendazim in Germany according to GAP were <0.02 mg/kg in the pods and seeds at about 56 days PHI. In three other trials at higher rates and in five trials in France at or below the GAP rate and longer PHIs than recommended, residues in the seeds and pods were again below the LOD (0.05 or 0.02 mg/kg).

Four trials were carried out with thiophanate-methyl in France, but no GAP was reported.

On the basis of the carbendazim trials, the Meeting estimated a maximum residue level of 0.05* mg/kg to replace the existing CXL of 0.1 mg/kg. As trials with applications above the recommended rate also yielded residues below the LOD, the Meeting estimated an STMR of 0 for carbendazim in rape seed.

Hops. Four trials with carbendazim on hops in Germany were with 2 applications of 0.225 or 0.38 kg ai/ha. The residues at PHIs of 17 or 26 days were 16, 18, 29 and 49 mg/kg. As no GAP was reported, the Meeting recommended the withdrawal of the existing CXL.

Peanuts. Ten trials with benomyl in the USA with applications above the recommended GAP rate gave residues in the kernels of <0.06 mg/kg 11 to 86 days after the last application.

As no data from trials according to GAP were submitted, the Meeting recommended the withdrawal of the CXLs for carbendazim in peanut and peanut fodder.

Coffee. In one trial with carbendazim in Brazil with a higher application rate than the recommended GAP and in six trials in Kenya (no GAP) the residues in the beans after 44-81 days were <0.1 mg/kg.

As no data from trials according to GAP were reported, the Meeting recommended the withdrawal of the CXL for carbendazim in coffee beans.

Tea. In six trials with thiophanate-methyl in Japan at a lower rate than the recommended GAP, the residues were 1.1-1.8 mg/kg after 7-21 days.

As there were no data from trials according to GAP, the Meeting could not recommend an MRL.

Processing studies

In two processing studies with benomyl on oranges in Brazil and one in the USA which simulated commercial practices, the processing factors (PF) for juice were 0.016, 0.36 and 0.83, with an average of 0.40. In the US study the PF was 1.36 in orange oil and ranged from 0.012 in finisher pulp to 0.88 in dried peel.

On the basis of an STMR for benomyl in oranges of 0.325 mg/kg and the calculated processing factors, the Meeting estimated STMRs of 0.13 and 0.442 mg/kg for benomyl, as carbendazim, in orange juice and orange oil respectively.

Two processing studies were carried out in the USA with benomyl on apples, one simulating household and commercial preparation and the other industrial processing. Washing and packing normally decreased the residues on apples, with PFs ranging from 0.26 to 1.2 (mean 0.55 ± 0.28) and from 0.36 to 1.0 (0.68 ± 0.29) respectively. Residues in peeled and unpeeled apples decreased after cooking, with PFs of 0.80 and 0.24 respectively. Residues in peeled and cored apple slices were decreased by factors of 0.23-0.38 (0.24 ± 0.10). Canned apple slices, apple sauce and gradeout fruit

had PFs of 0.14, 0.13 and 0.57 respectively, and the average PF for apple purée was 0.47. Residues in juice decreased by factors of 0.26 and 0.23.

On the basis of an STMR for benomyl in pome fruits of 0.60 mg/kg and the calculated processing factors, the Meeting estimated STMRs of 0.147, 0.282 and 0.078 mg/kg for benomyl, as carbendazim, in apple juice, apple purée and apple sauce respectively.

In two separate studies on peaches in the USA, washing and peeling processing factors were 0.18 and 0.37, and 0.02 and 0.12 respectively. The PFs for sliced and puréed peaches were <0.01 and 0.06 respectively. In seven studies on plums in California, the processing factors for prunes ranged from 0.08 to 0.83, with an average of 0.24 ± 0.27 (n = 25).

In four processing studies on grapes in Switzerland and two in the USA, the processing factors for wine averaged 0.53 (n = 4), for raisins 1.3 (n = 2) and for raisin waste 4.1 (n = 2).

On the basis of an STMR for benomyl in grapes of 0.84 mg/kg and the calculated processing factors, the Meeting estimated STMRs of 0.445, 1.09 and 3.44 mg/kg for benomyl, as carbendazim, in wine, raisins and raisin waste respectively.

A single processing study on tomatoes treated with benomyl was conducted in the USA in a pilot-scale plant, with processing factors of 0.29, 0.48, 0.27, 0.66, and 0.62 for wet tomato pomace, dry tomato pomace, juice, purée and ketchup respectively. The Meeting estimated corresponding STMRs of 0.013, 0.022, 0.012, 0.023, 0.030 and 0.028 mg/kg from the STMR of 0.045 mg/kg for benomyl in tomatoes.

In two processing studies in the USA with soya beans, the processing factors were 0.71, 1.9, <0.1, 0.23, 3.3 and 19.2 in meal, hulls, refined oil, crude oil, soap stock and aspirated fractions (assortment of seeds, stems, leaves, straw, hay, hulls, mill, sand and dirt) respectively, but there was no STMR for soya beans.

Two processing studies on rice in the USA in a pilot-scale plant closely simulated commercial practice. Processing factors from whole grain were 0.01, 0.31 and 2.3 in white rice, rice bran and rice hulls.

When benomyl was added to whole milk at a level of 1 mg/kg it appeared to be degraded during the production of commercial sterile evaporated canned milk (PFs of 0.64 and 0.43 for whole and skimmed milk respectively), but pasteurization did not affect residue levels. Residues tended to concentrate in mother liquor (PF=5.2) and cream (PF = 1.5 and 1.7).

As the STMR for benomyl in milk is 0, the STMR for cream is also 0.

Food of animal origin

Livestock feeding studies were conducted with benomyl or carbendazim at concentrations (in benomyl equivalents) ranging from 5 to 450 ppm in poultry and from 2 to 75 ppm in cattle. In two studies with cows at feeding levels above 10 ppm, residues in the milk of 4-HBC and 5-HBC ranged from <0.007 mg/kg after 7 days depuration to 0.09 mg/kg after 28 days of exposure. In four studies on poultry the residues of carbendazim, 4-HBC and 5HBC in the tissues and eggs were at or below the LOD (0.02 to 0.05 mg/kg) from levels of 5 ppm in the diet. A separate study showed that benomyl residues in liver reached a plateau within two weeks.

The STMRs for raisin waste and dry tomato pomace were equivalent to 5.2 and 0.033 mg/kg benomyl respectively, and the STMRs in barley, rice and wheat grain corresponded to 0.076, 0.076 and 0.045 mg/kg benomyl. On the basis of these estimates of the STMRs for animal feed items, the

Meeting concluded that the levels used in the feeding studies were adequate to estimate maximum residue levels in animal commodities.

The Meeting recommended the withdrawal of the CXLs for milks, cattle meat, chicken fat, poultry meat and eggs and estimated maximum residue levels of 0.05* mg/kg to replace them. As the lowest feeding levels used in the animal studies were much higher than the estimated dietary burdens, the Meeting estimated STMRs of 0 for cattle and poultry commodities (meat, milks, edible offal, chicken fat and eggs).

Residues in food in commerce or at consumption

Monitoring or surveillance data for carbendazim residues generated in the UK during 1995 and 1996 from samples of fruits, vegetables, cereals and processed products of UK or imported origin were submitted. In 1995, 1135 samples were analysed, of which 62 samples (55%) of apples, apple juice, fruit-based infant food, plums, strawberries, lettuce and blackcurrants had detectable levels of carbendazim (0.1 to 0.9 mg/kg). Of the 1375 samples analysed in 1996, 16 samples or 1.2% (apples, celery, dessert grapes and pears) had levels above the limit of determination, ranging from 0.1 to 1.1 mg/kg.

Monitoring data generated by the food industry in the UK were also reported. Residues of carbendazim were above the limit of determination in 36 samples. It was not clear from the report how many samples were analysed. Bananas had the highest frequency of positive samples (20%). Residues in bananas, apples, grapes, fruit conserve, oranges, pineapples and cabbages ranged from 0.2 to 1.5 mg/kg.

RECOMMENDATIONS

The maximum residue levels estimated to arise from the use of benomyl are covered by the MRLs recommended for carbendazim listed in the carbendazim monograph. The list also includes the STMRs estimated for benomyl, carbendazim and thiophanate-methyl.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: sum of benomyl and carbendazim, expressed as carbendazim.

DIETARY RISK ASSESSMENT

The residues of benomyl, carbendazim and thiophanate-methyl are all expressed as carbendazim, which has the lowest ADI of the three compounds. A total of 34 STMRs were estimated for benomyl, 8 for carbendazim and 5 for thiophanate-methyl. If STMRs were estimated for more than one compound in a commodity, the highest STMR was used for the calculation. No MRLs were used.

International Estimated Daily Intakes of benomyl, carbendazim and thiophanate-methyl for the five GEMS/Food regional diets were in the range of 1 to 6% of the carbendazim ADI.

The Meeting concluded that the intake of residues of benomyl, carbendazim and/or thiophanate-methyl resulting from their uses that have been considered by the JMPR is unlikely to present a public health concern.

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BENTAZONE (172)

EXPLANATION

Bentazone was evaluated by the JMPR in 1991, 1994 and 1995. At the CCPR in 1995, the delegations of Germany and France suggested that the definition of the residue for animal products should exclude the metabolite, as no residues of the metabolite had been found.

The 1995 Joint Meeting confirmed the previous recommendation for plant commodities but recommended that the definition of the residue in animal products should be changed to bentazone alone.

In 1997 the CCPR requested the JMPR to consider revising the definition of the residue for plant commodities (ALINORM 97/24A, para 71).

In order to respond to the CCPR request the Meeting considered the information provided in the 1991, 1994 and 1995 JMPR evaluations and that submitted to the manufacturer, which included summaries of new studies on plant metabolism and environmental fate, analytical methods and reports of supervised trials.

METABOLISM AND ENVIRONMENTAL FATE

The 1991 Meeting concluded that the degradation of bentazone in plants, animals, soil, and soil/water suspensions followed similar pathways, but with quantitative differences. In plants the aromatic ring is hydroxylated at the 6 and 8 position of the molecule; 6-hydroxy bentazone is a major part of residue during degradation.

Animal metabolism

Animal metabolism studies showed that bentazone was the main compound eliminated in the urine and faeces, 6-hydroxy-bentazone was present at low levels in the urine and only traces of 8-hydroxy-bentazone were found. Studies on hens and lactating goats evaluated by the 1995 JMPR concluded that the major residue component in meat, milk and eggs was the parent bentazone with smaller amounts of the glucuronide conjugate.

Plant metabolism

New metabolism studies on soya beans, rice, maize, green beans and potatoes were reported.

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 ethanol-extractable residues in forage and hay were up to 62 and 9% of the TRR respectively, and the corresponding total methanol-extractable ^{14}C residues were 4 and 6% of the TRR. When the residue in the methanol extract was hydrolysed with 2N HC1, the hydrolysate contained bentazone and 6- and 8-hydroxy-bentazone. The bound residues (not extracted with methanol) were associated with polysaccharides, hemicellulose fractions and lignin. It was estimated that 57% of the TRR in the beans was associated with protein and 16 % with carbohydrate.

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. In grain samples 63 days after

treatment only 6.6% of the TRR was extractable and 93.4% 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. The residues of bentazone and 6-hydroxy-bentazone were below the detection limit (0.02 mg/kg).

The metabolism of bentazone was also 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 to 1.68 kg ai/ha of bentazone. Samples were taken 0, 1, 2, 3, 6, 9 and 18 weeks (harvest) after application. In forage samples taken 14 and 21 days after treatment only bentazone and 6-hydroxy-bentazone were found in the methanol extract. Analysis of the final harvest grain, cobs, husk and stover showed no residues of bentazone or 6-hydroxy- or 8-hydroxy-bentazone ([0.05mg/kg).

The magnitude and nature 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 TRR was determined in forage at 9 and 36 days PHI, and in hay and beans at 79 days (harvest). The residues consisted of bentazone and 6- and 8-hydroxy-bentazone.

The metabolism in potato plants was studied after two foliar spray applications of 1.12 kg ai/ha [^{14}C]bentazone formulation 23 and 44 days after planting. Samples were taken at 41 and 62 days PHI. The identified extractable residues were bentazone (4% of the TRR) and conjugates of 6-hydroxy-bentazone (about 12%). Most of the radioactivity was incorporated into starch.

The metabolism and distribution of [^{14}C]bentazone were studied in leafy vegetable, root and grain rotational crops grown in confined plots, after soil was treated at a nominal application rate of 2.24 kg ai/ha. Cropping intervals were 39 days to represent emergency replanting, 102 to 145 days for autumn planting and 316 to 369 days for annual planting of rotational crops. The residues of bentazone and the metabolites 6-hydroxy- and 8-hydroxy-bentazone were quite low in emergency replant crops (0.005-0.04 mg/kg) and essentially absent in autumn and annual crops (0.001-0.02 mg/kg).

Residues in succeeding crops

Field trials were carried out with alfalfa, maize, lettuce, mustard, radishes, snap beans, sorghum, spinach, sugar beets, turnips and wheat, representing cereal, root, legume, leafy and oil crops.

The rates applied to the preceding crop, soya beans in all the trials, reflected a “worst-case” situation: 2 applications at 1.12 kg ai/ha each with an interval of 14 days (GAP: 1.44-1.99 kg ai/ha, 1 application). Soil samples collected before and after each application to the soya beans and at planting and harvest of the rotational crops were analysed. The residues of bentazone and 6-hydroxy- and 8-hydroxybentazone in the replanted crops were all below the LOD (0.05 mg/kg).

METHODS OF RESIDUE ANALYSIS

Analytical methods

The analytical method described in the 1991 evaluation (BASF, method No. 197) was modified to extend its range, and the modified method was described in the 1994 monograph. The reported LOD was 0.05 mg/kg. The method determines bentazone and the hydroxy metabolites.

Definition of the residue

New 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, depending whether a monocotyledonous or dicotyledonous crop was treated.

Animal metabolism studies showed that the parent bentazone was the major component of the residue.

Analytical methods are suitable for the determination of bentazone and both hydroxy metabolites.

The Meeting noted that existing and proposed MRLs for plant commodities are based on the sum of bentazone and its hydroxy metabolites, agreed that it was necessary to review all the studies on metabolism before taking a decision and recommended that the definition of the residue should be considered at the next periodic review.

USE PATTERN

Detailed information on national use patterns was given in the 1994 evaluation.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Supervised field trials were evaluated by the JMPR in 1991 and 1994. Bentazone and its hydroxy metabolites were determined in all the trials. A summary of the results is given below.

Crop	No. of trials	Applic. rate, kg ai/ha	PHI, days	bentazone, 6-OH- and 8-OH-bentazone, mg/kg	Recommended MRL, mg/kg
Onion	8	0.7-2.0	48-95	Bent <0.02-0.05 6-OH <0.02 8-OH <0.02	0.1 (1991) (CXL, 1995)
Beans, dry		1.44	21-35	Bent <0.02 6-OH <0.02 8-0H <0.02	0.05 (1991)
Common bean		1.44	21-35	6-OH <0.02 8-OH <0.02	0.2 (1991)
Broad bean, dry		1.44	21-35	6-OH <0.02 8-OH <0.02	0.05(1991)
Field pea (dry)	6	0.96- 1.44	30-40	Bent <0.05 6-OH <0.05 (3 trials); 0.06-0.43 (3 trials) 8-OH 0.31 (1 trial); <0.05 (5 trials)	1 (1994)
Lima bean	3	1.1		Bent, 6-OH and 8-OH<0.05	0.05 (1991) (CXL 1995)
Soya beans, dry		0.9-1.4	30-90	Bent, 6-OH and 8-OH < 0.02	0.05 (1991) (CXL, 1995
Barley		0.5-2.0	40-90	Bent, 6-OH and 8-OH <0.02	0.1 (1994)
Oats		1.0-2.0		Bent, 6-OH and 8-OH < 0.02	0.1 (1994)
Rye	4	1.0-1.9	64-91	Bent, 6-OH and 8-OH < 0.02	0.1 (1994)
Sorghum	9	1.0	97-134	Bent, 6-OH and 8-OH<0.02	0.1 (1994)
Wheat	15	1.0-1.9	60-110	Bent, 6-OH and 8-OH<0.02 6-OH B = 0.06 (1 sample)	0.1 (1994)
Maize	12	0.7 - 1.9	69-110	6- OH > Bentaz. (2 trials, 1991)	0.2 (1994)

Crop	No. of trials	Applic. rate, kg ai/ha	PHI, days	bentazone, 6-OH- and 8-OH-bentazone, mg/kg	Recommended MRL, mg/kg
Maize fodder	12	0.7-1.9	69 - 110	6-OH> Bent (3 trials) 8-OH> Bent (1 trial)	0.2 (1994)
Linseed	5	0.9-1.4	62 - 77	6-OH > Bent. 8-OH > Bent. (1 sample)	0.1 (1991)
Peanuts		0.75 3.6	20 - 155	Bent., 6-OH and 8-OH <0.05	0.05 (1991)
Potatoes	31	0.96 - 1.44	35 - 84	6- OH >bent. (2 samples)	0.1 (1991)
Alfalfa	3	0.9 - 1.4	32 - 58	8-OH < 0.02 6-OH> Bent in all trials	2 (1991)

APPRAISAL

Bentazone was originally evaluated in 1991 and subsequently in 1994 and 1995. The 29th (1997) Session of the CCPR requested the JMPR to consider revising the residue definition for plant commodities.

In order to respond to the CCPR request the Meeting considered the information provided in the 1991, 1994 and 1995 JMPR evaluations and that submitted by the manufacturer, which included summaries of new studies on plant metabolism and environmental fate, analytical methods and reports of supervised trials.

Metabolism studies in rats showed that bentazone is poorly metabolized. The parent compound was the predominant metabolite, with 6-hydroxy-bentazone identified as a minor metabolite and 8-hydroxy-bentazone found in trace amounts.

Metabolism studies in lactating goats and hens showed that the major residue component in meat, milk and eggs was the parent bentazone with small amounts of 6- or 8-hydroxy-bentazone and their glucuronide and sulfate conjugates.

New metabolism studies on soya beans, rice, maize, green beans and potatoes showed that the main residues in plants were bentazone and one or both of its conjugated metabolites, 6- and 8-hydroxy-bentazone, depending whether a monocotyledonous or dicotyledonous crop was treated. The nature of residues in succeeding crops was also investigated, but residues in replanted crops were all below the LOD. Details of these studies were not provided since bentazone was not scheduled for a full re-evaluation.

Multi-residue analytical methods do not determine residues of bentazone and its hydroxy metabolites. In a specialized analytical method suitable for the determination of bentazone and conjugated 6- and 8-hydroxy-bentazone, each of the residue components can be determined with an LOD of 0.02 mg/kg. The 1995 JMPR recommended a practical limit of determination of 0.05 mg/kg for regulatory purposes for each component.

Residue definitions for national MRLs include bentazone alone and the sum of bentazone and its metabolites.

In most of the supervised trials, residues of the metabolites were below the LOD. Residues of 8-hydroxy-bentazone above the LOD were found in three samples of maize fodder and one of linseed in trials evaluated in 1991. Residues of 6-hydroxy-bentazone were found at higher concentrations than bentazone in some samples of field peas (dry) (1 of 31), potatoes (2 of 31), wheat (1 of 15), maize (3 of 12), maize fodder (3 of 5), linseed (1 of 5) and alfalfa (3 of 3).

The Meeting noted that existing and proposed MRLs are based in the sum of bentazone and its hydroxy metabolites, agreed that it was necessary to review all the studies on metabolism before taking a decision and recommended that the definition of the residue should be considered at the next periodic review.

DIETARY RISK ASSESSMENT

Although no maximum residue levels were estimated, a risk assessment was carried out because the compound was on the agenda of the FAO Panel. The International Estimated Daily Intakes for the five GEMS/Food regional diets were in the range of 0 to 1% of the ADI. The Meeting concluded that the intake of residues of bentazone resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

REFERENCES

BASF. Bentazone dossier prepared according to Annex II of Directive 91/414/EC.

CARBENDAZIM (072)

[See also BENOMYL (069)/THIOPHANATE-METHYL (077)]

EXPLANATION

Carbendazim was evaluated in 1973 and again in 1994 (residues) and 1995 (toxicology and environmental). The CCPR recommended that the definition of the residue should be reconsidered on the basis of information that had been provided by the UK and that a risk assessment would be required (ALINORM 97/24, para 51). The UK propose the residue definition as the sum of thiophanate-methyl, benomyl and carbendazim, expressed as carbendazim. MRLs cover carbendazim residues, resulting from direct use, or occurring as a metabolic product. Data was provided by the main manufacturers and by The Netherlands Government.

IDENTITY

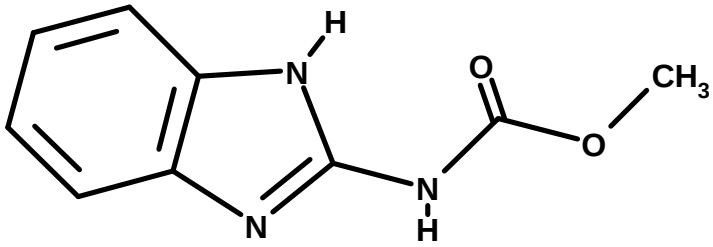
ISO common name: carbendazim

Chemical names**:**

IUPAC:	Methyl benzimidazol-2-ylcarbamate
CA:	Methyl 1*H*-benzimidazol-2-ylcarbamate

CAS registration number: 10605-21-7

Structural formula:



Molecular formula: $C_9H_9N_3O_2$

Molecular weight: 191.21

Physical and chemical properties

<u>Pure active ingredient</u>

Melting point: 302-307 C with decomposition

Relative density: 1.45 ± 0.05 g/ml at 20°C

Vapour pressure: 9.0×10^{-5} Pa at 20°C; 1.5×10^{-4} Pa at 25°C

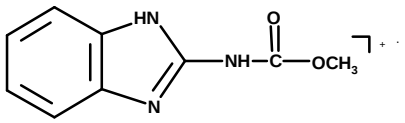
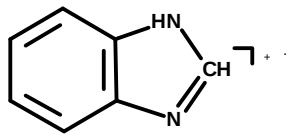
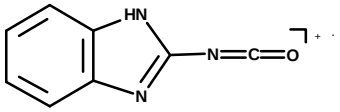
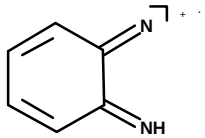
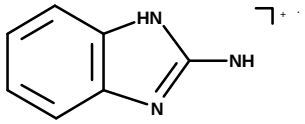
Volatility: 3.6×10^{-3} Pa x m^3 x mol^{-1} at 24°C

Physical state: almost colourless, odourless crystalline powder

Solubility (mg/l at 24°C):
water: 29 (pH 4); 8 (pH 7); 7 (pH 8)
ethanol: 300
benzene: 36.0
hexane: 0.5
ethyl acetate: 135.0
methylene chloride: 68.0
methanol: 480.0

Octanol water partition coefficient at 25 ± 1°C: K_{ow} = 30 (pH 5, 7 and 9)
24 (pH 5); 32 (pH 7); 31 (pH 9)

Mass spectral data

Molecular fragment	m/z	Molecular fragment	m/z
	191		118
	159		105
	132		

Hydrolysis: stable at 22 and 25°C, pH 5 and 7. At pH 9, half-life 22 days at 22°C; 54 days at 25°C

Photolysis: stable for 166 hours to simulated sunlight (290-490 nm), under sterile conditions and pH 5

Dissociation constant: $pK_a = 4.2$

Stability in air/photochemical degradation: $k_{OH} > 60 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}; half-life <0.27 days

<u>Technical material</u>

Purity: not reported

Melting point: >295°C under decomposition

Relative density: approx. 1.5 g/ml at 20°C

Physical state: sand-coloured to light grey odourless crystalline powder

Flammability: class 3 (topical burning or glowing without diffusion). Not flammable.

Auto-flammability: no spontaneous ignition up to 400°C. Not auto-flammable.

Explosive properties: capable of strong dust explosion but not sensitive to percussion.

Oxidizing/reducing properties: neither oxidizing nor reducing.

Stability at 25 ± 5 °C: dry: 2-3 years; alkaline solution: slowly decomposes; acid solution: water-soluble salts are formed.

Formulations

Table 1 shows the main formulations registered for use internationally, mainly foliar and soil application, with limited use as seed treatment.

Table 1. Formulations of carbendazim.

Product	Formulation	Active ingredient	Concentration, %
Derosal 50 Dispersion	SC	carbendazim	50
Derosal Flüssig	SC	carbendazim	36
Derosal 80	WG	carbendazim	80
Derosal 60	WP	carbendazim	59.4
Derosal 50	WP	carbendazim	50
Bavistin FL	SC	carbendazim	50 36
Bavistin	WP	carbendazim	50
Bavistin, Bavistin DF	WG	carbendazim	50
Delsene 50	WP	carbendazim	50
Delsene 75	WP	carbendazim	75
Carbendazim DP	WG	carbendazim	50
Carbendazim WDG 80	WG	carbendazim	80
Carbendazim	SC	carbendazim	51.1
Sportak Alpha HF	EC/SC	carbendazim prochloraz	10 26.7
Sportak Alpha	EC/SC	carbendazim prochloraz	83.0 30
Sportak® PF	EC/SC	carbendazim prochloraz	8.0 30
Sumico Botrylon	WP	carbendazim diethofencarb	25 25
Troika	EC	carbendazim prochloraz fenbuconazole	8.0 21.3 4.0

Product	Formulation	Active ingredient	Concentration, %
Vista C	SC	carbendazim fluquinconazole	10l 8.3
Alert S	SC	carbendazim flusilazole	25 12.5
Delsene MX 200	WP	carbendazim mancozeb	6.2 77.4
Delsene M	WP	carbendazim mancozeb	10 64
Kombak WDG	WG	carbendazim mancozeb	12.4 63.3
Prelude SP	DS and WS	carbendazim prochloraz manganese chloride complex	40 10.8
Prestige	FS	carbendazim prochloraz copper chloride complex	25 25

EC = emulsifiable concentrate; FS=flowable concentrate for seed treatment; DS = powder for dry seed treatment; SC = suspension or flowable concentrate; WG = water-dispersible granule; WP = wettable powder; WS = wettable powder for seed treatment.

METABOLISM AND ENVIRONMENTAL FATE

Abbreviations:

2AB:	2-aminobenzimidazole
ADDB:	2-amino-4,5-dihydro-4,5-dihydroxy-1*H*-benzimidazole
BUB:	*N*-(1*H*-benzimidazol-2-yl)-*N'*-butylurea
4,5-DDBC:	methyl (4,5-dihydro-4,5-dihydroxy-1*H*-benzimidazol-2-yl)carbamate
5,6-DDBC:	methyl (5,6-dihydro-5,6-dihydroxy-1*H*-benzimidazol-2-yl)carbamate
4,5-DHHBC-G:	*S*-[4,5-dihydro-5-hydroxy-2-(methoxycarbonylamino)-1*H*-benzimidazol-4-yl]glutathione
5,6-DHHBC-G:	*S*-[5,6-dihydro-5-hydroxy-2-(methoxycarbonylamino)-1*H*-benzimidazol-6-yl]glutathione
5,6-DHBC:	methyl (5,6-dihydroxy-1*H*-benzimidazol-2-yl)carbamate
4-HBC:	methyl 4-hydroxy-1*H*-benzimidazol-2-ylcarbamate
5-HBC:	methyl 5-hydroxy-1*H*-benzimidazol-2-ylcarbamate
5,6-HOBC N-oxide:	methyl (5-hydroxy-6-oxo-6*H*-benzimidazol-2-yl)carbamate N_1-oxide
STB:	3-butyl-1,3,5-triazino[1,2-*a*]benzimidazol-2,4(1*H*,3*H*)-dione

Animal metabolism

In early investigations the metabolism of benomyl was studied in rats, mice, rabbits, dogs, sheep and cows. Animals were dosed orally or peritoneally at 0.1g benomyl/kg/bw. The basic route involves cleavage of the 1-butylcarbamoyl side chain to yield carbendazim. Detoxification proceeds through hydroxylation and hydrolysis, the major metabolite being methyl 5-hydroxybenzimidazol-2-ylcarbamate (5-HBC). The hydroxylated metabolites appear to readily form excretable sulfate and glucuronide conjugates (Douch, 1973, Gardiner *et al*., 1974, Sherman and Clayton, 1968).

Rats. When [^{14}C]carbendazim (specific activity 25 mCi/g), was administered by gavage to Wistar rats at 2 mg/kg for 10 consecutive days, 59% of the radioactivity was eliminated in the urine and 36% in the

faeces at a rapid rate for the first 3 days and thereafter more slowly. The residues in the liver were 0.12 µg/kg as carbendazim (0.3%) 7 days after the last dose and 0.03 µg/kg (0.08%) after 14 days. The levels in the blood, kidneys, fat, muscle and gonads were [0.01 µg/kg after 7 days (Christ and Kellner, 1973). Single oral doses of 12 mg/kg [2-^{14}C]carbendazim (specific activity 5.7 mCi/mol) given to male albino rats in diethylene glycol-ethanol were rapidly absorbed. The bioavailability based on the urinary excretion data was about 85% (Krechniak and Klosowska, 1986).

After oral administration of about 3 mg/kg [2-^{14}C]carbendazim to rats of both sexes an average maximum concentration C_{max} of 1.03 ± 0.49 µg/ml carbendazim equivalents was reached in the blood within 15-40 min. A dose of about 300 mg/kg resulted in a disproportionately lower C_{max} of 16-17 µg/ml 0.4-4 h after dosing. The blood levels were the same when the rats were given the same daily dose for 14 and 29 days. Excretion in the urine within 6 h after administration was 46-63% of 3 mg/kg and 8-19% of 300 mg/kg. Between 0.01 and 1.08% of the applied dose was in the faeces. Under the same experimental conditions, mice displayed a similar C_{max} in the blood (1.12 ± 0.59 µg/ml) after a single oral dose of 3 mg/kg but a higher C_{max} at 300 mg/kg (36-53 µg/ml). The mice excreted 33-75% of the low dose in the urine and up to 10% in the faeces. At doses of 300 mg/kg, renal excretion was 10-24% and faecal excretion 27%. Pre-treatment with unlabelled carbendazim had no effect on the excretory pattern in either species. In rats 6 h after oral dosing the highest concentrations in males were found in the kidneys and in females in the liver irrespective of the dose, while in both male and female mice the liver contained the highest concentration, up to 3.6 times that in the rats. Notably, the concentrations in the gonads were near or below the blood concentrations (Kellner and Eckert, 1983).

The distribution patterns in rats and mice were confirmed by whole-body autoradiography after intravenous injection in DMSO or oral dosing with a suspension in starch mucilage of 3 mg/kg [2-^{14}C]carbendazim. The concentration in the liver was higher in mice than in rats and there was a high concentration in the bile (gall bladder). The radioactivity was almost completely excreted after 24 hours (Kellner, 1983).

In Wistar rats (of about 200 g body weight) dosed orally with 8 mg [^{14}C]carbendazim for 10 days, approximately 60% of the radioactivity was excreted in the urine and 35% in the faeces during the first 5 days. The main metabolite 5-HBC was identified in both the urine and faeces in conjugated form and in the faeces as the free compound. Small amounts of the conjugated metabolite were also found in the liver after 10 days (0.7 mg/kg, calculated as parent). The nature of the conjugate was not investigated (Gorbach *et al*., 1974).

When the metabolic transformation of [2-^{14}C]carbendazim was compared in Wistar rats and NMRI mice given an oral dose of 3 or 300 mg/kg, the same metabolites were found in the urine with quantitative differences between the species. A 14-day or 29-day pre-treatment of the animals with the unlabelled compound (rats 50 and 5000 ppm in the diet; mice 30 and 3000 ppm) had no influence on the metabolic profile. In rats 5-HBC was the major metabolite in the urine, being present as the glucuronide and sulfate. Less than 10% (low dose) and 2% (high dose) of the total radioactivity in the urine was attributed to a second sulfate ester, the hydrolysis product of which was neither hydroxylated carbendazim nor 2-aminobenzimidazole (2-AB). In the mouse urine this "sulfate ester II" represented 30% of the total radioactivity at the low dose and 4-10% at the high dose. In the liver carbendazim residues as a percentage of the extractable radioactivity were generally lower in rats pre-treated with unlabelled carbendazim. This was not so in pre-treated mice. Thus, the 29-day administration of the high dose to mice saturated the detoxification capacity of the liver, an effect not observed at the low dose. In contrast, the rats increased their detoxification capacaity more efficiently and showed higher elimination

and lower retention than mice. This may explain the development of hepatotoxicity in mice (Dorn *et al*., 1983; Table 2).

Table 2. Residues of carbendazim in the livers of rodents 6 h after oral dosing.

Dose, mg/kg		Rat, % of dose	Mouse, % of dose
Single dose	3	12	29
	300	18	26
29-day repeated dose	3	2	<2
	300	4	28

In a further gavage study (Monson, 1990) single oral doses of 50 mg/kg or 1000 mg/kg phenyl-labelled [^{14}C]carbendazim were given to Sprague-Dawley rats of both sexes, and single oral doses of 50 mg/kg were given after dosing by gavage with unlabelled carbendazim at 50 mg/kg for 14 days. 5-HBC was identified as the main metabolite in the urine of male rats. Female rats also excreted 5,6-HOBC N-oxide, mainly as the glucuronide. Both the sulfuric and glucuronic acid conjugates of 5,6-DHBC were identified as minor metabolites in the urine of the male and female rats. Free 5-HBC was the main metabolite in the faeces of the low-dose rats but 5,6-HOBC N-oxide was also identified after pre-conditioning. In addition to 5-HBC, carbendazim was identified as a major component in the faeces of the high-dose rats. Postulated metabolic pathways of carbendazim in rats are shown in Figure 1.

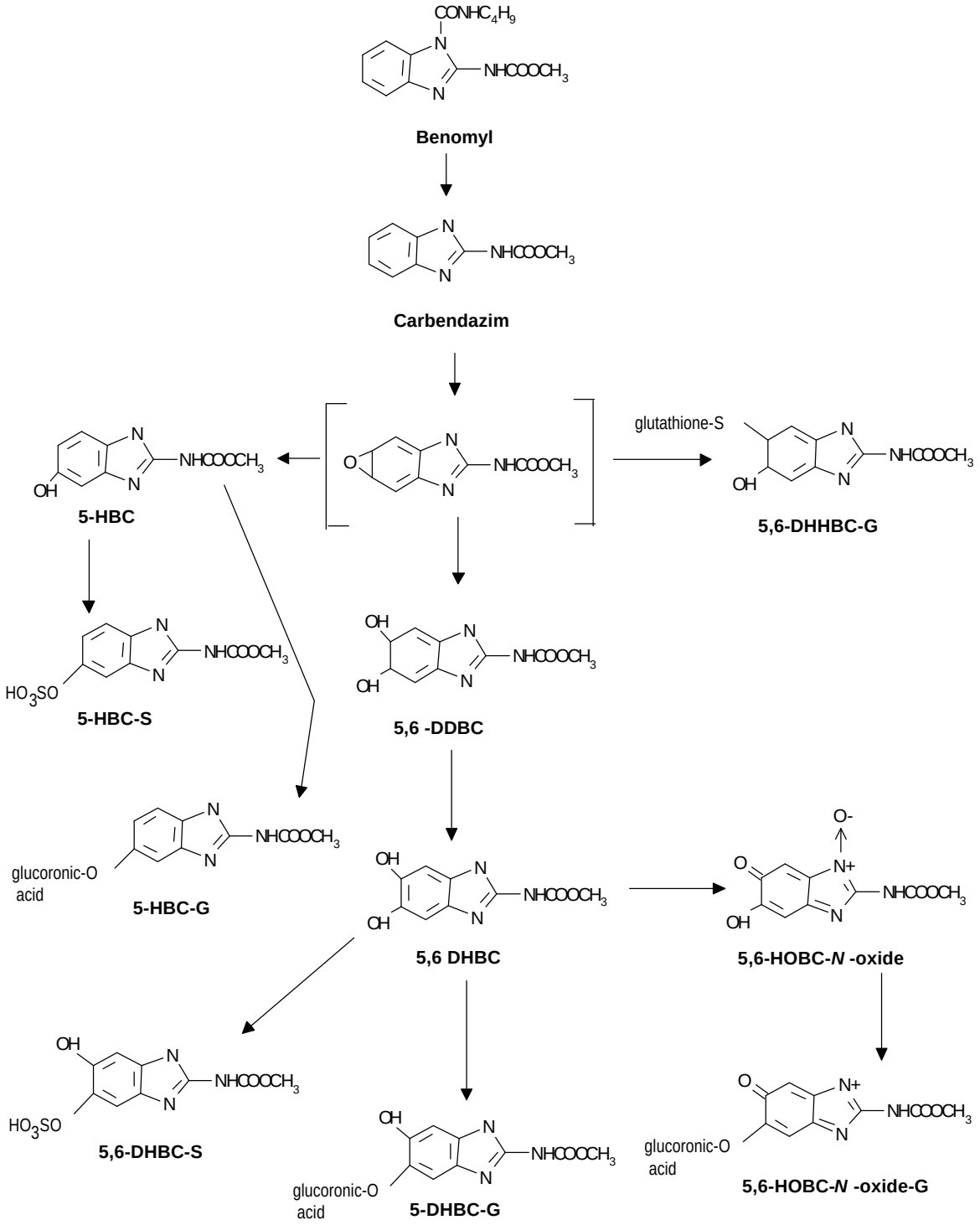


Figure 1. Metabolic pathways of benomyl and carbendazim in rats.

Ruminants. Metabolism was studied in cows and goats dosed with either [2-^{14}C]benomyl or [2-^{14}C]carbendazim. The recovery of ^{14}C was typically >80% (Table 3). The animals were dosed for 5 consecutive days at levels higher than the predicted maximum possible level of residues in livestock feed (17 mg benomyl equivalents/kg feed). Most of the radioactivity was excreted in the urine and faeces as either [^{14}C]benomyl of [^{14}C]carbendazim, with only a small fraction of the dosed radiolabel in the tissues or milk.

The distribution of radioactive residues in the cows dosed with benomyl and carbendazim was similar, as was the distribution of benomyl-derived residues in the cows and goats, although the lactating goat excreted a higher proportion of the ^{14}C in the milk. The liver and kidneys of both cows and goats contained the highest levels of the tissues, and the fat and muscle only traces. The non-lactating goat and lactating goat had similar residues in their liver and kidneys.

Metabolites were identified by mobility, retention times, mass spectra and chemical reactions. The main extractable metabolites in the tissues of cows dosed with either [^{14}C]benomyl or [^{14}C]carbendazim were 5-HBC and 4-HBC, but a high proportion of the ^{14}C represented polar, probably bound, residues. Three previously unknown metabolites were identified: 4,5-DDBC methyl 4,5-dihydro-4,5-dihydroxybenzimidazol-2-yl)carbamate, ADDB (2-amino-4,5-dihydro-4,5-dihydroxybenzimidazole) and 4,5-DHHBC-G, a glutathione conjugate (Figure 2). In the carbendazim-dosed cows, 4,5-DDBC (<0.06 mg/kg, <25%) was found in the milk in addition to 4-HBC (0.05 mg/kg, 21%) and 5-HBC (0.11 mg/kg, 42%). 4,5-DDBC, ADDB, DHHBC-G and 4-HBC and 5-HBC occurred in urine, while 4-HBC (3%) and 5-HBC (41%), 4,5-DDBC and DHHBC-G were the major residues in the kidneys. In the liver, 4,5-DHHBC-G and other sulfur-bound dihydrohydroxy-carbendazim conjugates (15.2%) predominated, with smaller amounts of 4,5-DDBC, ADDB (0.8%) and 5-HBC (2.7%). The metabolites seen in benomyl-treated cows were similar, indicating the loss of the butylcarbamoyl group before further metabolism occurs.

Table 3. Distribution of the administered dose (percentage of dose or mg test substance/kg) in cows and goats.

Sample	Lactating cow[a]		Goat[b]	
			Lactating	Non-Lactating
	50 mg/kg [^{14}C]benomyl	50 mg/kg [^{14}C]carbendazim	36 mg/kg [^{14}C]benomyl	88 mg/kg [^{14}C]benomyl
Urine	57.14 %	65.05 %	58.37 %	84.97 %
Faeces	27.94 %	20.88 %	24.44 %	14.57 %
Milk	0.37 %	0.42 %	2.20 %	ND
	0.20[c] mg/kg	0.26[c] mg/kg	1.38[c] mg/kg	ND
Muscle	0.02 mg/kg	0.01 mg/kg	<0.01 mg/kg	<0.01 mg/kg
Fat	0.03[c] mg/kg	0.04[c] mg/kg	<0.01 mg/kg	<0.01 mg/kg
Liver	4.12 mg/kg	2.62 mg/kg	3.8 mg/kg	3.6 mg/kg
Kidney	0.25 mg/kg	0.45 mg/kg	0.09 mg/kg	0.17 mg/kg

[a] Monson, 1985a,b
[b] Han, 1977, 1988
[c] Average value
ND = Not determined

Simple organic extraction removed 4- and 5-HBC from the liver and kidneys, but left a significant amount of unextractable residue. Characterization of this required reductive cleavage of the bound residues with Raney nickel and subsequent identification of the products carbendazim and 5-HBC. This led to the hypothesis that the bound residues in liver and kidney were sulfhydryl derivatives of an epoxide intermediate.

In the goats 5-HBC was the principal identified residue in milk, excreta and tissues, with lesser amounts of 4-HBC. There was also evidence that some of the benomyl-derived residues had been incorporated into the natural products casein, whey, lactose, glycogen, general protein, fatty acids and cholesterol. The apparent incorporation into proteins agrees with the observation that some liver and kidney residues in cows could only be released through reductive cleavage. The hypothesised residue in this case would be a cysteine adduct similar to DHBC-G which was incorporated into protein. A high proportion of the residue in the goats was identified as 5-HBC, following hydrolytic extraction under extreme conditions using trifluoroacetic anhydride. Since 5-HBC can be formed from the cow metabolites such as 4,5-DDBC by dehydration under acidic conditions the apparent absence of DDBC, ADDB and DHBC-G in goats is likely to be an artefact of the extraction procedure.

In another study, 4 groups of 2 dairy cows were treated with 0, 2, 10 or 50 mg/kg benomyl for 32 days. One cow of each treatment group was slaughtered at the end of the treatment period and the other one week after the withdrawal of benomyl. Samples of milk, urine and faeces were collected throughout the treatment period. Benomyl was found to be metabolized mainly to 5-HBC, which was conjugated and excreted in the urine (up to 40%). No residues of carbendazim or its metabolites could be detected in the meat at any dose level. In milk 0.1 mg/kg of 5-HBC was detected from the 10 mg/kg dose and 0.1 mg/kg of 4-HBC and 5-HBC from the 50 mg/kg dose. Levels of the metabolites in the milk became constant within 24 hours. No residues could be detected 48 hours after the last treatment. (Gardiner *et al*., 1974).

In a study by Johnson (1988) twelve non-lactating goats were given single capsules containing [^{14}C]carbendazim daily for up to 30 days. The equivalent rates in the diet were in the range 50-101 ppm, depending on feed consumption. Two goats were slaughtered on days 8, 15, 22, 29 and 36 and one goat on days 43 and 50.

^{14}C was determined in serial blood samples collected one hour before dosing on days 1 to 30. Residues were below the limits of detection in these samples and in skeletal muscle. The terminal half-life for the elimination of ^{14}C from the blood was 10.2 hours, as calculated from a pharamacokinetic experiment with one goat on day 21. A plateau residue level was reached in the liver within two weeks with a mean value of 9.48 mg/kg and accounted for less than 1% of the total administered dose. When dosing was discontinued after 30 days, the residue level in the liver decreased with a half-life of about 1.3 weeks (Table 4).

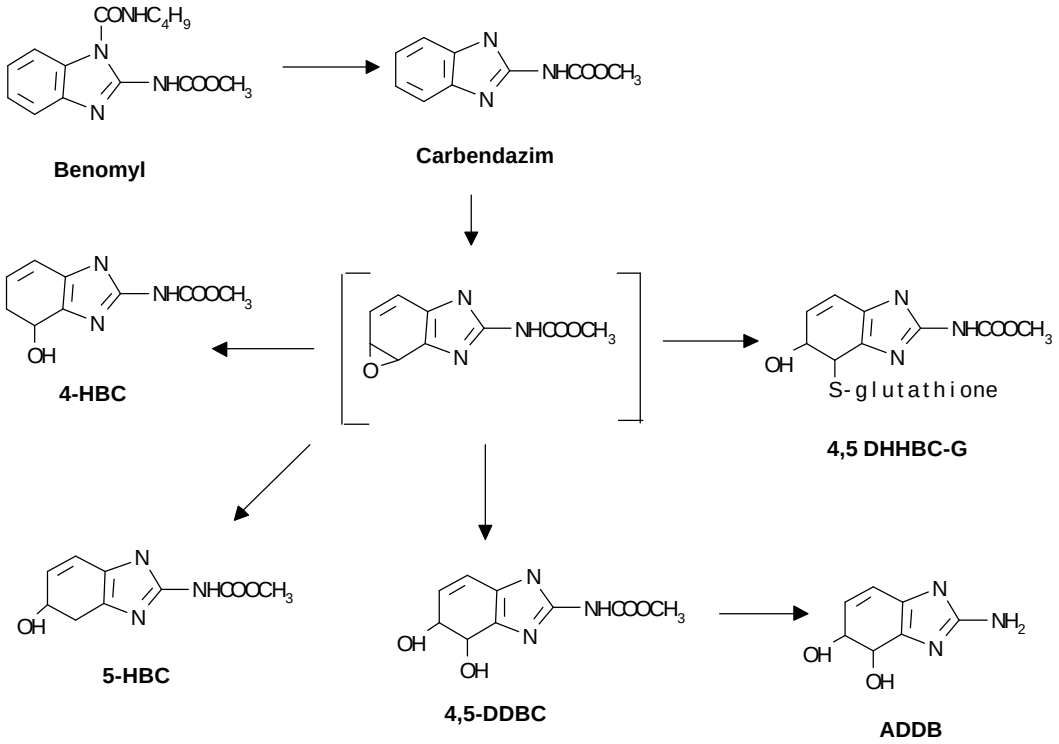
Table 4. ^{14}C in livers of goats dosed daily with radiolabelled carbendazim for 30 days, expressed as carbendazim.

Day	^{14}C, mg/kg	Total ^{14}C, mg	Total ^{14}C administered, mg	% of total dose
8	6.77	4.17	522.69	0.80
15	9.79	7.02	1052.38	0.67
22	13.44	7.08	1542.85	0.46
29	9.74	6.49	2007.42	0.32
36	5.37	3.74	2150.48	0.17
43	3.55	2.00	2150.48	0.09
50	1.67	1.05	2150.48	0.05

Residues were characterized in the pooled livers from the goats killed on day 29. Approximately 40.4%, 49.1% and 11.4% of the ^{14}C was in the ethyl acetate, aqueous and unextractable fractions respectively. The major labelled compound found upon TLC and HPLC analysis of the ethyl acetate fraction was 5-HBC (2.3 mg/kg as carbendazim, 64.1% of the total radioactive residues (TRR) in the fraction), while carbendazim amounted to 0.19 mg/kg (5.3% of the TRR). In addition three unidentified metabolites accounted for about 30% of the TRR in the ethyl acetate fraction. When lyophilised liver from a goat dosed with benomyl at the equivalent of 500 ppm was fed to rats, less than half of the residue consumed was excreted in the urine, mainly as the glucuronide conjugate of 5-HBC (Hardesty, 1983).

The metabolism of benomyl in ruminants is best defined by the results from the cow metabolism studies of Monson. Benomyl initially lost the butylcarbamoyl group to yield carbendazim, which was then oxidised to a postulated epoxide intermediate, which in turn would be further metabolized to the observed 4-HBC, 5-HBC, 4,5-DDBC, ADDB and DHHBC-G. The postulated metabolic pathways for benomyl and carbendazim in ruminants is shown in Figure 2.

Figure 2. Postulated metabolic pathways for benomyl and carbendazim in ruminants



Poultry. In two studies (Monson, 1986a,b) laying hens were dosed orally by capsule with [2-^{14}C]carbendazim, [2-^{14}C]benomyl or [U-*phenyl*-^{14}C]benomyl at doses equivalent to 5-120 ppm of the test substance in the feed. These dose levels were all in excess of the maximum anticipated dietary exposure of laying hens (5 mg benomyl equivalents/kg feed). The birds dosed with carbendazim received 6 daily doses, while those dosed with benomyl received 3 daily doses. Faeces and eggs were collected at each dosing and the hens were killed after the last dose. Essentially all the dosed radiolabel was excreted and only traces remained in the tissues, where levels generally increased with an increase in the dose (Table 5). The level of radiolabel in the tissues and eggs of benomyl-dosed birds was essentially the same for the two labels. The liver and kidneys contained the highest residues in all the birds, irrespective of the test substance and label position. Residues in the eggs increased during the course of dosing.

Table 5. Distribution of administered ^{14}C as mg test substance/kg tissue, or % of dose in laying hens dosed with [^{14}C]carbendazim.

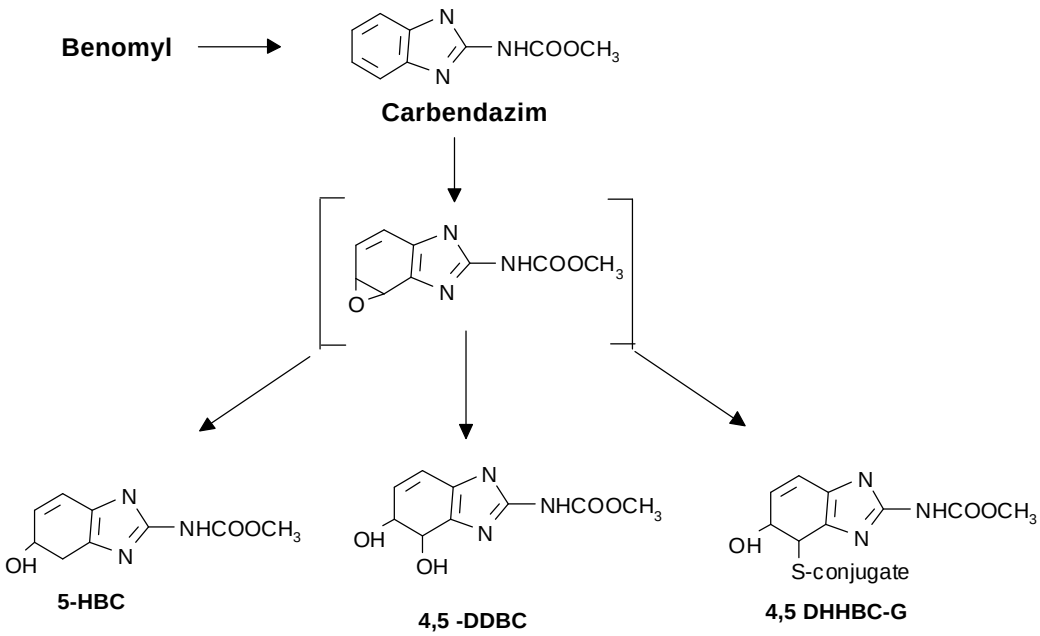
Sample	Carbendazim		Benomyl	
	5 mg/kg feed	120 mg/kg feed	27 mg/kg feed	29 mg/kg feed
	[2-^{14}C]	[2-^{14}C]	[2-^{14}C]	[U-*phenyl*-^{14}C]
Muscle	<0.01	0.06	0.02	0.01
Fat	<0.01	0.03	0.05	0.02
Liver	0.16	2.63	0.54	0.41
Kidney	0.08	1.74	0.28	0.16
Eggs	0.03	0.63	0.08	0.05
Excreta, % of dose	95	92	107	95

Carbendazim was extensively metabolized (no unchanged fungicide in the faeces after six days) to 5-HBC, 4,5-DDBC and the postulated glutathione conjugate 4,5 DHHBC-G (in tissues only). Approximately 73% of the radioactivity in day 6 eggs was identified as 5-HBC (0.26 mg/kg) and unchanged carbendazim (0.15 mg/kg). Most of the liver radioactivity was in polar and bound residues, tentatively identified as dihydro(di)-hydroxy-carbendazim sulfide conjugates. These sulfide conjugates were identified by their dehydration products after treatment with Raney nickel and hydrolysis with phosphoric acid. The metabolism of benomyl was similar. The residues in day 3 eggs from both labels contained 5-HBC (0.03 mg/kg) and carbendazim (<0.01 mg/kg)

These results confirmed those from an earlier study in which three groups of eight white leghorn hens were treated with 0, 5, or 25 ppm benomyl in the feed for 4 weeks (Gardiner *et al*., 1974). Four hens of each group were killed at the end of the treatment period and the remaining four animals one week later. Samples of eggs and faeces were analysed throughout the treatment period. Benomyl was found to be metabolized mainly to 5-HBC, which was conjugated and excreted in the faeces and urine. No residues of benomyl or its degradation products were present in muscle or fat at either dose level. 5-HBC was present in eggs collected at 7, 14 and 28 days in the 25 ppm group, at 0.03-0.06 mg/kg.

The nature of the identified residues suggested that in poultry, benomyl was metabolized to carbendazim, which in turn was converted to a postulated epoxide intermediate. Further metabolism of the intermediate was then by epoxide reductase to form 5-HBC, hydrolysis by epoxide hydrolase to 4,5-DDBC, or sulfide conjugation. A postulated metabolic pathway for benomyl in poultry is shown in Figure 3.

Figure 3. Postulated metabolic pathway for benomyl in poultry



Plant metabolism

In a study to test the stability of [2-^{14}C]benomyl when sprayed on crops in aqueous suspension, Baude *et al*. (1973) found that benomyl itself accounted for 48, 60, 77, 53 and 62% of the composite residue of benomyl plus carbendazim on the leaves of apple, cucumber, banana, orange and grape plants respectively, 21-23 days after treatment. The total ^{14}C residue on the treated cucumber and banana leaves decreased to about 10-35% of the original amount applied. To determine the amount of applied benomyl remaining, the plant tissue samples were refluxed under caustic conditions to convert benomyl to the stable derivative *N*-(benzimidazol-2-yl)-*N'*-butylurea (BUB); carbendazim under these conditions is converted to 2-aminobenzimidazole (2-AB). Since this harsh treatment could potentially destroy some base-sensitive metabolites, separate samples were usually extracted with organic solvents such as ethyl acetate or methanol.

The metabolism of [U-*phenyl*-^{14}C]benomyl in Williams 82 variety soya beans was determined following foliar application of a WP formulation (Bolton *et al*., 1986). The plants were treated twice, 14 days apart, with 1.1 kg ai/ha (twice the maximum label rate) at the early pod stage of growth. Mature plants were harvested 35 days after the second application. The total radioactivity was equivalent to 22, 8 and 0.7 mg/kg as benomyl after the first and second applications and at harvest respectively. The main residues in mature beans were 2-AB (0.42 mg/kg), benomyl (0.05 mg/kg) and carbendazim (0.14 mg/kg). Unextractable residues accounted for 13% of the total radioactivity.

In a metabolism study of [U-*phenyl*-^{14}C]benomyl in New Bonnet Semi-Dwarf paddy rice with 2 applications of 2.2 kg ai/ha, twice the label rate (Bolton *et al.*, 1986b), the concentrations of total radioactivity in the treated plants decreased by 43% between the first and second applications. At harvest after 21 days, the benomyl levels were 2.7 and 8.1 mg/kg and carbendazim levels 7.3 and 21.7 mg/kg in the rice grain and straw respectively. Minor metabolites, tentatively identified as 2-AB, benzimidazole, *o*-aminobenzonitrile, and aniline and/or *o*-phenylenediamine, accounted for about 4.0 mg/kg. In another study under similar conditions (McEuen and Stringer, 1993), carbendazim was 66% of the total radioactive residue after 30 days, at levels of 7.1 and 41 mg/kg in the grain and straw respectively. The residue in the hulls was 100 times that in the kernels. No benomyl was detected.

In a metabolism study by Baude (unknown date) [2-^{14}C]benomyl was applied to the basal sections of apple, orange and cucumber leaves on young seedlings, with the upper portions of the leaves protected. Each group of treated plants was connected to a metabolism system equipped with gas traps. During a seven-day test period, no ^{14}C was evolved from the plants, indicating that no ring degradation took place. After 7 days, only 0.6% of the applied activity had moved into the untreated, upper-leaf sections of the apple plants and the residue in the basal leaf sections consisted of 8% parent compound and 92% carbendazim. After 13 days, 0.1% of the applied radioactivity had moved into the untreated orange leaves and 0.002% was found in the winged petiole of the leaves, indicating that translocation into the leaves in either a downward or upward direction occurs to a very small extent. Translocation was higher in cucumber leaves, where 9% of the applied radioactivity had moved into the upper leaf portions after 7 days. Approximately 69% of this radioactivity was identified as being from carbendazim. At the original application site, 21% of the radioactive residue was the parent compound and 79% was carbendazim.

In a second experiment with cucumbers [2-^{14}C]benomyl was applied to the stems of young seedlings and the plants were analysed eleven days later. Approximately 35% of the applied radioactivity moved up into the cotyledon and true leaves, of which 45% was from carbendazim and 8% was tentatively identified by TLC as being from 2-AB. At the application site, 61% of the ^{14}C was from the parent compound and 39% from carbendazim; 64% of the total detected activity remained unextracted.

Oranges were dipped, dried and dipped again in a suspension of 2.5 kg ai/100 l of formulated [2-^{14}C]benomyl, then air-dried and exposed outdoors. Dried aliquots of the dipping suspension on glass plates were treated similarly. After 15 days, 61 and 19% of the total identified residue on the peel and the glass respectively was the parent compound. The ^{14}C in the peeled oranges (0.05 mg/kg as benomyl) was too low for identification. In a similar experiment with apples, 34 and 17% of the ^{14}C residue after 16 days on the apple surface and the glass plates respectively was the parent compound. The remainder of the activity in both cases was from carbendazim.

The metabolism of [U-*phenyl*-^{14}C]benomyl was studied in peaches after the formulated compound had been applied twice to the plants at rates of 1.4 and 1.1 kg ai/ha (Stevenson, 1985). Fruits were harvested approximately 20 minutes after each spraying. After the first application, [^{14}C]benomyl and [^{14}C]carbendazim were present at 0.65 and 0.72 mg/kg respectively. After the second application, the concentrations were 0.33 and 0.92 mg/kg. A similar experimental design was used with formulated [U-*phenyl*-^{14}C]carbendazim and fruits were harvested immediately after each spraying. Carbendazim was not metabolized under these conditions and the residue levels were 0.95 and 1.2 mg/kg after the first and second applications respectively.

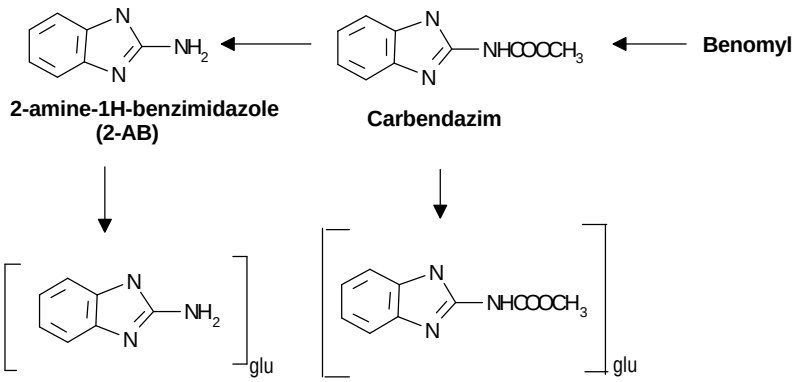
Pinto beans were germinated and grown for 13 days in soil drenched with [2-^{14}C]benomyl (Gardiner, unknown date). Carbendazim was identified as the major metabolite in leaves (48% of the radioactivity) and 2-AB accounted for 4%. When beans plants were treated with foliar applications of [2-^{14}C]carbendazim (2 x 1.1 kg ai/ha) and samples of mature beans were picked 1, 2, 3 and 4 weeks after the last treatment the total ^{14}C residues decreased from 0.06 mg/kg at the first sampling to 0.02 mg/kg after 4 weeks in the edible beans and from 4.7 to 0.2 mg/kg in the foliage. In both cases, 89-95% of the residue was free carbendazim and 1-8% was 2-AB. An additional 1-3% was found as β-glycoside conjugates of the free compounds.

[U-*phenyl*--^{14}C]benomyl was applied 3 times to sugar beet plants at 0.55 kg ai/ha, twice the recommended rate (McEuen and Stringer, 1994a). Mature plants were harvested 3 weeks after the final treatment. Carbendazim represented 41% (3.4 mg/kg) and 19% (0.05 mg/kg) of the total residue in the tops and roots respectively and 2-AB accounted for 1.9 and 0.36%. In another metabolism study with 5 applications of benomyl at the same rate (Tolle, 1988), mature sugar beets were harvested 19 weeks after planting. The main extractable radiolabelled residues in the tops were carbendazim (6.8 mg/kg, 63% of the total radioactivity), benomyl (0.40 mg/kg, 3.7%) and 2-AB (0.01 mg/kg, 0.7%). In the roots, only carbendazim (0.01 mg/kg) and 2-AB (<0.01 mg/kg, 4.4% of the total radioactivity) were detected.

Although none of the studies was designed to determine the half-life or DT_{90} of benomyl it was possible to estimate a combined half-life of benomyl/carbendazim ranging from 8 days in rice and soya beans to 23 days in cucumbers from the available data. In general, an approximate half-life of 14 days for combined benomyl/carbendazim residues on plants is appropriate.

A postulated metabolic pathway of benomyl in plants includes loss of the butylcarbamoyl group to form carbendazim. Significant loss of the methoxycarbonyl moiety to form 2-AB occurred only in soya beans. Carbohydrate conjugation with 2-AB and carbendazim was observed only in kidney beans. The postulated pathways are shown in Figure 4.

Figure 4. Metabolic pathways of benomyl and carbendazim in plants.



Residues in rotational crops

The use of benomyl or carbendazim for disease control in plants can lead to soil residues which might be taken up into succeeding crops. This is not an issue for the most benomyl or carbendazim uses, since the same crops of pome fruit, stone fruit and grapes are grown in the same area year after year. However, for crops such as tomatoes and cucurbits, uptake into succeeding crops is possible.

A crop rotation study with lettuce and radishes grown on soil containing aged residues of carbendazim was conducted in Germany (Otto, 1976). Lettuce and radishes were sown in soil treated with 3 mg/kg carbendazim and aged for 224 days. On the day of planting the soil contained residues of 0.23 mg/kg carbendazim and a total ^{14}C residue of 2 mg/kg as carbendazim. Over a period of 84 days, the plants absorbed only a negligible amount of the radioactivity present in the soil (0.02 to 0.04 mg/kg in radishes and 0.03 to 0.06 mg/kg in lettuce).

In the USA two trials were conducted with loamy sand soil in a greenhouse treated with [2-^{14}C] carbendazim at the rate of 1.1 kg ai/ha and aged for 30 days or with 3.4 kg ai/ha and aged for 120 or 145 days. The soils were then planted with beet, cabbage and barley crops (Rhodes, 1987). In the first study, at the final harvest of the mature crop cabbage plants had total ^{14}C residues of about 0.03 mg/kg carbendazim equivalents, intact carbendazim representing <0.005 mg/kg. Barley straw had total ^{14}C residues of 0.05 mg/kg, with about 0.01 mg/kg intact carbendazim. Barley grain, beets and beet foliage contained total residue of <0.01 mg/kg at harvest, while levels in /barley straw and cabbage were 0.053 and 0.026 mg/kg respectively. Concentrations of carbendazim in the soil decreased from 0.69 mg/kg at treatment to 0.15 mg/kg at planting. Intact carbendazim constituted 25-51% of the ^{14}C residues in the soils at final harvest. In the second study beets, beet foliage, cabbage, barley grain and barley straw at final harvest contained total residues of 0.012, 0.013, 0.053, 0.025 and 0.129 mg/kg respectively. The carbendazim concentration was about 0.03 mg/kg in cabbage and 0.005 mg/kg in barley straw. Accumulation factors, calculated as the ratio of radiolabel in the crop to that in the corresponding soil, were 0.04 in beet foliage, 0.03 in beet roots, 0.2 in cabbage and barley grain and 0.9 to 1.2 in barley straw.

Snap beans, sweet corn, carrots and tomatoes were planted in soil which had been treated with [2-^{14}C]benomyl at a rate of 2.2 kg/ha about one year before planting (Rhodes, unknown date). No detectable levels of ^{14}C (<0.01 mg/kg as benomyl) were found in the edible portions. The soil itself contained 0.9 mg/kg total residue at harvest. Leaves and stems from the plants showed trace residues (<0.1 mg/kg benomyl equivalents). Despite its full fibrous root system, rye as the cover crop did not pick

up detectable residues from the soil. Soil residues were consistently lower in the crop areas than in the bare soil areas. They remained essentially confined to the top 10 cm of soil.

Plants were grown in soil treated with unlabelled carbendazim and 2-AB. Alfalfa contained 0.05 and 0.08 mg/kg of carbendazim and 2-AB respectively at the first cutting, but no detectable residues of either compound at the second and third cuttings. Ryegrass contained 0.08-0.48 mg/kg of carbendazim but no detectable 2-AB (<0.05 mg/kg) in six cuttings. Mature soya bean plants contained 0.59 mg/kg of carbendazim and no detectable 2-AB (<0.1 mg/kg). Total ^{14}C residues in crops grown in soil treated with an 80:20 mixture of labelled carbendazim and 2-AB were 0.13-0.30 mg/kg in alfalfa, 0.09-0.19 mg/kg in ryegrass and 0.32-0.53 mg/kg in mature soya bean plants (Rhodes *et al.*, unknown date).

Environmental fate in soil

Degradation

Three mg/kg of [^{14}C]carbendazim was added to a sandy soil (2.6% organic matter) and incubated at 40% maximum field capacity and 22 ± 2°C for 224 days in the dark (Otto, 1976). Radioactivity in the soil decreased with incubation time owing to the formation of volatile mineralization products (36% of the applied activity). At the end of the experiment only 8% of the radioactivity in the soil was identified as being from carbendazim. Unextractable residues steadily increased to 57% of the initially applied radioactivity. In another study under the same conditions, carbendazim accounted for 6.3 and 5.3% of the applied radioactivity in sand (2.6% organic carbon, C_{org}) and loamy sand (1.0% C_{org}) respectively after 380 days (Otto, 1975).

In a third study [2-^{14}C]carbendazim was applied at concentrations of 10, 20 and 100 mg/kg to sterile and non-sterile sandy loam soil samples and incubated for 250-270 days at 45% maximum water holding capacity and 25°C (Helweg, 1977). A separate sample was pre-treated with 2100 mg/kg of unlabelled carbendazim 6 months before the addition of 20 mg [^{14}C]carbendazim/kg (Table 6). A higher proportion of the applied radioactivity was recovered as carbendazim in the 10 mg/kg samples under sterile than non-sterile conditions, while degradation to CO_2 was higher under non-sterile conditions. From 30 to 40% of the radioactivity could be recovered as $^{14}CO_2$ from soils treated with 10 or 20 mg/kg, but after treatment at 100 mg/kg the recovery was only 9%, comparable to that from pre-treated soil. 2-AB was found in non-sterile and sterile soil samples at the equivalent of 4 to 8% of the total applied radioactivity.

Table 6. Degradation of [^{14}C]carbendazim in loamy sand soil, % of applied dose.

Test system	Dose, mg/kg	Carbendazim	2-AB	CO_2
non-sterile	10	5-13	4-8	30-40
	20	30	NR	30
	100	70	NR	9
	20 + 2100 ^{12}C	70	NR	7
sterile	10	50-70	4-8	10

NR = not reported

When ^{14}C-labelled 2-AB was incubated with loamy sand soil there was a lag-phase of 1 to 2 weeks. After 112 days, 32 to 61% of the radiolabel was converted to $^{14}CO_2$ whereas only 6 to 22% WAS recovered as unchanged 2-AB (Helweg, 1977).

Degradation studies with [U-*phenyl*-^{14}C]benomyl, [2-^{14}C]benomyl or [2-^{14}C]carbendazim, in soil under aerobic or anaerobic conditions were conducted in the USA (Marsh and Arthur, 1989; Han, unknown date) and are summarized in Table 7. In all the studies, carbendazim was the main component of the residue, followed by STB or BUB. There was detectable but slow further conversion to 2-AB.

No formation of CO_2 (<0.1%) from benomyl was observed in sterilized aerobic soil or under strictly anaerobic conditions, but the production of carbendazim was similar in sterile and non-sterile soil. The further degradation of carbendazim was more rapid in non-sterile soil. Unextractable radiolabelled material accounted for a significant proportion of the radiolabel applied to the soil, ranging from 20 to 36.2%. Most of the unextractable ^{14}C was recovered in the insoluble humin fraction.

Table 7. Components of ^{14}C residues in soil incubated with ^{14}C-labelled benomyl or carbendazim.

Soil Compounds applied	pH	Carbendazim	^{14}C, % of applied			
			STB/BUB	2-AB	Unextracted	CO_2
Keyport silt loam soil benomyl – aerobic[1]	6.5					
non-sterile		34.3	1.2	nd	35.6	9.2
sterile		57.6	2.1	nd	26.0	<0.1
Fallsington sandy loam soil[2] benomyl	6.5	41	Nd	1.2	21	NR
carbendazim		54	Nd	0.8	20	
Keyport silt loam soil[2] benomyl	6.4	47	Nd	0.8	20	NR
carbendazim		49	Nd	1.5	28	

[1]1 year incubation (Marsh and Arthur, 1989
[2]Six month anaerobic incubation after 1 month aerobic ageing (Han, unknown date)
NR= not reported; nd = not detected

In another study with [^{14}C]benomyl incubated for 6 weeks in a greenhouse with two limed soils at pH 8.2 and 6.9, the residues of STB or BUB were 5 and <1% of the applied benomyl respectively (Morales, unknown date). No 2-AB was detected in a field soil dissipation study with benomyl in Illinois (Otto and Pease, 1972). In soils treated with 5.6 kg/ha of [2-^{14}C]benomyl in Delaware, North Carolina and Florida, 65-100% of the activity was identified as carbendazim and 0-35% as 2-AB after one year of exposure (Baude, unknown date).

The half-life of carbendazim in loamy and sand soils was determined to be approximately 40 days under aerobic incubation conditions in the laboratory. The DT_{90} was in the range of 85 to 240 days for sand soil and 120 to 240 days for loamy sand soil (Otto, 1975). A further study determined the rate of degradation of carbendazim (2.7 mg/kg) in a sand soil (2.7% organic carbon) at 40% maximum water holding capacity during 28 days. Carbendazim was rapidly degraded with computed half-lives of 21, 25

and 28 days at 25, 20 and 15°C respectively, indicating more rapid degradation substance with increasing temperature.

In 4 field trials with silty sand, loam, clay loam and loamy sand, formulated carbendazim was sprayed at concentrations of 0.482 and 0.540 kg ai/ha. The field plots were regularly sampled until 368 to 381 days after treatment (Krebs and Baedelt, 1990a-d). Half-lives were computed to be 32 days in sandy loam, 9 days in loam, 8 days in clay loam and 22 days in loamy sand. The DT_{90} values were 357, 250, 83 and 244 days respectively.

About 9-12 months were required for the disappearance of 50% of the total residues from bare soil after direct benomyl treatment in Delaware and North Carolina, and less than 6 months in Florida (Pease *et al*., unknown date). However in two other studies in Delaware and Illinois, using Fallsington sandy loam and Flanagan silt loam soil, the half-life of benomyl was estimated to be from 15 to 30 days.

Under laboratory non-sterile aerobic conditions, benomyl was degraded rapidly in soil to carbendazim, with a half-life of 19 hours (Marsh and Arthur, 1989) or 2 hours (Arthur *et al*., 1989a,b). The half-life of the carbendazim produced was estimated to be 320 and 1000 days under non-sterile and sterile conditions respectively (Marsh and Arthur, 1989). Under laboratory anaerobic conditions the half-life of formed carbendazim was 743 days in a pond sediment. In a field soil dissipation study using formulated benomyl and carbendazim in California (McNally, 1990), the half life of benomyl after degradation to carbendazim was determined to be 83 days.

Additional soil degradation studies with radiolabelled benomyl were conducted in North Carolina, Delaware and Florida (Baude, unknown date). The total radioactive residues fell to 61-78% of the applied radiolabel after six months, 49-57% after 12 months, and in Florida 27% after 24 months. The half-life for total ^{14}C residues was about one year at all three sites.

A photodegradation study of [U-*phenyl*-^{14}C]benomyl was conducted in Keyport silt loam soil. Twenty four treated samples (1.1 kg ai/ha) were exposed to summer sunlight or shielded from light for 48 hours. The degradation of benomyl was equal in the irradiated and control samples, with half-lives of 5.2 and 5.7 hours respectively. Carbendazim was the major degradation product, accounting for 92.2 and 93.4% of the applied radioactivity in the irradiated and control soil respectively, while 2-AB accounted for 2.6 and 2.1% (Monson and Hoffman, 1990). In another photodegradation study conducted for 32 days (Hoffman, 1985) the half life for the conversion of benomyl to carbendazim was estimated to be 3 days and was not significantly affected by photolysis. CO_2 accounted for 3.3% of the applied radioactivity.

Carbendazim concentrations in the 0 to 5 cm soil layers were estimated by assuming a maximum number of treatments at the highest rates to field crops (e.g. strawberries), vines and orchards (pome and stone fruits). Initial PEC values (time-weighted average concentrations) resulting from single applications are listed in Table 8. The bulk density of the soil was stated to be 1.5 g/cm^3. Residues were estimated for 50 and 10% deposition although the figures for 10% of deposition are the more relevant as carbendazim is sprayed at later growth stages of the crops when leaves are fully developed and cover the soil. The estimates of maximum carbendazim residues were based on a first-order decline and a half-life of 32 days, obtained in the field dissipation studies. Estimates of time-weighted concentrations were based on the estimated maximum carbendazim residue using the following formula.

$$PEC_i = [(PEC_{max}\, DT_{50})/t_i \ln 2](1-e^{\{-t_i \ln 2/DT_{50}\}})$$

where PEC_i = average concentration at time t_i; PEC_{max} = maximum concentration, DT_{50} = half-life.

Table 8. Estimated initial concentrations of carbendazim in the 0-5 cm soil layer at different single application rates.

Application rate (g/ha)	Initial concentration mg/kg	
	50% deposition	10% deposition
150	0.100	0.020
180	0.120	0.024
280	0.187	0.037
300	0.200	0.040
420	0.280	0.056
450	0.300	0.060
560	0.373	0.075
600	0.400	0.080

Adsorption/desorption

The adsorption of carbendazim was determined in three standard soils. Concentrations of the active substance in the aqueous phase were measured 16 hours after fortification with 0.24, 0.48, 1.21 and 2.42 mg carbendazim/l. The adsorption coefficients of carbendazim, calculated from the Freundlich adsorption isotherm, were found to be in the range of 1.6 to 6.3, corresponding to K_{oc} values between 200 and 246 (Goerlitz and Kloeckner, 1986). Slopes of the logarithmic Freundlich adsorption isotherm (b) were 0.87 to 1.12 (Table 9). Desorption coefficients were greater than adsorption coefficients and were in the range 9 to 51.

Table 9. Soil/water adsorption coefficients for carbendazim in three different soils.

Soil	$C_{org.}$ (%)	K	a	b	K_{oc}
Sand	0.80	1.6 ±0.3	1.9	0.87	200 ±40
Sand	2.58	6.3 ±0.9	5.6	1.12	246 ±35
Sandy loam	1.00	2.3 ±0.2	2.5	0.91	230 ±20

Mobility

The mobility of carbendazim in sandy and sandy loam soil was determined with a commercial preparation of [^{14}C]carbendazim. The results from column and container leaching studies with unaged and aged carbendazim are shown in Table 10.

Table 10. Mobility of carbendazim in column and container leaching studies.

Test design	Applied concentration, kg ai/ha	Sampling interval, days	% of applied ^{14}C in leachate		Study no./ref
Column leaching, 200 mm simulated precipitation	0.8 SC	2	< 2		1/Gildemeister and Jordan (1981)
Column leaching, 200 mm simulated precipitation	0.525 WP	2	<0.15		2/Spitzer and Buerkle (1990)
Container leaching, 38.1, 25.4 and 25.4 mm precipitation on days 1, 3 and 7 after application	11.3 WP		run-off water	leaching water	3/Rhodes and Long (1994)
		1	0.05	< 0.01	
		3	0.39	< 0.01	
		7	0.24	0.19	
Container leaching, 38.1, 25.4 and 25.4 mm precipitation on days 1, 3 and 7 after application	22.4 WP	1	< 0.1	< 0.1	4/Rhodes and Long (1974)
		3	0.39	< 0.1	
		7	0.24	0.19	

In the first experiment, all percolates contained <8.1 µg/l of carbendazim and the potential degradation product 2-AB, corresponding to <2% of the applied dose. In the second experiment, using the same arrangement, the leachate accounted for <0.15% of the applied radioactivity.

In the container studies with 11.3 or 22.4 kg ai/ha the soil was irrigated with 38.1 or 25.4 mm of water 1-7 days after the application. Following the first precipitation (one day after the treatment) 0.05% in study 3 and <0.1% in study 4 of the applied ^{14}C was measured in the run-off water. The percolates contained less than 0.01% and 0.1% of the applied dose respectively. In study 4, further investigations were made to determine the R_f values of carbendazim and 2-AB on soil thin-layer chromatographic plates. The soils used for this experiment were a muck (41.8% $C_{org.}$), two silt loams (1.1 and 3% $C_{org.}$) and a loamy sand (0.35% $C_{org.}$). The R_f values showed that according to the EPA mobility classification carbendazim is a class 1 substance (immobile, R_f 0.0-0.09) and 2-AB belongs to class 2 (low mobility, R_f 0.10-0.34).

In the container leaching experiments (studies 3 and 4) the run-off and leaching of aged residues (3 and 7 days after application) were determined. At both applied concentrations, the run-off water contained 0.39% of the original amount after 3 days and 0.24% after 7 days of ageing. In the percolate, less than 0.01 and 0.1% was found on day 3 and only 0.19% on day 7.

Benomyl was well adsorbed to two sandy loam soils (K_a = 6.1 and 13 µg/kg) and strongly adsorbed to two silt loam soils (K_a = 50 and 90 µg/kg), at a pH ranging from 5.2 to 6.6 (Priester, 1985). The adsorption was not correlated with the organic content of the soil (1.1-4.7%) and was not affected by the benomyl concentration (0.2-2.3 µg/kg). Desorption occurred very slowly, with K_d = 2.4-2.5 µg/kg. Aharonson and Kafkafi (1975), studying benzimidazole fungicides on kaolinite clay, suggested that adsorption of the compounds occurs on mineral clay surfaces through a cationic mechanism.

Benomyl was immobile when measured by soil thin-layer chromatography (Priester, 1985). In a greenhouse run-off experiment where benomyl was applied to turf at 2.2-22 kg ai/ha and then held at an angle with artificial rainfall applied, benomyl and/or its degradation products carbendazim and 2-AB were highly immobile (<0.1% of the applied ^{14}C detected in the run-off water). In soil, 0.1 to 0.7% of the applied radioactivity was detected in the run-off water. The compounds did not move significantly from the site of application (Rhodes and Long, 1974). The mobility of [U-*phenyl*-^{14}C]benomyl was studied in 4 sandy and silt loam soils (Chang, 1985). Benomyl and its major product carbendazim were highly retained in all the soils, being more tightly bound to silt loam. Less than 1% of the applied radioactivity was eluted from the soil column and most of the radioactivity remained in the upper 0-5 cm section.

In a study to investigate the soil leaching potential of benomyl in water-saturated silty clay loam soils with low organic matter content, typical for rice culture in the USA, 94% of the applied radioactivity was found in the 0-5cm soil segment. About 9% was found at 5-10 cm (Ryan, 1989).

Environmental fate in water and water/sediment systems

Water

Table 11 indicates the rates and routes of the hydrolytic, photochemical and biological degradation of carbendazim in aquatic systems.

The hydrolytic degradation of carbendazim was determined in two studies at pH 5.0, 7.0 and 9.0 in the dark under sterile (Goerlitz *et al*., 1982; Priester, 1984) and non-sterile conditions (Purser, 1987). Under sterile conditions, carbendazim was found to be stable at pH 5 and 7, while significant degradation was observed after 9 days at pH 9. Similar results were found with the degradation of 7.0 and 0.7 mg/l [^{14}C]carbendazim at 25°C during 30 days incubation. The proportion of 2-AB never exceeded 3% at pH 5 and 7, but at pH 9 approximately 30% of the carbendazim had hydrolysed to 2-AB. The half-lives at pH 9 were calculated to be 58 days at 7 mg/l and 50 days at 0.7 mg/l. The rates of degradation were 0.011 and 0.014/day respectively; independent of concentration within experimental error.

A third study was at 22°C, 50°C and 70°C with concentrations of 8 mg/l at pH 5 and 4 mg/l at pH 7 and pH 9, incubated up to 30 days under non-sterile conditions (Purser, 1987). At the environmentally relevant temperature of 22°C, significant degradation of carbendazim was observed only at pH 9. The corresponding half-life was calculated to be 22 days. The half-life of carbendazim in pH 5 acetate buffer at 22°C, 50°C and 70°C was 457, 108 and 29 days, in pH 7 phosphate buffer at 50°C and 70°C 43 and 12 days, and in pH 9 borate buffer at 22°C, 50°C and 70°C 22, 1.4 and 0.3 days.

The hydrolysis of [U-*phenyl*-^{14}C]benomyl was determined in sterilized aqueous solutions maintained at 25°C in the dark and buffered at pH 5, 7 and 9 (Wheeler, 1985). The half-lives were approximately 3.5 hours, 1.5 hours and less than 1 hour respectively. Benomyl was hydrolyzed primarily to carbendazim at pH 5, while at pH 9 STB was the primary transformation product. At pH 7 the ratio of carbendazim to STB was approximately 3:1. Once formed, STB was stable at pH 7 and 9 but appeared to be degraded at pH 5.

Tests designed to determine the stability of benomyl under simulated spray tank conditions indicated that benomyl in suspension can be transformed to STB (Baude, unknown date). At 23°C STB was detected after 6 hours at pH 9 and after 25 hours under neutral conditions. At 50°C detectable levels of STB appeared at the first sampling, with 44 and 55% conversion to STB at pH 7.3 and pH 9.0 respectively after 49 hours and detectable levels of BUB. After 4 hours at room temperature, there was <1% conversion to BUB at pH 7.3 and only 1% conversion to BUB at pH 9.0. No 2-AB was formed under any of these conditions.

Table 11. Degradation of carbendazim in aquatic systems.

Initial concentration	Duration, days	Conditions	Half-life, days	Products at termination (% of applied concentration)	Ref.
Hydrolytic degradation					
2.16 mg/l	9	pH 5, 22°C[)] pH 7, 22°C[)] pH 9, 22°C	>350 >350 124	NR	Goerlitz *et al*. (1982)
7.0/0.7 mg/l	30	pH 5, 25°C pH 7, 25°C pH 9, 25°C	NR NR 50-58	< 3% 2-AB < 3% 2-AB 30% 2-AB < 6% others	Priester (1984)
8 mg/l (pH 5) 4 mg/l (pH 7 and 9)	30	pH 5, 22°C pH 5, 50°C pH 5, 70°C pH 7, 22°C pH 7, 50°C pH 7, 70°C pH 9, 22°C pH 9, 50°C pH 9, 70°C	457 108 29 NR 43 12 22 1.4 0.3	NR	Purser (1987)
Photochemical degradation					
4.75 mg/l	166 h, = 35 days natural sunlight	pH 5, 25°C	>35	0.1-1.4% organic volatiles	Schwab (1992)
Biological degradation					
27.0 mg/l	21	aerobic, 20°C; oxygen uptake	>21	NR	Wellens (1984)
27.0 mg/l	0.125	aerobic, 20°C; Zahn-Wellens test	<0.125	NR	Wellens (1984)
10/20 mg/l	28	aerobic, 22°C, modified Sturm test	>28	NR	Voelkow (1990)

NR = not reported

The photodegradation of carbendazim in aqueous solution (pH 5) was determined under sterile conditions at 25°C ± 1°C. [^{14}C]carbendazim (4.75 mg /l) was added to the buffer and irradiated up to 166 hours by means of a “Sun-test” photoreactor (Schwab, 1992). The intensity of the radiation was determined with a uranyl sulfate/oxalate actinometer. The laboratory period of 166 hours corresponds to 35 days under natural conditions and is comparable to a mean daylight intensity in June in middle Europe (52° N). Only traces of radioactivity could be detected in the volatile traps (0.1 to 1.4% of the applied radioactivity) and no CO_2 was found.

The photolysis of [U-*phenyl*-^{14}C]benomyl at a concentration of 1 µg/ml was studied in sterilized solutions buffered at pH 5 (Powley, 1985). The irradiated and dark control test solutions showed similar degradation kinetics, with a half-life of 4 and 3 hours respectively. Carbendazim was the only significant degradation product, accounting for 99% of the initial radioactivity, with STB constituting the remaining 1% in both the exposed and control solutions.

The biological degradation of carbendazim was determined by two different experimental methods, OECD guidelines 301F and 302B (Zahn-Wellens test). Test vessels containing 27 mg carbendazim/l were incubated under aerobic conditions at 20°C. They contained inoculum and active substance, inoculum only, or inoculum and reference compound. The consumption of oxygen was measured continuously with a manometric respirometer for 21 days. The COD (chemical oxygen demand) for the Zahn-Wellens test was determined after 3 hours (Wellens, 1984). According to OECD Guideline 301F the oxygen uptake by the microbial population was less than 10% of the COD after 21 days incubation. The Zahn-Wellens test (OECD Guideline 302B) showed an elimination of more than 95% of the test substance within 3 hours. The rapid disappearance of the test substance from the water in the Zahn-Wellens test was mainly owing to strong adsorption to the sludge and not to biodegradation.

A further study determined the biodegradability of carbendazim under the conditions of the modified Sturm test. Duplicate vessels with inoculum and test substance (10 and 20 mg carbendazim/l), inoculum and reference compound and inoculum only were incubated under aerobic conditions at 22 ± 2°C for 28 days. The evolved CO_2 was trapped with NaOH and directly injected into a carbon analyser (Voelskow, 1990). The CO_2 evolution was less than 20% of the theoretical maximum after 28 days at both concentrations.

Water/sediment systems

The degradation of [^{14}C]carbendazim and the nature of the products were investigated in two aquatic model systems consisting of natural waters (Rhine and pond) and 2% of the corresponding sediment. The Rhine sediment was a loamy sand with a pH of 8.0 and 0.8% $C_{org.}$; the sediment from the pond was a clay loam/loam with pH 7.4 and 5.4% C_{org}. The active substance was applied at a concentration of 2.0 mg/l (Gildemeister, 1987). After 91 days, approximately 61.2 and 40.3% of the applied [^{14}C]carbendazim was mineralised to carbon dioxide in the Rhine and pond water respectively. The calculated half-lives were 31 days in the Rhine water and 22 days in the pond water. In both systems CO_2 was the only volatile compound evolved, accounting for 61.2% in the Rhine water and 40.3% in the pond water. 2-AB accounted for 10.8% of the ^{14}C after 30 days, 1.2% after 61 days and could not be detected after 91 days in the Rhine water and accounted for 2.0% after 30 days in the pond water. Additionally, two unknown compounds were detected in minor amounts. In the soils, besides the parent

compound and traces of 2-AB, three unknown products were detected in amounts ranging from 0.1% to 0.3% after 91 days.

The biodegradation of benomyl in sewage sludge from Devon, UK, was investigated for 28 days at 20 ± 2°C. No significant evidence of biodegradation was observed, indicated by an unchanged biological oxygen demand upon addition of benomyl (Mather and Roberts, 1993).

The fate of benomyl in two water/sediment systems from the South West of England was studied by Roberts and Gillings (1994). After equilibration of the system, benomyl was applied to the water surface (450 µg/l) and the systems were kept in the dark at 20°C for 100 days. The radioactivity in the aqueous phase declined with a corresponding increase in the sediment. At the end of the study, 46-57% of the radioactivity was associated with the sediment. The major compounds in both water/sediment systems were carbendazim and STB, with minor amounts of 2-AB. Carbendazim was degraded in these systems with a half-life of 84-131 days and a DT_{90} of 151-236 days.

When [^{14}C]benomyl was incubated with a pond water/sediment system in Ohio for one year at pH 7.4 (Arthur *et al.*, 1989a) 55.6% of the applied ^{14}C was accounted for by carbendazim, 7.6% by STB and BUB, and 36.2% was unextractable. 2-AB was undetectable and CO_2 <0.1%. Most of the unextractable ^{14}C in the sediment was divided roughly equally between the β-humins and insoluble humin fractions

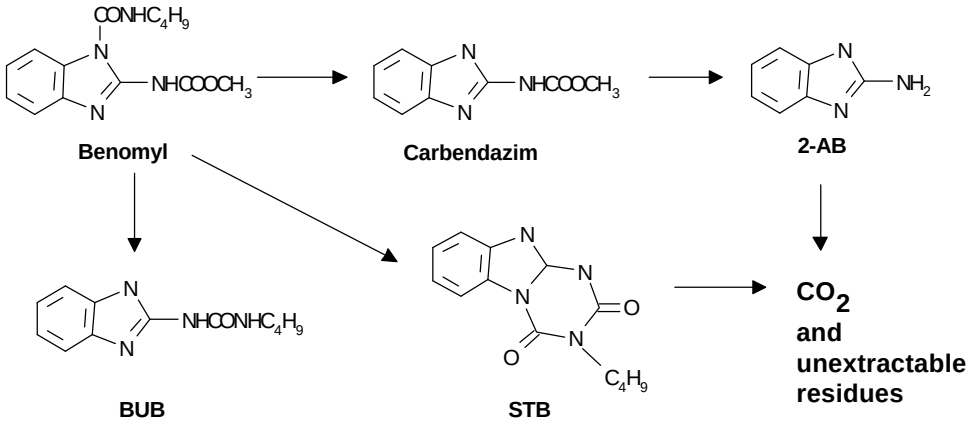
Similarly, in a Mississippi pond water/sediment study, benomyl was degraded rapidly to carbendazim and STB, and carbendazim was degraded with a half-life of 61 days in non-sterile conditions and 303 days in a sterile system (Arthur, *et al.*, 1989b). STB decreased from 29.5% of the applied radioactivity on day 0 to 21.6% on day 30 in the non-sterile system. In sterilized systems, STB decreased from 24.1% of the applied radioactivity at day 0 to 14.9% after 30 days.

Volatisation and degradation in air

The volatilisation of carbendazim from bare soil and leaves was tested under outdoor conditions. Carbendazim was applied as a suspension concentrate at a rate of 0.18 kg ai/ha to loamy sand soil and to mature bush beans (Buerstel *et al.*, 1993a,b). After 6 hours, a range from 76 to 117% of the applied compound was still in the soil and from 83-100% was found in the leaves. A model calculation according to Atkinson (1988), which took into consideration the reaction of the OH radical with nitrogen of the imidazole ring system, showed that carbendazim would be degraded rapidly in the troposphere (Gleisberg, 1991). The calculated half-life amounted to less than 0.27 days.

The postulated degradation pathways for benomyl and carbendazim in soil, under aerobic and anaerobic conditions, water and water/sediment systems is shown in Figure 5.

Figure 5. Degradation pathways of benomyl and carbendazim in the environment.



METHODS OF RESIDUE ANALYSIS

Analytical methods

The methods used for benomyl and carbendazim studies are considered together below.

Plants

In the first method used extensively for residues of benomyl in crops (Pease and Gardiner, 1969) samples were extracted with ethyl acetate, the extracts were acidified to convert any benomyl residue to carbendazim and cleaned up by liquid-liquid partition. The residue was determined by fluorimetric analysis at 335 nm, or colorimetric analyisat 445 nm after bromination. Both methods were acceptable down to 0.1 mg/kg with average recoveries of about 87%. Modifications of the fluorimetric method were introduced by Pease and Holt (1971) for analysis of citrus crops. To prevent quenching, the extracted residue was dissolved in methanolic NaOH for determination of the fluorescence. Recoveries ranged from 61 to 90%. In a method developed in France (Mestres *et al*, 1971), crop samples were extracted with ethyl acetate in the presence of concentrated ammonia. A series of liquid-liquid partitions was followed by spectrophotometric analysis at 282 nm. Recoveries were about 90% from a range of crops.

In a method tested on apples, cucumbers, grapes, sugar beets, strawberries and cherries for the determination of carbendazim (Gorbach and Kuenzler, 1972) the sample is homogenized with ethyl acetate, HCl, $NaHCO_3$ and Na_2SO_4. The aqueous phase is adjusted to pH 4.5, extracted with ethyl acetate and re-extracted with 1N HCl. The aqueous phase is analysed by UV spectrometry. The limit of detection was 0.05 mg/kg and average recovery 90 ± 5%. In a method for the determination of carbendazim in hops, residues are extracted with ethyl acetate, partitioned into sulfuric acid and back into chloroform for spectrophotometric determination at 281 nm. Recoveries from a range of crops fortified at 0.1 to 0.5 mg/kg were between 70 and 80% (Otto, 1972).

In a modification of this method, Kirkland *et al*. (1973) used ethyl acetate extraction and liquid-liquid partitions for clean-up, with the introduction of HPLC with UV detection for the determination of carbendazim and 2-AB. Approximately 20 crops were tested, most of them for recoveries of benomyl but some of carbendazim and 2-AB within the range 0.05 mg/kg (the limit of determination) to 2.2 mg/kg. Recoveries were generally well above 70%. Miller *et al*. (1990) developed a version of the

Kirkland method using extraction with ethyl acetate, acidification with hydrochloric acid, liquid-liquid partitions and HPLC determination. The method is suitable for enforcement purposes, with a limit of determination of 0.05 mg/kg and recoveries ranging from 77 ± 6 to 93 ± 11%.

Another HPLC method was developed for carbendazim residues in plant tissues by Prince (1984). After samples are extracted several times with ethyl acetate, the combined extracts are acidified and the ethyl acetate evaporated. The aqueous phase is washed with hexane, adjusted to pH 10 and re-extracted with ethyl acetate. After evaporation of the organic phase, the residues are dissolved in 0.1 N H_3PO_4 and determined with UV detection. The limit of determination was 0.05 mg/kg and recoveries ranged from 76% from rice to 120% from lettuce.

McNally (1989) developed an analytical method for the determination of benomyl and its derivatives in pineapples involving extraction with acetone followed by acidification with hydrochloric acid and cation exchange chromatography. A 1.0 N potassium hydroxide eluate from the exchange column was extracted with ethyl acetate, transferred to methanol solution and analysed by reverse-phase HPLC with UV detection at 280 nm. Recoveries from pulp and peel were 67-120% for benomyl, 68-114% for carbendazim and 73-124% for 2-AB. The same method was applied to tomatoes and their processed products. The limit of determination was 0.05 mg/kg for all the substrates except dry tomato pomace (0.25 mg/kg). Mean recoveries were about 80% (Loo, 1991).

A method was developed to determine residues of benomyl, carbendazim and 2-AB in soya beans and their processed fractions (Adams, 1994). The extraction solvent consisted of acidified aqueous ethanol containing a detergent. After filtration and evaporation, the crude extracts were cleaned up on solid-phase extraction cartridges and by liquid-liquid partitions, and the residues were determined by capillary electrophoresis with UV detection. Mean recoveries ranged from 72 to 107% for benomyl, carbendazim and 2-AB. A similar extraction was used for soya bean meal, soya oil, grapes, raisins, pears and apples (Bramble *et al*., 1996; Trubey and Bramble, 1996). The extract was neutralized, diluted with 10% acetonitrile/water, filtered and the residues determined by thermospray LC-MS-MS. Juice samples were simply diluted before analysis. The limit of determination was 0.03 mg/kg as carbendazim and recoveries were close to 100% for both carbendazim and 2-AB. Standard deviations ranged from 7% to 14%.

A method validated for application to peaches, plums, cucumbers, tomatoes, grapes, peas, beans and Brussels sprouts with a limit of determination of 0.05 mg/kg differs from others in using no organic solvent for the extraction. Samples were extracted with hot hydrochloric acid, followed by filtration and partition into dichloromethane. Subsequent liquid-liquid partitions eventually led to reconstitution of the residue in orthophosphoric acid for determination by ion-exchange HPLC with UV detection (Du Pont, 1996).

A modified enzyme immunoassay with a photodiode array detector was developed for the determination of carbendazim in juices and concentrates (Bushway *et al*., 1990). The analysis is complete within 30 minutes and up to eight samples can be run simultaneously. The detector response was linear from 1 to 26 ng/g and the limit of detection was 10 ng/g for juices and 30 ng/g for concentrates. Coefficients of variation ranged from 12 to 25%.

Residues of carbendazim can be extracted from plant material (tomato, barley and wheat) with ethyl acetate, partitioned into 0.2 M HCl and back into ethyl acetate after adjusting the pH to 12. If necessary, further clean-up is effected through an amino-bonded solid-phase extraction cartridge, before

HPLC with UV detection. The limit of determination was 0.05 mg/kg and mean recoveries were 89% for tomato and 78.5% for cereals (Taylor, 1996; Taylor and Ferreira, 1997).

In another method for tomatoes, combined extraction and clean-up was achieved with methanol and solid-phase extraction columns. Elution of the residue with acetone and methanol was followed by HPLC with UV detection. The limit of determination was 0.01 mg/kg and recoveries at 0.02 to 0.5 mg/kg ranged from 74 to 90% (Melkebeke and Geuijen, 1996).

The Netherlands Government reported two methods for the determination of benomyl, carbendazim and thiabendazole in fruits and vegetables. In a quantitative method, the fungicides are extracted with a mixture of acetone/dichloromethane and petroleum ether. The extract is cleaned up by solid-phase extraction on diol-bonded silica cartridges and the fungicides determined by HPLC with UV and fluorescent detectors in tandem. The limit of determination was 0.05 mg/kg (as carbendazim) and recoveries ranged from 90 to 110%. A qualitative and semi-quantitative determination for screening was also described, where the fungicides are extracted with ethyl acetate and applied to a TLC plate. After development of the chromatogram in ethyl acetate, a suspension of fungal spores of *Penicillium cyclopium* is applied to the plate. After incubation, white spots appear on a green background. The diameters of the spots are proportional to the logarithms of the amounts applied on the plate. The limit of determination ranges from 0.01 to 0.1 mg/kg and recovery is over 90% (Netherlands, 1996).

Animal products

Kirkland (1970, 1973) developed a method for the determination of benomyl, carbendazim, 5-HBC and 4-HBC in cow milk, tissues, urine and faeces. Samples of cow milk or tissues were hydrolysed with phosphoric acid, the fat removed by partitioning with hexane, the pH adjusted to 6.5, and the residues extracted into ethyl acetate and determined by cation exchange HPLC. Recoveries of the metabolites were about 80% from milk, 50-80% from tissues and 65 to 86% from faeces and urine. Limits of determination were 0.01-0.02 mg/kg in milk, 0.05-0.10 mg/kg in tissues and faeces and 0.1 mg/kg in urine. The method is suitable for enforcement purposes. A similar method was used by Hughes and McIntosh (1985) with reverse-phase HPLC. In one method applied to eggs residues were extracted with acidified ethyl acetate, neutralized, cleaned up by liquid-liquid partitions, and determined by UV spectrophotometry. The limit of determination was 0.05 mg/kg in both whites and yolks and recoveries were 88 and 100% respectively (Hollander *et al*, 1977).

Soil

Plant material, water or soil can be analysed for carbendazim after the sample is homogenized with $NaHCO_3$, ethyl acetate and celite for 3 min. The organic phase is extracted with sulfuric acid and the residues re-extracted with dichloromethane. The organic extract is evaporated to dryness, the residue dissolved in acetone and potassium carbonate solution and the compounds derivatized with pentafluorobenzyl bromide. The solution containing the derivative is purified on a mini silica gel column and the residues determined by GLC with an ECD. The limit of determination was 0.05 mg/kg and recoveries were 65-90% in cereals, 56-64% in soil and 60-95% in water (Specht, 1985).

In another method for the analysis of soils, samples were extracted with acidic aqueous methanol, cleaned up by liquid-liquid partitions and analysed by HPLC. 2-AB was also determined. From a range of soil types the mean recoveries were 92, 88 and 71% for benomyl, carbendazim and 2-AB respectively (Kirkland *et al*, 1973). A method recommended for regulatory enforcement purposes for benomyl-derived residues in soil was developed by Brookey *et al*. (1991). Residues were extracted with a mixture of acetonitrile and aqueous ammonia. The extract was evaporated and the residues

dissolved in the mobile phase for HPLC/UV analysis, although some soil types needed a liquid-liquid partition clean-up. The limit of quantification was 0.05 mg/kg and recoveries from a range of soil types averaged 84%.

Water

A method applicable to the determination of benomyl and carbendazim as carbendazim in industrial waste effluents was developed by Mohammed (1984). The procedure involves the conversion of benomyl by acid hydrolysis to carbendazim, followed by a pre-column concentration and HPLC on a strong cation exchange column with UV detection. The average recovery of carbendazim was 99% at 0.5-1.5 µg/l.

In a method for the determination of benomyl-derived residues in water, with reverse-phase HPLC with UV detection, benomyl was separated from carbendazim by treatment of the aqueous sample with alkali which did not affect carbendazim but formed STB from any unchanged benomyl. The limit of determination for both compounds was 0.03-0.05 mg/l and recoveries ranged from 97 to 107% (Chiba and Singh, 1986). This method is suitable for enforcement purposes, and was also applied to soil and sediment samples (Marsh and Arthur, 1989).

An ELISA immunoassay method was developed for the determination of benomyl residues (as carbendazim) in water. It performed satisfactorily between 0.1 and 5 µg/l but the limit of determination was given as 0.65 µg/l after the recommended 2-fold dilution of water samples before analysis. The mean recovery was 100% (Charlton, 1991).

A method for the determination of carbendazim in groundwater involved C-18 solid-phase extraction and HPLC with acetonitrile as eluant. Recoveries at the limit of determination of 0.05 µg/l varied from 32 to 70%. (Du Pont, 1991). For reagent water, the analysis was by high performance thin-layer chromatography (HPTLC) with a recovery of 105% at the limit of quantification of 0.02 µg/l. A similar method with HPTLC was reported by Zietz (1991) for ground-water, with methanol as the eluant and automated multiple development (AMD) with methanol and carbon disulfide. Recoveries at 0.05 µg/l varied from 33 to 93% and at 0.1 µg/l from 63 to 120%.

Air

A method for carbendazim in air reported by Buerstell *et al*. (1992) involves adsorption to Tenax, cold extraction with ethyl acetate + acetic acid (96 + 4) and determination by HPLC with UV detection. The limit of determination was 10 ng/l with 94% recovery.

Stability of residues in stored analytical samples

The recoveries of benomyl, determined as carbendazim, after storage at approximately -20°C were 90% after 18 months from apples and processed apple fractions, 90% after 26 months from peaches and processed peach fractions (Hoesterey and Tomic, 1995a,b), 74 to 82% after 30 months from tomatoes and green beans (Goldberg, 1989a) and 107% after 24 months from wheat grain and straw (107%) (McNally, 1991a). The metabolite 2-AB was stable in tomatoes for 24 months (Tomic, 1994), and carbendazim was stable up to 36 months (95% recovery) in soya beans (Goldberg, 1989b; McNally, 1991b).

Benomyl, carbendazim and 2-AB were stable for at least 9 months in soil at -20°C (Deardorff, 1991).

USE PATTERN

Table 12 shows the registered uses of carbendazim on the crops discussed in this evaluation as of February 1998.

Table 12. Registered uses of carbendazim.

Crop	Country	Product, % ai	Application				PHI, days
			No.	kg ai/ha	kg ai/hl	F/G	
Fruits	Tunisia	WG 50	-	0.1	0.25	F	-
	Vietnam	SC 50	1	0.1-0.2	-	F	14
	Zaire	SC 50	1	0.25	0.063	F	-
Citrus	Argentina	SC 50	2	-	-	F	7
	Australia	SC 50	-	-	0.1	F	-
	Brazil	SC 50	1-2	-	0.05	F	7
	Cyprus	WP 75	1-2	1.4-2	0.035	F	7
	Greece	SC 50/WP 50	-	0.13	-	F	-
	Malaysia	WP 60	1	1.188	0.12	F	14
		SC 50	1	0.8	0.84	F	14
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
		SC 50		0.06-0.12	dipping	F	-
	New Zealand	SC 50	-		0.025	F	-
	Pakistan	SC 50	1		0.035	F	14
	South Africa	SC 50	1		0.014-0.042	F	14
Pome fruits	Italy	SC 50/WG 80	1	0.4-0.5	0.04-0.05	F	15
	Spain	WP 50	-	0.375-0.6	0.025-0.03	F	15
	Turkey	WP 60	1-6	0.356	0.024	F	14
	UK	SC 50		0.25-0.55	0.031-0.55	F	7
					0.051	F	*
		WP 50			0.015-0.025	F	-
		WG 80	1	0.024-0.55	0.003-0.55	F	21*
Apples	Argentina	SC 50	2		-	F	7
	Australia	SC 50	-		0.02- 0.025	F	7
	Belgium	SC 50/WG 50	2	0.25-0.3	0.025-0.03	F	14
	Chile	WP 50/SC 50			-	F	5
	Cyprus	WP 75	2	1.2-1.6	0.04	F	7
	Greece	SC 50	-		0.03-0.046	F	15
		WP 50			0.03-0.05	F	15
	Indonesia	WP 60	1	0.134-0.267	0.045-0.089	F	14
	Israel	WP 50	-		-	F	7
	Italy	SC 50	1		-	-	15
	Netherlands	SC 50/ WG 80	2		0.025-0.05	F	14
	New Zealand	SC 50	-		0.0125	F	7
	Pakistan	SC 50	1		0.025-0.035	F	14
	UK	SC 50			0.06-0.112	F	7
		WG	3		0.03-0.56	F	7
	South Korea	WP 60	1		-	F	15
	Turkey	WP 50	-		0.015	F	14
Stone fruit	Australia	SC 50	-		0.0125-0.025	F	1
	Cyprus	WP 75	1-2	0.6-0.9	0.03	F	7
	Greece	SC 50	-		0.031-0.046	F	15
	Italy	SC 50/WG 80	1-3	0.3-0.4	0.03-0.04	F	15
	New Zealand	SC 50	-	-	0.025	F	1

Crop	Country	Product, % ai	Application				PHI, days
			No.	kg ai/ha	kg ai/hl	F/G	
	Spain	WP 50	-	0.375-0.6	0.025-0.03	F	15
		SC 50	-	0.5	0.05	F	15
	Turkey	WP 60	1-2	5.346-7.128	0.267-0.475	F	14
Peach	Argentina	SC 50			-	F	7
	Chile	SC/50WP 50	2-3		-	F	5
	Italy	WG 50			0.05-0.1	F	15
Plum	Ireland	WG 50	1-2	0.55	-	F	-
	Italy	WG 50	-		0.05-0.1	F	15
	Netherlands	WG 50	2-3		0.05	F	-
Cherries	Belgium	SC 50/WG 50	1	0.25	0.025	F	14
	Greece	SC 50			0.031-0.046	F	15
		WP 50			0.03-0.04	F	15
	Ireland	WG 50	1-2	0.55	-	F	14
	Italy	WG 50	-		0.05-0.06	F	15
	Luxembourg	WG 50	1		0.05	F	14
	Netherlands	SC 50/WG 80	-	-	0.025	F	-
		WG 50	2-3	-	0.05	F	-
Grape	Argentina	SC 50	3-5		-	F	14
	Australia	SC 50	-	0.55	0.05	F	1
	Chile	SC 50	3-5	-	-	F	20
	Italy	WG 50	4	-	0.05-0.1	F	15
	Luxembourg	WG 50	-	-	0.1	F	-
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
	Pakistan	SC 50	1	-	0.025-0.35	F	14
	Portugal	WP 60	4	-	0.08	F	-
	South Africa	SC 50	-	-	0.025	F	-
	Spain	WP 50	-	0.1-0.25	0.025	F	15
	Thailand	SV 50	1	0.375-0.75	-	F	14
Grape, wine	Cyprus	WP 75	1-2	0.35-0.50	0.05-0.07	F	14
	Germany	WP 25	1-2	0.156-0.5	0.01-0.083	F	35
	Italy	SC 50/WG 80	1-3	0.3-0.4	0.03-0.04	F	15
	Switzerland	WP 25	1	0.6	-	F	-
	Tunisia	WP 60	1-3	1.536-1.92	0.256-0.48	F	-
Strawberry	Argentina	SC 50	3	-	-	F	3
	Australia	SC 50	-	-	0.02-0.025	F	2
	Belgium	SC 50/WG 50	-	0.4-0.5	0.08-0.1	F	14
	Chile	WP 50	-	0.5	0.167	F	7
		SC 50	3	0.5	0.167	F	0
	Cyprus	WP 75	3	0.3-0.4	0.035	F/G	3
	Dominican Republic	WP 60	1-2	0.119-0.238	0.03-0.119	F	-
	Ecuador	WP 60	1-2	0.119-0.238	0.03-0.119	F	-
	Greece	SC 50	-	-	0.046-0.061	F/G	-
		WP 50	-	-	0.04-0.12	F	-
	Ireland	WG 50	1-4	0.55	0.05	F	-
	Israel	WP 50	-	-	-	F	7
	Luxembourg	WG 50	-	0.5	-	F	14
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
		SC 50		0.06-0.12	-	F	*
	Netherlands	WG 50	1-3	-	0.06-0.075	F	14
		SC 50/WG80	-	-	0.025-0.03	F	14
	Portugal	WP 60	2-3	0.45-0.6	0.045-0.06	F/G	7
	South Korea	WP 60	1	-	-	F	12

Crop	Country	Product, % ai	Application				PHI,
			No.	kg ai/ha	kg ai/hl	F/G	days
	Spain	WP 50/SC 50	-	0.2-0.25	0.025	F	15
	Switzerland	WP 25	1-2	0.313	-	F	14
	UK	SC 50	1-3	0.25-0.55	0.013-0.55	F	2
		WG 80	1-3	0.48	0.024	F	2
Cucurbits	Australia	SC 50		-	0.020-0.025	F	0
	Belgium	SC 50	-	0.5	0.025	F	3
	Chile	WP 50/SC 50	-	0.5	0.167	F	3
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
	Pakistan	WG 80	1	0.148-0.247	0.06-0.1	F	7
	Turkey	WP 60	1-5	0.297	0.03	F/G	28
Cucumber	Argentina	SC 50	-	-	-	F	7
	Belgium	SC 50	-	-	0.025	F	3
	Brazil	SC 50	1	0.3-0.5	0.03-0.085	F	3
	Costa Rica	SC 50	1-2	0.03-0.08	0.15-0.08	F	-
	Cyprus	WP 75	2-3	0.35-0.40	0.035-0.04	F/G	2
	Dominican Republic	WP 60	1-3	0.119-0.178	0.03-0.089	F	-
		SC 50	1-2	0.03-0.08	0.015-0.08	F	-
	Ecuador	WP 60	1-3	0.119-0.178	0.03-0.089	F	-
		SC 50	1-2	0.03-0.08	0.015-0.08	F	-
	Greece	SC 50/WP 50	-	0.31	-	F	7
			3	0.31	-	G	14
		WP 25	3	-	0.025	G	5
	Ireland	WG 50	-	0.55	-	F	-
	Luxembourg	WG 50	1	0.5	-	F	3
	Malaysia	WP 60	1	0.398-0.659	0.04-0.06	F	3
		SC 50	1	0.26-0.44	0.26-0.04		3
	Netherlands	WG 50	1-3	-	0.05	F	3
	Panama	SC 50	1-2	0.03-0.08	0.015-0.08	F	-
	Switzerland	WP 25	1	0.313	-	F	3
	Spain	SC 50	-	0.3	0.03	F	15
	UK	SC 50	6	-	0.025	F	2
		WG 80	1-6	0.24-0.48	0.024	F	2
	UK	SC 50/WG 80	1-6	0.025	0.025	G	2
Vegetables	Dominican Republic	WP 60	1-4	0.059-0.119	0.015-0.059	F	-
	Ecuador	WP 60	1-4	0.059-0.119	0.015-0.059	F	
	Thailand	SC 50	1	0.25-0.5	-	F	14
	Vietnam	SC 50	1	0.1-0.2	-	-	14
	Zaire	SC 50	1	0.25	0.063	F	-
Tomato	Argentina	SC 50	-	-	-	F	7
	Brazil	SC 50	1	0.35	0.035	F	1
	Chile	WP 50	-	0.5	0.167	F	3
	Cyprus	WP 75	2-3	0.35-0.40	0.035-0.04	F/G	2
	Greece	SC 50/ WP 50	-	0.31	-	F	7
			3	0.31	-	G	14
		WP 25	3	-	0.025-0.031	G	5
	Indonesia	WP 6	7	3.2	0.2-0.4	F	20
	Ireland	WG 50	-	1	-	F	-
	Israel	WP 50	-	-	-	F	7
	Malaysia	WP 60	1	0.659-0.927	0.06-0.09	F	3
		SC 50	1	0.44-0.64	0.04-0.06	F	3
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
		SC 50		0.06-0.12	-	F	*
	Netherlands	WG 50	1-3	-	0.04	F	3

Crop	Country	Product, % ai	Application				PHI, days
			No.	kg ai/ha	kg ai/hl	F/G	
		WG 80	-	-	0.02	F/G	3
	New Zealand	SC 50	-	1	0.06-0.1	F	3
	Portugal	WP 60	2-3	0.45-0.6	0.045-0.06	F/G	4
	Switzerland	WP 25	1	0.313	-	-	3
	Spain	SC 50	-	0.3	0.03	F	15
	UK	SC 50	1-6	0.5	0.5	G	2
		WG 80	1-6	0.48-0.96	0.048	G	2
Beans	Argentina	SC 50	-	-	0.12	F	7
	Belgium	SC 50/WG 50	2	0.4	0.08	F	6
	Brazil	SC 50	1	0.25	0.083	F	17
	Greece	SC 50	1	-	0.031-0.046	F	15
		WP 50	-	0.175-1.25	-	F	15
	Ireland	SC 50	1-2	0.5	-	F	-
		WG 80	1-2	0.625	-	F	-
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
	Netherlands	WG 50	1-2	1	-	F	14
	New Zealand	SC 50	-	1	0.06-0.1	F	14
	Poland	WP 40	1	-	-	F	NA
	Senegal	SC 50	1-4	0.35-0.5	0.087-0.2	F	8
	Spain	WP 50	-	0.15-0.24	0.025-0.03	F	15
	Switzerland	WP 25	1-2	0.313	-	F	14
	UK	SC 50/WG 80	1-2	0.5-0.55	0.25-0.275	F	21
Beans, dwarf	Ireland	WG 50	-	0.55	0.25	F	-
Sugar beet	Austria	WP 60	1	0.119-0.178	-	F	14
	Greece	SC 50		0.18	-	F	-
	Belgium	SC 50/WG 50	1	0.15	0.05	F	-
		SC 10	1	0.125	0.063		28
	Italy	SC 50	1	0.1-0.125/quintal of seed	-	F	NA
	Netherlands	SC 50	1	0.25	-	F	-
	Pakistan	WG 80	1	0.099-0.148	0.04-0.06	F	20
	Romania	S 25	1-2	0.075-0.15	0.012-0.025	F	14
	Russia	WP 50	1-3	0.3-0.4	-	F	20
	Spain	SC/EC 10	1	0.15-0.2	-	F	30
	Turkey	WP 60	1-2	0.238	0.079	F	14
		WP 50	-	0.4	-	F	14
	UK	WP 50	1-2	0.075-0.20		F	-
	Yugoslavia	SC 25	1-2	0.15	0.05-0.037	F	35
Cereals	Austria	WP (60)	1	0.178		F	35
	Belgium	SC 50/WG 50	1	0.15-0.2	0.05-0.67	F	28
	Chile	WP 50/SC 50	1	0.35	-	F	3
	France	SC 50	1	0.2	0.1	F	30
	Italy	WP 60	1	0.03	F	F	NA
	Luxembourg	WG 50	1-2	0.15	-	F	28
	New Zealand	SC 50	-	0.15-0.25	-	F	60
	Pakistan	WG 80	1	0.119-0.198	0.048-0.08	F	35
	Romania	SC 50	-	0.3	-	F	-
	Spain	WP 50	-	0.1-0.12	0.025	F	15
Barley	Czech Republic	SC 25	1	0.3	0.25	F	42
	France	SC/EC 8	1	0.12-0.144	0.096	F	-
	Germany	SC/EC 8	1	0.12	-	F	56
	Greece	SC 50/WP 50	-	0.31	-	F/G	35
	Indonesia	SC 50	-	0.25	-	F-	
	Ireland	WG 80	1	0.312	-	F	-

Crop	Country	Product, % ai	Application				PHI, days
			No.	kg ai/ha	kg ai/hl	F/G	
		WG 50	1-2	0.125-0.25	0.05-0.1	F	-
		SC 50	1	0.25	-	F	-
	Italy	SC/EC	1	-	-	F	-
	Poland	WP 40	1	-	-	F	NA
	Romania	S	1-2	0.1-0.2	0.03-0.06	F	14
	Russia	WP 50	1-2	0.15-0.3	-	F	30
	Saudi Arabia	SC/EC 8	1	0.12	-	F	-
	Slovakia	SC 25	1	0.3	0.25	F	42
	South Africa	SC/EC 8	-	0.064-0.08	-	F	56
	Spain	SC/EC 10	1	0.15-0.2	-	F	60
		SC 50	-	0.3	0.03	F	15
		WP 40	1	-	-	F	NA
	Turkey	SC/EC 8	1-2	0.12	0.04	F	15
	Ukraine	SC 50	1-2	0.25	-	F	30
			1	1-1.25	-	F	NA
	UK	WG 80	1-2	0.25	0.125	F	-
Barley, spring	UK	SC 50	1	0.25	0.125	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
Barley, winter	Czech Republic	WP 50	1	0.178	0.089	F	-
	Germany	SC 36	1	0.18	-	F	56
	Ireland	WG 50	1-2	0.25	0.1	F	-
	Poland	SC/EC 8	1	0.12	0.03-0.06	F	35
	UK	WG 12	1-2	0.28-1.42	-	F	-
		SC 50	1	0.25	0.125	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
Maize	France	SC 8	-	0.18	0.12	F	-
	Italy	EC/SC 8	1	-	-	F	NA
		WG 50	-	-	0.15	F	NA
	South Africa	SC/EC 8	2	0.032	0.08	F	14
Rape, oil seed	Czech Republic	SC/EC 8	1	0.12	0.171	F	56
	France	SC 50	1	0.5	0.167	F	45
		SC/EC 8	1	0.12	0.096-0.12	F	-
	Indonesia	SC 50		0.5	-	F	-
	Ireland	WG 80	1	0.625	-	F	-
		WG 50	1-2	0.25-0.5	0.114-0.227	F	-
		EC/SC 10	1-2	0.075-0.494	0.019-0.247	F	42
	Poland	SC/EC	1	0.12	0.03-0.06	F	42
	Slovakia	SC/EC 8	1	0.12	0.06	F	56
	UK	SC 50/WG 80	1-2	0.5	0.25	F	21
Rape oil seed, winter	Germany	SC 36	1	0.36	-	F	56
	UK	WG 12	1-2	0.28-1.42	-	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
Rye	Czech Republic	WS 40	1	0.8	-	F	NA
		WP 50	1	0.178	0.089	F	-
	Germany	SC/EC 8	1	0.12	-	F	56
	Greece	SC 50/WP 50	-	0.31	-	F/G	35
	Poland	WP 40	1	-	-	F	NA
	Russia	WP 50	1	0.15-0.3	-	F	30
	Ukraine	SC 50	1-2	0.25	-	F	30
Rye, winter	Germany	SC 36	1	0.018	-	F	56
		EC/SC 8	1	0.12	-	F	56
	Poland	SC/EC 8	1	0.12	0.03-0.06		35
Wheat	Czech Republic	SC/EC 8	1	0.12	0.06	F	42
		WP 50	1	0.178	0.089	F	-

Crop	Country	Product, % ai	Application				PHI, days
			No.	kg ai/ha	kg ai/hl	F/G	
		SC 25	1	0.3	0.25	F	42
		WS 40	1	0.8		F	NA
	France	SC/EC 8	1	0.12	-	F	-
	Germany	SC/EC 8	2	0.12	-	F	42
	Greece	SC 50/WP 50	-	0.31	-	F/G	35
	Indonesia	SC 50	-	0.25	-	F	-
	Ireland	WG 80	1	0.312	-	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
	Italy	SC 50	1	0.175-0.225	-	F	30
		SC/EC 30	1	0.12-0.15	0.015-0.025	F	30
		SC/EC 8	1	0.12-0.16	0.02-0.04	F	40
		SC/EC 8	1	-	-	F	NA
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
	Netherlands	SC 50/ WG 80	1	0.25	-	F	35
	Poland	WP 40	1	-	-	F	NA
	Portugal	WP 60	1	0.18-0.24	0.018-0.024	F	35
	Romania	SC 25	1-2	0.1-0.2	0.03-0.06	F	14
	Russia	WP 50	1-2	0.15-0.30	-	F	30
	Saudi Arabia	SC/EC 8	1	0.12	-	F	-
	Slovakia	SC/EC 8	1	0.12	0.06	F	42
		SC 25	1	0.3	0.25	F	42
	South Africa	SC/EC 8	2	0.08	-	F	14
	Spain	SC/EC 10	1	0.15-0.2	-	F	60
		WP 40	1				NA
	Turkey	SC/EC 8	1-2	0.12	0.04	F	15
		WP 60	1	-	-	F	NA
	Ukraine	SC 50	1-2	0.25	-	F	30
	UK	WG 80	1	0.25	0.125	F	-
	Yugoslavia	SC 25	1-2	0.15	0.05-0.037	F	35
Wheat, soft	Brazil	SC 50	1-2	0.3	0.1	F	35
	Italy	WG 50	-	0.3	-	F	30
			-	-	0.15	F	NA
	Netherlands	WG 50	1	0.25	-	F	35
Wheat, spring	UK	SC 50	1	0.25	0.125	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
Wheat, winter	Germany	SC 36	1	0.18	-	F	56
	Ireland	WG 50	1-2	0.25	0.114	F	-
	Poland	SC/EC 8	1	0.12	0.03-0.06	F	35
	Spain	SC 50	-	0.3	0.03	F	15
	UK	WG 124	1-2	0.28-1.42	-	F	-
		SC 50	1	0.25	0.125	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
Coffee	Brazil	SC 50	1-2	0.12-0.16	0.048-0.08	F	-
	Dominican Republic	WP 60	1-2	0.059-0.119	0.015-0.059	F	-
		SC 50	1-2	0.12-0.16	0.048-0.08	F	-
	Ecuador	WP 60	1-2	0.059-0.119	0.015-0.059	F	-
		SC 50	1-2	0.12-0.16	0.048-0.08	F	-
	Malaysia	WP	1	-	0.659-0.927	F	3
	Panama	WC 50	1-2	0.12-0.16	0.048-0.08	F	-

* Post harvest application (dipping). Figure in PHI column is withholding period
F = field; G = greenhouse;- = not stated; NA= not applicable (seed dressing) Application by foliar spray unless otherwise indicated

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of residue trials are shown in Tables 13 to 28. Trials with the same entry in the Tables were carried out at the same site. Some trial sites were divided into sub-plots separated from each other by a sufficient distance to avoid the possibility of contamination by spray drift. Residue data from sub-plots treated with exactly the same application regime are regarded as being from a single trial. Unless otherwise indicated, all trials were conducted outdoors with foliar sprays. Underlined or double underlined residues were from trials according to GAP or maximum GAP (± 30%) respectively, and were used to estimate maximum residue levels and STMRs. In cases where the sample analysed is both the portion to which the MRL applies and the edible portion, the underlined residues will be considered for the estimation of both MRLs and STMRs.

Oranges. Two trials were conducted in France with post-harvest treatments but no GAP was reported. One trial in South Africa according to GAP (1 x 0.014-0.042 kg ai/hl) gave residues at a PHI of 15 days of 0.07 and 1.6 mg/kg in the pulp and whole fruit respectively. In another trial at a double rate the residues were 0.27 and 3.2 mg/kg in the pulp and whole fruit (Table 13).

Table 13. Results of residue trials with carbendazim on oranges.

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Product	No	kg ai/ha	kg ai/hl				
France A06406 1973 Corsica	SC	NA	NA	0.0495% dipping	0 0	pulp rinsed peel[1]	<0.05; <0.05 0.9; 1.3	A06406 A06408
	SC	NA	NA	0.099% dipping	0 0	pulp rinsed peel[1]	<0.05 1.5: 2.1	A06407 A06407
South Africa A59510 1984[2]	SC	1		0.041	0 0 7 7 15 15 21 21	pulp/peel whole fruit[1] pulp/peel whole fruit[1] pulp/peel whole fruit[1] pulp/peel whole fruit[1]	0.08/4.4 1.1 0.06/4.3 1.1 0.07/7.0 1.6 0.10/5.6 1.3	Author unknown, 1984
	SC	1		0.085	0 0 7 7 15 15 21 21	pulp/peel whole fruit[1] pulp/peel whole fruit[1] pulp/peel whole fruit[1] pulp/peel whole fruit[1]	0.25/12 2.9 0.08/13 2.9 0.27/14 3.2 0.27/11 2.3	Author unknown, 1984

[1]Calculated from weights of pulp and peel
[2]Results corrected for recovery (pulp 73%, peel 92%)

Apples. Eight residue trials were conducted in Germany in 1986/1987 with 3 or 4 applications of 0.0288 kg ai/hl. Although no GAP for Germany was reported, the trials complied with UK GAP (1-12 x 0.015-0.5 kg ai/hl). The residues at the GAP PHI of 7 days ranged from 0.30 to 0.90 mg/kg (Table 14).

Table 14. Results of residue trials with carbendazim on apples in Germany with 0.0288kg ai/hl of SC formulation.

No. of applications	PHI, days	Residues, mg/kg	Report N° A53860 Trial number (year)
3	0	0.79	A39727 (1996)
	7	0.49	
	14	0.50	
	56	0.82	
	98	0.48	
	140	0.39	
	182	0.58	
3	0	0.70	A39728 (1996)
	7	0.90	
	14	0.28	
	56	0.60	
	98	0.69	
	140	0.53	
	182	0.67	
3	0	0.31	A39729 (1986)
	7	0.36	
	14	0.26	
	56	0.18	
	98	0.29	
	140	0.17	
	182	0.22	
3	0	0.86	A39730 (1986)
	7	0.70	
	14	0.71	
	56	0.56	
	98	0.51	
	140	0.66	
	182	0.37	
4	0	0.28	A39723 (1987)
	7	0.30	
	14	0.18	
	56	0.26	
	98	0.28	
	140	0.23	
	182	0.23	
4	0	0.51	A39724 (1987)
	7	0.84	
	14	0.16	
	56	0.30	
	98	0.22	
	140	0.35	
	182	0.34	
3	0	0.93	A39725 (1987)
	7	0.42	
	14	0.33	
	56	0.17	
	98	0.24	
	140	0.21	
	182	0.17	
3	0	0.41	A39726 (1987)
	7	0.35	
	14	0.20	
	56	0.24	

No. of applications	PHI, days	Residues, mg/kg	Report N° A53860 Trial number (year)
	98	0.25	
	140	0.23	
	182	0.18	

Peaches and plums. A total of 12 trials were conducted in Europe where normal PHIs are 14-15 days. In all the trials reported, samples were harvested at the earliest after 40 days, giving residues in fruit from <0.05 to 0.44 mg/kg (Table 15).

Table 15. Results of residue trials with WG formulations of carbendazim on peaches and plums.

Country Report No. year location	Application			PHI, days	Sample analysed	Residues, mg/kg	Reference
	No	kg ai/ha	kg ai/hl				
Germany	2	0.6-1.2	0.12	42	fruit	0.06	AGR/06/96
9711340				61		<0.05	
1996				70		<0.05	
Nordrhein-				82		<0.05	
Westfalen				91		<0.05	
				102		<0.05	
				112		<0.05	
	2	0.6-1.2	0.12	42	fruit	0.07	AGR/07/96
				61		<0.05	
				70		<0.05	
				82		<0.05	
				91		<0.05	
				102		<0.05	
				112		<0.05	
Italy	2	0.3-0.6	0.06	41	fruit	<0.05	560-1
9810178				51	fruit	<0.05	
1996				62	fruit	<0.05	
Brescia				71	pulp	<0.05	
				83	pulp	<0.05	
Pavia	2	0.3-0.6	0.06	40	fruit	0.44	560-2
				52	fruit	0.46	
				62	fruit	0.55	
				73	pulp	0.42	
				82	pulp	0.45	
Alessandria	2	0.3-0.6	0.06	40	fruit	0.07	560-3
				52	fruit	<0.05	
				62	fruit	<0.05	
				73	pulp	<0.05	
				82	pulp	<0.05	
Mantova	2	0.3-0.6	0.06	40	fruit	0.08	560-4
				52	fruit	0.07	
				62	fruit	<0.05	
				73	pulp	0.10	
				82	pulp	0.45	
Netherlands	2	0.6-1.2	0.12	50	fruit	<0.05	AGR/08/96
9711340				60		<0.05	
1996				71		<0.05	
Gelderland				81		<0.05	
Plums				91		<0.05	
				50	fruit	<0.05	AGR/09/96

Country Report No. year location	Application			PHI, days	Sample analysed	Residues, mg/kg	Reference
	No	kg ai/ha	kg ai/hl				
				60 71 81 91		<0.05 <0.05 <0.05 <0.05	
Spain 9810084 1997 Sevilla	2	0.6-1.2	0.12	49 60 71 81	fruit	<0.05 <0.05 <0.05 <0.05	ALO/14/97
	2	0.6-1.2	0.12	49 60 71 81	fruit	<0.05 <0.05 <0.05 <0.05	ALO/15/97
	2	0.6-1.2	0.12	49 60 71 80	fruit	<0.05 <0.05 <0.05 <0.05	ALO/16/97
	2	0.6-1.2	0.12	71 81	fruit	<0.05 <0.05	ALO/17/97

Cherries. In six residue trials with carbendazim in Germany during 1971 and 1972 the application conditions were close to GAP in Europe but the sampling intervals were much longer than the usual PHIs of 14-15 days (Table 16).

Table 16. Results of residue trials on cherries in Germany with two applications of a WP formulation.

Application		PHI,	Residues,	Report N°A53867 Trial No.
g ai/tree	kg ai/hl	days	mg/kg	
8	0.04	85	0.14	A00440
6	0.03	85	<0.05	A00441
6	0.03	85	<0.05	A00442
8	0.04	85	<0.05	A00443
12	0.075	75	0.07	A00990
12	0.075	75	0.10	A00991

Grapes. In ten trials on wine grapes in France with 3-4 applications of 0.35-0.5 kg ai/ha, residues were 0.8 -2.4 mg/kg after PHIs of 14-35 days. No GAP was reported.

In nine trials in Germany at rates higher than GAP (1-2 x 0.5 kg ai/ha) the residues at a PHI of 35 days were 0.04 to 1.1 mg/kg. In two trials in Italy and two in Spain at higher rates than GAP in Italy (1-3 x 0.3-0.4 kg ai/ha, 14 days PHI) the residues in the fruit after 0 or 35 days were 0.55 to 2.7 mg/kg (Table 17).

Table 17. Results of residue trials on grapes with a WP formulation.

Country Report No. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
France A52377 1986 Ry	4	0.5	0.25	0 7 14 21 30	fruit fruit fruit fruit fruit wine (y) wine(ny)	3.1 2.6 2.7 2.6 2.3 3.2 1.4	S 405.86
Hautvillers	3	0.5	0.25	0 28 35 42 49 58	fruit fruit fruit fruit fruit fruit wine (y) wine(ny)	2.6 2.2 2.4 2.2 2.5 1.4 2.3 1.4	S 406.86
	4	0.5	0.25	14 21 27	fruit fruit fruit wine(y) wine(ny)	1.8 2.1 1.4 0.92 0.69	S 433.86
	4	0.5	0.25	0 7 14 21 29	fruit fruit fruit fruit fruit wine (y) wine(ny)	1.7 1.1 1.4 2.2 1.7 1.5 1.5	S 434.86
Nitray	4	0.5	0.25	0 28 35 42 49 57	fruit fruit fruit fruit fruit fruit wine (y) wine(ny)	1.7 0.8 1.0 1.0 1.3 1.0 0.85 0.85	P628.86
Liergues	4	0.5	0.42	13 20 31 38 45 56	fruit	3.3 2.6 2.0 2.1 1.8 1.4	P 713.86
Le Breuil	4	0.5	0.42	13 20 31 38 45 55	fruit	1.5 1.8 1.8 1.1 1.2 1.0	P 714.86
Sarrians	4	0.5	0.25	14 20 30 30 35 41	fruit fruit fruit wine fruit fruit	1.2 0.8 1.6 0.54 1.9 1.4	P 309.86

Country Report No. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
				51 51	fruit wine	0.8 0.39	
A58410 1996 Caumont	4	0.35	0.035	0 34	fruit	0.26 0.21	F-54150
Pian sur Garone	4	0.35	0.035	0 34	fruit	0.35 0.15	F.33409
Germany A53870	4	0.41	0.0625-0.0938	0 7 14 28 35	fruit	2.2 1.3 1.4 0.83 1.1	D5515
	4	0.41	0.0625-0.0938	0 6 14 28 35	fruit	2.9 1.5 1.0 0.75 0.54	D6909
	4	0.41	0.0625-0.0938	0 7 14 28 35	fruit	1.2 1.3 1.8 0.57 0.57	D6520
	4	0.41	0.0625-0.0938	0 7 14 28 35	fruit	1.2 1.1 1.2 1.0 1.0	D6706
	4	0.41	0.0625-0.0938	0 7 14 28 35	fruit	1.8 1.5 1.2 0.48 0.49	D6507
	4	0.41	0.0625-0.0938	0 7 14 28 35	fruit	1.6 1.4 1.4 1.4 1.1	D6706
	4	0.41	0.0625-0.0938	0 7 14 28 35	fruit	0.86 1.8 0.82 0.68 0.82	D6909
	4	0.41	0.0625-0.0938	0 7 14 28 35	fruit	0.94 0.45 0.48 0.27 0.36	D7104
	4	0.41	0.0625-0.0938	0 7 14 28 35	fruit	0.76 0.49 0.30 0.07 0.04	D7800
Italy A58410 1996	4	0.35	0.035	0 35	fruit	0.30 0.39	I-15057

Country Report No. Year Location Tortora	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
La Morra	4	0.35	0.035	0 35	fruit	0.62 0.63	I-12054
Spain A58410 1996 Calabarra	4	0.35	0.035	0 35	fruit	0.66 0.55	E-46389
Campo Arcis	4	0.35	0.035	0 36	fruit	2.7 1.4	E-46352

y = with yeast; ny = no yeast

Strawberries. In six trials in Germany with 3 applications of 0.6 to 2.16 kg ai/ha, the residues in the fruit after PHIs of 14 to 39 days were 0.07 to 0.85 mg/kg. Two trials in the UK and one in Finland conducted according to GAP in The Netherlands (1-3 x 0.025-0.075 kg ai/hl) with PHIs of about 15 days gave residues of 0.30 to 2.0 mg/kg. One trial in Italy at 2.25 kg ai/ha could not be evaluated as no information on GAP was given (Table 18).

Table 18. Results of residue trials on strawberries with a WP formulation.

Country Report no. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
Germany A53868 1971 Eddersheim	3	0.9	0.045	39	fruit	0.14	A-00900
Hattersheim	3	0.6	0.03	25	fruit	0.76	A-00901
	3	0.9	0.045	25	fruit	0.40	A-00902
1972 Weiterstadt	3	2.16	0.09	22 26 30 34	fruit	0.85 0.70 0.63 0.71	A-00051
Hattersheim	2	0.96	0.04	14 18 22 26	fruit	0.14 0.20 0.09 0.07	A-00049
Weiterstad	3	0.96	0.04	22 26 30 34	fruit	0.25 0.25 0.25 0.25	A-00050
UK A53868 1972 March, Cambs	3	-	0.045	9 16	green fruit	1.2 (2) 0.9; 1.2	A01158, A01159 A00431, A00435
	3	-	0.036	9 16	green fruit	0.9 0.3	A00428 A00435
Italy A53868 1972 Masi Torelo	4	2.25	0.045	0 1 2 5 7 14	fruit	2.5 2.5 2.5 1.8 1.4	A-02203

Country Report no. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
				21 28		1.4 0.6	
Finland A53868 1976	3	0.9	0.045	19	fruit	2.0	A-14179

Cucumbers and gherkins. Trials were conducted in Europe on gherkins and cucumbers (1971-75) and in Brazil on cucumbers (1985). Four trials in Belgium and The Netherlands were at or above GAP rates (1-3 applications of 0.025 and 0.05 kg ai/hl respectively, 3 days PHI) but the raw fruit was not analysed. Residues in washed fruit and peel after 3-12 days were <0.05 mg/kg.

Ten trials in Germany on gherkins according to GAP in Belgium or The Netherlands gave residues in the fruit of <0.05 mg/kg at PHIs of 3 or 14 days. Decline studies showed that residues were <0.05 mg/kg from day 0 to day 28 (Table 19).

Table 19. Results of residue trials on cucumbers with a WP formulation.

Country Report No. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
Belgium A53865 1972 glasshouse	4 2	- -	0.06 0.03	1 1 2 2 3 3	peel washed fruit peel washed fruit peel washed fruit	0.64 0.60 0.26 <0.05 0.22 <0.05	A01206
Brazil A53865 1985	4	0.3066- 0.4906	0.05	3	fruit	<0.05	A-35946
	2	0.3066- 0.3679	0.05	5	fruit	<0.05	A-35947
Germany A53865 1971 Harttersheim	1	0.18	0.03	0 3 7 14 21 28	fruit (gherkins)	<0.05 <0.05 <0.05 <0.05 <0.05 <0.05	A00905
	1	0.36	0.06	0 3 7 14 21 28	fruit (gherkins)	<0.05 <0.05 <0.05 <0.05 <0.05 <0.05	A00906
	1	0.27	0.045	0 3 7 14 21 28	fruit (gherkins)	<0.05 <0.05 <0.05 <0.05 <0.05 <0.05	A00907
	2	0.27	0.045	0 3 7	fruit (gherkins)	<0.05 <0.05 <0.05	A00908

Country Report No. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
				14 21 28		<0.05 <0.05 <0.05	
	1	0.36	0.06	0 3 7 14 21 28	fruit (gherkins)	<0.05 <0.05 <0.05 <0.05 <0.05 <0.05	A00916
	2	0.27	0.045	0 3 7 14 21 28	fruit (gherkins)	<0.05 <0.05 <0.05 <0.05 <0.05 <0.05	A01136
	2	0.36	0.06	0 3 7 14 21 28	fruit (gherkins)	<0.05 <0.05 <0.05 <0.05 <0.05 <0.05	A01137
	2	0.12	0.02	0 3 7 14 21 28	fruit (gherkins)	<0.05 <0.05 <0.05 <0.05 <0.05 <0.05	A01138
	2	0.15	0.025	0 3 7 14 21 28	fruit (gherkins)	<0.05 <0.05 <0.05 <0.05 <0.05 <0.05	A01139
1975 Kruemsa glasshouse	4	0.3g/plant	0.03	0 1 2 3 4	peel fruit peel fruit peel fruit peel fruit peel fruit	0.06 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05	A04905
The Netherlands A53865 1972	4	0.12 g/plant	0.06	1 2 3	peel washed fruit peel washed fruit peel washed fruit	0.51 <0.05 0.32 <0.05 <0.05 <0.05	A01161
	4	0.096 g/plant	0.048	1 2 3	peel washed fruit peel washed fruit peel washed fruit	0.29 <0.05 0.15 <0.05 <0.05 <0.05	A011162
	3	0.6g/plant	0.12	12	peel	<0.05	A01297

Country Report No. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
				12 13 13 14 14	washed fruit peel washed fruit peel washed fruit	<0.05 <0.05 <0.05 <0.05 <0.05	(gherkins)

Tomatoes. Trials in glasshouses were conducted in Finland, France, Italy, Spain and The Netherlands.

The two trials in Finland with two applications of 1.8 kg ai/ha with PHIs of 4 and 7 days gave residues of <0.05 mg/kg; three each in France and Italy and two in Spain with four applications at 0.6 kg ai/ha and a PHI of 3 days gave residues of <0.05 to 0.21 mg/kg. None of these trials could be evaluated as no information on GAP was provided.

Seven of the 10 trials in The Netherlands were according to GAP (0.02 kg ai/hl, PHI 3 days) and gave residues of 0.08 to 0.22 mg/kg in the fruit. One trial at a higher rate gave the same residues and the two others gave residues in the pulp of <0.1 mg/kg at a PHI of 3 days (Table 20).

Table 20. Results of residue trials on tomatoes in glasshouses with a WP formulation.

Country Report No. Year, Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
Finland A53869 1977	4	1.8	0.036	4	fruit	<0.05	A14185
	4	1.8	0.036	7	fruit	<0.05	A14186
France A58405 1996 Marcellus	4	0.6	0.1	0 3	fruit fruit	0.16; 0.17 0.17;0.18	
	4	0.6	0.1	0 3	fruit fruit	0.13; 0.14 0.18(2)	
Razimet	4	0.6	0.1	0 3	fruit fruit	<0.05; 0.06 <0.05; 0.05	
Italy A58405 1996 Verona	4	0.6	0.1	0 3	fruit fruit	0.15; 0.18 0.09; 0.21	
Ascoli Piceno	4	0.6	0.1	0 3	fruit fruit	0.24 0.18	
	4	0.6	0.1	0 3	fruit fruit	0.33 0.16	
Spain A58405 1996 Muchante	4	0.6	0.1	0 3	fruit fruit	0.23 0.13	
Tudela	4	0.6	0.1	0 3	fruit fruit	0.12; 0.14 0.12; 0.14	
The Netherlands A53869 1972	6	0.8g/plant	0.04	1 2 3	washed peel pulp washed peel pulp washed peel	1.4 <0.1 1.3 <0.1 0.9	A01174

Country Report No. Year, Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
					pulp	<0.1	
	15	0.4g/plant	0.02	1	washed peel	1.2	A01175
					pulp	<0.1	
				2	washed peel	1.1	
					pulp	<0.1	
				3	washed peel	1.3	
					pulp	<0.1	
A57011 1995	2	0.375	0.025	0	fruit	<0.01 (2)	01
				1	fruit	0.17; 0.21	
				2	fruit	0.17; 0.22	
				3	fruit	0.15; 0.18	
				7	fruit	0.16; 0.21	
	2	0.375	0.025	0	fruit	0.06; 0.11	02
				1	fruit	0.15; 0.16	
				2	fruit	0.12; 0.13	
				3	fruit	0.11(2)	
				7	fruit	0.10; 0.15	
A58414 1996	2	0.375	0.025	3	fruit	0.08	01
	2	0.375	0.025	3	fruit	0.12	02
	2	0.375	0.025	3	fruit	0.17	03
	2	0.375	0.025	3	fruit	0.16	04
A57012 1995	2	0.5	0.033	0	fruit	0.18; 0.26	01
				1	fruit	0.23; 0.16	
				2	fruit	0.22; 0.17	
				3	fruit	0.16; 0.22	
				7	fruit	0.13; 0.17	
	2	0.375	0.025	0	fruit	0.28	02
				1	fruit	0.24	
				2	fruit	0.31	
				3	fruit	0.22	
				7	fruit	0.20	

Beans. Thirteen trials on dwarf and field beans in the UK were according to recommended GAP (1-2 applications of 0.5 kg ai/ha) or at higher or lower rates. The residues in the beans or pods at PHIs of 22 to 53 days were at or below the LOD of 0.01 mg/kg (Table 21).

Table 21. Results of residue trials on beans in the UK (1973) with a WP formulation.

Report N° Bean	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
A53861 dwarf	1	0.67	0.15	22	beans	<0.10	A01179
	1	1.34	0.3	22	beans	0.10	A01180
	1	0.58	0.13	22	beans	<0.10	A01181
	1	1.12	0.25	22	beans	<0.10	A01182
	1	0.50	0.11	22	beans	<0.10	A01183
	1	1.04	0.23	22	beans	<0.10	A01184
field	2	0.34	0.075	32	pods	<0.10	A01557
	1	0.67	0.15	53	pods	<0.01	A01558
	2	0.34	0.085	32	pods	<0.10	A01561
	2	0.34	0.075	32	pods	<0.10	A01555

Report N° Bean	Application No	kg ai/ha	kg ai/hl	PHI, days	Sample	Residues, mg/kg	Trial reference
	1	0.674	0.15	53	pods	<0.10	A01556
	2	0.34	0.075	32	beans	<0.10	A01559
	1	0.674	0.15	53	beans	<0.10	A01560

Sugar beet. Six trials were conducted in France and nine in Germany. No GAP was reported for these crountries but one of the trials in Germany was according to Belgian recommended GAP (1 x 0.125-0.15 kg ai/ha) and the residues at the GAP PHI of 28 days were <0.05 mg/kg in the roots. In all the trials residues in the roots from day 0 to 42 were close to or below the LOD of 0.05 mg/kg except in one sample at 21 days (Table 22).

Table 22. Results from residue trials with carbendazim on sugar beets

Country Report No. Year Location	Application Form.	No	kg ai/ha	kg ai/hl	PHI, days	Sample	Residues, mg/kg	Trial reference
France A53862 1986 Guitry	SC	1	0.0625	0.04	99	leaves root	<0.05 <0.05	A52965
	SC	1	0.05	0.03	99	leaves root	<0.05 <0.05	A52965
Oppoy	SC	1	0.0625	0.016	65	leaves root	<0.05 <0.05	A52965
	SC	1	0.05	0.013	65	leaves root	<0.05 <0.05	A52965
Rouvre-en-Plaine	SC	1	0.0625	0.016	26	leaves root	<0.05 0.05	A52965
	SC	1	0.05	0.013	26	leaves root	<0.05 0.06	A52965
Germany A53862 1971 Hattersheim	WP	3	0.09	0.015	0 7 14 21 28	leaves/root	2.0/<0.05 0.80/<0.05 0.70/<0.05 0.14/<0.05 0.5/<0.05	A00910
	WP	3	0.09	0.015	0 7 14 21 28	leaves/root	4.8/<0.05 1.9/<0.05 1.9/<0.05 0.74/<0.05 0.50/<0.05	A00911
1972 Gersthofen	WP	1	0.36	0.06	0 8 14 21 28 42	leaves	11 4.7 2.0 0.3 1.7 2.5	A01025
	WP	1	0.36	0.06	0 8 14 21 28 42	root	<0.05 <0.05 <0.05 0.26 <0.05 <0.05	A01027
	WP	1	0.4	0.066	0 8	leaves	5.5 1.2	A01024

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	kg ai/hl				
					14 21 28 42		0.6 0.2 1.0 0.6	
	WP	1	0.18	0.03	0 8 14 21 28 42	root	0.13 <0.05 <0.05 <0.05 <0.05 <0.05	A01035
	WP	1	0.2	0.033	0 8 14 21 28 42	leaves	5.2 1.1 0.50 0.20 0.70 0.50	A01026
	WP	1	0.2	0.033	2 14 21	root	<0.05 <0.05 <0.05	A01034
	WP	1	0.4	0.067	2 14 21	root	<0.05 <0.05 <0.05	A01036

Barley. 27 trials were conducted in Europe where GAP PHIs vary from 15 to 56 days. In three trials in France at nearly twice the maximum recommended rate of 0.144 kg ai/ha the residues at PHIs of 34 to 44 days were <0.05 mg/kg in the grain and from 0.27 to 0.83 mg/kg in the straw. In six trials in Germany approximating the GAP rate (0.12-0.18 kg ai/ha) residues at the GAP PHI of 56 days were 0.02 to 0.05 mg/kg in the grain and <0.05 to 0.77 mg/kg in the straw or stalks. Three trials in Italy and Spain at higher rates than Spanish GAP (1 application of 0.15-0.3 kg ai/ha, PHI 15 or 60 days) residues in the grain and straw after 35 days were 0.10-0.81 mg/kg and 0.58-3.8 mg/kg respectively. In the UK, two trials with 2 applications of SC formulations at 0.25 kg ai/ha gave residues at 42 or 45 days PHI of <0.05 to 0.36 mg/kg in the grain and 0.49 to 0.98 mg/kg in the straw (Table 23). The UK PHI is “up to and including grain watery ripe”.

Table 23. Results from residue trials on barley.

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	Kg ai/hl				
France A58409 1996 Inchy-en-Artois	SC	2	0.25	0.1	0 44 44	whole plant grain straw	1.0 <0.05 0.49	X966203
A58408 1996 Isère	SC	2	0.25	0.1	0 34 34	whole plant grain straw	3.6 0.15 0.27	96EZI0101PE
A67186 1997 Champaing	SC	2	0.241-0.25	-	0 37 37	whole plant grain straw	4.2 <0.05 0.83	PRE-A97006
Germany	SC	2	0.254-	-	0	whole plant	3.6	AT97/002-1

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	Kg ai/hl				
A67186 1997 Hesse			0.262		46 46	grain straw	<0.05 0.29	
LowereSaxony	SC	2	0.246- 0.261	-	0 44 44	whole plant grain straw	6.4 <0.05 0.41	AT-97/002-2
A58409 1996 Hustentten	SC	2	0.25	0.1	0 40 40	whole plant grain straw	1.7 <0.05 0.87	96/07796-DIII
Ettlingen	SC	2	0.25	0.1	0 44	whole plant grain straw	2.1 <0.05 0.77	96/07796-DIV
1982	SC	1	0.18	0.015	35	grain straw	0.01 0.90	A24446
	SC	1	0.18	0.015	0 25 57 57	whole plant whole plant grain straw	5.5 0.07 0.03 0.1	A24447
1983	SC	1	0.25	0.0625	0 21 35 72 72 56	whole plant whole plant whole plant whole plant grain straw	4.1 0.28 0.14 <0.01 0.29 0.36	A28197
	SC	1	0.258	0.063	0 21 35 72 72 56	whole plant whole plant whole plant grain straw straw	3.1 0.2 0.12 <0.01 0.2 0.18	A28201
1984	WP	1	0.198	0.0495	0 28 56 56 56 73	whole plant whole plant ear grain straw straw	5.7 0.1 <0.02 <0.02 0.2 0.3	A3009
	WP	1	0.196	0.049	0 28 56 56 73 73	whole plant whole plant ear straw grain straw	7.1 0.2 <0.02 0.2 <0.02 0.2	A31542
1986	EC	2	0.08/0.1	-	44	grain	0.05	A52961
	EC	2	0.08	0.04	69	grain	<0.05	
	EC	2	0.08	0.04	63	grain	<0.05	
	EC	1	0.08	0.04	88	grain	<0.05	
	EC	1	0.08	0.04	77	grain	<0.05	
	EC	1	0.08	0.04	65	grain	<0.05	
	EC	1	0.15	-	0 21 42 56 56 71 71	whole plant whole plant whole plant ears plant grain straw	5.0 0.20 0.10 <0.05 0.06 0.05 0.11	A52962

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	Kg ai/hl				
	EC	1	0.15	0.375	0 21 42 56 56 80 80	whole plant whole plant whole plant ears stalks grain straw	2.9 0.21 0.1 <0.05 <0.05 <0.05 0.06	A52963
1988	WP	1	0.175	0.04	0 22 42 56 56 56 70	whole plant whole plant whole plant ears stalks grain straw	2.0 0.64 0.14 0.09 0.77 0.05 <0.05	52960
Italy A58408 1996 Turin	SC	2	0.25	0.1	0 37 37	whole plant grain straw	1.1 0.18 1.3	96EZI0201PE
Spain A58408 1996 Valencia	SC	2	0.25	0.1	0 35 35	whole plant grain straw	3.6 0.81 3.8(2)	96EZI0301PE
Albacete	SC	2	0.25	0.1	0 35 35	whole plant grain straw	1.7 0.10 0.58	96EZI0401PE
UK A58409 1996 Wilson	SC	2	0.25	0.1	0 42 42	whole plant grain straw	1.5 0.29 0.98	AS/344/IF
A67186 1997 Hants	SC	2	0.245-0.26	-	0 45 45	whole plant grain straw	5.5 ≤0.05 0.54	FTU/00/001-2

Maize. In six trials in France in 1988 at the GAP rate (0.18 kg ai/ha) or lower residues in the kernels after 10 to 31 days were <0.05 mg/kg (Table 24). The submitted labels do not specify the PHI or number of applications.

Table 24. Results from residue trials in France on maize with an SC formulation.

Application			PHI, days	Sample	Residues, mg/kg	Trial reference
No	kg ai/ha	kg ai/hl				
1	0.1	0.025	14 28	kernels	<0.05 <0.05	Josse
1	0.21	0.0525	14 18	kernels	<0.05 <0.05	Josse
1	0.107	0.027	10 30	kernels	<0.05 <0.05	Lamont
1	0.21	0.0525	10 30	kernels	<0.05 <0.05	Lamont
1	0.11	0.025	15 31	kernels	<0.05 <0.05	Lacguy
1	0.21	0.0525	15	kernels	<0.05	Lacguy

Application			PHI,	Sample	Residues,	Trial
No	kg ai/ha	kg ai/hl	days		mg/kg	reference
			31		<0.05	

Wheat. 36 trials were conducted in Germany from 1980 to 1997, where GAP is either two applications of 0.12 kg ai/ha and a PHI 42 days or 1 application of 0.18 kg ai/ha and a PHI of 56 days. Most of the trials were at higher rates and/or samples were not taken at the recommended PHI. In five trials with 1-3 applications of 0.25 kg ai/ha, the residues in grain after 42-56 days were <0.01 to 0.05 mg/kg. In six trials according to GAP, residues in the straw and stalks were <0.03 to 0.2 mg/kg at a PHI of 56 days.

Seven trials in France, three in Italy and one in Spain were at higher rates than GAP (one application of 0.12-0.2 kg ai/ha). Residues in the grain after 31-42 days were at or below the LOD (<0.05 mg/kg) and in the straw from <0.05 to 5.3 mg/kg. In the UK, where 1 or 2 applications up to 0.28 kg ai/ha can be used, in one trial according to GAP residues in the grain and straw were <0.05 and 0.66 mg/kg at a PHI of 42 days. In two trials, one at a higher and the other at a lower rate than GAP, residues in the grain after 25 days were <0.1 mg/kg (Table 25).

Table 25. Results of supervised trials on wheat.

Country Report No. Year	Application				PHI,	Sample	Residues,	Trial
	Form.	No	kg ai/ha	kg ai/hl	days		mg/kg	Reference
France A58406 1996 Crest	SC	3	0.25	0.1	0 34 34	whole plant grain straw	2.9 <0.05 0.38	96EZ10202P E
Saint Quentin	SC	3	0.25	0.1	0 34 34	whole plant grain straw	2.5 <0.05 0.51	96EZ10102P E
A58407 1996 Inchy-en-Artois	SC	3	0.25	0.1	0 45 45	whole plant grain straw	1.4 <0.05 0.74	X966201
Aire	SC	3	0.25	0.1	0 42 42	whole plant grain straw	2.1 <0.05 5.3	X96202
A59515 1997 Ile de France	SC	3	0.25		0 42 42	shoot grain straw	2.2 <0.05 <0.05	FRA0001
1997 A59514 Poitou-	SC	3	0.25		0 35 35	shoot grain straw	2.6 <0.05 0.69	FRA00 01
Charentes	SC	3	0.25		0 35 35	shoot grain straw	2.3 <0.05 0.66	FRA00 02
German A53863 1980	SC	1	0.216	0.09	110	grain	<0.05	A20790
	SC	1	0.216	0.09	95	grain	<0.05	A20791
	SC	1	0.216	0.09	97	grain	<0.05	A20792
	SC	1	0.216	0.09	103	grain	<0.05	A20793
	SC	1	0.216	0.09	100	grain	<0.05	A20794
	SC	1	0.216	0.09	106	grain	<0.05	A20795
	SC	1	0.216	0.09	102	grain	<0.05	A20796
	SC	1	0.216	0.09	119	grain	<0.05	A20797
	SC	1	0.216	0.09	95	grain	<0.05	A20798
1983	SC	1	0.252	0.063	0	shoot	6.1	A28203

Country Report No. Year	Application				PHI, days	Sample	Residues, mg/kg	Trial Reference
	Form.	No	kg ai/ha	kg ai/hl				
					21	shoot	0.17	
					35	shoot	0.06	
					56	shoot	0.28	
					72	grain	<0.01	
					56	straw	0.23	
	SC	1	0.252	0.063	0	shoot	8.2	A28202
					21	shoot	1.4	
					35	shoot	0.26	
					56	grain	<0.01	
					56	straw	1.2	
	SC	2	0.145/0.18	0.045	0	shoot	4.2	A30361
					36	shoot	0.2	
					62	ears	<0.02	
					62	straw	<0.01	
					100	grain	0.02	
					100	straw	<0.01	
					171	plant	1.2	
					171	shoot	0.2	
	SC	2	0.18/0.145	0.045	223	shoot	4.1	A30360
					259	shoot	0.3	
					285	ears	<0.02	
					285	straw	0.01	
					323	grain	<0.01	
					323	straw	<0.01	
	SC	1	0.25	0.0625	0	shoot	7.5	A28198
					21	shoot	1.4	
					35	shoot	0.05	
					56	grain	<0.01	
					56	straw	0.46	
	SC	1	0.25	0.0625	0	shoot	17	A28199
					21	shoot	0.32	
					35	shoot	0.07	
					56	shoot	0.26	
					72	grain	<0.01	
					72	straw	0.11	
1984	WG	1	0.198	0.0495	0	shoot	9.6	A30171
					28	shoot	0.2	
					56	ear	<0.02	
					56	straw	<0.03	
					109	grain	<0.02	
					109	straw	<0.03	
	WG	1	0.198	0.06	0	shoot	9.6	A30172
					29	shoot	0.1	
					56	ear	<0.02	
					56	straw	<0.03	
					114	grain	<0.02	
					114	straw	<0.03	
	WP	1	0.196	0.049	0	shoot	11	A30173
					28	shoot	0.07	
					56	ear	<0.02	
					56	straw	<0.03	
					109	grain	<0.02	
					109	straw	<0.03	
	WP	1	0.196	0.049	0	shoot	8.6	A30174
					29	shoot	0.05	
					56	ear	<0.02	

Country Report No. Year	Application				PHI, days	Sample	Residues, mg/kg	Trial Reference
	Form.	No	kg ai/ha	kg ai/hl				
					56 114 114	straw grain straw	<0.03 <0.02 <0.03	
1986	EC	3	0.1-0.125	0.05/0.04	75 144	grain	<0.05; 0.07 <0.05	A52961
	EC	3	0.1-125	0.05/0.04	67 113	grain	<0.05 (2) <0.05	A52961
	EC	1	0.15	0.375	0 22 42 56 56 87 87	shoot shoot shoot ears stalks grain straw	7.2 0.33 0.08 0.06 <0.05 <0.05 0.11	A52961
	EC	1	0.15	-	0 21 42 77 77	shoot shoot shoot grain straw	5.5 0.13 0.07 <0.05 0.12	A52961
1988	WG	1	0.175	0.04	0 21 42 56 56 98 98	shoot shoot shoot ears stalks grain straws	13 2.4 0.34 <0.05 0.2 <0.05 0.11	52960
1989	SC	1	0.18	0.06	0 44 56 56 108 108	shoot shoot ears shoot grain straw	5.7 0.04 <0.02 <0.02 <0.02 <0.02	A44093
	SC		0.18	0.06	0 39 56 56 98 98	shoot shoot ear shoot grain straw	3.5 <0.02 <0.02 <0.02 <0.02 <0.02	A44094
	SC	1	0.18	0.06	0 52 63 120 120	shoot shoot shoot grain straw	8.6 <0.02 <0.02 <0.02 <0.02	A44095
	SC	1	0.18	0.06	0 41 49 56 56 108 108	shoot shoot shoot ear shoot grain straw	6.8 0.11 0.05 <0.02 0.05 <0.02 <0.02	A44096
	WG	1	0.18	0.06	0 44 56 56 108	shoot shoot ear shoot grain	6.7 0.16 <0.02 <0.02 <0.02	A44097

Country Report No. Year	Application				PHI, days	Sample	Residues, mg/kg	Trial Reference
	Form.	No	kg ai/ha	kg ai/hl				
					108	straw	<0.02	
	WG	1	0.18	0.06	0 39 56 56 56 98 98	shoot shoot ear shoot shoot grain straw	4.6 0.09 <0.02 <0.02 <0.02 <0.02 <0.02	A44098
	WG	1	0.183	0.061	0 52 63 120 120	shoot shoot shoot grain straw	10 0.18 0.03 <0.02 <0.02	A44099
	WG	1	0.18	0.06	0 41 49 56 56 108 108	shoot shoot shoot ear shoot grain straw	10 0.21 0.07 <0.02 0.03 <0.02 <0.02	A44100
A58407 1996	SC	3	0.25	0.1	0 45 45	whole plant grain straw	2.2 0.05 0.33	96/07798-D-IV
A59515 1997 Bayern	SC	3	0.25		0 42 42	shoot grain straw	4.0 <0.05 0.15	DEU0301
Hessen	SC	3	0.25		0 42 42	shoot grain straw	4.9 <0.05 0.11	DEU0401
Nordrhein-Westfalen	SC	3	0.25		0 42 42	shoot grain straw	3.3 <0.05 0.19	DEU0501
Italy A58406 1996 Govone	SC	3	0.25	0.1	0 31 31	whole plant grain straw	2.4 0.05 0.39	96EZ10302PE
A59514 1997 Emilia	SC	3	0.25		0 35 35	shoot grain straw	1.4 <0.05 0.42	ITA00 01
Romagna	SC	3	0.25		0 35 35	shoot grain straw	2.1 <0.05 0.40	ITA00 02
Spain A58406 1996 Albacet	SC	3	0.25	0.1	0 35	whole plant grain straw	2.1 <0.05 0.66	96EZ10402PE
UK A53863	WP	2	0.0336	0.075	25	grain	<0.1	A01587
1973	WP	2	0.672	0.15	25	grain	<0.1	A01588
A58407 1996 Wilson	SC	3	0.25	0.1	0 42 42	whole plant grain straw	1.7 <0.05 0.66	AS/3323/IF

Rye. Four of six trials in Germany were at the GAP rate (0.12-0.18 kg ai/ha) but in none was the grain harvested at the GAP PHI (56 days). In two of the trials the residues in the stalks after 56 days were 0.33 and <0.05 mg/kg (Table 26).

Table 26. Results from residue trials in Germany on rye.

Application				PHI, days	Sample	Residues, mg/kg	Trial reference
Form.	No	kg ai/ha	kg ai/hl				
SC	1	0.18	0.045	0	whole plant	13	A24448
				19	whole plant	0.4	
				36	ear	0.1	
				75	grain	<0.01	
				75	straw	0.08	
SC	1	0.252	0.063	0	whole plant	3.1	A28200
				19	whole plant	0.45	
				34	whole plant	0.26	
				90	grain	<0.01	
				90	straw	0.13	
SC	1	0.25	0.0625	0	whole plant	3.7	A28196
				19	whole plant	0.75	
				34	whole plant	0.41	
				90	grain	<0.01	
				90	straw	0.43	
WG	1	0.175	0.04	0	whole plant	6.2	A52960
				21	whole plant	0.56	
				42	whole plant	0.34	
				56	ears	0.05	
				56	stalks	0.33	
				94	grain	<0.05	
				94	stalks	<0.05	
EC	1	0.15	0.375	0	whole plant	4.5	A52962
				22	whole plant	0.22	
				42	whole plant	0.15	
				56	whole plant	0.06	
				56	ears	<0.05	
				83	grain	<0.05	
				83	stalks	0.05	
EC	1	0.15	0.375	0	whole plant	5.1	A52963
				21	whole plant	0.51	
				42	whole plant	0.14	
				56	ears	<0.05	
				56	stalks	0.05	
				120	grain	<0.05	
				12	straw	0.05	

Rape seed. The recommended rate in France with the SC 50 formulation is one application of 0.5 kg ai/ha and a PHI of 45 days. Four trials in France at about the recommended rate for the SC/EC 8 formulation (0.12 kg ai/ha) gave residues of <0.05 mg/kg in the seed after 60-76 days. In one trial at the same rate (unspecified PHI) the residue was 0.09 mg/kg and in another at a lower rate <0.05 mg/kg. In Germany, 10 trials were at or near the recommended rate (one application, 0.36 kg ai/ha) and three trials were at a higher rate. The residues in the pods, shoots and seed were <0.02 mg/kg at PHIs of 56 or more days (Table 27).

Table 27. Results from residue trials on rape.

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	kg ai/hl				
France A53866 1986	SC	1	0.08	0.02	60	seed	<0.05	A52964
Dampiere-et- Flay	SC	1	0.1	0.025	60	seed	<0.05	A52964
Mery en Bois	SC	1	0.125	0.089	76	seed	<0.05	A52964
	SC	1	0.1	0.071	76	seed	<0.05	A52964
Chateauvillain	SC	1	0.125	-	-	seed	0.09	A52964
Hilaire le Grand	SC	1	0.1	0.027	78	seed	<0.05	A52964
Germany A53866 1984	WP	1	0.297	0.0743	65 83	pod seed	<0.02 <0.02	A30362
	WP	1	0.297	0.0743	62 82	pod seed	<0.02 <0.02	A30363
	WP	1	0.297	0.0743	62 82	pod seed	<0.02 <0.02	A30364
	WP	1	0.594	0.1485	65 83	pod seed	<0.02 <0.02	A30365
	WP	1	0.594	0.1485	62 82	pod seed	<0.02 <0.02	A30366
	WP	1	0.594	0.1485	65 83	pod seed	<0.02 <0.02	A30367
1985	SC	1	0.36	0.09	0 28 56 56 76	shoot shoot pod shoot seed	6.2 <0.02 <0.02 <0.02 <0.02	A36445
	SC	1	0.36	0.09	0 28 56 56 73	shoot shoot pod shoot seed	5.2 <0.02 <0.02 <0.02 <0.02	A36446
	SC	1	0.36	0.09	0 28 56 56 84	shoot shoot pod shoot seed	6.1 <0.02 <0.02 <0.02 <0.02	A36447
	SC	1	0.36	0.09	0 28 56 56 77	shoot shoot pod shoot seed	6.6 0.11 <0.02 <0.02 <0.02	A36448
	SC	1	0.36	0.09	0 28 56 76	shoot shoot shoot seed	3.8 2.1 0.08 <0.02	A36449
1987	SC	1	0.36	0.09	0 28 56 56 86	shoot shoot pod shoot seed	4.6 0.1 <0.02 <0.02 <0.02	A38137
	SC	1	0.36	0.09	0 28 56 56 90	shoot shoot pod shoot seed	6.4 0.25 <0.02 0.11 <0.02	A38138
	SC	1	0.36	0.09	0	shoot	7.9	A38139

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	kg ai/hl				
					31 56 56 62	shoot pod shoot seed	0.04 ≤0.02 <0.02 <0.02	
	SC	1	0.36	0.09	0 28 56 56 71	shoot shoot pod shoot seed	6.3 0.31 ≤0.02 0.07 <0.02	A38140

Coffee. In one trial in Brazil at a higher application rate than recommended GAP (1-2 applications, 0.12-0.16 kg ai/ha) and in six trials in Kenya (no GAP reported) the residues in the beans after 44-81 days were below the limit of determination of 0.1 mg/kg (Table 28).

Table 28. Results from residue trials on coffee.

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	kg ai/hl				
Brazil A02025 1972/73 São Paulo	SC	5	0.5	0.0874	69	beans	<0.1	A02025
Kenya 1972	WP	7	1.17	0.09	44	beans	<0.1	A01028
A01029	WP	6	0.66	0.06	69	beans	<0.1	A01029
A01030	SC	7	0.66	0.045	45	beans	<0.1	A01030
A01031	WP	6	0.58	0.06	81	beans	<0.1	A01031
A01032	SC	7	1.04	0.08	45	beans	<0.1	A01032

Hops, dry. Four trials on Hallertau hops in Germany in 1972 were with 2 applications of 0.225 or 0.38 kg ai/ha of WP formulation. The hops were harvested, dried and analysed. Residues at PHIs of 17 or 26 days were 16, 18, 29 and 49 mg/kg. Residues on the hops before drying were not reported. No information on GAP was provided to evaluate the trials.

Food of animal origin

Dairy cows were fed either carbendazim (Hughes and McIntosh, 1985) or benomyl (Kirkland and Pease, 1970) at levels of 2, 10, or 50 ppm of each substance/kg in the diet for four weeks. Samples of milk collected during treatment and at slaughter and of tissues at slaughter were analysed for benomyl, carbendazim, 4-HBC and 5-HBC. No benomyl residues were found in samples of lean muscle, liver, kidney or fat (Kirkland and Pease, 1970). In the study by Hughes and McIntosh, low-level residues of 5-HBC were observed in the liver (0.01 mg/kg) and kidneys (0.06 mg/kg) of cows in the group receiving 50 ppm carbendazim. However residues of this compound were also apparent in a kidney sample in the control group. One week after the end of treatment with the test material no residues were detectable in any tissue sample. Quantifiable residues in milk were observed in cows whose feed contained 10 ppm or

more. Residues reached a maximum at three weeks and were mainly 5-HBC and 4-HBC. No carbendazim was observed in the milk. Residues were below the limit of determination within two days after the test material was removed from the diet (Table 29). Residues in the cream and skimmed milk were similar to those in whole milk.

Table 29. Average residues in the milk from cows fed either carbendazim or benomyl at levels higher than 10 ppm in the diet.

Day	5-HBC, mg/kg	4-HBC, mg/kg	Equivalent mg carbendazim/kg
3	0.05	0.02	0.07
7	0.05	0.03	0.07
14	0.05	0.03	0.07
21	0.06	0.04	0.08
28	0.06	0.04	0.09
D1[1]	0.02	<0.01	0.02
D2	<0.01	<0.01	<0.007
D7	<0.01	<0.01	<0.007

[1]D refers to the decline phase after removing test material from diet, and the number following is the number of days after removal of test material.

In a study by Johnson (1988) benomyl residues in goat liver reached equilibrium within two weeks at a concentration equivalent to 9.48 mg carbendazim/kg, which was less than 1% of the total administered dose.

In four poultry studies laying hens were fed for 28 days with carbendazim at levels from 5 to 100 mg/kg diet (Singh *et al*., 1985; Hollander *et al*., 1977) or benomyl at levels of 5 to 450 mg/kg diet (Blanchfield *et al*., 1973; Kivimäe, 1971). Eggs were collected during treatment and at slaughter and fat, liver, kidneys and thigh meat at slaughter. The samples were analysed for carbendazim, 4-HBC and 5-HBC. Residues in the tissues were at or below the limit of determination (0.02-0.05 mg/kg). The maximum residues in eggs found during the treatments are shown in Table 30. In all the studies, the residues in whole eggs decreased to below detection levels after the treatment was withdrawn. Singh *et al*. (1985) found that egg yolks contained two to four times the residues in egg whites, reaching 0.12 and 0.42 mg/kg of carbendazim and 5-HBC after three weeks of treatment.

Table 30. Residues in eggs from hens feed with carbendazim or benomyl.

Dietary concentration , mg/kg	Carbendazim, mg/kg	4-HBC, mg/kg	5-HBC, mg/kg	Ref.
5 [a] 15 100	<0.05 <0.05 <0.05-0.1	<0.05 <0.05 <0.05	<0.05 <0.05 <0.05-0.36	Singh *et al.*, 1985
10 [a]	<0.05	NA	NA	Hollander *et al.*, 1977
5 [b] 25	<0.02 <0.02	<0.02 <0.02	<0.02 0.03-0.06	Blanchfield *et al.*, 1973
230[b] 450	0.07 0.18	<0.04 <0.04	0.26 1.0	Kirvimäe, 1971

a. carbendazim; b. benomyl NA = not analysed

Exposure of cattle and poultry to benomyl/carbendazim

A discussion of the maximum potential exposure of cattle and poultry to residues in the crops on which benomyl is used in the European Union was submitted. The percentage dry matter and the maximum percentage of each commodity in the diet obtained from the revised Livestock Feeds Tables published by the US EPA in June 1994 (Saito and Zager, 1994b) are shown in Table 31. No information on metabolism was available on the crop commodities and fractions listed in Table 31, but the residue data indicate clearly that carbendazim is the major, if not the only, residue of benomyl present in them.

Table 31. Livestock feed commodities relevant to benomyl in the EU.

Commodity	% dry matter	Maximum % in diet of		
		Beef cattle	Dairy Cattle	Poultry
Apple pomace, wet	40	40	20	0
Citrus molasses	68	10	15	0
Citrus pulp, dry	91	25	20	0
Citrus pulp, wet	21	40	30	0
Grape pomace, dry	89	20	0	0
Grape pomace, wet	15	20	0	0
Grape raisin culls	85	25	20	0
Grape raisin waste	79	25	0	0
Tomato pomace, dry	92	25	10	10
Tomato pomace, wet	15	30	20	0

The residue intake was calculated according to the method outlined by the US EPA (Saito and Zager, 1994a, Lundehn 1993). The residue burden in the relevant raw agricultural commodity (RAC) was determined either from a JMPR MRL recommendation (e.g. pome fruit) or from an estimated maximum residue level calculated from residue data collected by the registrant from treatments in accordance with GAP and the appropriate processing factor applied. In the cases where processing included drying the MRL value in the calculation was multiplied by the ratio of the dry matter content of the dried commodity to that of the fresh or wet commodity. This assumed that all the residue stayed with and was stable in the dry matter. For instance, wet citrus pulp was assumed to have the same maximum residue level as that propoesd for whole citrus by the manufacturer, 3 mg/kg. This commodity contains 21% dry matter, whereas dry citrus pulp contains 91% dry matter. Therefore, the maximum residue level for dry citrus pulp was calculated as 3 mg/kg x 91/21 = 13 mg/kg. These assumptions produced the highest theoretical residues in animal feed for the commodities listed in Table 32.

Table 32. Maximum potential residues (as benomyl) in feed components.

Commodity	Maximum residue, mg/kg	mg-benomyl/day		
		Beef cattle	Dairy cattle	Poultry
Apple pomace, wet[1]	2.0	30	20	0
Citrus molasses[3]	10	21	43	0
Citrus pulp, dry[3]	13	54	57	0
Citrus pulp, wet[2]	3.0	86	86	0
Grape pomace, dry[3]	18	60	0	0
Grape pomace, wet[2]	3.0	60	0	0
Grape raisin culls[3]	17	75	80	0
Grape raisin waste[3]	16	75	0	0
Tomato pomace, dry[3]	18	75	40	0.24

Commodity	Maximum residue, mg/kg	mg-benomyl/day		
		Beef cattle	Dairy cattle	Poultry
Tomato pomace, wet[2]	3.0	90	80	0

[1]Estimated by JMPR
[2]Proposed by manufacturer
[3]Derived from proposed MRL adjusted for dry matter content

The theoretical intakes for poultry and cattle shown in Table 33 were calculated using data from Tables 31 and 32. Residues in meat and other animal products derived from these intakes would be the maximum expected residue levels.

Table 33. Theoretical dietary intakes of benomyl in example diets.

Livestock	Item	% in diet	mg benomyl per day	mg/kg diet*
Beef cattle	Citrus pulp, wet	40	86	
	Tomato pomace, wet	30	90	
	Grape raisin culls	25	75	
	Grape raisin waste	5	15	
	Total	100	266	18
Dairy cattle	Citrus pulp, wet	30	86	
	Citrus pulp, dry	20	57	
	Grape raisin culls	20	80	
	Tomato pomace, wet	20	80	
	Tomato pomace, dry	10	40	
	Total	100	343	17
Poultry	Tomato pomace, dry	10	0.24	2.0

*Daily food consumption was assumed to be 14, 20 and 0.12 kg dry matter/day for beef cattle, dairy cows and poultry respectively.

Maximum residue levels of benomyl in food of animal origin were calculated by multiplying the dietary concentrations in Table 33 by the residue transfer coefficients (RTCs). Each RTC is the average of RTCs derived from the highest dietary concentrations administered in the cow and poutry feeding studies (Hughes and McIntosh, 1985; Kirkland and Pease, 1970; Singh *et al*., 1985; Blanchfield *et al*., 1973). For commodities with residues <LOD, the residues were taken to be at the LOD.

Table 34. Calculated maximum residue levels of benomyl, expressed as carbendazim.

Livestock	Commodity	RTC	Benomyl in diet, mg/kg	Maximum residue level
Cattle	Whole milk	0.0034	17	0.038
	Cream	0.0021	17	0.024
	Skimmed milk	0.0023	17	0.025
	Edible muscle	0.0034	18	0.040
	Edible offal	0.0034	18	0.040
Poultry	Whole egg	0.0043	2.0	0.0056
	Egg yolk	0.0055	2.0	0.0072
	Egg white	0.0018	2.0	0.0024
	Edible muscle	0.0012	2.0	0.0016
	Edible offal	0.0015	2.0	0.0020

	Fat	0.0012	2.0	0.0016

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

No information.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Tables 35 and 36 show data on carbendazim residues in the UK found during government monitoring in 1994 and 1995, the two most recent years for which the data have been published (Ministry of Agriculature, Fisheries and Food and Health and Safey Executive, 1995, 1996). Fruit and fruit products, celery and lettuce were the only commodities in which carbendazim was detected, apple being the commodity with the highest number of positive results.

Table 35. Residues of carbendazim in food found in monitoring in the UK in 1994.

Commodity	Reporting LOD, mg/kg	MRL	Samples					
			UK origin		Imported		Unknown origin	
			No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)
Bread	0.05	-	255	-	2	-	4	-
Potato	0.1	-	174	-	24	-	20	-
Apple	0.2	5	31	23 (0.2-2.7)	42	6 (0.2-0.8)	-	-
Apple juice	0.2	-	31	9 (0.2-0.7)	9	-	4	-
Artichoke	0.2	-	1	-	19	-	2	-
Asparagus	0.1	-	6	-	20	-	-	-
Beans, broad	0.05	-	14	-	1	-	1	-
Blackcurrant	0.1	5	18	1 (0.5)	1	-	4	-
Blackcurrant-based drinks	0.1	-	8	-	-	-	20	-
Chinese cabbage	0.2	-	13	-	10	-	2	-
Infant food, fruit-based	0.2	-	32	3 (0.3-0.5)	21	4 (0.2-0.4)	-	-
Lettuce	0.2	5	53	3 (0.2-1.2)	30	1 (0.3)	-	-
Onion	0.05	-	35	-	12	-	2	-
Peas, frozen	0.1	-	14	-	4	-	6	-
Plum	0.1	2	1	-	39	5 (0.2-0.9)	1	2 (0.4-0.6)
Pumpkin	0.1	-	2	-	-	-	-	-
Squash	0.1	-	2	-	15	-	7	-
Strawberry	0.1	-	28	-	15	4 (0.1-0.6)	-	1 (0.2)
Wheat bran	0.05	-	12	-	-	-	-	-
Wheat germ	0.05	-	6	-	-	-	-	-

Table 36. Residues of carbendazim in food found in monitoring in the UK in 1995.

Commodity	Reporting LOD, mg/kg	MRL	Samples					
			UK origin		Imported		Unknown origin	
			No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)
Bread	0.05	-	239	-	-	-	-	-
Potato	0.1	-	170	-	28	-	12	-
Apple	0.3	-	19	7 (0.5-1.1)	47	-	-	-
Carrot	0.05	-	63	-	2	-	7	-
Celery	0.3	2	11	1 (0.7)	36	1 (0.6)	-	-
Courgette	0.2	-	9	-	9	-	6	-
Grape, dessert	0.3	10	-	-	54	3 (0.4-0.8)	-	-
Infant food, fruit-based	0.05	-	28	-	27	-	5	-
Kiwi	0.1	-	-	-	36	-	-	-
Loganberry	0.2	-	-	-	11	-	-	-
Marmalade	0.05	-	27	1 (0.1)	1	-	19	-
Okra	0.1	-	-	-	24	-	-	-
Orange	0.1	-	-	-	72	-	-	-
Pear	0.3	-	11	2 (0.5-0.9)	31	1 (0.4)	4	-
Pepper, sweet	0.1	-	12	-	33	-	5	-
Persimmon	0.05	-	-	-	24	-	-	-
Pomegranate	0.1	-	-	-	23	-	-	-

Commodity	Reporting LOD, mg/kg	MRL	Samples					
			UK origin		Imported		Unknown origin	
			No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)
Sweet potato	0.1	-	-	-	26	-	-	-
Tomato	0.05	-	15	-	27	-	6	-
Flour (various)	0.05	-	52	-	1	-	7	-
Infant food, cereal-based	0.05	-	78	-	35	-	7	-

Table 37 shows monitoring data generated by the food industry in the UK for commodities in which residues of carbendazim above the limit of determination were found. It is not clear from the report how many crops were analysed for carbendazim. As in the government data fruit was the commodity in which residues of carbendazim were most frequently found.

Table 37. Monitoring data on carbendazim generated by the food industry in 1995.

Commodity	No.	No. >LOD (mg/kg)	MRL, mg/kg
Apple/apricot conserve	1	1 (0.16)	-
Banana	20	4 (0.29-0.38)	1
Banana conserve	1	1 (0.16)	-
Apple	4	1 (0.44)	2
Cabbage	3	2 (0.6-1.5)	-
Grape, white	6	1 (1.0)	-
Orange	1	1 (1.9)	-
Pineapple	1	1 (0.2)	0.1

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country	Commodity	MRL, mg/kg
Australia	Citrus, ginger root, litchi, mushrooms, stone fruits	10
	Berries and other small fruits (except grape), mango, pome fruit	5
	Wine grapes, avocado, vegetables (except fruiting vegetables, curcubits, fruiting vegetables)	3
	Fruiting vegetables (except mushrooms), curcubits	2
	Banana	1
	Edible offal (mammalian), mammalian meat, peanut	0.2
	Sugar cane,	0.1
	Eggs, milks, poultry meat, poultry eligible offal,	0.1*
	Cereal grain	0.05*
Austria	Citrus	7
	Table grapes, wine grapes	3
	Pineapple, pome fruits	2
	Small fruits	1.5
	Other vegetables, citrus (without peel), banana	1
	Cereals, cucumber	0.5
	Banana (without peel)	0.2
	Other foodstuffs	0.1
Belgium	Citrus	4

Country	Commodity	MRL, mg/kg
	Potato	3
	Other vegetables, other fruit	2
	Cereals, mushrooms, cucumber (inc. cornichons), melon, sweet pepper	0.5
	Escarole	0.3
	Other foodstuffs	0.1
Brazil	Cucumber	0.5
Canada	Peach, citrus	10
	Raspberry, blackberry, loganberry	6
	Carrot, plum, sweet cherry, wine grapes, apricot, mushrooms, sour cherry,	5
	Pear,. Apple, strawberry	5
	Tomato	2.5
	Pineapple (without peel), bean	1
	Pumpkin, melon, cucumber, summer squash	0.5
Chile[1]	Wine grapes, citrus, peach	10
	Tomato, pear, apple, lettuce,	5
	Plum (dried), plum, bean	2
	Rice, rye, barley, wheat	0.5
	Potato, sugar beet	0.1
Denmark	Stone fruits, pome fruits, small fruits, citrus, carrot, leaf, stem vegetables	5
	Other fruit, other vegetables	2
	Mushrooms	1
	Cereals, other root vegetables, almond, other nuts, potato, onion	0.1
Finland[3]	Citrus, boysenberry	2
	Apple, pear	1
	Other foodstuffs	0.5
France	Other fruit, other vegetables	2
	Banana (whole fruit), mushrooms (champignon de couche), peach	1
	Banana (without peel), cereals	0.5
	Hop, rape, potato,	0.1
	Pea	0.05
Germany	Citrus	7
	Wine grapes	3
	Pome fruits, pineapple	2
	Small fruits	1.5
	Citrus (juice), banana, other vegetables,	1
	Cereals, cucumber,	0.5
	Banana (without peel)	0.2
	Other foodstuffs	0.1
Hungary	Sweet pepper, red currant, gooseberry, lettuce, strawberry, apple, raspberry, black currant, pear, celery, garden parsley, apricot, sweet cherry, sour cherry, sorrel, common, spinach,	2
	Wine grapes, onion (green), horseradish, watermelon, carrot, melon, pumpkin, radish, Nectarine, peach, sugar beet	1
	Cereals (grain), rice (grain), sorghum, common (grain), maize (grain)	0.5
Israel	Tomato, pear, strawberry, sugar beet (leaves), sweet pepper,	5
	Barley (straw), mango, pea, peanut, plum, celery	2
	Mushrooms, banana, almond	1
	Other cereals, eggplant, avocado, watermelon, melon, cucumber, pumpkin	0.5
	Peanut, pecan nut, sugar beet (beet), potato	0.1
Italy[2]	Pear, wine grapes, apple	1
	Stone fruits, wheat (grain)	0.5
Luxembourg	Wine grapes	3
	Other fruit, other vegetables	2
	Cereals, cucumber (inc. Cornichons),	0.5

Country	Commodity	MRL, mg/kg
	Other foodstuffs	0.1
Mexico	Pineapple (without peel)	35
	Citrus, wine grapes, grapefruit, lemon, orange, lime	10
	Pear	7
	Apple, head lettuce, sweet pepper, strawberry, tomato	5
	Avocado, celery, mango	3
	Bean, garlic	2
	Banana, cucumber, melon, summer squash, watermelon	1
	Pecan nut, eggplant	0.2
	Coffee (coffee beans)	0.1
Netherlands	Citrus	4
	Vegetables, potato, other fruit	3
	Mushrooms	0.5
	Cereals, other foodstuffs	0.1
New Zealand	Fruit	5
	Vegetables	2
	Cereals	1
South Africa	Citrus	5
	Pear, apple	3
	Peanut	0.1
Spain[2]	Citrus, blueberry, strawberry, dewberry, common, apricot, table grapes, wine grapes, cherry, lettuce, watercress, chicory, loganberry, raspberry, currant, gooseberry, peach, plum	5
	Pome fruits, celery, sweet pepper, Brussels sprouts, head cabbage, legumes (fresh/green), Tomato, broccoli, gherkin, cucumber, cauliflower, onion	2
	Olive, mushrooms, banana,	1
	Summer squash, barley (grain), eggplant, melon	0.5
	Soya bean	0.2
	Other food/foodstuffs of plant origin, nuts	0.1
Switzerland	Citrus	7
	Other fruit, tomato	3
	Wine grapes (wine), champignon	2
	Citrus (without peel), banana	1
	Cereals	0.3
	Bean, banana (without peel)	0.2
	Celeriac, sugar beet, rape, cucumber	0.1
Taiwan	Lemon, jujube, plum, apple (wax-apple), pineapple, banana, carambola, table grapes, apple,	2
	Strawberry, guava, wine grapes, kaki plum, papaya, pear, peach, loquat,	2
	Mango, lychee, leek, welsh onion, amaranth (edible), chives, asparagus, lettuce, garlic,	1
	Mustard, Chinese mustard, spinach, celery, garden parsley, Chinese cabbage, Swiss chard	1
	Rice, pea, bean, soya bean, mushrooms	0.5
Turkey	Apple, pear	2
UK	Nectarine, grapefruit, peach, mandarin, wine grapes, orange, lime, lemon, pear	10
	Lettuce, apple, strawberry, raspberry, currant, tomato, other leaf, stem vegetables	5
	Potato	3
	Celery, onion, plum	2
	Mushrooms, banana	1
	Wheat (grain), barley (grain), cucumber, Brussels sprouts, rye (grain), oat (grain)	0.5
Yugoslavia[4]	Citrus	7
	Other fruit	2
	Other vegetables, banana (without peel)	1
	Cereals, cucumber	0.5
	Other foodstuffs	0.1

[1]Sum of carbendazim and 2-aminobenzimidazole, calculated as carbendazim
[2]Sum of benomyl, carbendazim and 2-aminobenzimidazole, calculated as carbendazim
[3]Sum of benomyl, carbendazim, thiophanate-methyl, calculated as carbendazim
[4]BCM generators either alone or combined, calculated as carbendazim

APPRAISAL

See the monograph on benomyl. (See also that on thiophanate-methyl).

RECOMMENDATIONS

On the basis of the results of supervised residue trials the Meeting estimated the maximum residue levels and STMRs listed below, which also cover residues arising from the use of benomyl and thiophanate-methyl. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and the estimation of dietary intake: carbendazim.

Note. The recommendations cover carbendazim arising from the direct use of carbendazim or (as a metabolite and/or a hydrolysis product formed during analysis) from the use of benomyl or thiophanate-methyl.

Commodity		Recommended MRL, mg/kg		STMR, mg/kg
		New	Previous	
JF 0226	Apple juice			0.147 (B)
	Apple purée			0.282 (B)
	Apple sauce			0.078 (B)
FS 0240	Apricot	W	0.1 (B)	
VS 0621	Asparagus	W	0.1* (B)	
FI 0326	Avocado	W	0.5 (B)	
Fl 0327	Banana	0.2 (B)	1 Po (B,C,Th)	0.03 (B)
GC 0640	Barley	0.5 (C)	0.1 (C,Th)	0.05 (C)
AS 0640	Barley straw and fodder, dry	2 (C)	2 (B)	0.345 (C)
VD 0071	Beans (dry)	0.5 (Th)	2 (B)	0.165 (Th)
FB 0018	Berries and other small fruits	W	1 (B, Th)	
VP 0522	Broad bean (green pods and immature seeds)	W	2 (Th)	
VB 0402	Brussels sprouts	0.5 (B)	0.5 (B)	0.065 (B)
VR 0577	Carrot	0.2 (B)	-	0.04 (B)
MM 0812	Cattle meat	0.05* (B)	0.1* (B)	0 (B)
VS 0624	Celery	W	2 (B, C)	
GC 0080	Cereal grains	W	0.5[1] (B,C,Th)	
FS 0013	Cherries	W	2 (Th)	
PF 0840	Chicken fat	0.05* (B)	0.1* (Th)	0 (B)
SB 0716	Coffee beans	W	0.1* (C)	
VP 0526	Common bean (pods and/or immature seeds)	W	2 (B,C,Th)	
VC 0424	Cucumber	0.05* (B, C)	0.5 (B,C,Th)	0.03 (B) 0.05 (C)
MO 0105	Edible offal (Mammalian)	0.05* (B)	-	0 (B)
VO 0440	Egg plant	W	0.5 (C)	
PE 0112	Eggs	0.05* (B)	0.1* (B,Th)	0 (B)
VP 0529	Garden pea, shelled (succulent	0.02 (Th)	-	0.01 (Th)

		Recommended MRL, mg/kg		
	seeds)			
VC 0425	Gherkin	0.05* (B,C)	2 (C,Th)	0.03 (B) 0.05 (C)
FB 0269	Grapes	3 (B,Th)	1 (B,Th)	0.84 (B) 0.87 (Th)
DH 1100	Hops, Dry	W	50 (C)	
VL 0482	Lettuce, Head	W	5 (Th)	
FI 0345	Mango	W	2 (B)	
VC 0046	Melons, except Watermelon	W	2 Po (B,C)	
ML 0106	Milks	0.05* (B)	0.1* (B)	0 (B)
	Milk cream			0 (B)
VO 0450	Mushrooms	W	1 [2](Th)	
FS 0245	Nectarine	W	2 (B)	
GC 0647	Oats	W	0.1 (C)	
VA 0385	Onion, Bulb	W	2 (C,Th)	
FC 0004	Oranges, Sweet, Sour	1(B)	-	0.325 (B)
JF 0004	Orange juice			0.13 (B)
	Orange oil			0.442 (B)
FS 0247	Peach	2 (B)	2 (B)	0.255 (B)
SO 0697	Peanut	W	0.1* (B,C)	
AL 0697	Peanut fodder	W	5 (B,C)	
VO 0051	Peppers	W	0.1 (Th)	
FI 0353	Pineapple	5 (B)	-	0.03 (B)
FS 0014	Plums (including Prunes)	0.5 (B)	0.5 (Th)	0.06 (B)
FP 0009	Pome fruits	3 (B,C,Th)	2 (B,C,Th)	0.60 (B) 0.455 (C) 0.555 (Th)
VR 0589	Potato	W	3 Po (B,C)	
PM 0110	Poultry meat	0.05* (B)	0.1* (B,Th)	0 (B)
DF 5263	Raisins			1.09 (B)
	Raisin waste			3.44 (B)
SO 0495	Rape seed	0.05* (C)	0.1* (C)	0 (C)
CM 0649	Rice, husked	2 (B)	-	0.05 (B)
AS 0649	Rice straw and fodder, dry	15 (B)	15 (B,C,Th)	2.5 (B)
GC 0650	Rye	W	0.1 (C,Th)	
MM 0822	Sheep meat	W	0.1* (B)	
VD 0541	Soya bean (dry)	W	0.2 (C)	
AL 0541	Soya bean fodder	W	0.1* (C)	
VC 0431	Squash, Summer	W	0.5 (B)	
VR 0596	Sugar beet	W	0.1*(B,C,Th)	
AV 0596	Sugar beet leaves or tops	W	5 (B,Th)	
VR 0497	Swede	W	0.1* (C)	
VR 0508	Sweet potato	W	1 (B)	
VR 0505	Taro	W	0.1* (B)	
VO 0448	Tomato	0.5 (B,C)	0.1 (Th)	0.16 (C) 0.045 (B)
JF 0448	Tomato juice			0.012 (B)
	Tomato purée			0.030 (B)
	Tomato ketchup			0.028 (B)
	Tomato pomace, wet			0.013 (B)
	Tomato pomace, dry			0.022 (B)
TN 0085	Tree nuts	W	0.1* (B)	
GCO 654	Wheat	0.05* (B,Th)	0.1 (B,C,Th)	0.03 (B) 0.01(Th)

		Recommended MRL, mg/kg		
AS 0654	Wheat straw and fodder, dry	1 (B,C)	5 (B)	0.1 (B) 0.03 (C)
	Wine			0.445 (B)
VC 0433	Winter squash	W	0.5 (B)	

[1]To be replaced by MRLs for barley, oats, rye and wheat (1994 JMPR)

[2]Group MRL for berries and other small fruits

Letters in parentheses in columns 3 and 4 indicate the compounds for which sufficient data from trials complying with GAP were provided (B = benomyl; C = carbendazim; Th = thiophanate-methyl). Bold letters indicate the source(s) of the data on which the recommendation is based.
Letters in parentheses in column 5 indicate the compound to which the STMR applies. Recommendations cover carbendazim arising from the direct use of carbendazim or (as a metabolite and/or a hydrolysis product formed during analysis) from the use of benomyl or thiophanate-methyl.

DIETARY RISK ASSESSMENT

The residues of benomyl, carbendazim and thiophanate-methyl are all expressed as carbendazim, which has the lowest ADI of the three compounds. A total of 34 STMRs were estimated for benomyl, 8 for carbendazim and 5 for thiophanate-methyl. If STMRs were estimated for more than one compound in a commodity, the highest STMR was used for the calculation. No MRLs were used.

International Estimated Daily Intakes of benomyl, carbendazim and thiophanate-methyl for the five GEMS/Food regional diets were in the range of 1 to 6% of the carbendazim ADI.

The Meeting concluded that the intake of residues of benomyl, carbendazim and/or thiophanate-methyl resulting from their uses that have been considered by the JMPR is unlikely to present a public health concern.

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2,4-D (20)

EXPLANATION

2,4-D was first evaluated in 1970 (T, R), and the last evaluations are from 1986/87 (R) and 1996 (T). The 1997 JMPR evaluated effects on the environment.

2,4-D was proposed for re-evaluation by the Working Group on Priorities at the 1989 CCPR as the ADI was established before 1976 (ALINORM 89/24A, para 299 and Appendix V). It was stated at the 1990 CCPR that there was continued use and manufacturers might be able to submit data (ALINORM 91/24 para 360, Appendix V part I). The review was tentatively scheduled for 1994. The compound was later rescheduled to the 1996 JMPR, and then to the 1998 Meeting.

The present evaluation is within the CCPR Periodic Review Programme.

The members of the industry taskforce which supplied most of the information were AGRO-GOR, Dow Elanco, Nufarm and Rhône Poulenc, who provided data on metabolism and environmental fate, analytical methods, use patterns, residue trials and national MRLs. Information on residue analytical methods, GAP and national MRLs was also provided by the government of The Netherlands.

IDENTITY (Free acid)

ISO common name: 2,4-D
Chemical name

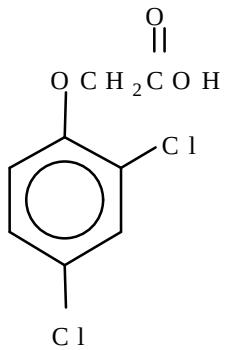
IUPAC: 2,4-dichlorophenoxyacetic acid

CA: (2,4-dichlorophenoxy)acetic acid

CAS Registry No.: 94-75-7

CIPAC No.: 1

Structural formula:



Molecular formula: $C_8H_6Cl_2O_3$

Molecular weight: 221.0

Physical and chemical properties

Pure active ingredient

Appearance: white to brown crystals, granules, flakes, powder or lumps

Vapour pressure: 1.9×10^{-5} Pa at 25°C (Chakrabarti and Gennrich, 1987a)

Melting point: 140.5°C

Octanol/Water partition coefficient at 25°C:
log P_{OW} = 2.7 at pH 1; 0.18 at pH 5; -0.83 at pH 7; -1.01 at pH 9
(Bailey and Hopkins, 1987)

Solubility: in water at 25°C (Hopkins,1987c)

pH 1 buffered	311 ± 4 mg/l
pH 5 buffered	20031± 1149 mg/l
pH 7 buffered	23180 ±590 mg/l
pH 9 buffered	34196 ± 1031 mg/l
pH 5 unbuffered	29934 ± 2957 mg/l
pH 7 unbuffered	44558 ± 674 mg/l
pH 9 unbuffered	43134 ± 336 mg/l

Hydrolysis: stable at pH 5, 7, 9 at 25°C (Anon. 1989a)

Photolysis: aqueous photolysis pH 7 $t_{1/2}$ = 13 days (Anon. 1989b)
soil photolysis very stable

Rate of dissociation: ~200 minutes at 25°C

Dissociation constant: pK_a 3 at 25.2°C (Reim, 1989a; Gallacher, 1991)

Thermal stability: stable at melting point

Technical material

Minimum purity: 96%

Main impurities:

water	1.5% max.
free phenols	0.3% max. (calculated as 2,4-dichlorophenol)
sulphated ash	0.5% max.
triethanolamine insolubles	0.1% max.

Melting range: 137-141°C

Stability: stable indefinitely

Formulations

Commercially available formulations: TC, WP, SP, WG. Also compounded as alkali metal salts, organic amines and esters.

IDENTITY (dimethylamine salt)

ISO common name: 2,4-D-dimethylamine

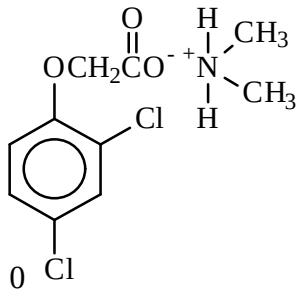
Chemical name
IUPAC: dimethylamine (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, dimethylamine salt

CAS Registry No.: 2008-39-1

CIPAC No.: 1

Synonyms: 2,4-D DMA

Structural formula:



Molecular formula: $C_{10}H_{13}Cl_2NO_3$

Molecular weight: 266.13

Physical and chemical properties

<u>Pure active ingredient</u>

Appearance: amber to brown liquid; white to brown crystals or powder

Vapour pressure: <1.33 x 10^{-5} Pa at 26°C (Douglas, 1993a; MacDaniel and Weiler, 1987)

Octanol/Water partition coefficient: refer to 2,4-D acid

Solubility (water: Hopkins, 1987a,b; organic solvents: Kinnunen, 1994a):

water	pH 5	320632 ± 3645 mg/l at 25°C
	pH 7	729397 ± 86400 mg/l at 25°C
	pH 9	663755 ± 94647 mg/l at 25°C
acetonitrile		1.02 g/100 ml at 20°C
methanol		>50 g/100 ml at 20°C
hexane		3.59 g/100 ml at 20°C
1-octanol		5.37 g/100 ml at 20°C
toluene		0.165 g/100 ml at 20°C

Specific gravity: 1.23 - 1.24 g/cm^3 at 20°C (Dow Chemical Co., 1989a)

Hydrolysis: refer to 2,4-D acid

Photolysis: refer to 2,4-D acid

Rate of dissociation: <1 minutes

Thermal stability: stable

pH: 6.8 -9

Technical material

Minimum purity: to be prepared from 2,4-D acid 96% min.

Main impurities: proportional to 2,4-D content except water

Melting range: 118–120°C ± 1°C (Murphy, 1993a)

Formulations

Commercially available formulations: TK, SL, SP.

IDENTITY (2-ethylhexyl ester)

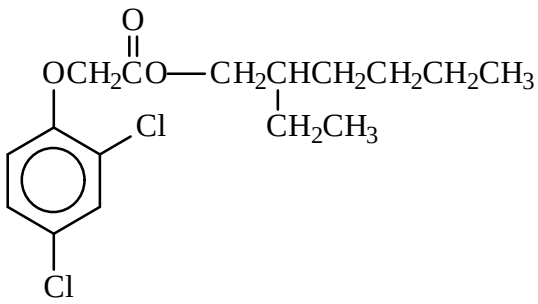
ISO common name: 2,4-D-ethylhexyl

Chemical name
IUPAC: 2-ethylhexyl (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, 2-ethylhexyl ester

CAS Registry No.: 1928-43-4

CIPAC No.: 1

Synonyms: 2,4-D EHE
0
Structural formula:



Molecular formula: $C_{16}H_{22}Cl_2O_3$

Molecular weight: 333.27

Physical and chemical properties

Pure active ingredient

Appearance: amber to brown liquid

Vapour pressure: 4.8×10^{-4} Pa at 25°C (Chakrabarti and Gennrich, 1987b)

Boiling point: >200°C under degradation (Kinnunen, 1994b)

Octanol/Water partition coefficient: log P_{OW} = 5.78 at 25°C (Helmer, 1987a)

Solubility: water 0.0867 mg/l at 25°C (Helmer, 1987b)
industrial water 0.0324 ± 0.0032 mg/l at 12°C (Potter, 1990)

Specific gravity: 1.152 g/cm^3 at 20°C (Dow Chemical Co., 1989b)

Hydrolysis: in sterile aqueous solutions at 25°C (Concha *et al.*, 1993a):
pH 5 $t_{1/2}$ 99.7 days
pH 7 $t_{1/2}$ 48.3 days
pH 9 $t_{1/2}$ 52.2 hours
in natural water (river water) pH 7.8 at 25°C:
$t_{1/2}$ 6.2 hours
in soil slurries at 25°C (Concha *et al.*, 1993b):
$t_{1/2}$ in Catlin silty clay soil slurry 1.25 hours
$t_{1/2}$ in Hanford sandy loam soil slurry 1.45 hours

Photolysis: sterile aqueous photolysis 25°C $t_{1/2}$ 128 days (Concha and Shepler, 1993b)
UV stable (Schriber and Tiszai, 1991)

Technical material

Minimum purity: 92%

Main impurities: proportional to 2,4-D content except:
free acid 1.5% max., suspended solids 0.1% max., water 1% max.

Stability: no appreciable change in 2 years in sealed containers. will decompose before boiling.

Formulations

Commercially available formulations: TK, EC, EW and OL.

IDENTITY (diethanolamine salt)

ISO common name: 2,4-D-diethanolamine

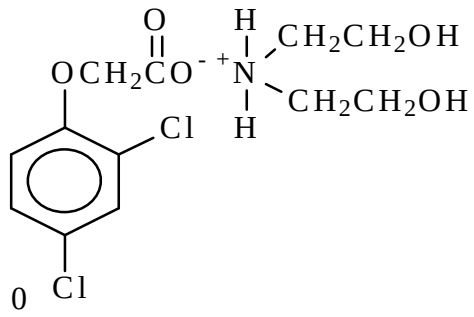
Chemical name
IUPAC: diethanolamine (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, diethanolamine salt

CAS Registry No.: 5742-19-8

CIPAC No.: 1

Synonyms: 2,4-D DEA

Structural formula:



Molecular formula: $C_{12}H_{17}Cl_2NO_5$
Molecular weight: 326.18

Physical and chemical properties

Pure active ingredient

Appearance: cream solid powder

Vapour pressure: <1.33 x 10^{-5} Pa at 25°C and 45°C (Douglas, 1993a)

Melting point: 83°C (Malone, 1993)

Octanol/Water partition coefficient: log P_{OW} = -1.65 at 25°C (Douglas, 1993b)

Solubility:			
	acetonitrile	47 mg/g	at 25°C
	ethanol	280 mg/g	at 25°C
	n-octanol	36 mg/g	at 25°C
	water	806 mg/g	at 25°C (Douglas, 1993c)

Specific gravity: 0.762 g/cm^3 at 25.5°C (Wojcieck, 1992a)

Photolysis: stable under light

Rate of dissociation: 3 minutes at 25°C

Thermal stability: stable up to 150°C (Malone, 1993)

pH: 7.48 at 25°C (Furlong, 1992)

Technical material

No information was received.

FORMULATIONS

Commercially available formulations: SL.

IDENTITY (2-butoxyethyl ester)

ISO common name: 2,4-D-butoxyethyl

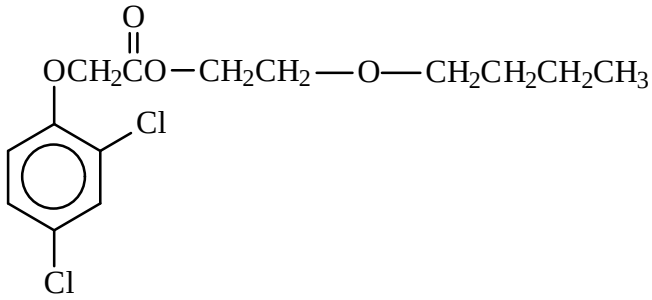
Chemical name
IUPAC: 2-butoxyethyl (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, 2-butoxyethyl ester

CAS Registry No.: 1929-73-3

CIPAC No.: 1

Synonyms: 2,4-D BEE

Structural formula:



Molecular formula: $C_{14}H_{18}Cl_2O_4$

Molecular weight: 321.20

Physical and chemical properties

Pure active ingredient

Appearance: amber liquid

Vapour pressure: 3.2×10^{-4} Pa at 25°C (Chakrabarti, 1989)

Boiling point: 89°C (Kinnunen, 1994c)

Octanol/Water partition coefficient: log P_{OW} = 4.1 at 25°C (Heimerl, 1990)

Specific gravity: 1.0 - 1.2 g/ml at 20°C (Dow Chemical Co., 1989c)

Hydrolysis: in sterile water buffered at 25°C (Shepler *et al.*, 1990)
pH5 $t_{1/2}$ 196 days
pH7 $t_{1/2}$ 74 days
pH9 $t_{1/2}$ 55 minutes
soil/water slurry (Racke, 1989)
61% hydrolysed in 20 minutes

Photolysis: (aqueous) $t_{1/2}$ 74 days, stable to photodegradation (Marx and Shepler, 1990)

Thermal stability: stable up to 50°C (Schriber, 1992)

Technical material

Minimum purity: 92.0%

Stability: stable for a minimum of 2 years in sealed container.

Formulations

Commercially available formulations: EC, TK.

IDENTITY (isopropylamine salt)

ISO common name: 2,4-D-isopropylamine

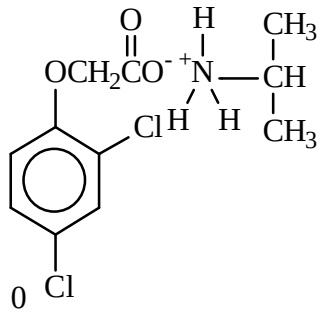
Chemical name
IUPAC: isopropylamine (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, isopropylamine salt

CAS Registry No.: 5742-17-6

CIPAC No.: 1

Synonyms: 2,4-D IPA

Structural formula:



Molecular formula: $C_{11}H_{15}Cl_2NO_3$

Molecular weight: 280.04

Physical and chemical properties

<u>Pure active ingredient</u>

Appearance: amber liquid

Vapour pressure: <1.33 x 10^{-5} Pa (Chakrabarti, 1990a)
(salt decomposed in temperature range -3.9 to 24°C)

Octanol/Water partition coefficient: refer to 2,4-D acid

Melting point: 121°C ± 1°C (Murphy, 1993b)

Solubility (Kinnunen, 1994d):

water	pH5	17.4 g/100 ml
	pH7	43.6 g/100 ml
	pH9	33.1 g/100 ml
acetonitrile		2.1 g/100 ml

methanol	>50	g/100 ml
hexane	4.36×10^{-3}	g/100 ml

Specific gravity: 1.15 g/ml at 20°C (Dow Chemical Co., 1989d)

Photolysis: refer to 2,4-D acid

Dissociation rate: <1 min at 21°C (Reim, 1989b)

Thermal stability: stable up to 50°C (Schriber, 1991a)

Technical material

Minimum purity: 48.4%

Stability: stable for minimum of 2 years in sealed container

Formulations

Commercially available formulations: SL.

IDENTITY (isopropylamine salt)

ISO common name: 2,4-D-isopropylamine

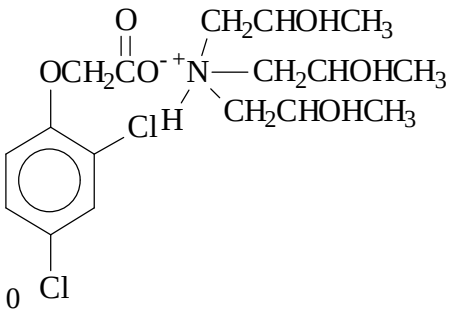
Chemical name
IUPAC: tri-isopropanolamine (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, tri-isopropanolamine salt

CAS Registry No.: 32341-80-3

CIPAC No.: 1

Synonyms: 2,4-D TIPA

Structural formula:



Molecular formula: $C_{17}H_{27}Cl_2NO_6$

Molecular weight: 412.31

Physical and chemical properties

Pure active ingredient

Appearance: amber liquid

Vapour pressure: <1.33 x 10^{-5} Pa at 14.2 - 28.0°C (Chakrabarti, 1990b)

Octanol/Water partition coefficient: refer to 2,4-D acid

Melting point: 88.0°C - 110.5°C (Kinnunen, 1994)

Solubility (Schriber, 1991b):

water	pH5	46.1 wt % ai
	pH7	46.1 wt % ai
	pH9	10.4 wt % ai
acetonitrile		12.3 wt % ai
acetone		11.7 wt % ai
n-octanol		7.6 wt % ai

Specific gravity: 1.2 g/ml at 20°C (Dow Chemical Co., 1989e)

Photolysis: refer to 2,4-D acid

Dissociation rate: <1 min at 21°C (Reim, 1989b)

Thermal stability: stable up to 50°C (Schriber, 1991c)

Technical material

Minimum purity: 68.8%

Melting range: 88°C - 110.5°C (Kinnunen, 1994e)

Stability: stable at minimum for 2 years in sealed container

Formulations

Commercially available formulations: SL.

IDENTITY (isopropyl ester)

ISO common name: isopropyl

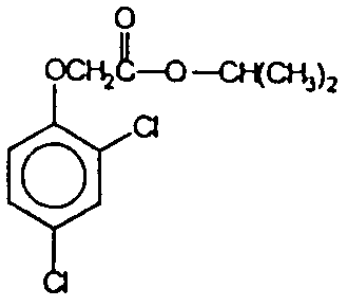
Chemical name
IUPAC: (2,4-dichlorophenoxy)acetate, isopropyl ester
CA: (2,4-dichlorophenoxy) acetic acid, isopropyl ester

CAS Registry No.: 94-11-1

CIPAC No.: 1

Synonyms: 2,4-D IPE

Structural formula:



Molecular formula: $C_{11}H_{12}Cl_2O_3$

Molecular weight: 263.12

Physical and chemical properties

Pure active ingredient

Appearance: light amber liquid

Vapour pressure: 1.87 Pa at 25°C (Fisher, 1989)

Octanol/Water partition coefficient: log P_{ow} = 4.2 at 25°C (Fisher, 1989)

Solubility: practically insoluble in water (Fisher, 1989)

Specific gravity: 1.25 g/cm^3 at 20°C (Fisher, 1989)

Hydrolysis: under sterile conditions at 25°C
pH 5 no hydrolysis in 30 days
pH 7 $t_{1/2}$ 89 days
pH 9 $t_{1/2}$ 22.4 hours (Burke, 1994a)

Thermal stability: stable to approximately 240°C (Fisher, 1989)

Technical material

Minimum purity: 92%

Main impurities: proportional to 2,4-D content (except free acid 1,5% max. suspended solids 0.1% max., water 1% max.)

Stability: no appreciable change in 2 years in sealed containers. Decomposes before boiling.

Formulations

Commercially available formulations: TK and EC.

METABOLISM AND ENVIRONMENTAL FATE

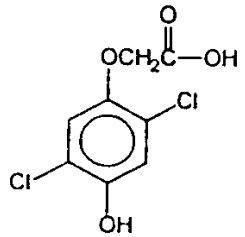
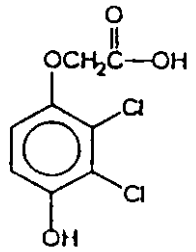
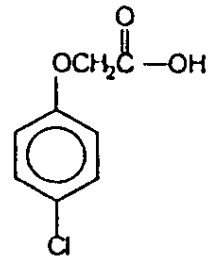
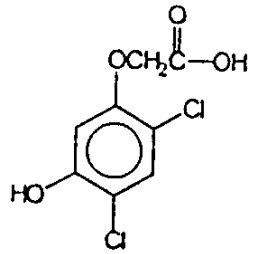
Metabolism and environmental fate studies were conducted with uniformly ring-^{14}C-labelled 2,4-D:

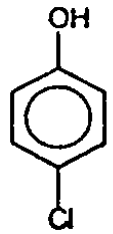
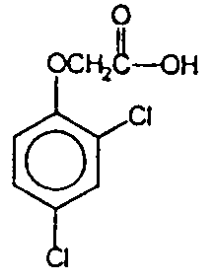
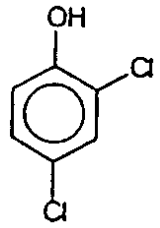
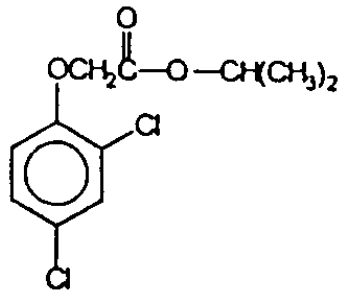
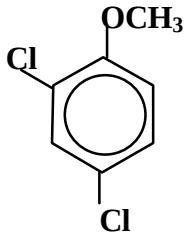
^{14}C-labelled 2,4-dichlorophenoxyacetic acid ([^{14}C]2,4-D): mouse, rat, goat, poultry, fish.
^{14}C-labelled 2,4-dichlorophenoxyacetic acid dimethylamine salt ([^{14}C]2,4-D DMA): apple.
^{14}C-labelled 2,4-dichlorophenoxyacetic acid 2-ethylhexyl ester ([^{14}C]2,4-D EHE): potato, wheat.
^{14}C-labelled 2,4-dichlorophenoxyacetic acid isopropylester ([^{14}C]2,4-D IPE): lemon.

Furthermore, the label on the ester moiety is also used:
2,4-Dichlorophenoxyacetic acid 2-ethylhexyl-1-^{14}C ester (2,4-D EHE-1-^{14}C): rat.

For the chemical names, structures and abbreviations of metabolites used in the text see Table 1.

Table 1. Structures of metabolites of 2,4-D.

Chemical name, abbreviation	Structure
2,5-Dichloro-4-OH-phenoxyacetic acid (4-Hydroxy-2,5-D)	
2,3-Dichloro-4-OH-phenoxyacetic acid (4-Hydroxy-2,3-D)	
4-Chlorophenoxyacetic acid (4-CPAA)	
2,4-Dichloro-5-OH-phenoxyacetic acid (5-Hydroxy-2,4-D)	

Chemical name, abbreviation	Structure
4-Chlorophenol (4-CP)	
2, 4-Dichlorophenoxyacetic acid (2,4-D)	
2,4-Dichlorophenol (2,4-DCP)	
2,4-Dichlorophenoxyacetic acid isopropyl ester (2,4-D IPE)	
2,4-Dichloroanisole (2,4-DCA)	

Animal metabolism

Mice (Eiseman, 1984). The pharmacokinetics of [^{14}C]2,4-D (purity, 98%) were studied in groups of 26 male B6C3F1 mice after single oral doses at 5, 45, or 90 mg/kg bw and single intravenous

administrations of 90 mg/kg bw. To evaluate the excretion balance groups of five mice were given the same single doses of [^{14}C]2,4-D by gavage or intravenous doses of 5 or 90-mg/kg bw. Plasma, liver and kidneys were analysed for the radiolabel 0.083, 0.25, 0.5, 1, 2, 4, 6, 8, 12, 24, 36, 48 and 72 hours after treatment. Urine was collected before and after treatment at 0-6, 6-12, 12-24, 24-36, 36-48, 48-72 hours and then every 24 hours up to 168 hours. Faeces were collected before and 0-12, 12-24 and every 24 hours up to 168 hours after treatment. The animals were then slaughtered and the blood, liver, kidneys and residual carcases were sampled for measurement of total radioactive residues (TRR).

The disappearance of the label from plasma in animals at each dose was examined by reiteratively weighted non-linear regression analysis to obtain the apparent pharmacokinetic parameters by both the oral and intravenous routes. Because of the apparent lag in clearance at the higher doses and the high levels of 2,4-D-derived ^{14}C in plasma during the first 4 hours after dosing, a two-compartment model with Michaelis-Menten limited clearance was used. The half-lives were calculated to be 28-45 hours. At least 50% of the dose was cleared within 12 hours however, suggesting that the estimates are lower than the actual clearance constants.

After oral administration, the area under the curve (AUC) of time v. concentration increased more than proportionally with the dose.

The main route of elimination of ^{14}C was the urine, accounting for 63, 84, 71, 53 and 65% of doses at 5 mg/kg bw orally, 5 mg/kg intravenously, 45 mg/kg bw orally, 90 mg/kg bw orally, and 90 mg/kg intravenously respectively. 7.6% of the dose in animals receiving 5 mg/kg bw orally and 5.2% at 5 mg/kg bw intravenously was excreted in the faeces. The proportions increased to 15% at 45 mg/kg bw orally, 16% at 90 mg/kg bw orally, and 12% at 90 mg/kg bw intravenously. Most of the TRR was eliminated in the urine 0-6 hours after treatment at 5 mg/kg bw intravenously, 0-12 hours after at 5 mg/kg bw orally, and 6-24 hours after at 45 or 90 mg/kg bw. 168 hours after treatment very little ^{14}C was detected. None was found in blood or plasma in the animals dosed intravenously, and only one animal of those dosed orally had a detectable, low level of radiolabel in the plasma. The liver and kidneys contained similar levels of TRR at each dose. Less than 1.1% of the dose was retained in the animals seven days after administration of [^{14}C]2,4-D, irrespective of the dose and administration route. The urinary clearance of 2,4-D appeared to be a saturable process in male mice at doses of $\geq$45 mg/kg bw.

Rats. Smith *et al.* (1980) examined the pharmacokinetics of the elimination of [^{14}C]2,4-D (radiochemical purity, >99%) after oral and intravenous administration to several groups of male Fischer 344 rats to investigate the fate of the compound as a function of the dose and to identify the approximate dose at which the kinetics of elimination begin to show evidence of saturation. Three groups of three rats with jugular cannulae received oral doses of 10, 50, or 150 mg/kg bw, and two similar groups received intravenous doses of 5 or 90 mg/kg bw. The concentrations of TRR were determined 1, 2, 3, 6, 9, 12,15, 18, 24, 36, 48, 60 and 72 hours after treatment; ^{14}C levels in the urine were measured at 6-hourly intervals for the first 24 hours and at 12-hour intervals thereafter up to 72 hours; faecal samples were collected at 24-hour intervals.

To determine the effect of dose five groups of six rats were given single oral doses of 10, 25, 50, 100 or 150 mg/kg bw and were killed 6 hours after treatment. Absorption of 2,4-D after oral administration was complete as >85% of the dose within the first 12 hours and a total of 97% of the 10 mg/kg bw oral dose and 95% of the 150 mg/kg bw dose was excreted in the urine. After intravenous doses 99 and 86% of the 5- and 90-mg/kg bw doses were recovered within the first 12 hours and 100 and 91% after 72 hours. Saturable clearance from the plasma was detected and was confirmed by the disproportionate increase in the AUC, which probably reflects saturable urinary excretion, in view of the concomitant increasing ratio of plasma:kidney ^{14}C concentrations with increasing dose.

The elimination was biphasic. The mean half-lives for the intravenous and oral routes were 55 minutes and 1 hour respectively for the ∀-phase and 14 and 18 hours for the ∃-phase. The rapid elimination of the ^{14}C in the urine and the small contribution of the ∃-phase indicate low potential accumulation of 2,4-D in rats.

Timchalk (1990) examined the absorption, distribution, metabolism and excretion of [^{14}C]2,4-D after oral and intravenous administration to Fischer 344 rats. Four groups of five male and five female rats each received [^{14}C]2,4-D as a single oral dose by gavage at 1 or 100 mg/kg bw, or as a single intravenous dose at 1 mg/kg bw, or were given 14 daily oral doses of unlabelled 2,4-D at 1 mg/kg bw followed by a single oral dose of [^{14}C]2,4-D at the same rate on day 15. Two additional groups of four male rats were given single oral doses and then 1 or 100 mg/kg bw through jugular cannulae to define the concentration-time course in the plasma. Plasma concentrations were determined for 24 hours after treatment.

In all groups >94% of the dose was recovered within 48 hours after treatment, mainly in the urine (85-94%), with 2-11% in the faeces. No sex-related difference was seen, and repeated oral dosage did not alter the excretory route. Peak plasma levels were attained about 4 hours after treatment. The disproportionate AUCs and the delayed urinary excretion of ^{14}C strongly imply dose-dependent non-linear kinetics however. Although the elimination of the radiolabel was saturated during the first few hours after the 100 mg/kg bw dose its excretion was rapid, most of the dose having been excreted 36 hours after treatment in all groups. Rapid excretion of [^{14}C]2,4-D is also indicated by the approximate half-life of 5 hours for urinary excretion after oral administration. The analysis of all major tissues and organs for residual ^{14}C activity indicated that only a small fraction of the dose was present 48 hours after treatment. The tissues and organs of animals treated at the low dose contained <0.7% of the administered [^{14}C]. These results indicate that the fate of [^{14}C]2,4-D in rats is independent of dose and sex and that the compound is rapidly and almost completely eliminated, essentially by the urinary route, and is unlikely to accumulate.

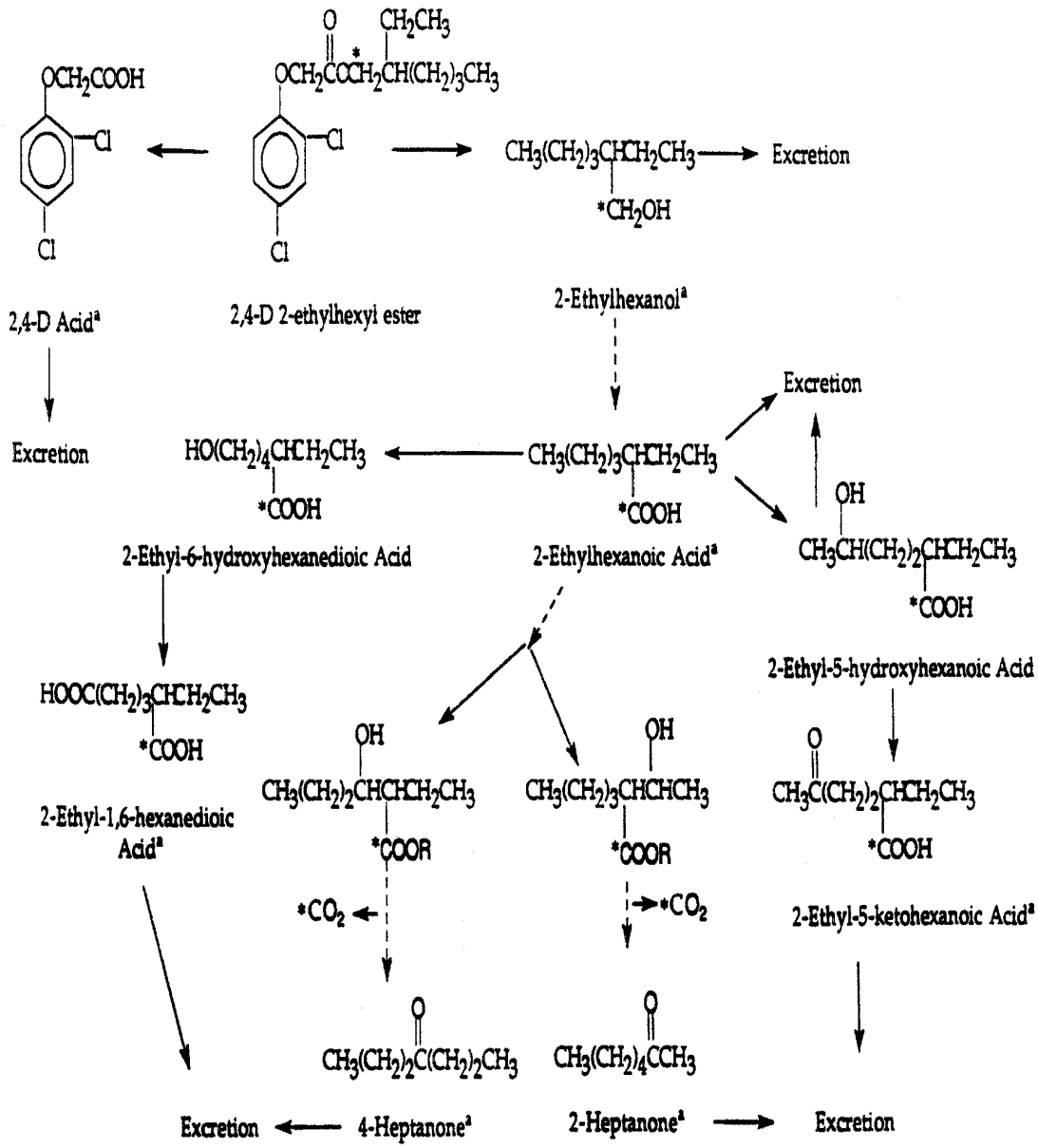
Unlabelled 2,4-D EHE was administered as a single oral dose to male and female 11 week old Fischer 344 rats to investigate the pharmacokinetic characteristics of this ester in relation to 2,4-D itself (Frantz and Kropscott, 1984). Eight groups of animals (3/sex/group) were given oral doses of 130 mg/kg of the 2-ethylhexyl ester (equivalent to 86.3 mg/kg 2,4-D acid) in maize oil and killed after 15 and 30 min, and 1, 2, 4, 8, 24 and 72 hours for blood samples. Urine samples were taken at 12 hour intervals from the 72-hour group. A control group (3/sex) was dosed with maize oil only and a terminal blood sample was taken after 3 hours. Both ester and acid were determined by GLC and GC-MS with detection limits of 0.01 and 0.1 :g/ml respectively.

The most significant finding was the absence of any 2-ethylhexyl ester ([0.01 :g/ml) in either blood or urine as measured up to 72 hours after dosing. The acid was found in both blood and urine. Log-linear plots of 2,4-D acid concentration in the blood v. time were similar for male and female rats, with peak blood levels appearing at 2 hours for females and 4 hours for males. No acid was detectable at 72 hours in either male or female blood samples. Urine levels of 2,4-D acid peaked at 12 hours in both sexes and clearance was nearly complete by 36 hours; only small amounts of acid were detectable at 72 hours. The cumulative recovery of 2,4-D acid in urine (as a percentage of the equivalent administered) was 94.8 ± 9.2% for males and 84.3 ± 4.5% for females. These data indicate that the 2-ethylhexyl ester of 2,4-D is converted very rapidly to 2,4-D acid, and the acid is then excreted in the urine.

The absorption, distribution, excretion and biotransformation of [*EHE*-1-^{14}C]2,4-D were studied in male Fischer 344 rats after a single oral dose of 15 mg/kg bw (Dryzga *et al.*, 1992). Blood was collected from each rat 0.5, 1, 1.5, 2, 4, 6, 8, 12, 18 and 24 hours after treatment and the plasma was analysed for the radiolabel; urine was collected 6, 12, 24 and 48 hours after treatment, and the radiolabel in the urine and the cage rinse was combined for each collection interval and expressed as radiolabel excreted in the urine. Faeces were collected at 24-hour intervals and analysed for

radiolabel; expired [^{14}C]carbon dioxide collected at 6, 12, 24 and 48 hours was trapped in a solution of monoethanolamine and 1-methoxy-2-propanol, and the TRR was quantified. No tissue samples were analysed. Metabolites were characterized in pooled urine (0-6 and 6-12 hours) and in faeces (0-24 hours) by GC-MS, and unchanged ester in the urine and faecal extracts was determined by HPLC.

Figure 1. Proposed metabolic pathways of 2,4-Dd EHE in rats (Dryzga *et al.*, 1992).



[a] Compounds actually identified

,4-D EHE-1-^{14}C was rapidly absorbed, with a peak plasma concentration of 1.0 mg/g 4 h after treatment, decreasing with a half-life of 9 hours. Once absorbed, the ester was extensively metabolized and eliminated in the urine and faeces, and as expired $^{14}CO_2$. It was rapidly hydrolysed to 2,4-D and 2-ethylhexanol, since no ester was found in the blood, urine, or faeces. The principal route of excretion was the urine (62-66%), with less in the faeces (14-21%) and expired carbon dioxide (9-12%). The metabolites in both urine and faeces were 2-ethylhexanol, 2-ethylhexanoic

acid, 2-ethylhexane-1,6-dioic acid and 2,4-D. Metabolites found in only in the urine were 2-ethyl-5-oxohexanoic acid, 2-ethyl-5-hydroxyhexanoic acid, 2-heptanone and 4-heptanone (Figure 1). These metabolites were previously reported as metabolites of [^{14}C]2-ethylhexanol. The ethylhexyl ester of 2,4-D is thus converted rapidly to 2,4-D, which is then excreted in the urine.

Goats. Guo and Stewart (1993) dosed a lactating goat orally with [^{14}C]2,4-D at a level equivalent to 483 ppm in the feed intake, for 3 consecutive days. Urine, faeces and milk were sampled during the dosing phase and tissues were collected after slaughter. ^{14}C was determined by combustion and/or liquid scintillation counting. Approximately 82 and 8% of the total dose was recovered in the urine and faeces respectively. Less than 0.1% of the dose was recovered in the other samples.

The ^{14}C residues in the samples except excreta and liver were extracted with organic and aqueous solvents. Liver was first treated with pancreatin and then extracted with organic solvents. Urine was analysed directly by HPLC with radiometric detection. HPLC was used to determine the total ^{14}C as 2,4-D equivalents in the various extracts. The major ^{14}C component was identified as 2,4-D by mass spectrometry, HPLC and thin-layer chromatography. The results of these analyses are shown in Table 2.

Table 2. Metabolism of 2,4-D in goats. Identity and distribution of ^{14}C components in the extractable fractions urine, milk and tissues (Guo and Stewart, 1993).

Sample	Total ^{14}C mg/kg	% 2,4-D	% DCP[1]	% CPAA[2]	% NP1	% NP2[3]	% NP3	% Not[4] identified
Urine	320	97.8	ND[5]	1.8	ND[5]	ND[5]	ND[5]	0.4
Milk	0.202	47.0	5.0	6.9	1.0	ND[5]	ND[5]	35.1
Liver	0.224	20.5	ND[5]	ND[5]	14.7	17.9	5.4	36.6
Kidney	1.44	53.6	ND[5]	ND[5]	10.3	22.0	4.1	9.9
Fat	0.088	45.4	2.3	ND[5]	3.4	13.6	ND[5]	21.7
Muscle	0.037	37.8	ND[5]	ND[5]	2.7	24.3	ND[5]	19.0

[1]DCP: 2,4-dichlorophenol
[2]CPAA: 2-*o* and 2-*p*-chlorophenoxyacetic acid
[3]The GC/MS profile for NP2 matched 2,4-dichloroanisole, but the compound was not later confirmed (Guo and Stewart 1994)
[4]Total % extracted - Total % identified. In general, this radioactivity is associated with several different fractions and with radioactivity that was unaccounted for after HPLC analysis. Thus, no single unidentified component is present at the level shown here.
[5]Not detected

2,4-dichlorophenoxyacetic acid was found to be the predominant component in the urine, kidneys, fat, liver and muscle. Free 2,4-D and polar conjugates hydrolysed to 2,4-D under acidic conditions were the major ^{14}C components in the milk. Low levels of DCP were tentatively identified in the milk and fat by HPLC.

The ^{14}C in the am and pm milk samples ranged from 0.22 to 0.34 mg/kg and 0.036 to 0.055 mg/kg, as 2,4-D respectively. Free [^{14}C]2,4-D was identified as the most significant residue in milk (38% of the TRR, 0.077 mg/kg). Certain polar conjugates were observed in the milk, from which 2,4-D was readily released by acid hydrolysis. The total 2,4-D after a 1-hour hydrolysis was about 47.0% of the TRR or 0.095 mg/kg. Approximately 0.009 mg/kg (4.5% of the TRR) and 0.01 mg/kg (5.0% of the TRR) of the residues in milk were tentatively identified as *o*- and *p*-

chlorophenoxyacetic acid (CPA) and 2,4-dichlorophenol (DCP) respectively. It is possible that CPA derived from an impurity in the original test substance.

The highest ^{14}C concentration in the tissues was in the kidneys (1.4 mg/kg). Lower levels were found in the liver (0.22 mg/kg), fat (0.088 mg/kg) and muscle (0.037 mg/kg). The main component identified in the residues of each tissue was 2,4-D. About 0.002 mg/kg of DCP (2.3% of the TRR) was found in the fat.

Poultry. Residues in the tissues, eggs and excreta were measured in laying hens (3 groups of 5, each bird weighting 1.5 kg) dosed orally for 7 days with radiolabelled capsules of 2,4-D approximately equivalent to 18 ppm in the feed intake (112-119 g/bird/day). The eggs and excreta were collected throughout the 7 days, and the birds were killed 22-24 hours after the final dose (Puvanesarajah and Bliss, 1992).

Samples collected included excreta, egg, fat, gizzard, heart, kidney, liver, breast muscle and thigh muscle. Except for the eggs (production of which from each treatment group was good) all the samples were composited for each group before analysis. The weights of the comparable samples from the three groups were very similar.

The TRR levels in the samples were determined either by direct radio-analysis or combustion and radio analysis (the latter corrected for sample and oxidizer recoveries). Recoveries in the hens ranged from 95.8 to 101.6%, approximately 90% in the excreta. The residues in the breast muscle were <0.002 mg/kg; thigh muscle 0.006 mg/kg; fat 0.028 mg/kg and liver 0.03 mg/kg. The mean residue levels in eggs increased steadily from less than quantifiable at day 1 to 0.018 mg/kg at day 7. The tissues and eggs contained <0.1% of the total dose (Table 3).

Table 3. 2,4-D acid equivalents and % total dose recoveries in body tissues, eggs and excreta of hens (Puvanesarajah and Bliss, 1992).

Sample	Group II		Group III		Group IV	
	TRR, mg/kg[1]	% Total dose recovered	TRR, mg/kg[1]	% Total dose recovered	TRR, mg/kg[1]	% Total dose recovered
Egg 1[2]	<LOD[4]	<0.1	<MQL[4]	<0.1	<MQL[4]	<0.1
Egg 2	0.002	<0.1	0.003	<0.1	0.003	<0.1
Egg 3	0.006	<0.1	0.006	<0.1	0.006	<0.1
Egg 4	0.010	<0.1	0.010	<0.1	0.010	<0.1
Egg 5	0.014	<0.1	0.013	<0.1	0.009	<0.1
Egg 6	0.016	<0.1	0.016	<0.1	0.018	<0.1
Egg 7[3]	0.018	<0.1	0.017	<0.1	0.019	<0.1
Fat	0.029	<0.1	0.032	<0.1	0.023	<0.1
Kidney	0.705	<0.1	0.065	<0.1	0.791	<0.1
Liver	0.025	<0.1	0.019	<0.1	0.046	<0.1
Breast muscle	<MQL[4]	<0.1	<MQL[4]	<0.1	0.002	<0.1
Thigh muscle	0.005	<0.1	0.004	<0.1	0.008	<0.1
Heart	0.011	<0.1	0.008	<0.1	0.028	<0.1
Gizzard	0.142	<0.1	0.038	<0.1	0.118	<0.1
Excreta[5]	16 - 21	95.9	15 - 19	89.9	15 - 21	89.4
Total dose recovered		96.0		90.0		89.5

[1] Numbers listed are the means of triplicate determinations of pooled samples.
[2] First day of dose
[3] Last day of dose
[4] Limit of determination (0.002 mg/kg)
[5] Range of values for the day 1-7 samples

The ^{14}C components present as free residues in the eggs and liver were 2,4-D and 2,4-dichlorophenol (Table 4). A large proportion of the fat activity was released only after base hydrolysis, which suggested that 2,4-D conjugates constituted most of the extractable ^{14}C.

Table 4. Components of extractable ^{14}C residues in hens (Puvanesarajah and Bliss, 1992).

Sample	Total ^{14}C mg/kg	% of extractable ^{14}C (free and conjugated)		
		2,4-D	2,4-Dichlorophenol	Not identified
Egg	0.0178	23.0	7.3	56.8
Fat	0.0271	25.1		67.6
Liver	0.0297	18.2	4.4	59.7

Fish. Bluegill sunfish (*lepomis macrochirus*) were exposed to approximately 11 mg/kg of [^{14}C]2,4-D in their water under static conditions for 4 consecutive days (Premkumar and Stewart, 1994). The whole fish and the water were sampled daily and the fish on day 4 were dissected into fillet and viscera. The [^{14}C]2,4-D equivalent TRR levels in the whole fish, fillet and viscera and the water were determined by combustion and/or liquid scintillation counting.

The fillet and viscera residues were extracted with polar and nonpolar organic solvents. Most of the residues were acetonitrile-extractable. <5% of the TRR was hexane-soluble, and approximately 10% was unextractable with solvents. Acid and base hydrolyses released the unextractable residues in the fillets.

Radio analyses of the whole fish showed a steady increase from day 1 (0.41 mg/kg) to day 3 (0.6 mg/kg). The TRR in the day 4 viscera and fillet were 1.9 and 0.41 mg/kg respectively. The treated fillet had small amounts of hexane-soluble residues (0.005 mg/kg, 1.2% of the TRR) and unextractable ^{14}C (0.041 mg/kg, 10% of the TRR). Most of the ^{14}C was soluble in acetonitrile (0.34 mg/kg, 84% of the TRR).

HPLC radio-analysis was used to characterize the ^{14}C residues in the extracts (Table 5). 2,4-D (70.4% of the TRR, 0.29 mg/kg), 2,4-DCP (4.7% of the TRR, 0.019 mg/kg), and a conjugate (4.4% of the TRR, 0.018 mg/kg) were identified in the acetonitrile-soluble residue. Acid hydrolysis of the polar conjugate released 2,4-D and 2,4-DCP. Acid and base hydrolyses of the unextractable fillet pellet released additional 2,4-D (6.4 and 3.9% of the TRR, 0.029 and 0.016 mg/kg respectively) and 2,4-DCP (0.5% of the TRR, 0.002 mg/kg). The identities of 2,4-D and 2,4-DCP in the fillet tissue were confirmed by GC-MS.

Table 5. Components of extractable ^{14}C residues in fish exposed for 4 days to 11 mg/kg in their water (Premkumar and Stewart, 1994).

TRR		Extractable ^{14}C in					
		2,4-D	2,4-DCP	2,4-DCA	polar unknown	CPA and CP	not identified
Fillet, TRR	% of TRR[1]	80[2]	7.9[2]		2.2	N/A[3]	1.0
0.41 mg/kg	mg/kg[1,2]	0.33	0.03		0.009	N/A[3]	0.004
Viscera, TRR	% of TRR[1]	30[2]	28[2]	0.3[3]	5.8	40	1.6
1.9 mg/kg	mg/kg[1,2]	0.57	0.53	0.006	0.11	0.76	0.03

[1] Sum of free and conjugated
[2] Expressed as 2,4-D
[3] Identity confirmed by GC-MS

Plant metabolism

Apples. Smith (1991) sprayed [^{14}C]2,4-D on the turf beneath the canopy of a dwarf apple tree in accordance with label instructions. The test material consisted of the dimethylamine salt of 2,4-D acid in aqueous solution applied at 2.2 kg ae/ha (2 applications 42 days apart). Soil samples were taken after 42 days and 97 days, and fruit samples after 97 days (maturity) .

Combustion analysis and liquid scintillation counting were used to determine ^{14}C residues in the soil and plant samples. All residues were corrected for oxidizer recovery and matrix effects, and those in the soil for moisture content. Most residues were in the 0-7.5 and 7.5-15 cm layers with considerably less (<0.05 mg/kg as 2,4-D) in the 15-22.5, 22.5-30 and 30-45 cm layers. The TRR in was 0.53 mg/kg and 0.042 mg/kg 0-7.5 and 7.5-15 cm layers at day 42 and 0.93 mg/kg and 0.15 mg/kg at day 97. Combustion analysis of the apples gave TRR levels of 0.009 mg/kg. The apples were lyophilized and exhaustively extracted with methanol/acetic acid (95:5). The extract was then concentrated, re-suspended in water, and extracted with hexane/diethyl ether/acetic acid (47.5:47.5:5), leaving 56% as water-soluble residue with no quantifiable residue (<0.0008 mg/kg) in the organic extract and 44% remaining in the post-extraction solids as determined by combustion.

Lemons. Wu (1994) treated lemons with an aqueous emulsion of [^{14}C]2,4-D isopropyl ester resulting in an average residue level of 2.4 mg/kg expressed as 2,4-D on the fruit. The lemons were stored inside a constant temperature incubator at an average temperature of 5.5 ± 0.7°C, with relative humidity of about 85%. The stored lemons were sampled at 2 hours, 2, 7, 14 and 28 days, and 6, 8, 10, 12, 16, 20 and 24 weeks after treatment.

At sampling, each lemon was rinsed with 200 ml of acetone to remove the surface residues, then cut into eight slices and peeled and processed through a juice extractor. The peel was diced, and homogenized in liquid nitrogen and dry ice. The TRR level was determined for each type of sample.

All the samples were extracted twice with methylene chloride, and the remaining solids in the pulp and peel samples were extracted twice with a mixture of acetonitrile and 0.1 N hydrochloric acid. The distribution of ^{14}C in each extracted fraction was monitored. The acetone rinses and all organosoluble and aqueous fractions obtained at each sampling were analysed by both TLC and reversed-phase HPLC.

Most of the TRR was found in the peel and rinse at all samplings, with very little in the pulp and juice. Radioactivity in the peel increased from 57% of the TRR at 2 hours to 97% at 2 weeks, and remained at about the same level for the 24-week storage period. Radioactivity in the pulp increased from 0.17% at 2 hours to 3.8% at 24 weeks, and in juice from 0.09% at 2 hours to 2.5% at 10 weeks, maintaining a level of about 2% for the remaining weeks. Surface residues removed by acetone decreased from 43.02% to 0.85% after 24 weeks. Solvent extraction of the peel showed 76%, 23% and 1.15% of the peel radioactivity in methylene chloride, aqueous acetronitrile, and post-extraction solid (PES) fractions respectively 2 hours after treatment, and 19.9, 73.5 and 6.6% respectively 24 weeks after treatment. The corresponding proportions in the pulp were about 31-38%, 54-62% and 6-8%, and in juice about 32-44%, 29-33% and 26-35%.Table 6 shows the distribution of ^{14}C in the rinse, peel, pulp and juice at each sampling.

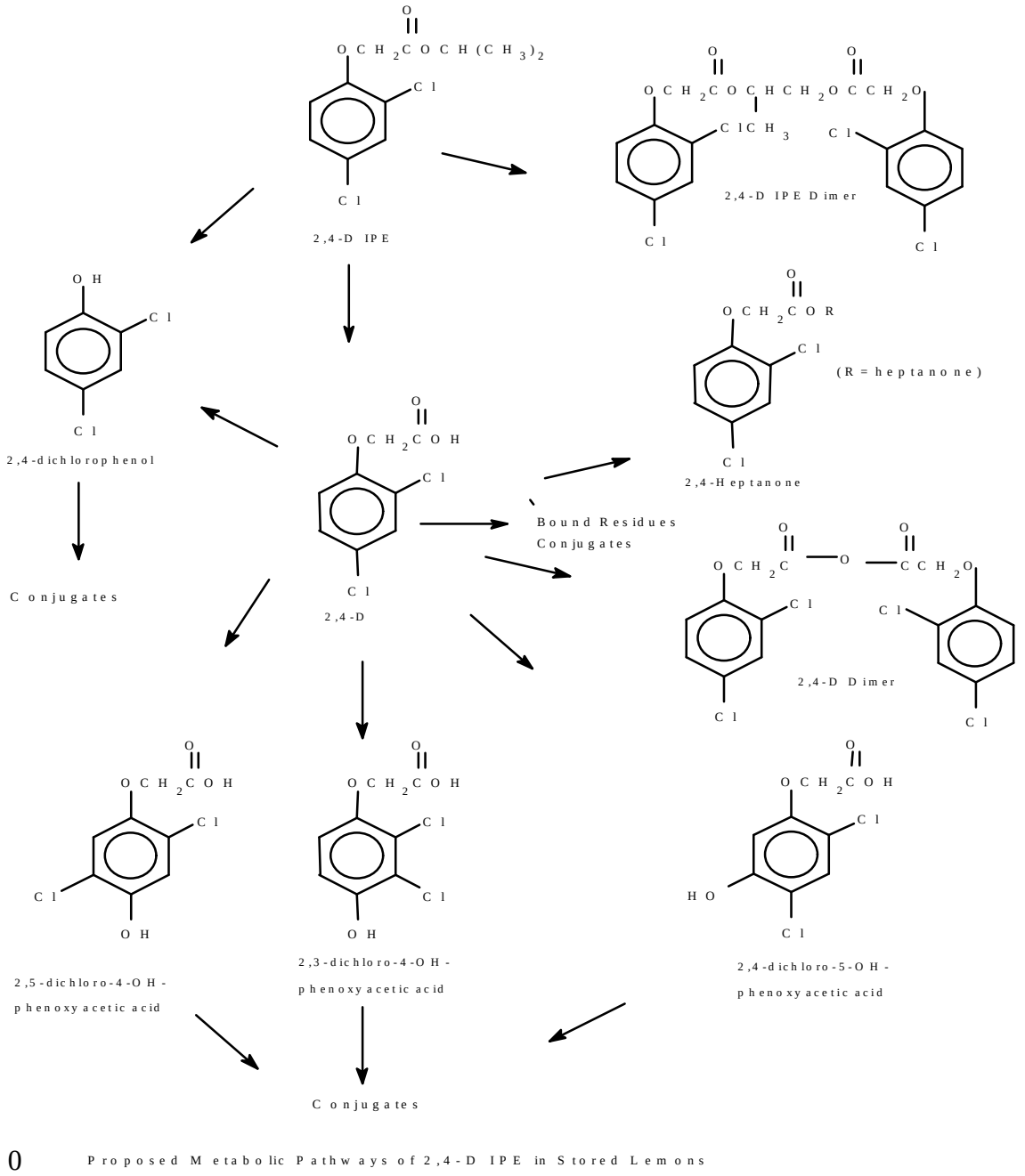
Table 6. Distribution of radioactivity in lemons at various sampling intervals (Wu, 1994).

Sampling	TRR, mg/kg as 2,4-D	Pan wash & rinse		Juice		Pulp		Peel	
		% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
2 h	2.8	43	1.2	0.09	0.003	0.17	0.005	56.7	1.6
2 days	2.3	4.9	0.11	0.10	0.002	0.20	0.005	94.8	2.2
7 days	2.3	3.2	0.07	0.31	0.007	0.55	0.01	96.0	2.2
14 days	2.3	2.1	0.05	0.51	0.01	0.66	0.02	96.8	2.3

Sampling	TRR, mg/kg as 2,4-D	Pan wash & rinse		Juice		Pulp		Peel	
		% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
28 days	2.1	1.6	0.03	0.93	0.02	1.3	0.03	96.1	2.0
6 weeks	2.2	1.2	0.03	1.2	0.03	1.7	0.04	95.9	2.2
8 weeks	2.3	1.1	0.03	1.8	0.04	2.3	0.05	94.8	2.2
10 weeks	2.4	1.1	0.03	2.5	0.06	3.1	0.07	93.3	2.3
12 weeks	2.4	1.0	0.025	1.9	0.05	2.7	0.07	94.4	2.3
16 weeks	2.3	0.80	0.02	1.5	0.035	2.3	0.06	95.4	2.2
20 weeks	2.3	0.93	0.02	2.0	0.05	3.5	0.08	93.5	2.1
24 weeks	2.4	0.85	0.02	1.9	0.05	3.8	0.09	93.4	2.3
Average	2.34								

Metabolites were determined by HPLC and TLC with radiometric detection. Most of the low-level residues (0.64% of the TRR, 0.015 mg/kg) in the 20-week rinse were detected at HPLC retention times of about 36-50 minutes. Four metabolites were tentatively identified by GC-MS: a heptanone ester of 2,4-D, a 2,4-D dimer postulated as 2,4-D anhydride, a dimer of 2,4-D IPE, and a substituted 2,4-dichlorophenol. 2,4-D (0.12% of the TRR, 0.003 mg/kg) and 2,4-D IPE (0.05% of the TRR, 0.001mg/kg) were also found in the rinse. The lemon peel at 20 weeks contained 93.5% of the TRR (2.1 mg/kg). Most of these residues consisted of free and conjugated forms of 2,4-D (64% of the TRR, 1.45 mg/kg). Other metabolites found in minor quantities were free and bound 2,4-D IPE (0.73% of the TRR, 0.017 mg/kg), 4-hydroxy-2,3-D or 5-hydroxy-2,4-D (0.58%, 0.013 mg/kg), 4-hydroxy-2,5-D (0.44%, 0.01 mg/kg) and 2,4-dichlorophenol (0.72%, 0.016 mg/kg). Small amounts of ester-like metabolites similar to those found in the rinses were detected (0.92% of the TRR, 0.02 mg/kg). The main metabolites found in the pulp and juice were also free and conjugated 2,4-D (2.9% of the TRR, 0.07 mg/kg, in the pulp, and 0.99% of the TRR, 0.02 mg/kg, in the juice).

Figure 2. Proposed metabolic pathways of 2,4-D IPE in stored lemons (Wu, 1994).



0 Proposed Metabolic Pathways of 2,4-D IPE in Stored Lemons

The post-extraction solid fraction PES-1 (5.3% of the TRR, 0.12 mg/kg) from the 20-week peel was hydrolysed with cellulase, then 1 *N* HCl and finally 6 *N* HCl. Each hydrolysate was partitioned with ethyl acetate (EtOAc). The organic and aqueous fractions, as well as the final PES, were monitored for ^{14}C. Cellulase released about 27% of the PES radioactivity; 17.6% was soluble in EtOAc (EtOAc-1), and 9.4% remained in the aqueous fraction (Aq-1). Hydrolysis of the resulting PES-2 with *N* HCl released 13.2% of the radioactivity; 10.2% was soluble in EtOAc (EtOAc-2), and 3% remained in the aqueous fraction (Aq-2). Hydrolysis of the remaining PES-3 with 6 *N* HCl released 43% of the radioactivity, 39.5% soluble in EtOAc (EtOAc-3) and 3.7% remaining in the aqueous fraction (Aq-3), while 57% remained in final PES-4. Owing to the low residue levels only the EtOAc-1 fraction was analysed by HPLC and two-dimensional TLC. Four metabolites were detected in this fraction; the main metabolite (about 89% of EtOAc-1, <0.1% of the TRR) had a similar TLC R_f value to 2,4-D, but the HPLC retention times did not match.

Potatoes. [^{14}C]2,4-D ethylhexyl ester was applied as an over-the-top spray to the immature foliage of potato plants grown in a greenhouse (Puglis and Smith, 1992). The diluted emulsified concentrate was applied twice at 0.067 kg acid equivalent (ae)/ha, the first application to three to four week-old plants and the second approximately one week later, according to the registered use of the herbicide on potatoes. Phytotoxicity was observed on the foliage, and the tuber yield was reduced by 56% compared to the control plant. The specific activity of the formulated [^{14}C]2,4-D ethylhexyl ester was 4.08 mCi/mmol (41,000 dpm/µg ae), and the radiochemical purity was 99%. The tubers were harvested at maturity 82 days after the last application. The TRR in the tubers was determined by combustion of tissue aliquots to $^{14}CO_2$ and subsequent radio-analysis. Aliquots of the ground potato tubers were extracted by two methods, one to determine free residues and the other total free and acid-hydrolysable residues. The free residues were isolated by extraction of a 5 *N* hydrochloric acid slurry of the ground potato tuber with diethyl/ether petroleum ether (3:1). The total free and acid-hydrolysable residues were isolated after heating a 5 *N* hydrochloric acid extract of the ground tuber with 5 *N* sulfuric acid and extracting the hydrolysate with the ether mixture (Table 7).

Table 7. Distribution of ^{14}C residues in potato tubers (Puglis and Smith, 1992).

Total ^{14}C, mg/kg as 2,4-D	Free ^{14}C, %		Sample of free and acid-hydrolysable ^{14}C, %	
	aqueous	ether	aqueous	ether
0.0054	46	17	65	30

The total ^{14}C residue in the potato tubers was very low. In an attempt to characterize the organosoluble residue, a 50 g sample was subjected to acid hydrolysis followed by extraction with diethyl ether. The ^{14}C activity in the partially purified extract was observed at an R_f value that did not match the R_f of either the 2-ethylhexyl ester or the free acid. The unknown ^{14}C-labelled compound from the TLC zone was fortified with unlabelled 2,4-D acid and reanalysed by TLC. The added 2,4-D was found at the same R_f value as the unknown compound, and the identity was confirmed by mass spectrometry and high-performance liquid chromatography. Thus, if 2,4-D were present in the treated tubers, it would chromatograph in the same region as the unknown ^{14}C activity. Further characterization of the unknown ^{14}C component(s) was not possible owing to the very low concentration (<0.001 mg/kg 2,4-D ae) and the significant interference of other sample components with the chromatography. An exaggerated application rate was not used to achieve higher residue levels in the tubers because an unacceptable phytotoxic response to rates above 0.067 kg ae/ha.

A second study was conducted with [^{14}C]2,4-D EHE formulated as an emulsifiable concentrate solution (Premkumar and Vengurlekar, 1994). Two foliar applications were made to the plants, the first when the tubers were about the size of a pea 58 days after planting, the second 14 days later. The average radiochemical purity of the formulated solution was 95.4%, and the specific activity 1.55 x 10^5 dpm/mg 2,4-D acid equivalents. The formulated [^{14}C]2,4-D EHE was applied at an average exaggerated rate of 0.35 kg acid equivalents/ha (0.33 and 0.37 kg ae/ha for the first and second applications respectively), 4.4 times the maximum label rate of 0.078 kg ae/ha.

Foliage, vine and tuber samples were analysed for ^{14}C. The vines sampled 1, 7 and 20 days after the second application had residues of 15, 10 and 6.3 mg/kg as 2,4-D respectively, and the tubers collected at the same times contained total ^{14}C residues of 0.32, 0.65 and 0.58 mg/kg respectively. Because the watering of the plants after application was directed to the soil to avoid wash-off from the foliage, these results suggest that the [^{14}C]2,4-D EHE and/or its metabolites were translocated from the plant tops to the tubers.

The ^{14}C residues in the mature tubers were extracted with acidified acetonitrile, which extracted 105% of the TRR (0.61 mg/kg) and 5.4% (0.031 mg/kg) remained unextracted. HPLC of

the extracts showed that 8.3% of the TRR (0.048 mg/kg) was the parent 2,4-D EHE. The main identifiable metabolite was 2,4-D (46% of the TRR, 0.27 mg/kg) and the remaining radioactivity was distributed among four or more polar components. When the extract was concentrated and re-analysed by HPLC the profile changed considerably in the polar region and the parent was found to be unstable during the concentration process, being reduced to 1.6% of the TRR, 0.009 mg/kg. Also the 2,4-D concentration decreased to 36.4% of the TRR (0.21 mg/kg).

The extraction, concentration and analysis procedure was validated by fortifying control samples with 2,4-D EHE at 0.62 mg/kg. Upon chromatographic analysis, 95% of the parent compound remained unchanged. The remainder was hydrolysed to 2,4-D (3.4%) and an unknown component (1.9%).

The treated tubers were then extracted with acetonitrile. This extracted 96% of the TRR (0.55 mg/kg) and 9% (0.052 mg/kg) remained in the post-extraction solids (PES). HPLC analysis of the acetonitrile extract demonstrated that 0.5% of the TRR (0.003 mg/kg) was present as 2,4-D EHE, and 40% (0.23 mg/kg) as free 2,4-D. The remaining radioactivity was distributed among several polar components. During concentration and analysis some parent was again lost and changes were observed in the polar components but the 2,4-D remained unchanged (43% of the TRR, 0.25 mg/kg) indicating that the parent ester and some polar components (perhaps conjugates) were not stable during concentration.

The extracted ^{14}C residues were subjected to acid hydrolysis. HPLC of the hydrolysate showed three major compounds which were tentatively identified as 4-hydroxy-2,5-D (15% of the TRR, 0.084 mg/kg), 4-chlorophenoxyacetic acid (4-CPAA; 24% of the TRR, 0.14 mg/kg) and 2,4-D (39.5% of the TRR, 0.23 mg/kg). The amount of 2,4-D in the extract remained unchanged after hydrolysis, suggesting that the polar components in the extract could be conjugates of 4-hydroxy-2,5-D and 4-CPAA. All three major products were isolated and methylated: GC-MS of the methyl esters confirmed the identification of 4-hydroxy-2,5-D, 4-CPAA and 2,4-D.

Acid hydrolysis released some bound ^{14}C residues from the PES (9.0% of the TRR, 0.052 mg/kg) and the pellet remaining after the concentration of the acetonitrile extract (4.9% of the TRR, 0.028 mg/kg). The acetonitrile phase contained 8.7% of the TRR (0.05 mg/kg) and 6.4% of the TRR (0.037 mg/kg) remained unextracted. HPLC radio-analysis of the released ^{14}C residues demonstrated the presence of 2,4-D (2.3% of the TRR, 0.013 mg/kg), 4-CPAA (1.6% of the TRR, 0.009 mg/kg) and 4-hydroxy-2,5-D (0.9% of the TRR, 0.005 mg/kg). The components were characterized on the basis of their retention times. A total of 1.4% of the TRR (0.008 mg/kg) was eluted in the void volume and remained unidentified.

Figure 3. Metabolic pathways of 2,4-D EHE in potato tubers (Premkumar and Vengurlekar, 1994).
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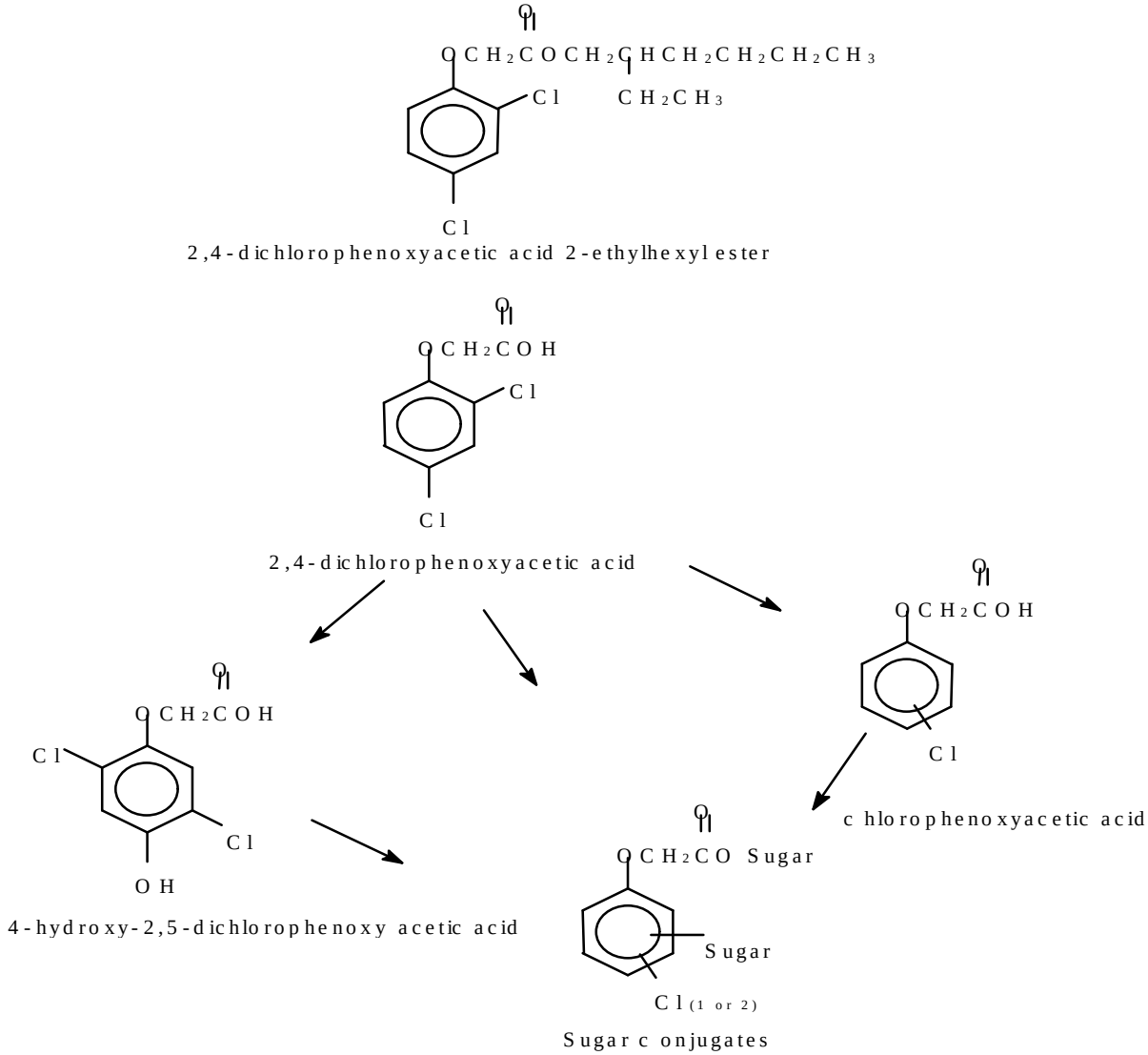

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The distribution of the ^{14}C components is shown in Tables 8 and 9.

Table 8. Distribution of ^{14}C residues (0.58 mg/kg) in extracts of mature potato tubers treated with 2,4-D EHE (Premkumar and Vengurlekar, 1994).

Residue component	Acidified acetonitrile extract		Acetonitrile extract	
	% TRR	mg/kg[1]	% TRR	mg/kg[1]
Polar unknown[2]	27.7	0.16	9.5	0.055
4-hydroxy-2,5-D	18.4	0.11	6.4	0.04
4-CPAA	1.0	0.006	4.3	0.025
2,4-D	46.3	0.27	40.4	0.23
2,4-D 2-EHE	8.3	0.05	0.5	0.003

Residue component	Acidified acetonitrile extract		Acetonitrile extract	
	% TRR	mg/kg[1]	% TRR	mg/kg[1]
Unidentifiable	3.3	0.019	28.6	0.17
Unaccounted for	-	-	6.0	0.03
Unextractable	5.4	0.031	9.0	0.05
Total	110.3	0.64	104.7	0.6

[1] 2,4-D acid equivalents
[2] Eluting in the void volume

Table 9. Distribution of ^{14}C residues in acid hydrolysates of unextracted ^{14}C residues (Premkumar and Vengurlekar, 1994).

Residue component	CH_3CN extract of acid hydrolysis		Post extraction solid (PES) from acid hydrolysate		Total in tuber	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
4-Hydroxy-2,5-D	14.6	0.08	0.9	0.005	15.5	0.09
4-CPAA	24.4	0.14	1.6	0.009	26.0	0.15
2,4-D	39.5	0.23	2.3	0.01	41.8	0.24
Unidentified	8.5	0.05	3.9	0.02	12.4	0.07

Wheat. In a wheat metabolism study [^{14}C]2,4-D EHE formulated as an emulsifiable concentrate solution was applied in a single over-the-top spray to spring wheat, at about the tiller stage, at 1.68 kg ae/ha which is in excess of the maximum label rate (Puvanesarajah, 1992). The radio purity of the formulated solution was 98% and the specific activity was 20,070 dpm/µg ae (2.0 mCi/mmol). The plants were grown under partially enclosed greenhouse conditions.

The TRR levels, as 2,4-D equivalents, in the forage, straw and grain samples were determined by combustion radio-analysis and liquid scintillation counting (LSC). The ^{14}C in the forage, straw and grain was extracted with organic and aqueous/organic solvents and 0.5 M KOH in aqueous methanol. The remaining residues were treated with enzymes. Diethyl ether and aqueous ethanol extraction recovered a large proportion of the residues in the forage and straw. Most of the residues recovered from the grain were in the aqueous and aqueous/methanolic KOH extracts. The distribution of the ^{14}C is shown in Table 10.

Table 10. Wheat. Distribution of ^{14}C in extraction solvents (Puvanesarajah, 1992).

Sample	Total ^{14}C, mg/kg[1]	% in ether	% in EtOH	% in AcN/H_2O	% in H_2O	% in KOH	% in enzyme digest	% in Aq. HCL	% un-extracted
10-day forage	34	20	66	N/A	N/A	12	0.04		0.4
49-day straw	56	14	63	N/A	N/A	19	1.7		0.4
49-day grain	0.30	N/A	N/A	3.7	7.7	28	10	22	8.9

[1] As 2,4-D ae

The radioactive residues in the extracts were separated by HPLC. Owing to the many metabolites and conjugates, quantification of the components by direct HPLC analysis of the extracts was not possible. Base and acid hydrolyses of the ether and ethanol extracts converted most of the metabolites to exocons which were separated by HPLC and their identities confirmed by MS and/or TLC (Table 11).

Table 11. Distribution of the components of extractable residues in wheat (Puvanesarajah, 1992).

Sample	Total ^{14}C, mg/kg [1]	% of Total ^{14}C extracts[4]					
		2,4-D EHE	2,4-D	2,4-dichloro phenol	Hydroxydichloro-phenoxyacetic acids[5]	In natural constituents	Not identified[6]
10-day forage	34	3.1 [2]	74 [2]	0.5 [3]	8 [3,]		9.8
49-day straw	56	2.0 [2]	70 [2]	0.9 [3]	8.5 [3]		12
49-day grain	0.3	-	6	-	-	45 [7]	41

[1] As 2,4-D acid ae
[2] Identity confirmed by MS, TLC and HPLC
[3] Identity confirmed by MS and HPLC
[4] Total of free and conjugated
[5] 4-Hydroxy-2,5-dichlorophenoxyacetic acid and two other structural isomers H_2 & H_3
[6] In general, this radioactivity is associated with many different fractions over a wide range of retention times and/or with radioactivity which was unaccounted for after HPLC analysis. Thus, no single unidentified component is present at the level shown.
[7] Incorporated into protein, starch and cellulose fractions

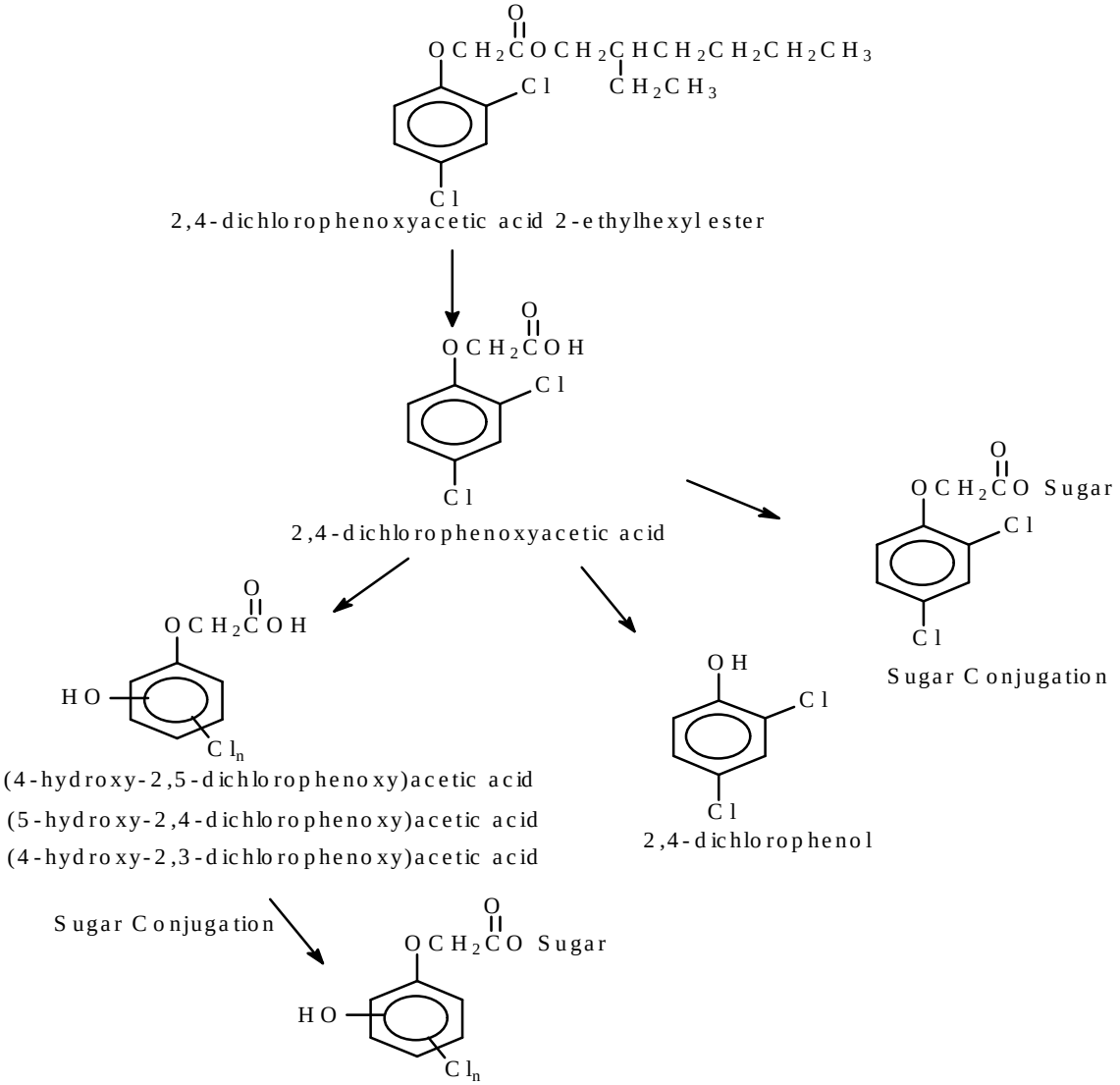
In forage and straw unconjugated 2,4-D was found at 9% and 6% respectively, and base-labile 2,4-D conjugates accounted for 64% of the total residues. The hydrolysis of these 2,4-D conjugates by a mild base suggests esterification with indigenous substances, presumably sugars. Approximately 33% of the total ring-hydroxylated 2,4-D derivatives identified in the forage were free residues extractable in ether, and the others were found as polar conjugates in the ethanol extract. These polar conjugates were stable to bases but were readily cleaved under acidic conditions, which suggests they were phenolic glycosides. A large portion (about 77%) of the ring-hydroxylated metabolites in the straw were polar conjugates. Side-chain degradation of 2,4-D to give 2,4-dichlorophenol was a minor pathway (see Table 11).

2,4-D residues identified in the grain extracts represented $\leq$6% of the total grain residues. 45% from the incorporation of ^{14}C into proteins, starch and cellulose. Untreated control samples had residues of 0.17 mg/kg. This ^{14}C contamination was attributed to the proximity of the control and treated wheat to another plot in which $^{14}CO_2$ was generated from the microbial breakdown of 2,4-D EHE applied to soil. Both the treated and control samples were analysed by the same schemes for the extraction of residues and isolation of natural products to distinguish between the residues resulting from treatment of wheat with [^{14}C]2,4-D EHE and that resulting from the uptake of $^{14}CO_2$. These parallel analyses demonstrated that the presence of ^{14}C in the control grain samples did not affect the conclusions on the nature of the residue in wheat grain after treatment of young wheat plants with [^{14}C]2,4-D EHE.

In later work on samples from the above study (Pither, 1992) the two isomeric hydroxydichlorophenoxyacetic acids reported as H_2 and H_3 in wheat forage and straw (at 1.4 to 2.5% of the total ^{14}C residue) were identified from their chromatographic mobilities and mass spectral data as 4-hydroxy-2,3-dichlorophenoxyacetic acid and 5-hydroxy-2,4-dichlorophenoxyacetic acid. These compounds had HPLC elution ranges of 15.0-17.5 min and 18.5-21.5 min respectively. The presence of the ^{14}C components with HPLC elution ranges similar to those of 2,4-D EHE and 2,4-D in the basic extract of control wheat grain was re-examined, and the presence of 2,4-D in the extracts of control and treated wheat grain was confirmed by the re-analysis. 2,4-D EHE could not be detected

in the basic extract from control wheat grain when precautions were taken to eliminate contamination by carry-over during HPLC analysis.

Figure 4. Metabolic pathways of 2,4-D EHE in spring wheat (Puvanesarajah, 1992; Puvanesarajah and Ilkka, 1992).



0 Metabolic Pathway for 2,4-D 2-EHE in Spring Wheat

Environmental fate in soil

Aerobic degradation

Concha. and Shepler (1994a) studied the aerobic degradation of [^{14}C]2,4-D in unsterilized Catlin silty clay soil applied at a rate of 5.1 mg/kg for 16 days. The samples were incubated at about 25°C throughout the study. Recoveries of radiocarbon averaged 95.6 ± 6.3%.

The 2,4-D was degraded rapidly and represented 0.5% of the applied dose after 16 days of exposure. The calculated half-life was 1.7 days based on pseudo-first order kinetics.

The main degradation product was CO_2, which accounted for 51.2% of the applied dose at the end of the study period. Two major products were 2,4-DCP (2,4-dichlorophenol) and 2,4-DCA (2,4-dichloroanisole) which rose and fell over the 16-day period. 2,4-DCP reached its maximum of 3.5% of the applied dose at day 2, then decreased to 0.4% at the end of the study period, while 2,4-DCA represented 2.5% of the applied dose at day 9 and decreased to 1.5%; and the unextractable residue was 36% of the TRR. Separation of the fulvic and humic acid fractions of an extracted sample at day 5 afforded 16% of the applied dose in the former and 11% in the latter. Further analysis of the fulvic acid fraction by HPLC recovered 6.1% of the applied dose as 2,4-D.

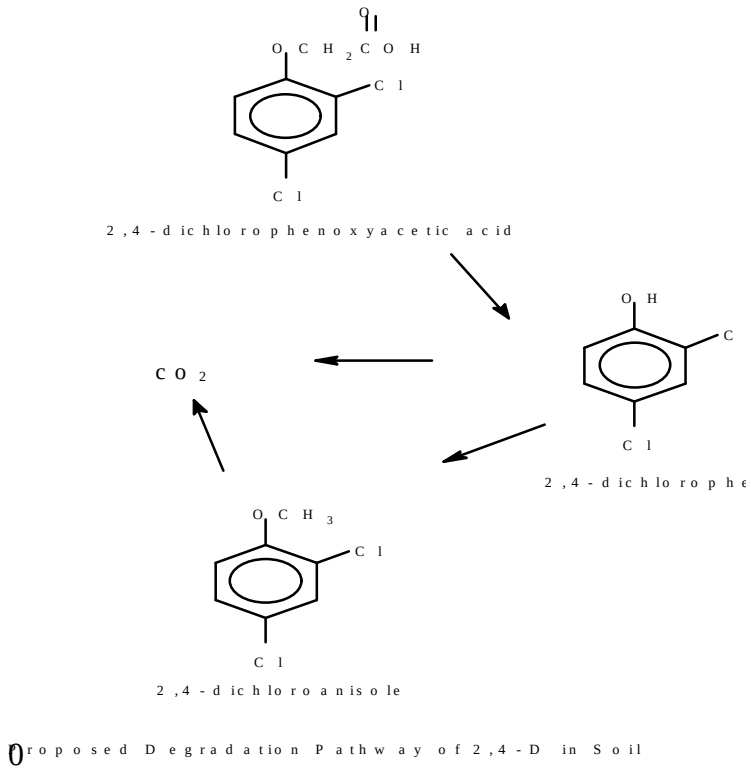
The results indicate that 2,4-D and its degradation products should dissipate rapidly from the soil environment mainly by mineralization and incorporation into the soil organic matter.

Reynolds (1994) determined the fate of the 2-ethylhexyl moiety of 2,4-D EHE by incubating ^{14}C-labelled 2-ethylhexanol in an aerobic soil system at 10 mg/kg under laboratory conditions at 25 ± 1°C in the dark. Sampling was at 0, 2, 4, 8, 12, 18, 24, 48, 168 and 336 hours after treatment.

Degradation was rapid. Initially most of the applied radioactivity was extracted into the organic solvent (methanol/methylene chloride) but the percentage of ^{14}C extracted decreased rapidly from 91% to 13% during the first 48 hours. By days 7 and 14, the organic extract accounted for 6.9% and 6.4% of the total applied radioactivity. The percentage of ^{14}C in the post-extraction solids (PES) remained fairly constant for the first 8 hours then began to increase dramatically, reaching its highest level (48% of the applied ^{14}C) at 48 hours. By day 14 the ^{14}C in the PES accounted for 22% of the total applied radioactivity.

During the first 24 hours the evolved acidic volatiles, including $^{14}CO_2$, increased gradually. Between 24 and 48 hours, however, the level detected in the KOH solution had quadrupled to 47%. Volatile ^{14}C accounted for a maximum of 70% of the applied ^{14}C on day 14.

Figure 5. Proposed degradation pathways of 2,4-D in soil (Concha and Shepler, 1994a).



Recoveries of ^{14}C from days 0 to 14 ranged from 93% to 108%. The average overall recovery of the applied radioactivity was 99%.

Analyses of the organosoluble fraction by reversed-phase HPLC showed one main product, which reached a maximum of 84% at 18 hours, in addition to 2-ethylhexanol. This was identified by GC-MS as 2-ethylhexanoic acid. Low levels of 5 other compounds were observed at later sampling times, but none of these exceeded 2.6% of the total applied radioactivity.

The PES fraction from day 14 was subjected to various procedures which included shaking for 4 hours with acetonitrile/water/acetic acid and refluxing for 1 hour with 0.25 *N* HCl, followed by shaking with 0.5 *N* NaOH for 24 hours to release the bound residues. The radioactivity extracted by $CH_3CN/H_2O/HOAc$ accounted for 1.6% of the total; 4% could be extracted from the solids following reflux with 0.25 *N* HCL for about 1 hour. The radioactivity that was extracted into the acid hydrolysate remained mostly in the aqueous fraction after partitioning with EtOAc. Less than 0.38% of the total applied radioactivity was detected in the EtOAc fraction. Most of the radioactivity in the solids appeared to be incorporated into natural soil constituents (fulvic acid, humic acid and humins). The ^{14}C in the fulvic and humic acids and humins was 4.2%, 4.6% and 7.5% of the total applied radioactivity respectively.

The half-life of 2-ethylhexanol in soil under the aerobic test conditions at 25°C was calculated to be 5.3 hours.

Reynolds (1995e) investigated the fate of the diethanolamine moiety from the diethanolamine salt by incubating diethanolamine with soil (10 mg/kg) under identical conditions to the above. [^{14}C]diethanolamine labelled on the 1-carbons was degraded rapidly with a calculated half-life in sandy loam soil of 1.35 days.

Analyses were by HPLC and TLC comparisons and LSC.

The parent compound steadily decreased throughout the study with the Hanford sandy loam soil. Two days after dosing, less than 38% of the total applied radioactivity was attributable to the parent compound. Its level had decreased to 0.9% of the applied ^{14}C by day 14 and to less than 0.6% at 90 days.

A total of ten products (M1-M10) were observed during the 90-day study. M2 accounted for 9.91% of the total applied radioactivity at day 0 but was not detected at day 1. Low levels of M2 appeared at day 2, reached a maximum of 1.4%, but then decreased to 0.1%.

The main product was M3 which, as determined by reversed-phase HPLC, reached 7.9% at day 2 and then steadily decreased to less than 1% at the end of the study. TLC analysis of the same fraction indicated that M3 consisted of three or four compounds, none of which exceeded 3% of the applied radioactivity.

Low levels of glycine (M4) and ethanolamine (M5) were also detected. Glycine reached a maximum of 5% at day 3, but at 90 days was less than 0.4%. Ethanolamine did not exceed 2.6% of the total radioactivity.

None of the products M6, M7, M8, M9 or M10 exceeded 0.8% of the dosed ^{14}C.

Up to 60% of the dosed ^{14}C in the sandy loam soil was converted to CO_2. The levels of bound residues reached a maximum of 33% at day 7. At day 90, the level of radioactivity detected in the post extraction solids (PES) accounted for 24% of the total applied ^{14}C.

The PES fraction from day 7 was subjected to acid hydrolysis for 4 hours followed by a 24-hour shaking with 0.5 *N* NaOH. Acid hydrolysis released 20% of the ^{14}C. Less than 1% of the radioactivity extracted by 0.25 *N* hydrochloric acid could be partitioned into ethyl acetate. TLC analysis of the aqueous fraction showed five or six compounds. The remaining radioactivity in the solids was incorporated into fulvic acid (4.4%), humic acid (3.7%) and humins (5%), indicating that diethanolamine is incorporated into the natural soil constituents and then mineralized to CO_2.

Adsorption/desorption

Cohen (1991b) determined the adsorption/desorption of unaged [^{14}C]2,4-D in unsterilized Louisiana rice paddy sediment by the batch equilibrium technique.

Two preliminary studies were conducted to determine the adsorption and desorption equilibrium times (24 and 8 hours respectively). It was also demonstrated that 2,4-D acid does not bind to glass surfaces.

A definitive study was conducted at five different concentrations (0.1, 0.51, 1, 2.47 and 5.02 mg/kg) at 22 ± 1°C. The K_d value for 2,4-D acid was 1.22 (K_{oc} = 58.1) indicating adsorption to sediment from water during the adsorption phase of the study. However, in the desorption phase, the K_d value of 1.64 (K_{oc} =78.1) indicated that 2,4-D is moderately to highly mobile in rice paddy sediment. The average ^{14}C recovery for the five concentrations tested was 98.9%.

Fathulla (1996b) studied the adsorption and desorption characteristics of [^{14}C]2,4-D on four representative agricultural soils. Samples were prepared at a soil:solution ratio of 1g:1ml, with nominal concentrations of [^{14}C]2,4-D in aqueous 0.01 *M* calcium chloride of 10, 5, 2.5 and 1 mg/ml. The samples were equilibrated in a shaking water bath for 24 hours at 25 ± 1°C, followed by vortexing and centrifugation. ^{14}C was measured in the resulting supernatant by LSC to determine the adsorption of the test material to the soil. The supernatant was then removed from each sample and replaced with an equal volume of untreated 0.1 *M* $CaCl_2$. The samples were equilibrated for 24 hours

at 25 ± 1°C, followed by vortexing and centrifugation. ^{14}C in the supernatant was determined by LSC and the radioactivity remaining in the soil after desorption was determined by oxidation followed by LSC.

Linear regression analysis of the adsorption and desorption data for all the soils demonstrated that adsorption and desorption of [^{14}C]2,4-D followed the Freundlich equation. The adsorption and desorption equilibrium constants (K_{d-a} and K_{d-d} respectively), and coefficients K_{oc-a} and K_{oc-d} are shown in Table 12.

Table 12. Adsorption and desorption data of 2,4-D in soils (Fathulla, 1996b).

Soil	Adsorption		Desorption	
	K_{d-a}	K_{oc-a}	K_{d-d}	K_{oc-d}
Plainfield sand	0.36	76	1.16	247
California sandy loam	0.17	70	0.81	338
Mississippi loam	0.28	117	1.48	617
Arizona silty clay loam	0.52	59	1.90	216

The test material was largely stable in the test system in all the soils. After 24 hours, the total amounts of unchanged [^{14}C]2,4-D in the adsorption solution and soil extract were 95% of the original for Arizona silty clay loam, 109% for California sandy loam, 97% for Mississippi loam, and 98% for Plainfield sand. [^{14}C]2,4-D was stable over a 24-hour period and in aqueous 0.01 *M* $CaCl_2$, 100% of radioactivity in the desorption solution was owing to unchanged [^{14}C]2,4-D after 48 hours,.

The potential for [^{14}C]2,4-D to leach though soil, based solely on estimations of relative mobility using K_{oc-a} values, is high for all the soils tested.

Fathulla (1996c) determined the adsorption and desorption characteristics of the soil degradation product 2,4-dichloroanisole (2,4-DCA) on the same four soils. Samples were prepared at a soil:solution ratio of 1g:5ml with nominal concentrations of [^{14}C]2,4-DCA in aqueous 0.01 *M* calcium chloride of 5, 2.5, 1 and 0.5 mg/ml. Other experimental details were as described above (Fathulla, 1996b).

Linear regression analysis of the data demonstrated that the adsorption and desorption of [^{14}C]2,4-DCA followed the Freundlich equation. The adsorption and desorption equilibrium constants and coefficients are shown in Table 13.

Table 13. Adsorption and desorption of 2,4-DCA in soils (Fathulla, 1996c).

Soil	Adsorption		Desorption	
	K_{d-a}	K_{oc-a}	K_{d-d}	K_{oc-d}
Plainfield sand	2.05	436	3.4	721
California sandy loam	1.6	667	2.4	996
Mississippi loam	3.46	1,442	4.5	1,867
Arizona silty clay loam	5.42	616	8.6	975

The test material was again stable in all the test systems. After 24 hours, the total amounts of unchanged [^{14}C]2,4-DCA in the adsorption solution and soil extract were 94% of the original for

Arizona silty clay loam, 105% for California sandy loam, 105% for Mississippi loam and 103% for Plainfield sand. After 48 hours 100% of the radioactivity in the desorption solution was due to unchanged [^{14}C]2,4-DCA.

The potential for 2,4-DCA to leach though the four soils, on the basis of the K_{oc-a} values is medium to low.

Fathulla (1996d) also studied the adsorption and desorption characteristics of 2,4-dichlorophenol in the four agricultural soils. Samples were prepared at a soil:solution ratio of 1g:2ml, with nominal concentrations of [^{14}C]2,4-DCP in aqueous 0.01 *M* calcium chloride of 10, 5, 2.5 and 1 mg/ml. Other experimental details were as described above (Fathulla, 1996b).

The adsorption and desorption of [^{14}C]2,4-DCP again followed the Freundlich equation. The adsorption and desorption equilibrium constants and the adsorption and desorption coefficients are shown in Table 14.

Table 14. Adsorption and desorption of 2,4-DCP in soils (Fathulla, 1996d).

Soil	Adsorption		Desorption	
	K_{d-a}	K_{oc-a}	K_{d-d}	K_{oc-d}
Plainfield sand	1.7	368	3.8	813
California sandy loam	1.97	821	6.3	2,625
Mississippi loam	2.9	1,204	5.6	2,325
Arizona silty clay loam	3.3	374	7.1	807

The test material was largely stable in all four test systems. After 24 hours, the total amounts of unchanged [^{14}C]2,4-DCP in the adsorption solutions and soil extracts were 92.5% of the original for Arizona silty clay loam, 93% for California sandy loam, 92% for Mississippi loam and 92% for Plainfield sand. [^{14}C]2,4-DCP was shown to be stable for 24 hours in aqueous 0.01 *M* $CaCl_2$, and for 48 hours in the desorption solution.

The potential for [^{14}C]2,4-DCP to leach though the tested soils is low, on the basis of the K_{oc-a} values.

Mobility

Burgener (1993) used lysimeters to represent an agricultural ecosystem in which to study the translocation of [^{14}C]2,4-D and its degradation products in a 120 cm soil and the effects of precipitation and vegetation of leaching. Information on the uptake of the pesticide by plants after soil application, as well as the ^{14}C balance after 725 days, was also obtained.

Two lysimeters were covered with summer wheat. On 15 June 1990, the herbicide was applied as the DMA salt at its recommended field rate, 750 g ae/ha. Husbandry and crop rotation followed common agricultural practice. Winter rye was sown in November 1990, followed by winter rape after harvest of the rye in summer 1991.

Water samples were taken regularly and ^{14}C was determined by LSC to estimate the contribution of dissolved $^{14}CO_2$ from the mineralization of the test compound. The remaining radioactivity was characterized by chromatographic techniques. The radioactivity taken up by the plants as well as that in the soil at the conclusion of the experiment was determined by combustion, while $^{14}CO_2$ and other volatile substances emitted to the atmosphere were calculated by difference.

In lysimeter 1 the ^{14}C recovered in the leachate after 2 years was 0.196% of the total applied radioactivity, corresponding to 0.14 mg parent equivalents. The total mean recovery of radioactivity, all leachate samples included, represented a concentration of 0.14 mg parent equivalents/l. After subtraction of $^{14}CO_2$, which represented 0.099% of the applied radioactivity, the remaining concentration was reduced to 0.07 mg/l. During the whole experimental period, 958 l of water (about 48% of the total precipitation, including irrigation) had been collected.

In lysimeter 2 the radioactivity in the water after two years was 0.25% of the total applied corresponding to 0.17 mg parent equivalents. The total mean recovery of radioactivity, all leachate samples included, represented 0.175 mg parent equivalents/l and 0.058% of the total applied radioactivity was $^{14}CO_2$. After subtracting this, the mean content of ^{14}C as 2,4-D was 0.13 mg/l. During this period, 994 l of water was collected, representing about 50% of the total precipitation, including irrigation.

No volatile substances except for $^{14}CO_2$ were detected in the leachates by TLC or HPLC.

[^{14}C]2,4-D DMA salt, the free acid and its known degradation products 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol were not detected in any of the leachates. In both lysimeters, a maximum of three unknown radioactive fractions were detected. The main unknown fraction was present in all the analysed leachate samples. It amounted in total to 0.043% of the applied radioactivity (AR) in lysimeter 1 and to 0.087% in lysimeter 2. The radioactivity evidently originated from very polar residues, and may be assumed in part to be derived from cleaved ring fragments bound to humic and fulvic acids.

At the conclusion of the experiment, soil cores were sectioned into 12 horizontal segments of about 10 cm thickness. In lysimeter 1, the TRR in the soil profile amounted to 21% of the AR, 11% in the top layer. For lysimeter 2 the corresponding proportions were 17% and 8.8%. In both lysimeters, only about 0.1% of the AR was found in the soil below 57 cm.

The extractable radioactivity in the soil again originated from three unknown fractions, the patterns and amounts of which in the soil extracts from the two lysimeters compared well and were nearly identical. Radioactivity was found as deep as 17 cm and amounted in total to 0.26% of the AR in the soil of lysimeter 1 and 0.29% in lysimeter 2. The decomposition products 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol were not detectable in any of the six analysed soil layers, which covered a depth of 57 cm.

The water collected during the experiment represented about 50% of the total precipitation. In June 1990, a series of exceptionally heavy rainfalls started one week before the application. Although the total amount in this month was nearly twice the monthly average for the region, the unfavourable conditions did not yield high concentrations of radioactivity.

The number and levels of the compounds found in the leachate and soil samples compared well in the two lysimeters. The results obtained indicated that [^{14}C]2,4-D and its decomposition products are not mobile in the sandy soil used in the experiment and 2,4-D is therefore not considered to have any potential to leach into ground-water. The leached radioactivity originated entirely from very polar unidentified residues.

Uptake by rotational crops

Burnett and Ling (1994) determined the level and nature of the 2,4-D residues taken up by rotational crops from soil treated with [^{14}C]2,4-D, applied by broadcast spray to bare ground on each of three plots at a rate equivalent to 2.2 kg ae/ha. Rotational crops, wheat, icicle white radish and lettuce, were planted 30 days after treatment (DAT) and 139 DAT.

Soil residues decreased significantly during the initial 30 DAT and chromatographic analysis of soil extracts indicated substantial degradation of 2,4-D during this period. Only 8.7% of the soil residues at 30 DAT were soluble in ether compared to an average of 97.5% at 0 DAT. The radioactivity recovered from soil cores at 0 DAT was identified as being from 2,4-D by HPLC, but at 30 DAT only 1.1% of the applied radioactivity was tentatively attributed to 2,4-D.

The TRR as 2,4-D equivalents in the 30 DAT crops except wheat forage ranged from 0.01 mg/kg to 0.06 mg/kg:

Sample	TRR, mg/kg as 2,4-D	
	30 DAT	139 DAT
Radish top	0.043	0.01
Radish root	0.01	0.011
Lettuce	0.019	0.013
Wheat forage	<0.001	0.03
Wheat straw	0.06	0.084
Wheat grain	0.049	0.06

No ether-soluble residues above 0.01 mg/kg were found in any plant samples, whereas in control tissues fortified with 2,4-D more than 65% of the activity was ether-soluble. All samples contained ethanol-soluble residues, but these exceeded 0.01 mg/kg only in radish tops and wheat straw (30 DAT radish tops 0.011 mg/kg, 30 DAT wheat straw 0.017 mg/kg, 139 DAT wheat straw 0.014 mg/kg).

Most of the radioactivity in the plants was not extractable with ether or acidic aqueous ethanol. Hydrolysis of the bound residues solubilized varying amounts of ^{14}C but only traces of ether-soluble residues, none above 0.004 mg/kg. Radioactive components at the retention times of 2,4-D and a hydroxylated product were observed on HPLC analysis of the ether extract of acid-hydrolysed radish tops at [0.001 mg/kg.

In the wheat straw at 30 DAT, crude lignin and cellulose contained 0.01 mg/kg and 0.007 mg/kg respectively. Wheat grain from both planting intervals was shown to contain ^{14}C incorporated into glucose isolated from the starch. The amount of [^{14}C]glucose was consistent with the amount of starch in typical wheat grain (60-70%).

The results showed no ether-soluble residues from free or conjugated 2,4-D or its known wheat metabolites at levels above 0.01 mg/kg after a 30-day planting interval. Extraction, hydrolysis and chromatographic characterization, supported by the detection of ^{14}C in glucose from starch, indicate that the radioactive residues in the rotational crops at both 30 and 139 DAT were owing to natural incorporation.

Terrestrial field dissipation

Fifteen terrestrial field soil dissipation studies were conducted with 2,4-D EHE (Barney, 1995a-d, j; Hatfield, 1995c-j; Silvoy, 1995a,b), and 18 with 2,4-D DMA (Barney, 1995e-i; Burgener, 1993; Hatfield, 1995k-r; Silvoy, 1994a-d). The results were summarized by Wilson *et al.* (1997).

Each test substance was characterized before use. Maximum label rates and treatment sequences were applied to each crop. In some of the trials, test plots were established in bare soil as well as in cropped areas.

In 1993, test sites in Colorado, North Carolina, and Texas (USA) were treated with commercial liquid formulations of 2,4-D DMA or 2,4-D EHE applied as diluted sprays. The Colorado and North Carolina trials included wheat and turf cropping practices with adjacent bare soil treatments, while the Texas plots included pasture cropping.

The wheat and bare soil plots had 1.4 kg ae/ha applied in May and again in July. In Colorado the soil was sandy clay loam with 1.3 to 1.8% organic matter (OM) and pH 7.8 to 8.1 (total precipitation plus irrigation 32 to 36 cm); in North Carolina sand with 0.77 to 1.4% OM, pH 5.4 to 6.9 pH (total precipitation plus irrigation 52 to 86 cm). Turf and adjacent bare soil treatments in North Carolina and pasture treatments in Texas consisted of 2.2 kg ae/ha applied in May and June. In Texas, the soil varied from sandy loam to silt loam with 1.5 to 1.6% OM, pH 6.0 to 6.1 (total precipitation plus irrigation 94cm).

In 1994 the test sites were in California, Nebraska, North Dakota, and Ohio. Sprays of both the amine salt and ester were applied to bare soil following a treatment regime for maize in Nebraska and Ohio, wheat in North Dakota, and pasture, bare soil, and turf in California. A commercial granular formulation of 2,4-D DMA was applied to bare soil and turf in North Dakota, and a 2,4-D EHE granular formulation to bare soil and turf in Ohio.

The maize treatment regime consisted of applications to bare soil of 2.2 kg ae/ha in May, 1.1 kg ae/ha in June, 0.56 kg ae/ha in July, and 1.7 kg ae/ha in September/October. In Nebraska the soil was silt loam with 2.9 to 3.5% OM and pH 5.7 to 6.7. Total precipitation plus irrigation was 79.5 cm. In Ohio the soils included a silty clay loam, clay loam, and silt loam with 2.0 to 5.0% OM and pH 6.5 to 7.1. Total precipitation plus irrigation was 47 to 97 cm. The wheat treatments consisted of 1.4 kg ae/ha applied in June and August. In North Dakota the soils ranged from sandy loam to loam with 2.9 to 6.4% OM and pH 5.9 to 7.7. The total precipitation plus irrigation ranged from 33 to 34 cm. Turf, pasture, and adjacent bare soil treatments consisted of 2.2 kg ae/ha applied in March through July with second applications in April through August. In California, soils varied from a sandy loam to loamy sand with 0.7 to 3.9% OM and pH 6.3 to 7.9. Total precipitation plus irrigation ranged from 67 to 142 cm.

In addition to 2,4-D, the analytical method employed was designed to extract and determine the ester 2,4-D EHE, 2,4-dichlorphenol and 2,4-dichloroanisole. The last two were shown to be relevant in soil degradation studies. The analytes were extracted from soil samples by a combination of three solvent systems and sonication. The combined extracts were diluted with water and concentrated on a C-18 solid-phase cartridge. The analytes were eluted sequentially with two solvent systems that yielded two eluates. The first eluate, containing 2,4-D EHE, 2,4-DCP, and 2,4-DCA, was chromatographed without derivatization. The second contained 2,4-D which was methylated with BF_3/methanol and partitioned into hexane. The first eluate and the hexane solution were combined for analysis by GC-MS. Recoveries of 2,4-D from fortified soil ranged from 91% at 0.01 mg/kg to 76% at 10 mg/kg with an LOD of 0.01 mg/kg.

Half-lives ($t_{1/2}$) for 2,4-D in soil were calculated for each trial by regression analysis of the residue data. Verification techniques showed applications to be generally close to the targeted levels. Soil half-life values were calculated using only the residues found in the 0- to 15-cm soil layer. The lower layers were not included because the residues were generally low (0 or <10% of those in the 0-15 cm layer), and the rate of degradation has been shown to decrease with increasing soil depth.

Tables 15 and 16 show 2,4-D residues found at various samplings after the maximum number of applications in the 1993 and 1994 trials respectively. For the 2,4-D EHE treatments, the residues shown are the sum of 2,4-D plus the remaining 2,4-D EHE expressed as 2,4-D. Half-lives are also shown for each trial. These were determined from regression analyses using all sampling intervals, and from analyses using the highest residue value found as the initial value. When two half-life values are shown, the first was calculated from all the samplings and the second by taking the highest residue as the initial value.

Table 15. 2,4-D residues and half-lives in 1993 trials. All spray applications (Wilson *et al.*, 1997).

Type of trial, location	Compound applied	$t_{1/2, days}$	Residues, mg/kg, at days after application

			0	1	3	7	14	30	64
Bare soil Wheat-CO	Amine Ester	5.1-4.3 2.2	0.35[1] 0.52[2]	0.38 0.48	0.36 0.35	0.53 0.16	0.05 0.01		
Bare soil Wheat-NC	Amine Ester	3.0 3.0-2.5	0.3 0.19	0.28 0.3	0.12 0.34[3]	0.14 0.05	0.01[4] 0.01[4]		
Wheat CO	Amine Ester	9.3-7.1 2.6-2.3	0.2 0.22	0.31 0.31	0.23 0.28[5]	0.27 0.04	0.08 <0.01		
Wheat NC	Amine Ester	3.1-2.9 6.1-6.5	0.26 0.12	0.28 0.12	0.1[5] 0.17[3]	0.17 0.06[6]	<0.01[4]	<0.01	
Bare soil Turf-NC	Amine Ester	2.5 1.7	0.89 0.62	0.38 0.63	0.16[3] 0.36[3]	0.03[7] 0.03[7]	0.013 <0.01		
Turf NC	Amine Ester	2.3 3.9	0.88 0.63	0.57 0.38	0.13[3] 0.39[3]	0.095[7] 0.04[7]	<0.01 <0.01	<0.01[8]	
Pasture TX	Amine Ester	10.7 12.8	0.44 0.33	0.38 0.29	0.21 0.22	0.15 0.1	0.09[4] 0.05[4]	0.05 0.05	<0.01 <0.01

[1]Residues from amine applications are 2,4-D acid
[2]Residues from ester applications are the sum of 2,4-D acid and 2,4-D EHE expressed as 2,4-D ae
[3]Two days
[4]Fifteen days.
[5]Four days.
[6]Eight days.
[7]Five days.
[8]Thirty five days.
[9]Twenty five days.

Table 16. 2,4-D residues and half-lives in 1994 trials, spray and granule applications (Wilson *et al.*, 1997).

Type of trial	Compound applied	$t_{1/2, days}$	Residues, mg/kg, at days after application						
			0	1	3	7	14	30	60
Spray									
Bare soil maize NE	Amine Ester	2.8 4.1	0.59[1] 0.52[2]			0.32 0.21	0.05 0.13	 0.003	
Bare soil maize OH	Amine Ester	16.1-15.9 6.7-5.2	0.47 0.59	0.75 0.59	0.73 0.87	0.5 0.78	0.44 0.48	0.07 0.03	0.01
Wheat ND	Amine Ester	4.5 5.3	0.64 0.51	0.53 0.49	0.21 0.39	0.11 0.19	0.07 0.09	0.005 0.009	
Pasture CA	Amine Ester	30.6-31.2 25.6-27.5	0.34 0.29	0.56 0.34	0.39 0.15	0.13 0.09	0.15 0.08	0.09[3] 0.08[3]	0.04[4] 0.04[4]
Turf CA	Amine Ester	7.5 8.5	0.12 0.15	0.09 0.13	0.08 0.04	0.21 0.09	0.02 0.02	 0.01[5]	 5
Bare soil turf CA	Amine Ester	2.3-2.1 11.0	0.83 0.42	1.4 0.29	0.82 0.30	0.13 0.28	0.02 0.15		
Granular									
Turf ND	Amine	5.1-4.0	0.1	0.11	0.74	0.07	0.02	<0.01	
Bare soil turf ND	Amine	14.6-14.5	1.2	1.6	1.9	1.7	0.89	0.27	0.03[7]
Turf OH	Ester	296-84	0.18	0.74	0.28	0.25	0.19	0.07[6]	<0.01[4]
Bare soil turf OH	Ester	9.9	1.6	1.1	1.3	1.3	1.5	0.05[6]	0.01[4]

[1]Residues from amine applications are 2,4-D acid.
[2]Residues from ester applications are the sum of 2,4-D acid and 2,4-D EHE expressed as 2,4-D.
[3]Twenty nine days.
[4]Fifty eight days.
[5]Twenty days.
[6]Thirty one days.
[7]Sixty two days

Environmental fate in water/sediment systems

Aquatic degradation

Cohen (1991a) studied the aerobic aquatic degradation of uniformly ring-labelled [^{14}C]2,4-D at a concentration of 4.6 mg/kg in a mixture of sieved (2-mm), unsterilized Louisiana rice paddy sediment (clay soil) and water (320 g sediment, 534 g water, 854 g total). The untreated mixture was pre-incubated under aerobic aquatic conditions in darkness at 25°C for 218 days to activate microbes, then [^{14}C]2,4-D in acetonitrile was mixed thoroughly with the sediment/water in the incubation flask and aerobically incubated in darkness at 25°C for 30 days. The soil was continuously purged with humidified air at 30 ml/minute to flush any volatile compounds formed into a series of trapping solutions (ethylene glycol, 1 *M* sulfuric acid and 5% sodium hydroxide).

Samples of the test system were taken immediately after treatment (day 0) and at 2, 5, 12, 20, 27 and 30 days after treatment. Sediment/water samples were separated by centrifugation and aliquots of sediment were combusted and the ^{14}C determined by LSC. The remaining sediment samples were extracted with 1.5 *M* phosphoric acid mixed with ethyl ether, washed with water, and re-extracted with 1 *N* sodium hydroxide solution. ^{14}C was measured in aliquots of all extracts and in duplicate samples of the supernatant and trapping solutions by LSC.

The sediment extracts and the water supernatant were analysed by HPLC with both UV (280 nm) and radio detection in series. Radioactive flow detection allowed identification of 2,4-D and its aerobic degradation products at a level of 0.01 mg/kg (limit of detection 0.005 mg/kg).

Analysis of the sediment/water samples showed that the half-life of 2,4-D acid was 15 days under aerobic aquatic conditions.

The degradation product chlorohydroquinone reached a maximum concentration of 17% (0.78 mg/kg) of the initial radioactivity on day 27 and decreased to 11% (0.52 mg/kg) by day 30. A minor product, 2,4-dichlorophenol, accounted for 4.9% (0.23 mg/kg) and CO_2 for 16% (0.74 mg/kg) of the initial ^{14}C by day 30.

The recovery of ^{14}C during the study (soil extractable and unextractable + water-soluble + cumulative volatiles) ranged from 69 to 100% of the initial radioactivity.

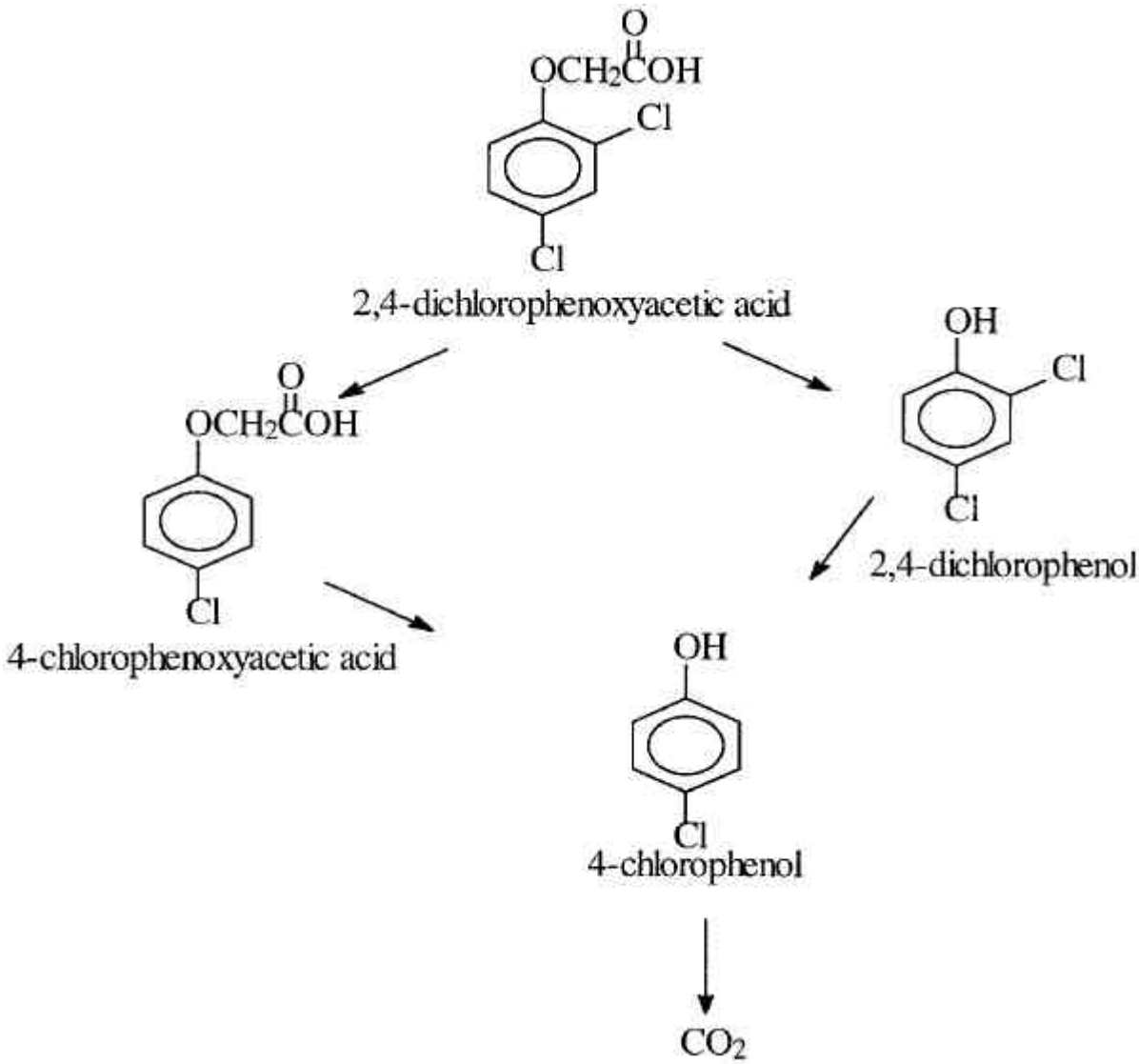
Concha and Shepler (1993a) studied aerobic aquatic degradation of [^{14}C]2,4-D in pond sediment and water samples from Henry County, Illinois with an application rate of 5 mg/kg for up to 46 days, and incubation at 25°C. The aqueous phase was monitored at each sampling for pH (7 to 8) and dissolved oxygen content (2.7 to 6.75 mg/kg).

[^{14}C]2,4-D acid was degraded slowly in the first 25 days and represented $\leq$75% of the applied dose at 25 days. It decreased rapidly n the next 10 days, and at 46 days it represented 0.5% of the applied radiocarbon. Its half-life was 4.5 days.

The main degradation product was CO_2 (64% of the applied radiocarbon at 46 days). 2,4-DCP, 4-CPA and 4-chlorophenol were present in both the water and sediment extracts. 2,4-DCP accounted for 1.1% of the applied ^{14}C at day 35 and decreased to 0.1% at day 46, and 4-CPA rose to 1.1% at day 14 and decreased to untraceable amounts. 4-chlorophenol represented 1.4% of the applied radiocarbon after 20 days and decreased slowly to zero by day 46. An unknown product was observed in the water phase of the samples after 35 days (1.1% of the applied dose); it was unstable when stored frozen or refrigerated and was converted to CO_2 and other volatile products upon acidification of the water-phase. No organic volatiles were detected above 0.1%. The unextractable residue increased with exposure time and constituted about 16% of the applied dose at day 46.

Radiocarbon recoveries averaged 93 ± 7%. During the lag time (25 days) most of the radiocarbon (>64%) was found in the water, and approximately 10 to 14% was extracted from the sediment in an alkaline solvent and about 4% in acidic acetone. After the lag time the radiocarbon distribution shifted dramatically as 2,4-D acid was degraded. At day 46 3% of the applied dose was recovered in the water phase, with 1.0% and 0.6% extracted in base and acidic solvents respectively. The overall material balance dropped slightly at day 35 but increased at day 46. This decrease is attributed to the rapid, massive production of CO_2 after the lag period that may not have been trapped efficiently which the trapping solutions were being changed. A separate sample was incubated and left unopened for 39 days, and higher recovery (92%) confirmed that the loss of radiocarbon was owing to the loss of untrapped CO_2 in the headspace.

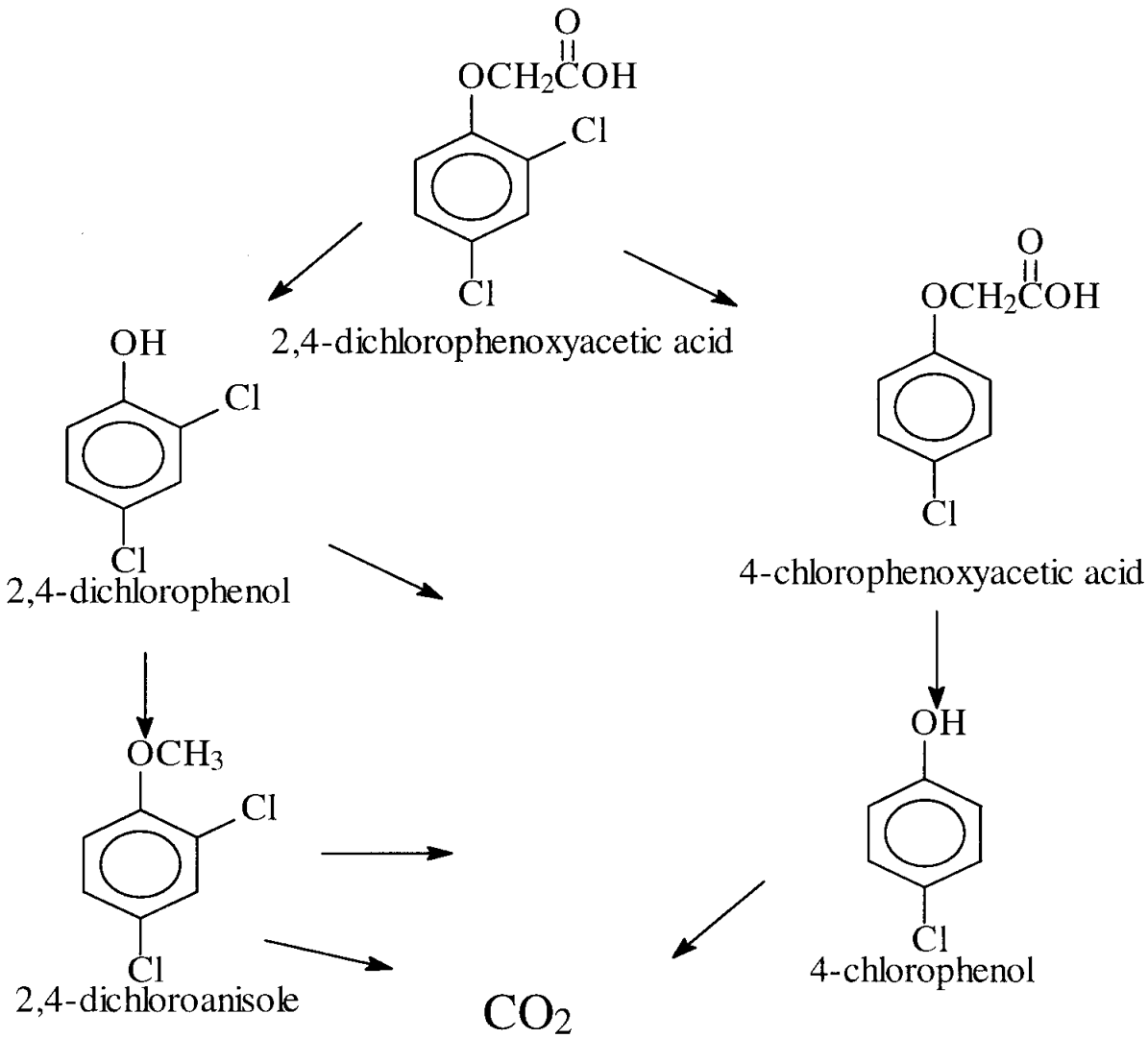
Figure 6. Degradation pathways of 2,4-D in an aerobic pond sediment/water system (Concha and Shepler, 1993a).



Concha and Shepler (1994b) studied the anaerobic aquatic degradation of [^{14}C]2,4-D (4.9 mg/kg) in raw pond sediment and water in Henry County, Illinois for one year. Samples were incubated at 25°C throughout the study and the aqueous phase was monitored at each sampling for pH (7.6-9.6). CLICK HERE for continue

Radiocarbon recoveries averaged 101 ± 5.2%. The distribution of ^{14}C varied depending on the extent of degradation observed in individual samples. The radiocarbon in the aqueous phase amounted to 24-85.5% of the applied ^{14}C and that in the organic extracts of sediment to 11-42%. Bound radiocarbon increased with increased degradation and after 240 days 35% of the applied ^{14}C remained unextracted. A sample taken on day 240 contained 2.4% of the ^{14}C in the humic acid and 14.9% in the fulvic acid fraction, with 23.5% remaining unextracted. Organic volatiles in the foam plugs accounted for up to 2.3% of the applied dose and $^{14}CO_2$ trapped in caustic solutions reached an average of 22% after 365 days.

Figure 7. Degradation pathways of 2,4-D in an anaerobic pond sediment/water system (Concha and Shepler, 1994b).



Compounds in the water, sediment extracts and foam plug extracts were identified by HPLC or two-dimensional TLC. The main component in the aqueous phase was 2,4-D, which represented 26% of the applied dose after 365 days. In the sediment extracts the parent compound constituted 13% of the applied radiocarbon at that time, giving a total of 39% 2,4-D in the test system. The two major degradation products were 2,4-DCP, which rose to 22% at day 30 and subsequently decreased to 4.2% after 365 days, and CO_2. Small unidentified peaks with various retention times were detected in some HPLC radiochromatograms. The largest unknown after 365 days represented 1.5%

of the dose. Small quantities of volatiles were extracted from the foam plugs, and at 365 days they included 4-chlorophenol (1.9%), 2,4-dichloroanisole (0.7%) and 2,4-DCP (0.7%).

The approximate half-life of 2,4-D was calculated to be 312 days ($r^2 = 0.69$).

Fathulla (1996a) studied the aerobic aquatic degradation of [^{14}C]2,4-D in representative sediment and water from Lake Mendota, Dane County, Madison, Wisconsin (USA).

Eighteen samples were prepared by placing approximately 3 g (dry-weight equivalent) of 2-mm sieved sediment and 30 ml lake water in glass containers. The test material was added to each sample in solution at a nominal concentration of 10 mg/kg. The day 0 samples were analysed as soon as possible after dosing. The other sample containers were gently shaken, and the water level was marked on each container. To maintain aerobic conditions and to collect volatile components, the sample vessels were connected to a glass manifold which was attached to a series of traps: ethylene glycol, 0.1 *N* sulfuric acid and two containing 2 *N* KOH. Air was sucked continuously through the traps and the test apparatus maintained in a dark, temperature-controlled room at 25°C. The pH, oxidation-reduction potential (Eh) and dissolved oxygen (DO) were monitored for all samples and throughout the study to ensure that the aerobic conditions were maintained.

The water layer and sediment were separated by centrifugation. The concentration of radioactivity in the water was determined by LSC, and the radioactive compounds separated by HPLC. The sediment samples were extracted first with 5% v/v acetic acid (HOAc) in methanol (MeOH), then with 50:50 MeOH/5% HOAc and finally with 5% aqueous HOAc. The three extracts were combined, the concentration of radioactivity was determined by LSC and the extract analysed by HPLC.

The recovery of radioactivity ranged from 97 to 103%, almost all of it (94-101%) in the water layer. The radioactivity in the sediment extracts did not exceed 3.1% of that applied, and the mean did not exceed 0.1%. Radioactive carbon dioxide was the only volatile component determined in the traps, increasing from 0.015% of the total applied radioactivity at day 1 to 0.28% at day 30.

The radioactivity in the water layers and sediment extracts from days 0 through 30 was almost entirely owing to [^{14}C]2,4-D, with mean percentages of the applied ^{14}C ranging between 103% at day 0 and 97% at day 8. Because no significant degradation was observed it was not possible to calculate the half-life. A single minor component, detected only in one replicate at day 30, accounted for 0.1% of the total applied radioactivity. The identity of [^{14}C]2,4-D was confirmed by two-dimensional TLC and HPLC co-chromatography with an unlabelled reference standard.

Under aerobic aquatic conditions, [^{14}C]2,4-D was not significantly degraded during a 30-day incubation period. In addition to [^{14}C]2,4-D, small amounts of $^{14}CO_2$ (accounting for 0.28% of the initial ^{14}C) and one other component (0.1%) were detected by day 30.

Levine (1990) studied the aquatic degradation of [^{14}C]2,4-D at a concentration of 4.9 mg/kg in sieved (2 mm), unsterilized Louisiana rice paddy sediment (clay soil) and water. The untreated mixture was pre-incubated under anaerobic conditions in darkness at 25 ± 0.8°C for approximately 138 days to activate soil microbes. After the activation period, [^{14}C]2,4-D acid in acetonitrile was mixed thoroughly with the sediment/water mixture in the incubation flask, which was then anaerobically incubated in darkness at 25 ± 0.8°C for 365 days. The mixture was continuously purged with humidified nitrogen at 45-50 ml/minute to flush any volatile compounds formed into a series of trapping solutions (ethylene glycol, 1 *M* sulfuric acid, ethanolamine and 5% sodium hydroxide).

Samples of the test mixture were taken immediately after treatment and after 1, 6, 13, 22, 35, 70, 85, 120, 160 224, 281, 338 and 365 days. The sediment and water were separated by centrifugation and replicate sediment samples were combusted and analysed for total radioactivity

by LSC. Additional duplicate samples were extracted with 1.5 *M* phosphoric acid mixed with ethyl ether, washed with water and finally re-extracted with 1 *N* sodium hydroxide solution. ^{14}C was measured in all the extracts and in replicate supernatant water samples and trapping solutions by LSC.

The water samples and sediment extracts were analysed by HPLC with a UV (280 nm) detector and a radioactive flow detector connected in series. Radioactive flow detection allowed identification of 2,4-D and its degradation products at µ0.01 mg/kg. TLC was used as a confirmatory method of identification.

Analysis showed that 2,4-D acid was degraded with a half-life of 41 days under anaerobic aquatic conditions. The main product formed during the 365-day incubation period was 4-chlorophenol, and 2-chlorophenol was a minor product. All ^{14}C residues at or above 0.01 mg/kg were identified.

CO_2 production reached 71% of the initial radioactivity (3.5 mg/kg as 2,4-D) by the end of the study.

The extraction of ^{14}C from the sediment samples ranged from 90 to 102% of the radioactivity present at each sampling, and the total recovery (sediment extractable and unextractable + water supernatant + cumulative volatiles) ranged from 52 to 98% of the day 0 radioactivity. The incomplete recovery was owing to loss of the volatile $^{14}CO_2$.

The results indicate that 2,4-D acid is not likely to remain long in the environment under anaerobic aquatic conditions.

Reynolds (1995b) showed that ^{14}C-labelled 2-ethylhexanol was degraded quickly when incubated at approximately 10 mg/kg in flooded soil under anaerobic conditions at 25 ± 1°C.

The percentage of ^{14}C in the supernatant fraction decreased from 75% at day 0 to 59% at day 3 where it seemed to stabilize throughout the remainder of the study. The proportion of radioactivity that could be extracted from the solid fraction into CH_3OH/CH_2Cl_2 remained at a level of 22 to 26% for the first 30 days. By 60 days, 14% of the initial radioactivity was found in the CH_3OH/CH_2Cl_2 fraction and this proportion stayed fairly constant throughout the remaining period. The percentage of ^{14}C in the post-extraction solids fraction ranged from 6.7% (day 3) to 1.9% (day 179) but remained fairly constant from day 14 to day 270.

The evolved acidic volatiles, including $^{14}CO_2$, increased gradually with time, accounting for 14% and 25% at 30 and 270 days respectively. Barium salt precipitation from the KOH solution at each sampling indicated that there were other volatiles besides $^{14}CO_2$. The mean $^{14}CO_2$ ranged from 1.1% (day3) to a maximum of 9.1% (day 179) of the applied radioactivity. Analysis of a composite of day 224 KOH samples showed the main component to be 2-ethylhexanol.

The water samples and organosoluble extracts were analysed by reversed-phase HPLC. The main compounds were 2-ethylhexanoic acid and 2-ethylhexanol.

The parent 2-ethylhaxanol decreased quickly accounting for 22% of the total applied radioactivity after 30 days, 5.1% after 60 days and was undetectable at 270 days. The 2-ethylhexanoic acid was first observed at day 7 (9.3%) and reaching a maximum of 61% at 120 days, then remaining stable. At 270 days, 59% of the applied dose was still 2-ethylhexanoic acid.

The radioactivity from 2-ethylhexanol in the CH_3OH/CH_2Cl_2 fraction decreased from 24% of the applied radioactivity at day 0 to 2% at day 30, 0-0.53% was detected in the remaining samples. The main product was again 2-ethylhexanoic acid, at 19% after 30 days. It decreased slightly thereafter but then remained stable until the last sampling.

There were four other minor products, none exceeding 2.4% of the total applied radioactivity. Recoveries of ^{14}C ranged from 97% to 105% with a mean of 99%.

In summary under anaerobic conditions, [^{14}C]2-ethylhexanol at an application rate of 10 mg/kg was degraded to 2-ethylhexanoic acid and further mineralized to $^{14}CO_2$ by micro-organisms in the sediment/water test system. Significant levels of 2-ethylhexanol were also detected in the KOH trapping solution together with $^{14}CO_2$. The half-life of 2-ethylhexanol was 14 days.

Reynolds (1995a) established that under laboratory conditions at 25 ± 1°C and in the dark, dimethylamine (DMA) was degraded very quickly in an aerobic water/sediment system containing approximately 10 mg/kg. The estimated half-life was 2.8 days.

Analyses were by comparative HPLC and TLC with LSC.

Quantitative recoveries of ^{14}C were obtained throughout the 14 days of the study from all samples, with an average of 99.6%.

Nine degradation products were observed. The main product, monomethylamine (MMA), was detected at day 0 and accounted for 5.9% of the total applied radioactivity. It gradually decreased with time and accounted for 1.2% of the total initial radioactivity at the end of the period. None of the other products accounted for more than 0.29% of the applied ^{14}C in any sample.

The evolved acidic volatiles trapped in KOH solution increased dramatically during the 14 days, accounting for an average of 63% of the applied radioactivity. Neutral volatiles trapped in ethylene glycol were negligible, amounting to about 0.08% of the applied ^{14}C. Barium salt precipitation from the KOH solution confirmed that most of the trapped radioactivity was due to $^{14}CO_2$.

Sediment-bound residues increased gradually to reach a maximum of 41% at 5 days; these were released by various techniques. Refluxing with 0.25 *N* HCl released 29% of the applied radioactivity which was not extracted by organic solvents. After the acid hydrolysed aqueous fraction was derivatized with benzoyl chloride organic solvent partition extracted 26% of the applied ^{14}C. Chromatographic analysis of the derivatized aqueous fraction showed the presence of a component which was identified as *N*,*N*-dimethylbenzamide, indicating that the parent compounds had become bound to soil constituents.

Soil fractionation of the remaining bound residues yielded 3.1%, 3.96% and 5.1% of the applied radioactivity in humic acid, fulvic acid and humin fractions respectively.

In an identical experiment ,but with an anaerobic water/sediment system (Reynolds, 1995c) DMA was degraded very slowly at 10 mg/kg. The estimated half-life was approximately 1610 days.

Analyses were as before and quantitative recoveries of ^{14}C were obtained throughout the 180-day test period for all samples. The average recovery was 109%.

The total DMA in the water and sediment ranged from an average level of about 99% of the applied chemical on day 0 to 88% by day 180. Eight degradation products were detected. The main one, monomethylamine appeared at day 0 when it accounted for 5.3% of the total applied radioactivity, with levels ranging from 5.5% at 14 days to 3.2% at 90 days with no obvious pattern of formation or decrease. None of the other seven products accounted for more than 0.63% of the initial ^{14}C.

Less than 2% of the applied ^{14}C was evolved as acidic volatiles, including $^{14}CO_2$, which was trapped in KOH solution. Barium salt precipitation confirmed that most of the trapped radioactivity was due to $^{14}CO_2$.

Acid hydrolysis released 7% of the applied ^{14}C, of which almost all (6.9%) remained in the aqueous fraction after partitioning with ethyl acetate. When the aqueous fraction was derivatized 5.9% of the initial ^{14}C could be extracted into dichloromethane and the main component of the extract was DMA, as *N,N*-dimethylbenzamide. A KOH trap used during the acid reflux procedure was found to contain 0.03% of the initial ^{14}C, indicating that no volatiles were formed during reflux. Low levels of radioactivity were detected as fulvic acid (0.51%), humic acid (0.38%) and humins (0.87%).

Reynolds (1995d) also incubated ^{14}C-labelled isopropanol in the dark at 25 ± 1°C in flooded sediment at 10 mg/kg under anaerobic conditions. Degradation was rapid. The evolved acidic volatiles trapped in 1 *N* KOH including $^{14}CO_2$ increased steadily and after 120 days accounted for 65% of the applied ^{14}C, but barium chloride precipitation and HPLC showed that much of the volatile ^{14}C consisted of acetone and isopropanol. Other minor products were observed but not identified.

The half-life of the [2-^{14}C]isopropanol was 15 days. Under the anaerobic aquatic test conditions isopropanol was degraded to acetone and further mineralized to $^{14}CO_2$.

Reynolds (1995f) showed that under the same laboratory conditions diethanolamine was degraded very quickly in an aerobic water/sediment system at 10 mg/kg. The estimated half-life was 10.3 days. Analyses were by HPLC and TLC with LSC.

Nine degradation products were observed in addition to the parent chemical and ethanolamine. The main product, described as M3, accounted for 4.1% of the total applied radioactivity at day 0, 8.2 % after 7 days, decreasing to 2.1% at the end of the study. None of the other products including ethanolamine exceeded 4.3% in any sample.

Sediment-bound residues increased gradually to reach 27% at 21 days. Those from day 14 were examined further. A refluxing solvent released 13% of the applied radioactivity which was not organosoluble. Chromatographic analysis of the polar residues identified a number of components, none of which exceeded 3% of the AR.

Soil fractionation of the remaining bound residues gave 3.4%, 2.2% and 5.5% of the ARR in humic acid, fulvic acid and humin fractions respectively.

In the corresponding anaerobic system, under otherwise identical conditions (Reynolds, 1996) degradation was too slow to estimate a half-life during the study period of 365 days.

Four degradation products in addition to the parent chemical and ethanolamine were observed. The main product, M1, accounted for 1.4% of the total applied radioactivity at day 0, and 6.4% after 14 days, but decreased to 0.84% at 365 days. None of the other products observed, including ethanolamine, exceeded 4.7% in any sample.

Sediment-bound residues accounted for 20% of the ARR at 59 days and 9.1% at 91 days. Acid hydrolysis of the PES from 59 days released 14% of the applied ^{14}C, less than 0.5% of which could be partitioned into ethyl acetate. TLC of the aqueous fraction showed a radioactive spot with the same Rf value as the parent compound. During acid refluxing a KOH trap was found to contain less than 0.25% of the applied dose, indicating that no volatiles were formed. Low levels of the applied radioactivity were detected in fulvic acid (2.75%), humic acid (1.4%) and humins (1.4%).

Recoveries of ^{14}C during the 365days ranged from 102 to 110%, with an average total recovery of 105%.

Aquatic field dissipation

In June 1993 a study was initiated in Louisiana to investigate the dissipation and mobility of 2,4-D DMA and its major products, 2,4-D, 2,4-DCP, 2,4-DCA, 4-CPAA and 4-CP when applied to rice in flooded Mowata silt loam (Barney, 1994). One aerial spray was applied at 2 kg ae/ha. Soil and water samples were taken from the treated and control plots before and after the application on day 0. Soil samples were also taken at 1, 3, 7, 15, 30, 45, 60, 90, 120 and 180 days and water samples at 1, 3, 7, 15 and 30 days. Soil was sampled to a depth of 30 cm at each sampling except on day 0 when samples were taken to a depth of 10 cm. The water samples were taken before soil cores to prevent contamination from disturbed sediment. At each sampling three subsamples of water, each about 200 ml, were collected from different parts of the test site.

Water samples were analysed for 2,4-D, 2,4-DCP, 2,4-DCA, 4-CPAA and 4-CP. The highest 2,4-D residue (mean 1.4 mg/kg) occurred on day 0 and then decreased to a mean of 0.54 mg/kg at day 1 and 0.19 mg/kg at day 3. No 2,4-D was detected above the LOD (0.01 mg/kg) in water samples at 7, 15 or 30 days. Residues of 2,4-DCP and 4-CPAA were detected in the first three samplings, but below the LOD (0.01 mg/kg). Apparent residues of 2,4-DCP and 4-CPAA at day 0 were undetectable at day 7. Traces of 2,4-DCP, 2,4-DCA, 4-CPAA and 4-CP were observed at day 15. The half-life for the dissipation of 2,4-D in water was 1.1 days.

Soil samples were analysed for 2,4-D, 2,4-DCP and 2,4-DCA in 10 cm increments to a depth of 30 cm. The highest 2,4-D residue (0.04 mg/kg; mean total of 3 depths) occurred 1 day after application and decreased to 0.013 mg/kg after 3 days. Residues of 2,4-D, slightly above the LOD of 0.01 mg/kg, were detected below 10 cm only at the day 1 sampling. This suggests contamination by the sampling equipment rather than any mobility to lower depths. Degradation products (2,4-DCP and 2,4-DCA) were not detected above the LOD (0.01 mg/kg) at any sampling. The half-life for the dissipation of 2,4-D in soil was calculated as 1.5 days.

Aquatic pond dissipation

Hatfield (1995a,b) studied the dissipation and mobility in soil of 2,4-D DMA, 2,4-D, 2,4-DCP, 2,4-DCA, 4-CPAA and 4-CP in an aquatic environment (small pond) in North Carolina (NC) and North Dakota (ND). The soils were Bibb sandy loam in NC and Runaff sandy loam in ND. Two applications were made by subsurface injection to the pond, the first at 45 kg ae/ha and the second 30 days later at 50 kg ae/ha in NC, and both at 47 kg ae/ha, 31 days apart, in ND. Soil and water samples were taken from the treated and control plots before and after the applications (day 0), and 1, 3, 7, 14 and 21 days after the first applications and 1, 3, 7, 14, 21, 30, 60, 90 and 120 days (and 180 days in ND) after the second. Soil was sampled to a depth of 20 cm at each sampling, and a composite sample of water was taken from the top 90 cm (NC) or 120 cm (ND) of the pond water.

In NC water residues of 2,4-D increased from 0.54 mg/kg (day 0, first application) to 2.1 mg/kg (day 3) and then decreased to 0.86 mg/kg just before the second application. The concentration of 2,4-D at day 0 after the second application was 2.8 mg/kg and decreased to 0.01 mg/kg by day 21. No subsequent samples had residues above the LOD (0.001 mg/kg).

The mean residues of 2,4-DCP in water fluctuated from 0.006 mg/kg (days 7 and 14 after the first application and the day of the second application) to the LOD at day 21 (second application). 2,4-DCA was undetectable throughout the study. The mean residues of 4-CPAA were similar to 2,4-DCP with the highest concentration (0.012 mg/kg) on day 0 and day 1 after the second application. Low levels of 4-CP were reported on day 14 (0.002 mg/kg) and day 30 (0.001mg/kg) after the second application.

The half-lives of 2,4-D in water were 20 and 7.6 days after the first and second applications respectively.

The average residues of 2,4-D in 0-5 cm soil/sediment layers were 1.1, 1.2, 1.3, 1.5 and 0.79 mg/kg at 0, 1, 3, 7 and 14 days after the first application. At day 21, 2,4-D was detected throughout the 0-20 cm depth at a total concentration of 0.33 mg/kg, and 2,4-DCP was found at 0.22 mg/kg.

After the second application the average residues of 2,4-D in the 0-5 cm soil fractions decreased from 0.62 mg/kg (day 0) to 0.13 mg/kg by day 14 and were undetectable thereafter. Low levels of 4-CP and 4-CPAA were reported from day 21 (first application) to day 7 (second application), but only in the 0-5 and 5-10 cm depths.

The half-life of 2,4-D in soil/sediment was calculated to be 7.6 and 2.0 days after the first and second applications respectively

In ND residues of 2,4-D in water decreased from 4.7 mg/kg (day 0, first application) to 1.2 mg/kg on the day before the second application. The concentration of 2,4-D on day 0 after the second application was 3.1 mg/kg and decreased to 1.5 mg/kg by day 30. Samples taken after day 60 had no residues above the LOD (0.001 mg/kg).

The mean residue of 2,4-DCP in water was 0.01 mg/kg on days -1, 3 and 21 after the second application and decreased to below the LOD after day 60. There were no detections of 2,4-DCA throughout the study. The mean residues of 4-CPAA followed 2,4-DCP with the highest concentration (0.008 mg/kg) on day 0 after the second application.

The half-lives of 2,4-D in water were 14 and 6.5 days for the first and second applications respectively.

The average residues of 2,4-D in the 0-5 cm soil/sediment layers were 0.25, 0.61, 0.35, 0.37 and 1.2 mg/kg at 0, 1, 3, 7 and 14 days after the first application respectively. At day 21, 2,4-D was detected throughout the 0-20 cm depth at a total concentration of 1.05 mg/kg.

After the second application the average residues of 2,4-D in the 0-5 cm fractions decreased from 1.6 mg/kg (day 3) to 0.016 mg/kg (day 180).

Low levels of 4-CP and 4-CPAA were reported only from day 21 (first application) and day 60 (second application) in the 5-10 and 10-15 cm depths.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The official method of analysis in The Netherlands (Anon. 1996) is based on the extraction of samples with a basic aqueous solution before solid-phase extraction (SPE) on a C-18 bonded silica cartridge for concentration and isolation of the analytes followed by clean-up on a silica- or aminopropyl-bonded cartridge. SPE extracts are further processed by column-switched reversed-phase LC using a pre-column packed with internal-surface reversed-phase (ISRP) material and a C-18 bonded analytical column. The analytes are detected by UV at 118 nm. The LOD was reported to be 0.02 mg/kg for meat and 0.05-0.1 mg/kg for cereals and vegetables.

Plants, general method

James (1994) validated EN-CAS method No. ENC-2.93 used to determine the residues in wheat forage, straw and grain.

Table 17 compares the 2,4-D concentrations reported in forage, grain and straw samples from a metabolism study conducted by ABC Laboratories (Puvanesarajah, 1992) with the averaged 2,4-D residues found in the same samples by the EN-CAS method. The results show that method ENC-2/93 is adequate for determining 2,4-D in wheat plants which have been treated during growth.

Table 17. Comparison of analytical methods for 2,4-D in wheat (James, 1994; Puvanesarajah, 1992).

Wheat fraction	^{14}C, mg/kg, 2,4-D equivalents					2,4-D, mg/kg by GLC in final volume from ENC-2/93
	Total ABC Labs	2,4-D, ABC Labs	Total, ENC-2/93	Extracted, ENC-2/93	in final volume from ENC-2/93	
Forage	33.6	24.8	32.2	32.3	24.8	30.6
Straw	55.7	39.0	53.1	53.8	37.1	52.4
Grain	0.299	0.017	0.323	0.120	0.025	0.037

The analytical procedure was as follows. The residues were extracted by shaking with 0.5 M KOH in 1:1 EtOH/H_2O and filtering. After the addition of 0.2 M HCl to an aliquot, the mixture was refluxed for 1 hour on a hot plate. The extract was cleaned up by octadecylsilyl solid-phase (ODS) extraction and solvent partitioning. The dry sample was methylated with boron trifluoride in methanol and the methyl ester was cleaned up by solvent partition followed by alumina column chromatography. ^{14}C was measured by liquid scintillation counting (Optiphase HiSafe® scintillation cocktail with LKB 1214 RackBeta counter).

The 2,4-D residues were determined as the methyl ester by GLC with an ECD. A fused silica 15 m x 0.32 mm DB-1701 column with a 0.25 µm film thickness was used for wheat grain and straw and a 30.m x 0.32 mm DB-17 column with a 0.25 µm film thickness for forage.

Most samples yield good recoveries for forage with good chromatographic baselines with the method as described. A permanganate oxidation as an extra clean-up step is needed for soya beans (forage and seed), rice straw and sugar cane.

Table 18 shows the recoveries of 2,4-D from fortified processed fractions by EN-CAS Method No. ENC-2/93.

Table 18. Recoveries of 2,4-D from fortified processed fractions by EN-CAS method No. ENC-2/93 (James, 1994).

Crop	Sample	Fortification level, mg/kg	Number of samples [1]	% Recovery
Wheat	patent flour	0.01 0.50	5 2	74-101 73, 80
	bran	0.01 0.50	2 2	86, 110 77, 79
	middlings	0.01 0.50	2 2	74, 76 84, 90
	shorts	0.01 0.50	2 2	77, 85 85, 97
	aspirated grain fractions	0.10 1.00	2 2(1)	113, 116 111, 125

Crop	Sample	Fortification level, mg/kg	Number of samples [1]	% Recovery
Maize	starch	0.01 0.50	6 (1) 2	65-87 75, 85
	grits	0.01 0.50	2 2	92, 105 89, 92
	meal	0.01 0.50	2 2	96, 100 86, 91
	flour	0.01 0.50	6 2	81-100 72, 80
	crude oil	0.01 0.50	6 2	71-104 84, 88
	refined oil	0.01 0.50	2 2	92, 98 81, 90
	aspirated grain fractions	0.01 0.50	2 2	93, 99 95, 97
Sorghum	starch	0.01 0.50	2 2	77, 86 82, 84
	flour	0.01 0.50	2 2	88, 94 73, 77
Sugar cane	molasses	0.01 5.00	6 2	82-98 87, 89
	bagasse	0.01 5.00	6 2	72-110 83, 83
	sugar	0.01 2.00	6 2	100-107 73, 80
Rice	hulls	0.01 0.10	2 (1) 2	68, 78 74, 82
	bran	0.01 0.50	2 2	87, 88 90, 97
	polished rice	0.01 0.10	6 2	70-90 78, 80

[1] Figures in parentheses are the numbers of samples with recoveries outside the 70-120% range

Table 19 shows concurrent recoveries of 2,4-D from fortified control samples of field maize, grass, rice, sorghum and sugar cane and processed fractions of field maize, rice, sorghum, sugar cane and wheat.

Table 19. Recoveries of 2,4-D from fortified samples (Carringer, 1995a-x, Rosemond, 1995a-c).

Crop (Reference)	Sample	Fortification level, mg/kg	Number of samples[1]	% recovery
Field maize	forage	0.01-10	15	73-95
(Carringer, 1995d,e,f)	silage	0.01-10	14	78-110
	grain	0.01-20	23	73-112
	fodder	0.01-100	22	80-109

Crop (Reference)	Sample	Fortification level, mg/kg	Number of samples[1]	% recovery
Field maize	starch	0.01, 1	2	93, 95
(Carringer, 1995c)	grits	0.01, 1	2	86, 86
	meal	0.01, 0.05	2	106, 109
	flour	0.01, 0.05	2	111, 121
	crude oil	0.05, 0.1	4	85-107
	refined oil	0.01, 0.05	2	100, 128
	grain	0.01-0.1	4	86-110
	aspirated grain fractions	0.01-5	4	79-102
Grass	forage	0.01-1000	65 (7)	64-112
(Carringer, 1995j,k,o,u,v,w,x) (Rosemond, 1995a,b,c)	hay	1.0-1500	58 (4)	65-100
Rice	grain	0.01-0.5	10	81-118
(Carringer, 1995p,q)	straw	0.01-0.5	8	72-97
Rice	grain	0.01, 0.05	2	70, 82
(Carringer, 1995n)	hulls	0.01, 0.5	2	99, 119
	bran	0.01, 0.5	2	84, 114
	milled white rice	0.01, 0.05	2	93, 103
Sorghum	forage	0.01-0.1	14 (1)	67-114
(Carringer, 1995g,h,i)	grain	0.01-0.1	14	74-93
	fodder	0.02-1	12 (3)	100-133
Sorghum	starch	0.01, 0.05	2	91, 94
(Carringer, 1995m)	flour	0.01, 0.05	2	96, 88
	grain	0.02-0.2	4	70-93
Sugar cane	forage	0.01-0.5	8	90-117
(Carringer, 1995r,s)	cane	0.01-0.2	8	76-108
Sugar cane	cane	0.05, 0.5	2	79, 93
(Carringer, 1995l)	molasses	0.01, 0.05	4	85-116
	bagasse	0.01, 0.05	2	90, 96
	sugar	0.01, 0.05	2	87, 100
Wheat	Forage	0.01-10	19 (1)	60-110
(Carringer, 1995a,b,t)	grain	0.001-20	15	71-113
	straw	0.01-20	17 (2)	69-127

Crop (Reference)	Sample	Fortification level, mg/kg	Number of samples[1]	% recovery
Wheat	bran	0.01-10	4	83-100
(Carringer, 1995a)	low grade flour	0.01, 0.05	2	97, 93
	patent flour	0.01, 0.05	2	97, 100
	middlings	0.01-5.0	4	76-107
	shorts	0.01-5.0	4	72-93
	grain	0.01, 0.05	2 (1)	63, 86
	aspirated grain fractions	0.10-100	3	86-107

[1] Figures in parentheses are the numbers of samples with recoveries outside the 70-120% range.

In an independent laboratory validation of EN-CAS Method No. ENC-2/93 by Centre Analytical Laboratories, Inc. (Zheng 1995) control samples of wheat forage, straw and grain were fortified with 2,4-D at 0.01 mg/kg (the LOD) and at either 5 or 20 mg/kg. Recoveries from all the samples averaged 94%, ranging from 82% for wheat forage to 103% wheat straw.

Citrus fruits

(Siirila 1995). 2,4-D residues in oranges and grapefruit were extracted from 10 g samples of citrus fruit by refluxing with 0.2 M NaOH for 1 hour. An aliquot of the extract was acidified with sulfuric acid and extracted with ethyl ether. The 2,4-D was then methylated with boron trifluoride in methanol. After the addition of water, the residue was extracted into hexane and determined by GC-MSS.

The same method was used for lemons, lemon juice and wet lemon pulp, except that 0.7 M NaOH solution was used for the initial extraction. For lemon molasses, dry lemon pulp and lemon oil, samples of 5, 2 and 1 g were extracted with 0.2, 0.7 and 0.2 M NaOH respectively.

The Olds were 0.05 mg/kg for oranges, grapefruit, lemons, lemon juice and wet lemon pulp, 0.2 mg/kg for dry lemon pulp and molasses and 0.5 mg/kg for lemon oil. Table 20 shows recoveries of 2,4-D from fortified control samples of citrus fruits and processed citrus commodities.

Table 20. Recoveries of 2,4-D from citrus fruit and processed fractions (Johnson and Strickland, 1995a-c).

Sample	Reference	Fortification level, mg/kg	Number of samples [1]	% recovery
Grapefruit	Johnson and Strickland, 1995c	0.5	16 (4)	70.8-140
	Johnson and Strickland, 1995a	0.05 0.1 0.25	10 (2) 6 (2) 4	79.2-133 110-138 90.4-100
Lemons	Johnson and Strickland, 1995c	0.5	6	85.0-104
	Johnson and Strickland, 1995a	0.05 0.25	11 (2) 11	76.6-191 84-114
Oranges	Johnson and Strickland, 1995a	0.05 0.25	6 6	89.6-118 92.8-107

Sample	Reference	Fortification level, mg/kg	Number of samples [1]	% recovery
Lemon juice	Johnson and Strickland, 1995c	0.5	6 (2)	90.2-126
	Johnson and Strickland, 1995b	0.05 0.25	6 6	107-114 96-104
Wet lemon pulp	Johnson and Strickland, 1995c	0.5	6	92.0-105
	Johnson and Strickland, 1995b	0.05 0.025	7 (1) 7	97.6-126 83.2-104
Dry lemon pulp	Johnson and Strickland, 1995c	0.5 1	2 6	98.2-104 76.4-97.6
	Johnson and Strickland, 1995b	0.4 2	6 6	85.5-114 94.0-103
Lemon molasses	Johnson and Strickland, 1995c	1	8	96.3-119
	Johnson and Strickland, 1995b	0.4 2	6 6 (1)	97.8-115 95.0-121
Lemon oil	Johnson and Strickland, 1995c	1	8	77.7-116
	Johnson and Strickland, 1995b	1 5	4 4	74.2-98.1 80.8-95.4

[1] Figures in parentheses are the numbers of samples with recoveries outside the 70-120% range.

Animal products

(Howard 1996a). Procedures were developed to extract and quantify residues of 2,4-D in beef muscle, liver, kidneys, fat and milk.

2,4-D is extracted from beef muscle by homogenizing the tissue with acidified acetonitrile. The homogenate is centrifuged, filtered and diluted with water. The analyte is partitioned into diethyl ether and then into 0.1% NaOH solution. The residual organic solvent is removed by rotary evaporation. The extract is acidified and passed through C-8 and C-18 solid-phase extraction (SPE) columns in series. The analyte is eluted with *tert*-butyl methyl ether (MTBE). The MTBE is concentrated, and the analyte is methylated with ethereal diazomethane or boron trifluoride in methanol (BF_3/MeOH).

Beef fat is homogenized in hexane and 2,4-D is extracted from the homogenate with 0.1% NaOH solution. The basic extract is acidified and partitioned with diethyl ether. The analysis is completed as described for beef muscle.

Beef liver is refluxed for one hour in 2 *N* hydrochloric acid. After cooling, the aqueous extract is diluted with acetonitrile and sodium chloride is added. After phase separation the acetonitrile layer is passed through a hand-packed Florisil column to remove some interferences, the eluate is diluted with 1% NaOH solution and the acetonitrile is removed by rotary evaporation. The aqueous extract is acidified and the analyte transferred to 10% ethyl acetate in hexane, which is passed through a hand-packed neutral alumina column. The analyte is eluted with a solution of 10% methanol in 1% NaOH which is acidified and partitioned with MTBE. The MTBE layer is concentrated and the analyte is methylated with ethereal diazomethane or BF_3/MeOH.

Beef kidney is homogenized in acidified acetonitrile. The homogenate is centrifuged and filtered, and the analysis is completed as described for beef liver.

Milk is acidified to 2 *N* with hydrochloric acid. It is then refluxed for one hour and allowed to cool. Acetonitrile and sodium chloride are added to the sample. The analysis is completed as for liver.

GLC conditions:

Instrument:	HP 5890
Column:	60 m, J&W DB-1, 0.32 mm, 5 µm film
Injector temperature:	250°C
Carrier:	Helium at 2 ml/min
Detector:	ECD at 325°C
Detector make-up:	Nitrogen at 58 ml/min
Column temperature programme	220°C, 5 min, 2°C/min 230°C, 30 or 40 min, 40°C/min 300°C, 10 or 15 min
Injector volume:	4 µl splitles
Retention time:	Approximately 28 to 30 minutes

The LOD was 0.05 mg/kg for beef muscle, beef liver, beef kidney and beef fat, and 0.01 mg/kg for milk.

Howard (1996b) developed and validated procedures to extract and quantify 2,4-D in poultry muscle, liver, fat and eggs.

Residues of 2,4-D are extracted from poultry muscle and fat as described for beef muscle and fat.

2,4-D is extracted from eggs by homogenization with acidified acetonitrile. The homogenate is centrifuged, filtered, and passed through a hand-packed Florisil column to remove interferences. The eluate is diluted with 1% NaOH solution and the acetonitrile removed by rotary evaporation. The aqueous extract is acidified and the analyte partitioned into 10% ethyl acetate in hexane. The organic phase is separated and passed through a hand-packed neutral alumina column. The analyte is eluted with a solution of 10% methanol in 1% NaOH and the eluate is acidified and partitioned with MTBE. The MTBE layer is concentrated and the analyte methylated with BF_3/MeOH. Water is added to the reaction mixture and the methyl ester of 2,4-D is partitioned into hexane for determination by GLC.

Poultry liver is refluxed for 1 hour in 2 *N* HCl. After cooling, acetonitrile and NaCl are added to the hydrolysate, the acetonitrile layer is removed and passed through a hand-packed Florisil column and the analysis is completed as described for eggs.

The GLC conditions are the same as for beef and milk.

The LOD was 0.05 mg/kg for poultry muscle, fat and liver, and 0.01 mg/kg for eggs.

Soil, water and sediment

(Hatfield 1995r). Soil samples were analysed for 2,4-D EHE (when applicable), 2,4-D acid, 2,4-DCP and 2,4-DCA. Residues of these analytes were extracted by sonicating successively with 5% acetic acid in methanol, 5% acetic acid in 50% aqueous methanol and finally 5% acetic acid in water. The combined extracts were diluted with water, acidified and concentrated on a C-18 SPE cartridge. The

cartridge was eluted with 2% acetone in hexane and then with 20% methanol in hexane. The first eluate contained 2,4-DCP, 2,4-DCA and 2,4-D EHE if present. The second contained 2,4-D which was concentrated, methylated with BF_3/methanol, partitioned into petroleum ether, and combined with the first (underivatized) eluate. The combined solution in hexane was concentrated and analysed by gas chromatography with a mass selective detector. The LOD was 0.01 mg/kg.

GC-MSD conditions

Instrumentation:	Hewlett-Packard model 5890 Series II gas chromatograph/model 5971A mass selective detector
Column:	Durabond-1 (DB-1), 15 m x 0.25 mm i.d., 0.25 µm with DF film
Pre-column:	Stabilwax, 1 m x 0.25 mm i.d., with 0.25 µm DF film
Oven temperature:	Hold at 60° for 2 minutes, then 60-150°C at 10°C/minute, then 150-200°C at 45°C/minute, then 200-240°C at 10°C/minute, then hold at 240°C for 2 minutes
Injector temperature:	250°C
Transfer line temperature:	280°C
Carrier gas:	Helium
Carrier gas flow rate:	~40-60 cm/second (internal flow sensor)
Head pressure:	5 psi
Injection mode:	Splitless
Injection liner:	Silanized dual taper
Injector purge delay:	1.5 minutes
Septum purge:	~7.5 ml/minute
Injection volume:	2 µl
Ionization potential:	70 eV
Electron multiplier voltage:	1400-1900 V (typical)
Dwell time:	50-200 msec

(Hatfield 1995b). Extraction, concentration on a C-18 column, and elution were identical to the procedures for soil. Water samples were analysed for 2,4-D acid, 2,4-DCP, 2,4-DCA, 4-CPA and 4-CP. The first eluate now contained 2,4-DCP, 2,4-DCA and 4-CP and the second contained 2,4-D and 4-CPA. The analysis was completed as for soil, with the same GC-MS condition. The LOD was 0.001 mg/kg.

(Hatfield 1995b). Sediment samples were analysed for 2,4-D acid, 2,4-DCP, 2,4-DCA, 4-CP and 4-CPA. A 10 g sample was vortexed and sonicated as before. The extracts were decanted and filtered after each extraction, combined and brought to a known volume. 2,4-D acid and its products were fractionated by liquid-liquid partition of separate aliquots. The residues were quantified by gas chromatography with mass selective detection. The LOD for all the analytes was 0.01 mg/kg.

GC-MS conditions:

Instrumentation:	Hewlett-Packard model 5890 Series II gas chromatograph/model 5972 mass selective detector
Column:	HP-5MS, 0.25 mm i.d. x 30 m, 0.25 µm film thickness
Oven temperature:	Hold at 50°C for 1 minutes, then 50-100°C at 5°C/minute, then 100-260°C at 10°C/minute then hold 5 minutes
Injector temperature:	240°C
Transfer line temperature:	280°C
Carrier gas:	Helium
Carrier gas flow rate:	1 ml/minute
Head pressure:	12 psi
Injection mode:	Splitless
Injection liner:	Silanized single taper
Injector purge delay:	1.5 minutes
Septum purge:	50 ml/minute
Injection volume:	2 µl
Ionization potential:	70 eV
Electron multiplier voltage:	1400-1900 V (typical)
Dwell time:	100 msec

Stability of pesticide residue in stored analytical samples

Barker (1995) determined the stability of residues of 2,4-D during freezer storage for one year (the longest period of storage of samples from the residue trials) in raw agricultural commodities (maize grain, forage and fodder, sorghum grain, wheat grain, forage and straw, sugar cane, rice grain, rangeland grass and hay and soya bean seed) and processed fractions (maize starch, flour and crude oil, wheat flour, sugar, molasses and bagasse, and rice bran and hulls). The results are shown in Tables 21 and 22. Freezer storage temperatures were monitored daily and were -12°C to -27°C. Fortification levels ranged from 0.1 to 5 mg/kg. Analyses of stored samples, but not 0-day samples, were corrected for procedural recoveries if these were less than 100%. Procedural recoveries from samples fortified at 0.1 to 5 mg/kg which were analysed concurrently with stored samples yielded an overall mean and standard deviation of 89 ± 10% (n = 232).

Table 21. Storage stability of residues of 2,4-D in raw agricultural commodities (Barker, 1995).

Sample	2,4-D, % of initial residue after days				
	0	30	90	180	365
Maize grain	95 118 88	82 104	101, 108	105 99	91 93
Maize forage	95 91 89	97 94	90 94	93 98	104 96

Sample	2,4-D, % of initial residue after days				
	0	30	90	180	365
Maize fodder	97 96 96	96 95	98 92	82 85	74 78
Sorghum grain	84 83 91	89 89	92 91	99 103	87 88
Wheat grain	79 80 84 87	105 105	90 81	92 94	98 98
Wheat forage	84 82	102 102	93 99	96 97	91 92
Wheat straw	81 86 93 99	103 102	95 93	100 88	100 105
Sugar cane	83 86 79	94 90	102 104	96 97	93 101
Rice grain	110 107 109	98 94	99 101	87 95	100 97
Rangeland grass	88 91 89 98	96 91	100 101	97 89	83 86
Rangeland hay	94 86 89	99 86	96 93	115 110	90 86
Soya bean seed	86 93	93 95	98 92	90 71	96 93

Table 22. Storage stability of incurred residues of 2,4-D in processed agricultural commodities (Barker, 1995).

Sample	2,4-D, % of initial residue after days				
	0	30	90	180	365
Maize starch	98 102 105	106 112	106 104	101 111	98 103
Maize flour	74 64 81	90 89	106 105	89 80	91 100
Crude maize oil	92 92 91	100 88	99 86	94 87	90 93

Sample	2,4-D, % of initial residue after days				
	0	30	90	180	365
Wheat flour	91 84 84	95 94	98 101	89 94	82 100
Cane sugar	94 86 81	95 95	92 89	91 83	88 77
Sugar molasses	84 85 86	98 95	95 98	114 112	100 94
Sugar bagasse	73 68 75	91 96	92 96	90 87	86 84
Rice bran	84 92 91	104 96	96 79	100 102	88 88
Rice hulls	72 73 70	98 98	103 105	81 78	99 80

Johnson and Strickland (1995c) determined the storage stability of 2,4-D in fortified grapefruit, lemons and lemon products stored at ≤-20°C (Table 23).

Table 23. Storage stability of 2,4-D in fortified citrus commodities (Johnson and Strickland, 1995c).

Sample	Fortification level, mg/kg	Storage period, days	Recovery, %	Corrected recovery, %[1]
Grapefruit	0.5	0	91, 90	--
		28	82, 83	92, 93
		56	111, 111	105, 105
		86	69, 93	96, 130
		119	104, 108	91, 95
		150	120, 125	103, 107
		181	134, 135	97, 98
		212	92, 96	79, 82
Lemons	0.5	0	101, 103	-
		28	98, 97	110, 109
		59	105, 104	103, 102
Lemon juice	0.5	0	120, 126	-
		28	129, 136	108, 114
		58	104, 87	111, 92
Wet lemon pulp	0.5	0	96, 94	-

Sample	Fortification level, mg/kg	Storage period, days	Recovery, %	Corrected recovery, %[1]
		28	102, 93	107, 98
		59	99, 101	95, 97
Dry lemon pulp	1	0	96, 78	-
		28	99, 97	123, 121
		58	61, 93	60, 92
		92	107, 107	112, 112
Lemon molasses	1	0	96, 102	-
		28	112, 112	103, 103
		59	108, 106	100, 98
		104	114, 108	98, 93
Lemon oil	1	2	106, 102	-
		28	107, 95	129, 114
		59	100, 99	112, 111
		97	112, 112	99, 99

[1] Corrected for average concurrent procedural recoveries

The stability of 2,4-D in other crops is shown in Table 24.

Table 24. Frozen storage stability of 2,4-D in other fortified crops.

Crop (Reference)	Sample	Fortification, mg/kg	Storage, days	Recovery [1], %
Apple (Barney and Kunkel, 1995b)	Fruit	0.1, 0.5	573	75-101
Asparagus (Kunkel, 1995a)	Spears	0.1	~630 [2]	56, 55, 56, 71
		1	~630 [2]	42, 54, 52, 49
		1	14 [3]	93, 92, 92
Cherry (Barney and Kunkel, 1995c)	Fruit	0.05	862	99, 97, 94
Cranberry (Barney and Kunkel, 1995a)	Fruit	0.05	876	96-102
Filbert (Kunkel, 1996a)	Kernel	0.5	151	77, 96, 99
Grapes (Kunkel, 1996b)	Fruit	0.5	467	101, 92, 101
	Juice	0.5	466	108, 103, 103
	Raisins	0.5	414	87, 91, 88
Peach (Barney and Kunkel, 1995d)	Fruit	0.1	271	99, 96
		0.5	271	94, 91
Pear (Kunkel, 1996d)	Fruit	0.1, 0.5	563-567	92-97

Crop (Reference)	Sample	Fortification, mg/kg	Storage, days	Recovery [1], %
Pecan (Kunkel, 1996c)	Kernel	0.5	182	89, 90, 99
Pistachio (Barney, 1995e)	Kernel	0.5	171	58, 88, 85
Plum/fresh prune (Barney and Kunkel, 1995f)	Fruit	0.02	235	77
		0.1	235	101
		0.5	235	107
Prune (Barney, 1995f)	Fruit	0.02	195	110
		0.1	195	70
		0.5	195	91
Potato (Barney and Kunkel, 1995g)	Tuber	0.05	747	93, 102, 102
Strawberry (Kunkel, 1995e)	Fruit	0.5	59	114-117
Sweet corn (Kunkel, 1995c)	Kernel and cob [4]	0.5	104	81-113

[1] Corrected for concurrent procedural recoveries of 89-117% for asparagus, 75% for cherries, 77% for peaches, 93% for pistachios, 83% for plums, 79% for prunes, 77% for grapes, 87% for grape juice and 69% for raisins.
[2] Storage stability study with fortified 1992 field trial control samples
[3] Storage stability study with fortified 1994 field trial control samples
[4] With husks removed

The stored fortified samples of asparagus showed an average decrease in 2,4-D content of 46% after about 20 months. As these samples were only analysed after a single storage period and 2,4-D residues are stable at -20°C in other commodities, it is unclear whether the decrease reflects actual degradation of 2,4-D or procedural error.

Krautter and Downs (1996) determined the storage stability of 2,4-D in frozen cattle liver, kidney, muscle, fat and milk. Homogenized tissue and milk were fortified with 2,4-D and analysed on the day of preparation and after about 2 and 4 months of frozen storage.

Mean recoveries of 2,4-D from freshly prepared liver, kidney, muscle, fat and milk samples were 99, 71, 111, 85 and 71% respectively. Results of analyses of stored samples were corrected for concurrently determined procedural recoveries. Mean corrected recoveries from liver, kidney, muscle, fat and milk were 115, 112, 106, 112 and 81% respectively after 2 months and 107, 124, 110, 117 and 109% after 4 months. These findings demonstrated that 2,4-D is stable in the analysed cattle products when stored frozen for at least 4 months.

USE PATTERN

2,4-D as acid, salt or ester is a selective hormone-type phenoxy herbicide. It is readily absorbed by leaves and roots causing abnormalities in growth and plant structure with subsequent necrosis. Plant protection products containing 2,4-D are used as foliar-applied herbicides for the post-emergence control of broad-leaved weeds. The registered uses are shown in Table 25.

Table 25. Registered uses of 2,4-D. Application rates are expressed as acid equivalents (kg ae/ha or ae/hl).

Crop	Country	Application					PHI, days
		Method	Rate, kg ae/ha	Minimum spray, l/ha	Spray conc, kg ae/hl	No.	
Almonds	USA	directed to the orchard floor	1.6	61		2	60

Crop	Country	Application					PHI, days
		Method	Rate, kg ae/ha	Minimum spray, l/ha	Spray conc, kg ae/hl	No.	
Apple	Nether-lands	spraying of aerial parts after flowering[1]	0.9-2.1	500		1	
	USA	directed to the orchard floor, retreatment interval of 75 days	2.2	183		2	14
Asparagus	Canada		1.3	50		1	
	USA		2.2	183		2	3
Barley	Australia	boom application aerial application	1.6 1.1	70 10		1	7
	Canada	aerial application ground application, depends on design	0.52	30 50		1	b
	USA	apply after grain is fully tillered but before forming joints in stems, apply when grain is in the dough stage	1.4 0.56	18 18		2	14
Barley, spring	EU[3]	forage application	0.42	200-600	0.07-0.21		
	Germany		0.75	200		1	F
	Poland		1.3	200-300	0.28-0.64	1	
Barley, winter	EU[3]	forage application	0.90	200-600	0.15-0.45		
	Germany		0.75	200		1	F
	Poland		1.3	200-300	0.28-0.64	1	
Blueberries	USA	directed or spot applications to row middles	1.6			2	30
Cereals	Belarus		0.6	200		1	
	France		1.4	200		1	
	Hungary		0.81	300		1	
	Kazakhstan		1.4	200		1	
	Poland		0.90	200		1	
	Russia		1.6	200		1	
	Ukraine		0.84	300		1	
Cereals, spring	Austria		0.72	200		1	
Cereals, winter	Austria		0.72	200		1	
	EU[3]	forage application (2,4-D EHE)	0.56	200		1	
	Nether-lands	spraying of aerial parts before coming of the ear	0.9-1	600		1	
Cherries	USA	directed to the orchard floor	1.6	183		2	14
Cranberry	USA	make directed wipe of spot applications, make directed or spot applications when weed tops are above crop	4.5 1.3			2	
Grapefruit	USA	ground application to increase fruit size			0.0012 - 0.0024	1	7
Grapes	USA	direct application at least 3 months before harvest	1.6	476		1	100
Grass, pastures cultures of grass seed	Australia	boom application aerial application	4.5 2.8	30 10		1	7
	Canada		3.1	100		1	b
	EU[3]	forage application	0.9-1.5	200-600	0.15-0.75		
	Germany		1.0	600		1	28
	Hungary		1.4	300		1	
	Poland		1.3-1.5	200-300	0.42-0.73	1	
	Nether-lands	spraying of aerial parts	0.9-1.5	600		1	d, e
	USA	allow 30 days between applications, do not cut for hay with in 7 days of application	2.2	18		2	
Hazelnuts	USA	spray to wet leaves and stems of			0.12	4	45

Crop	Country	Application					PHI, days
		Method	Rate, kg ae/ha	Minimum spray, l/ha	Spray conc, kg ae/hl	No.	
		suckers during April through August, 30 days between applications					
Lemon	USA	post harvest packing house application			0.050	1	
Maize	Australia	boom application aerial application	0.67 1.1	25 10		1	
	Belarus		0.6	200		1	
	Canada		0.52	50		1	b
	EU[3]	direct spray to weeds	1.2	200-600	0.2-0.6		
	Hungary		0.68	300		1	
	Kazakhstan		1.1	200		1	
	Nether-lands	spraying till crop height 5-60 cm	0.9-1	200		1	
	Russia		1.6	200		1	
	Slovakia		0.63	400		1	
	Thailand		0.71-1.0	500	0.15-0.20		
	Ukraine		0.84	300		1	
	USA	preplant or pre-emergence post-emergence, layby treatment, apply after hard dough stage	1.1 0.56 1.7	18 18 18		3	7
Millet	Australia	boom application aerial application	0.67 0.72	25 10		1	
	USA	1. apply after grain is fully tillered but before forming joints in stems, 2. apply when grain is in the dough stage	1.4 0.56	18 18		2	14
Oats	Australia	boom application aerial application	1.6 1.1	70 10		1	7
	Germany		0.75	200		1	F
	USA	1. apply after grain is fully tillered but before forming joints in stems, 2. apply when grain is in the dough stage	1.4 0.56	18 18		2	14
Oranges	USA	ground application to increase fruit size; aerial application; apply in fall oil, water or whitewash sprays, prevent pre-harvest drop			0.0012-0.0024 0.02 0.0004-0.0024	1 1 1	7 - -
Peach	USA	directed to the orchard floor	1.6	183		2	14
Peanut	Australia	boom application aerial application	2.3 2.3	25 10		1	
Pear	Nether-lands	spraying of aerial parts after flowering [6]	0.9-2.1	500		1	
	USA	directed to the orchard floor, retreatment interval of 75 days	2.2	183		2	14
Pecan	USA	directed to the orchard floor	1.6	61		2	60
Pistachio nut	USA	directed to the orchard floor, retreatment interval 30 days	1.6	183		2	50
Plums	Nether-lands	spraying of aerial parts of weeds after flowering[6]	1.8	600		1	
Plums (incl. Prunes)	USA	directed to the orchard floor	1.6	183		2	14
Pome fruits	Poland	ground application	0.72-0.90	200-300	0.24-0.45	1	
	USA	directed to the orchard floor,	2.2	183		2	14

Crop	Country	Application					PHI, days
		Method	Rate, kg ae/ha	Minimum spray, l/ha	Spray conc, kg ae/hl	No.	
		retreatment interval of 75 days					
Potato	Australia	aerial application	1.6	10		1	28
	USA	first application at pre-bud stage, second application 10-14 days later	0.078	183		2	
Raspberries	Canada	any time except during bloom	0.52	100		1	
	USA	24 days before harvest and post-harvest	3.1	275		2	24
Rice	Thailand		0.75-1.0	500	0.15-0.20		
	USA	usually 6-9 weeks after emergence	1.7	18		1	60
Rye	Australia	boom application aerial application	1.6 1.1	70 10		1	7
	Canada	aerial application ground application, depends on design	0.52	30 50		1	B
	USA	apply after grain is fully tillered but before forming joints in stems, apply when grain is in the dough stage	1.4 0.56	18 18		2	14
Rye, spring	Germany		0.75	200		1	F
	Poland		1.3	200-300	0.28-0.64	1	
Rye, winter	EU[3]		0.90	200-600	0.15-0.45		
	Germany		0.75	200		1	F
	Poland		1.3	200-300	0.28-0.64	1	
Sorghum	Australia	boom application aerial application	0.67 0.72	25 10		1	
	USA	apply when sorghum is 15 to 38 cm tall	0.56 (only EHE) 1.1	18		1	30 (for forage)
Soya bean	USA	apply not less than 7 days before planting, apply not less than 15 days before planting	0.56 (only EHE) 1.1	18 18		1	
Strawberry	Canada	after planting – before rooting of runners	0.52	100		1	
	Nether-lands	spraying of aerial part of weeds after harvest	1.4	500		1	
	USA	broadcast application, dormant	1.7	183		1	
Sugar cane	Australia	boom application aerial application	3.9 3.2	30 10		1	
	EU[3]		1.4	400-600	0.24-0.36		
	Thailand		0.75-1.0	500	0.15-0.2		
	USA	pre-emergence before canes appear, post-emergence after cane emerges and through canopy closure	2.2	18		2	
Sweet corn	Australia	boom application aerial application	0.67 1.1	25 10		1	
	USA	broadcast application, 1. pre-emergence 2. post-emergence	 1.1 0.56	 183		2	7 (for forage)
Tangelo	USA	apply in fall oil, water or whitewash sprays, prevent pre-harvest drop			0.0004-0.0024	1	
Tree nuts	USA	directed to the orchard floor	1.6	61		2	60
Triticale	Australia	boom application aerial application	1.6 1.1	70 10		1	7
	Germany[7]		0.75	200		1	F
	Poland		1.3	200-300	0.42-0.62	1	
Wheat	Australia	boom application	1.6	70		1	7

Crop	Country	Application					PHI, days
		Method	Rate, kg ae/ha	Minimum spray, l/ha	Spray conc, kg ae/hl	No.	
		aerial application	1.1	10			
	Canada	aerial application ground application	0.52	30 50		1	b
	USA	1. apply after grain is fully tillered but before forming joints in stems, 2. apply when grain is in the dough stage	1.4 0.56	18 18		2	14
Wheat, spring	EU[3]	forage application	0.42	200-600	0.07-0.21		
	Germany		0.75	200		1	F
	Poland		1.3	200-300	0.28-0.64	1	
Wheat, winter	EU[3]	forage application	0.9	200-600	0.15-0.45		
	Germany		0.75	200		1	F
	Nether-lands	spraying of aerial parts at crop height 15-20 cm, before coming of ears[8]	1	600		1	
	Poland		1.3	200-300	0.28-0.64	1	
Wild rice	USA	apply in the 1 to 2 aerial leaf through early tillering stage	0.28	18		1	60

[1]Other herbicides mixed with 2,4-D used for apples (trees over 3 years old): benazolin, dicamba, MCPA, mecoprop.
[2]Do not permit lactating dairy animals to graze treated fields within 7 days after application. Do not harvest forage of cut hay within 30 days after application. Withdraw meat animals from treated fields at least 3 days before slaughter
[3] Proposed uses
[4] Re-entry of cattle not within 1 week after application
[5] Other herbicides mixed with 2,4-D used for grass: benazolin, dicamba, MCPA, mecoprop
[6] Other herbicides mixed with 2,4-D used for pears or plums (trees over 2 years old): dicamba, mecoprop
[7] Pending
[8] Other herbicides mixed with 2,4-D used for wheat: benazolin, dicamba, MCPA

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of supervised residue trials on agricultural crops are shown in Tables 26-53. All trials were carried out in the USA.

Table 26. Grapefruit.
Table 27. Oranges.
Table 28. Lemons.
Table 29. Pome fruit.
Table 30. Stone fruit.
Table 31. Berries.
Table 31. Sweet corn.
Table 33. Potatoes.
Table 34. Asparagus.
Table 35. Maize forage.
Table 36. Maize fodder.
Table 37. Maize grain.
Table 38. Rice grain.
Table 39. Rice straw.
Table 40. Wild rice.
Table 41. Sorghum grain.
Table 42. Sorghum forage.
Table 43. Sorghum fodder.
Table 44. Wheat forage.
Table 45. Wheat grain.
Table 46. Wheat straw.
Table 47. Sugar cane forage.
Table 48. Sugar cane.
Table 49. Tree nuts.
Table 50. Soya bean forage.
Table 51. Soya bean hay.
Table 52. Soya bean seed.
Table 53. Pasture grass, forage and hay.

Residues, application rates and spray concentrations have generally been rounded to two significant figures or, for residues below 0.1 mg/kg, to one. Only when residues were quantifiable in control samples are they recorded in the Tables. Multiple values from the same trial are replicate field samples. Underlined residue values were used for the estimation of maximum residue levels and/or STMRs.

Treatment of citrus fruits

2,4-D is registered in the USA as a growth regulator (1) to reduce drop of mature fruit (2) to increase fruit size (3) to reduce leaf and fruit drop after pesticide sprays, and (4) to inhibit abscission of buttons on harvested fruit (lemons).

Treatments (1)-(3) are applied as diluted pre-harvest sprays to the trees, whereas (4) is a post-harvest packing house treatment applied in a water-wax emulsion or as a diluted flush or spray. Residue trials for (1)-(3) were carried out on grapefruit and oranges (Tables 26 and 27) and for (4) on lemons (Table 28).

Grapefruit . Critical GAP (USA): 1 x 2.4 g ae/hl, PHI 7 days. Trials were conducted at two sites in Riverside County, California, on grapefruit with three broadcast applications of 2,4-D IPE. The first application was at concentrations of approximately 2.4 g ae/hl in early July to trees bearing mature (1994) and immature (1995) fruit. The second application was about three months later at a rate of 0.4 g ae/hl in spray oil (1.25% v/v) to trees bearing immature (1995) fruit, and the final application after a further nine months at 2.3 g ae/hl with ground equipment (Johnson and Strickland, 1995a).

After the first application, three treated and control samples of mature fruit (1994) were collected from each trial site at PHIs of 0 and 7 days. After the second application, three treated samples of immature fruit (1995) were collected from each site at a 0-day PHI after the spray had dried. After the final application, three treated samples of mature fruit (1995) were collected at each site at PHIs of 0 and 7 days. Two of each set of samples were analysed for residues. The LOD for 2,4-D in grapefruit is 0.05 mg/kg.

Table 26. Residues of 2,4-D in grapefruit, Riverside County, California (Johnson and Strickland, 1995a).

	Crop variety	Application rate		Dates	Growth stage at treatment	Sample	Residue, mg/kg	PHI, days	Remarks
		g ae/ha (g ae/hl)	water l/ha						
Site 1	Marsh	113 (2.4)	4690	7/8/94	Mature fruit & immature fruit	Fruit	<0.05 (2) <0.05 (2)	0 7	
		83 (0.4)	20932	10/7/94	Immature fruit	Immature fruit	<0.05 (2)	0	Contained spray oil at conc. of 1.25% v/v
		113 (2.3)	4896	7/6/95	Mature fruit	Mature fruit	0.08 (2) 0.08, 0.07	0 7	
Site 2	Ruby Red	113 (2.5)	4477	7/7/94	Mature fruit & immature fruit	Fruit	<0.05 (2) <0.05 (2)	0 7	
		83 (0.4)	19982	10/7/94	Immature fruit	Immature fruit	<0.05 (2)	0	Contained spray oil at conc. of 1.25% v/v
		113 (2.4)	4674	7/6/95	Mature fruit	Fruit	0.05, 0.08 0.06, 0.07	0 7	

Oranges. Critical GAP (USA): 1 x 2.4 g ae/hl, PHI 7 days. Four trials were conducted in California on navel oranges harvested after a single pre-harvest application of 2,4-D IPE, applied alone or in hydrated lime solution using ground equipment, in two trials at each site.

Table 27. Residues of 2,4-D in navel oranges, California (Johnson and Strickland, 1995a).

Site/location	Application		Dates	Sample	Residue, mg/kg	PHI, days	Remarks
	g ae/ha (g ae/hl)	water l/ha					
Site 1	75 (1.6)	4628	11/15/94	Fruit	<0.05 (2) <0.05 (2)	0…… 7	
Tulare County	113 (2.4)	4628	11/15/94	Fruit	<0.05, 0.06 <0.05 (2)	0 7	included 56 kg/ha hydrated lime
Site 2	75 (1.6)	4572	11/21/94	Fruit	<0.05 (2) <0.05 (2)	0 7	
Kern County	113 (2.5)	4572	11/21/94	Fruit	<0.05 (2) <0.05 (2)	0 7	included 56 kg/ha hydrated lime

Lemons. Critical GAP: (USA) 1 x 0.05 kg ae/hl as post-harvest use. Lemon trees were treated once pre-harvest at 1.2-1.3 g ae/hl (approximately 56 g ae/h) with 2,4-D IPE. Lemons were picked before treatment, on day 0 (after the treated fruit had dried) and day 7.

On day 7, pre-harvest treated "light-green" lemons were treated according to GAP with a water-wax emulsion, with a commercial storage wax containing 50 g ae/hl. Samples were taken on the day of treatment after drying and some were stored at 5.6-16°C, and removed 28, 56 and 112 days after the post-harvest treatment for analysis.

Table 28. Residues of 2,4-D in lemons, California (Johnson and Strickland, 1995a).

Site/location	Variety	Application		Date	Growth stage at treatment	Sample	Residue, mg/kg	PHI or WHP, days	Remarks
		g ae/ha (g ae/hl)	water l/ha						
Site 1 Tulare County	Eureka	56 (1.3)	4456	12/6/94	Immature fruit	Fruit	0.06, 0.05 <0.05(2)	0 7	Pre-harvest
		(50)		12/15/94		Fruit	0.42 0.29 0.61 0.41	0 28 56 112	Post-harvest storage, days
Site 2 Ventura County	Lisbon	56 (1.2)	4663	12/20/94	Immature fruit	Fruit	<0.05, 0.05 <0.05(2)	0 7	Pre-harvest
		(50)		12/28/94		Fruit	0.54 0.4 0.52 0.5	0 28 56 112	Post-harvest storage, days

WHP: Withholding period (interval between post-harvest treatment and sampling)

Use as herbicide on fruits

2,4-D is directed to the orchard floor. Residue trials were carried out on apples and pears (Table 29), cherries, peaches and plums (Table 30) and on berries (Table 31). All broadcast spray treatments.

Pome fruits. Critical GAP (USA): 2 x 2.2 kg ae/ha, PHI 14 days. Five trials were conducted in four US states to determine the residues of 2,4-D in apples harvested 14 days after the second of two applications. In four of the trials, 2,4-D DMA was applied twice as a broadcast spray at 2.2 kg ae/ha with a retreatment interval of 69 to 110 days. In an additional trial in New York, 2,4-D was applied as above except that an exaggerated rate of 11 kg ae/ha was used. Samples from this trial were used for a related processing study (Barney and Kunkel, 1995b).

Six trials were conducted in four US states to determine the residues of 2,4-D in pears harvested about 14 days after the second of two applications of 2,4-D DMA at 2.2-2.7 kg ae/ha with a retreatment interval of 28 to75 days, with a total seasonal application rate of 4.5 kg ae/ha (Kunkel, 1995d).

The LOD for 2,4-D was 0.01 mg/kg.

Table 29. Residues of 2,4-D in apples and pears.

Crop, Reference Report no.,. Location	Variety	Application		Date	Sample	Residues, mg/kg	PHI, days
		kg ae/ha	water l/ha				
Apples (Barney and Kunkel, 1995b)							
4182.92-NY13	Oregon Spur & Bisbee	2.2 + 2.2	374	6/12/92 + 9/14/92	Fruit	<0.01 (4)	14
	Oregon Spur & Bisbee	11 + 11	374	6/12/92 + 9/14/92	Fruit	<0.01 (4)	14
					Juice	<0.01	14
					Wet pomace	<0.01	14
					Dry pomace	0.014	14
4182-92-MI09	spur MacIntosh MM106	2.2 + 2.2	187	6/17/92 + 8/25/92	Fruit	<0.01 (4)	14
4182.92-WA*14	Red Delicious	2.2 + 2.2	281	5/20/92 + 8/27/92	Fruit	<0.01 (4)	14
4182.92-CA55	Granny Smith	2.2 + 2.2	430	4/22/92 + 8/10/92	Fruit	<0.01 (4)	14
Pears (Kunkel, 1995d)							
4256.92-WA16	Bartlett	2.2 + 2.2	280	5/8/92 + 7/21/92	Fruit	<0.01 (2)	14
4256.92-NY18	Mixed	2.7 + 2.7	374	6/12/92 + 8/31/92	Fruit	<0.01 (2)	14
4256.92-CA64	Unknown	2.2 + 2.2	467	6/19/92 + 7/17/92	Fruit	<0.01 (2)	14
4256.93-OR21	Bartlett	2.2 + 2.2	187	6/10/93 + 8/24/93	Fruit	<0.01 (2)	14
4256.95-CA78	Bartlett	2.2 + 2.2	308	6/23/95 + 7/31/95	Fruit	<0.01 (2)	15
4256.95-CA79	Bartlett	2.2 + 2.2	308	6/14/95 + 7/28/95	Fruit	<0.01 (2)	13

Stone fruits. Critical GAP (USA): 2 x 1.6 kg ae/ha, PHI 14 days. Three trials each on cherries, peaches and plums were conducted in three US states. 2,4-D DMA was applied twice at 1.6 kg ae/ha with retreatment intervals of 7 to 28 (cherries), 35 to 78 days (peaches) and 77 to 93 days (plums) (Barney and Kunkel, 1995c,d,f).

Samples were harvested 12-14 days after the second application. Residues were below the LODs (<0.05 mg/kg cherries, <0.01 mg/kg peaches, plums) in control and in treated samples.

In an additional trial on fresh plums in Idaho, two directed applications of 2,4-D were made at 6.4 kg ae/ha/application. Fresh prunes from the fourfold treatment were processed to dried prunes.

Table 30. Residues of 2,4-D in cherries, peach, plums and prunes.

Crop/Reference Report no. Location	Variety	Application		Date	Sample	Residues, mg/kg	PHI, days
		kg ae/ha	water l/ha				
Cherries (Barney and Kunkel, 1995c							
4254.94-CA49	Bing	1.6 + 1.6	468	5/2/94 + 5/9/94	Fruit	<0.05 (2)	14
4254-92-MI10	Montmorency	1.6 + 1.6	187	6/12/92 + 6/26/92	Fruit	<0.05 (4)	14
4254.92-WA15	Chinook	1.6 + 1.6	281	5/4/92 + 6/1/92	Fruit	<0.05 (4)	12
Peach (Barney and Kunkel, 1995d)							
4255.93-GA08	Summer Prince	1.6 + 1.6	187	4/28/93 + 6/2/93	Fruit	<0.01 (4)	14
4255.93-NJ01	NJ 275	1.6 + 1.6	234+271	5/10/93 + 7/27/93	Fruit	<0.01 (4)	13
4255.93-CA12	Elegant lady	1.6 + 1.6	159	4/23/93 + 6/15/93	Fruit	<0.01 (4)	16
Plums/fresh prunes (Barney and Kunkel, 1995f)							
4257.93-WA01	Friar	1.6 + 1.6	281	5/18/93 + 8/5/93	Fruit	<0.01 (4)	14
4257.93-MI04	Stanley	1.6 + 1.6	187	6/9/93 + 8/24/93	Fruit	<0.01 (4)	14
4257.93-ID03	Italian	1.6 + 1.6	187	5/23/94 + 8/24/94	Fruit	<0.01 (2)	14
		6.4 + 6.4	187	5/23/94 + 8/24/94	Fresh prunes Dried prunes	<0.01 (2) <0.01 (2)	14

Blueberries. Critical GAP (USA): 2 x 1.6 kg ae/ha, PHI 30 days. In one trial on low bush blueberries, 2,4-D DMA was applied once as a solution containing 4.5 g ae/l of water to a cloth-covered stick that was wiped onto woody weeds growing above the crop during the summer. In a second trial, 2,4-D DMA in a mixture containing 12 g ae/l of oil was applied as a spot treatment to cut stems of woody weeds during the autumn. The blueberries were harvested at normal maturity the year after treatment, (55 weeks after the wipe treatment/41 weeks after the spot treatment). Samples were also collected from adjacent plants. All residues were below the LOD of <0.05 mg/kg (Kunkel, 1995b).

2,4-D was also applied twice at 1.6 and 3.1 kg ae/ha to the middle of rows of high bush blueberries. The first application was after harvest of the previous year's crop and the second in the following spring approximately 30 days before harvest. Care was taken to avoid contact of the spray solution with the crop foliage and berries. 2,4-D residues were below or at about the LOD of 0.01 mg/kg (Kunkel, 1997b).

Cranberries. Critical GAP (USA): 2 x 4.5 kg ae/ha, PHI not defined. Two trials were conducted on cranberries. In each, a broadcast application was made to dormant plants in the spring at 4.5 kg ae/ha and two further directed wipe applications were made during the summer to the weeds growing above the cranberry crop. The cranberries were harvested 30 days after the last application. Residues ranged from <0.02 to 0.11 mg/kg (Barney and Kunkel, 1995a).

Grapes. Critical GAP: 1 x 1.6 kg ae/ha, PHI 100 days. Two field trials were conducted in California on grapes and processed products. The vineyard floor was treated with one directed application of 2,4-D at 1.6 kg ae/ha about 100 days before harvest. Some grape samples were processed into raisins and juice. All residues were below the LOD of 0.05 mg/kg (Kunkel, 1996b).

Raspberries. Critical GAP: 2 x 3.1 kg ae/ha, PHI 24 days. 2,4-D was applied twice as a directed spray away from the raspberry plants into the row centres at 1.6 and 3.1 kg ae/ha, with the second application 24 days before harvest. All residues of 2,4-D were below the LOD of 0.05 mg/kg (Baron, 1988).

Strawberries. Critical GAP: 1 x 1.7 kg ae/ha, PHI not defined (timing defined by application to dormant plants). Dormant strawberry plants received one broadcast treatment of 1.7 kg ae/ha at 129 to 59 days before harvest. This range is representative of the normal variations of local production practices. This use is needed for established perennial strawberries. All residues were below the LOD of 0.05 mg/kg (Kunkel, 1995e).

Table 31. Residues of 2,4-D in blueberries, cranberries, grapes, raspberries and strawberries.

Crop/Reference Report No., Location	Variety	Application		Date	Sample	Residues, mg/kg	PHI, days
		kg ae/ha	water l/ha				
Blueberries[1] (Kunkel, 1997b)							
3085.93-OR18	Bluecrop	1.6 + 1.6	468	9/8/93 + 6/8/94	Fruit	<0.01 (4)	30
		3.1 + 3.1	468	9/8/93 + 6/8/94	Fruit	<0.01 (4)	30
3085.93-NC04	O'Neal	1.6 + 1.6	468	10/1/93 + 5/6/94	Fruit	<0.01 (4)	28
		3.1 + 3.1	468	10/1/93 + 5/6/94	Fruit	<0.01 (4)	28
3085.94-NJ16	Bluecrop	1.6 + 1.6	337	11/4/94 + 6/2/95	Fruit	<0.01, 0.01	31
3085.94-MI14	Jersey	1.6 + 1.6	187	8/22/94 + 6/26/95	Fruit	<0.01, 0.01	29
Low Bush Blueberry (Kunkel, 1995b)							
4295.92-ME07	Wild	4.5 g ae/l[2]		07/30/92	Fruit	<0.05 (4)	55 weeks
		12 g ae/l[3]		11/11/92	Fruit	<0.05 (2)	41 weeks
Cranberry[4] (Barney and Kunkel, 1995a)							
4297.92-MA01	Early Black	4.5		3/9/92 + 7/16/92 + 8/12/92	Fruit	0.11, 0.02, 0.05, 0.07	30
4297.92-WI07	Stevens	4.5		4/21/92 + 6/25/92 + 8/31/92	Fruit	<0.02 (4)	30
Grapes (Kunkel, 1996b)							
4298.94CA70	Thompson Seedless	1.6	449	5/14/94	Fruit	<0.05	104
					Raisin	<0.05	104
4298.94CA71	Thompson Seedless	1.6	458	5/14/94	Fruit	<0.05	101
					Juice	<0.05	101
Raspberries[5] (Baron, 1988)							
3718-MN	Red Raspberry	1.6 + 3.1	281	6/8/87 + 7/21/87	Fruit	<0.05 (4)	24
Strawberries (Kunkel, 1995e)							
4179.95-WA13	Sumas	1.7	206	1/24/95	Fruit	<0.05 (2)	129
4179.95-WA14	Red Crest	1.7	281	3/7/95	Fruit	<0.05 (2)	99
4179.95-WI17	Honey oye	1.7	187	4/17/95	Fruit	<0.05 (2)	59
4179.95-WI01	Honey oye	1.7	187	4/17/95	Fruit	<0.05 (2)	59
4179-95-NJ11	Chandler	1.7	327	3/16/95	Fruit	<0.05 (2)	75
4179-95-NH02	Earliglow	1.7	281	4/10/95	Fruit	<0.05 (2)	71

[1] Directed application to avoid plants
[2] Wipe treatment (solution containing 4.5 g ae/l)
[3] Directed spray applied to cut hardwoods (mixture containing 12 g ae/l of oil).
[4] First application was a granule followed by two wipe applications on weeds above the plants.
[5] Applications were made pre- and post-harvest

Use as herbicide on vegetables

2,4-D is directed to the ground for weed control in vegetables. Supervised residue trials were carried out on sweet corn (Table 32), potatoes (Table 33) and asparagus (Table 34).

Sweet corn. Critical GAP (USA): 1 x 1.1 + 1 x 0.56 kg ae/ha. Trials were conducted in nine US states to determine the residues in sweet corn harvested 22-48 days after the second of two

applications of 2,4-D, with side-by-side comparisons of amine salt and low ester formulations. Both formulations were applied initially as pre-emergence broadcast applications at 1.1 kg ae/ha and 33-50 days later as post-emergence directed applications at 0.56 kg ae/ha before tasselling when plants were 40 to 50 cm high. The LOD for 2,4-D residues in cobs ("kernels plus cobs with husks removed") was 0.05 mg/kg (Kunkel, 1995c).

Table 32. Residues of 2,4-D in sweet corn. Kernels plus cobs with husks removed analysed. DMA and EHE formulations. Two treatments, pre-emergence and just before tasselling.

Report, no. form	Variety	Sowing date	Application		Date	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha			
(Kunkel, 1995 c)							
4183.95-WA29 DMA, EHE	Golden Jubilee	5/1/95	1.1 + 0.56	206 + 300	5/2/95 + 6/30/95	<0.05 (4)	39
4183.95-SC11 DMA, EHE	Silver Queen	4/14/95	1.1 + 0.56	196 + 196	4/15/95 + 6/1/95	<0.05 (4)	22
4183.95-WI07 DMA, EHE	Excellency Hybrid	5/17/95	1.1 + 0.56	187 + 112	5/17/95 + 6/30/95	<0.05 (4)	45
4183.95-FL45 DMA, EHE	Challenger	5/9/95	1.1 + 0.56	281 + 281	5/9/95 + 6/14/95	<0.05 (4)	23
4183.95-NY09 DMA, EHE	Callco Belle	6/1/95	1.1 + 0.56	318 + 318	6/2/95 + 7/5/95	<0.05 (4)	42
4183.95-MI03 DMA, EHE	Champ	5/18/95	1.1 + 0.56	187 + 187	5/22/95 + 6/29/95	<0.05 (4)	39
4183.95-CA38 DMA, EHE	Sweetie	3/13/95	1.1 + 0.56	542 + 1356	3/13/95 + 5/1/95	<0.05 (4)	38
4183.95-OR20 DMA, EHE	Super Sweet Jubilee	5/24/95	1.1 + 0.56	178 + 178	6/6/95 + 7/19/95	<0.05 (4)	48
4183.95-IL02 DMA, EHE			1.1 + 0.56		5/595 + 6/26/95	<0.05 (4)	37

Potatoes. Critical GAP (USA): 2 x 0.078 kg ae/ha. Eight trials were conducted in seven US states to determine the residues of 2,4-D in red potatoes after two foliar applications at 0.078 kg ae/ha/application with a retreatment interval of 9-13 days. 2,4-D was formulated as an amine salt in seven of trials in different states, and as an ester in the eighth trial. In two additional trials, amine and ester formulations were applied as above except that exaggerated rates of 0.36 g ae/ha/application were used. Potatoes were harvested after the second application as soon as tubers reached marketable size, 24-67 days after treatment. Although samples from different trials were analysed by different methods, repeated analyses from individual trials indicated that similar results were obtained by the three GLC-ECD methods (Barney and Kunkel, 1995g).

Residues were <0.05-0.13 mg/kg in 30 potato samples taken 24-67 days after the second 0.078 kg ae/ha application and <0.05-0.08 mg/kg in 8 samples harvested 50 days after the second 0.36 kg ae/ha application. Residues were highest (0.07-0.13 mg/kg) with the shortest PHI (24 days), but were also quantifiable (0.05-0.08 mg/kg) after the trial with longest PHI (67days). There was no apparent difference between the residues resulting from the use of amine salt and ester formulations.

Table 33. Residues of 2,4-D in potatoes treated at pre-bud stages. Tubers analysed

Report no.	Variety	Form	Application		Date	Residues, mg/kg	PHI, days	Analytical method
			kg ae/ha	water l/ha				
(Barney and Kunkel, 1995g)								
4302.94CA*24	Red Lasoda	DMA	0.078	598	5/23/94 + 6/3/94	0.08 (2)	45	ENC-2/93-2
4302.92ID02	Norland	DMA	0.078	187	6/17/92 + 6/30/92	0.07 (2), 0.08, 0.13	24	KANN
						0.05, 0.08 (2), 0.09	24	ENC-2/93-2
4302.92ME04	La Reuge	DMA	0.078	281	7/17/92 + 7/29/92	<0.05 (4)	59	KANN
4302.92ND02	Red Norland	DMA	0.078	187	7/6/92 + 7/16/92	<0.05 (4)	50	KAN
						<0.05 (4)	50	ENC-KAN
			0.36	187	7/6/92 + 7/16/92	0.05, 0.06, 0.07, 0.08	50	KAN
						<0.05, 0.05 (2), 0.07	50	ENC-KAN
		2-EHE	0.078	187	7/6/92 + 7/16/92	<0.05 (4),	50	ENC-KAN
			0.36	187	7/6/92 + 7/16/92	<0.05, 0.05 (2), 0.06	50	ENC-KAN
4302.93NY08	Chieftain	DMA	0.078	374	6/22/93 + 7/2/93	0.05, 0.07, 0.08 (2)	67	KAN
4302.92WA25	Red Pontiac	DMA	0.078	281	6/1/92 + 6/10/92	<0.05 (4)	44	KAN
4302.92WI06	Norland	DMA	0.078	187	6/19/92 + 7/2/92	<0.05 (4)	28	KAN

Asparagus. Critical GAP (USA): 2 x 2.2 kg ae/ha, PHI 3 days. Two trials were conducted in the USA in Washington and Michigan during 1992 and again in 1994. Two post-emergence broadcast applications of 2,4-D DMA salt were made at 2.2 kg ae/ha with 29- to 31-day retreatment intervals. In the 1992 trials, samples were harvested 24 hours after the second application. In the 1994 trials samples were taken at 24, 48 and 72 hours in WA, but only a single 72-hour sample was collected in MI owing to cool weather. The LOD was 0.05 mg/kg.

The apparent residues of 2,4-D in the 1992 trials were 10-15 mg/kg in samples from MI and 4.8-5.3 mg/kg in samples from WA. The actual residues may have been higher as fortified control samples stored with the treated samples indicated that the residues may have decreased on average by 46% during the storage period of about 20 months.

In the 1994 trials residues were 2.3 and 2.8 mg/kg in two samples at 24 hours and 1.1 and 0.97 mg/kg at 48 hours. By 72 hours the residues were 0.09 and 0.1 mg/kg in WA and 3 mg/kg in MI. The 1994 samples were analysed within 34 days of sampling, so no data on frozen storage stability are required to support the results (Kunkel, 1995a).

Table 34. Residues of 2,4-D in asparagus. Spears analysed.

Report no. Location	Variety State	Application		Date	Residue, mg/kg	PHI, hours
		kg ae/ha	water l/ha			
(Kunkel, 1995a)						
400.92-WA12	Mary WA	2.2 + 2.2	561 + 281	4/20/92 + 5/20/92	4.8, 5.1, 5.3 (2)	24
4090.92-MI06	Viking MI	2.2 + 2.2	187	5/8/92 + 6/8/92	10, 10.5, 13.5, 15	24
4090.94-WA46	Glen Smith WA	2.2 + 2.2	238 + 238	5/10/94 + 6/9/94	2.8, 2.3 0.97, 1.1 0.09, 0.1	24 48 72
4090.92-MI28	Martha MI	2.2 + 2.2	187	5/2/94 + 5/31/94	3	72

Use as herbicide on cereals

2,4-D is used world-wide in pre-emergence, post-emergence and pre-harvest applications to winter and summer cereals. The residue data are summarized in Tables 35-46.

Maize. Critical GAP (USA): 1.1 + 0.56 + 1.7 kg ae/ha, PHI 7 days). Seven side-by-side trials were conducted in the USA with 2,4-D DMA salt and 2-EHE. In each study two or three applications were made with a total up to about 3.4 kg ae/ha/season; these included a pre-emergence application at about 1.1 kg ae/ha, a directed post-emergence application at 0.56 kg ae/ha (except one at 1.1 kg ae/ha) when the maize was 25-41 cm high, and a pre-harvest application at 1.7 kg ae/ha 14 days before normal crop maturity. Two additional concurrent trials with the same use pattern were conducted with 2,4-D acid. Applications were made using ground equipment with intervals of 30-48 days between the first and second applications and 83-113 between the second and third applications (Carringer, 1995d,e,f).

Forage samples were collected 7 days after the second application, and silage samples at the dough-dent stage about 54-89 days after the second application (1.7-2.3 kg ae/ha total applied). Grain and fodder samples were harvested 7 days (9 days in one trial) and 14 days after the third application.

Table 35. Residues of 2,4-D in maize forage and silage.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	Water, l/ha					
DMA (Carringer, 1995e)									
AA930208.IA	Querna 7670	5/18/93	1.1	47	5/21/93	Pre-emergence			
			0.57	48	6/22/93	25-40 cm	Forage Silage	1.0 <0.01	7 70
AA930208.IL	Querna 7670	5/14/93	1.1	47	5/17/93	Pre-emergence			
			0.57	48	6/22/93	25-40 cm	Forage Silage	0.09 <0.01	7 69
AA930208.MN	Pioneer 3861	5/21/93	1.1	47	5/26/93	Pre-emergence			
			1.1	47	7/7/93	25-40 cm	Forage Silage	0.25 <0.01	7 76
AA930208.NC	Pioneer 3165	4/23/93	1.2	58	4/26/93	Pre-emergence			
			0.5	48	5/28/93	25-40 cm	Forage Silage	1.0 <0.01	7 60
AA930208.NE	Pioneer 3162	5/3/93	1.1	47	5/3/93	Pre-emergence			
			0.56	47	6/21/93	25-40 cm	Forage Silage	0.01 <0.01	7 65
AA930208.OH	GL 235	5/20/93	1.2	48	5/20/93	Pre-emergence			
			0.58	47	6/23/93	25-40 cm	Forage Silage	0.25 <0.01	7 76
AA930208.PA	Jacques 7710	5/14/93	1.1	49	5/17/93	Pre-emergence			
			0.58	47	6/22/93	25-40 cm	Forage Silage	2.7 0.01	7 89
EHE (Carringer, 1995f)									
AA930209.IA	Pioneer 3861	5/21/93	1.1	47	5/21/93	Pre-emergence			
			0.58	47	6/22/93	25-40 cm	Forage Silage	5.2 <0.01	7 70
AA930209.IL	Pioneer 3165	4/23/93	1.2	47	5/17/93	Pre-emergence			
			0.58	47	6/22/93	25-40 cm	Forage	1.1	7

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	Water, l/ha					
							Silage	<0.01	69
AA930209.MN	Pioneer 3162	5/3/93	1.1	47	5/26/93	Pre-emergence			
			1.1	47	7/7/93	25-40 cm	Forage	0.69	7
							Silage	<0.01	76
AA930209.NC	GL 235	5/20/93	1.2	58	4/26/93	Pre-emergence			
			0.52	43	5/28/93	25-40 cm	Forage	0.88	7
							Silage	<0.01	60
AA930209.NE	Jacques 7710	5/14/93	1.1	47	5/4/93	Pre-emergence			
			0.56	47	6/21/93	25-40 cm	Forage	0.03	7
							Silage	<0.01	65
AA930209.OH	GL 235	5/20/93	1.1	50	5/20/93	Pre-emergence			
			0.58	48	6/23/93	25-40 cm	Forage	0.46	7
							Silage	<0.01	76
AA930209.PA	Jacques 7710	5/14/93	1.1	50	5/17/93	Pre-emergence			
			0.57	49	6/22/93	25-40 cm	Forage	3.0	7
							Silage	<0.01	89
Acid (Carringer, 1995d)									
AA930210.IA	Querna 7670	5/18/93	1.1	48	5/21/93	Pre-emergence			
			0.58	49	7/8/93	25-40 cm	Forage	0.61	7
							Silage	0.03	54
AA930210.NC	Pioneer 3165	4/26/93	1.15	52	4/29/93	Pre-emergence			
			0.53	44	5/29/93	25-40 cm	Forage	0.33	7
							Silage	<0.01	59

Table 36. Residues of 2,4-D in maize fodder.

Compound (Reference) Report no.. Location	Variety	Sowing date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
DMA (Carringer, 1995e)								
AA930208.IA	Querna 7670	5/18/93	1.1	48	5/21/93	Pre-emergence		
			0.57	48	6/22/93	25-40 cm		
			1.7	48	10/5/93	Pre-harvest	4.4	7
							1.4	14
AA930208.IL	Querna 7670	5/14/93	1.1	48	5/17/93	Pre-emergence		
			0.57	47	6/22/93	25-40 cm		
			1.7	48	10/4/93	Pre-harvest	9.1	7
							3.8	14
AA930208.MN	Pioneer 3861	5/21/93	1.1	47	5/26/93	Pre-emergence		
			1.1	47	7/7/93	25-40 cm		
			1.7	48	9/28/93	Pre-harvest	51	7
							22	14
AA930208.NC	Pioneer 3165	4/23/93	1.2	58	4/26/93	Pre-emergence		
			0.5	43	5/28/93	25-40 cm		
			1.8	49	9/2/93	Pre-harvest	3.2	7
							9.9	14
AA930208.NE	Pioneer 3162	5/3/93	1.1	47	5/4/93	Pre-emergence		
			0.56	47	6/21/93	25-40 cm		
			1.7	47	9/17/93	Pre-harvest	4.4	7
							4.2	14

Compound (Reference) Report no.. Location	Variety	Sowing date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
AA930208.OH	GL 235	5/20/93	1.2 0.58 1.7	50 48 46	5/20/93 6/23/93 9/22/93	Pre-emergence 25-40 cm Pre-harvest	 11, 15 3.6, 6.4	 7 14
AA930208.PA	Jacques 7710	5/14/93	1.1 0.58 1.7	50 49 53	5/17/93 6/22/93 10/13/93	Pre-emergence 25-40 cm Pre-harvest	 4.2 3.4	 7 14
EHE (Carringer, 1995f)								
AA930209.IA	Querna 7670	5/18/93	1.1 0.58 1.7	47 48 48	5/21/93 6/22/93 10/11/93	Pre-emergence 25-40 cm Pre-harvest	 14 30	 7 14
AA930209.IL	Querna 7670	5/14/93	1.2 0.58 1.7	49 48 48	5/17/93 6/22/93 10/4/93	Pre-emergence 25-40 cm Pre-harvest	 3.6 2.1	 7 14
AA930209.MN	Pioneer 3861	5/21/93	1.1 1.1 1.7	47 48 48	5/26/93 7/7/93 9/28/93	Pre-emergence 25-40 cm Pre-harvest	 7.3 4.3	 7 14
AA930209.NC	Pioneer 3165	4/23/93	1.2 0.52 1.75	58 45 49	4/26/93 5/28/93 9/2/93	Pre-emergence 25-40 cm Pre-harvest	 20 8.2	 7 14
AA930209.NE	Pioneer 3162	5/3/93	1.1 0.56 1.7	47 47 47	5/4/93 6/21/93 9/17/93	Pre-emergence 25-40 cm Pre-harvest	 5 5.7	 7 14
AA930209.OH	GL 235	5/20/93	1.1 0.58 1.7	49 49 47	5/20/93 6/23/93 9/22/93	Pre-emergence 25-40 cm Pre-harvest	 6.4 6.0	 7 14
AA930209.PA	Jacques 7710	5/14/93	1.1 0.57 1.7	52 48 68	5/17/93 6/22/93 10/13/93	Pre-emergence 25-40 cm Pre-harvest	 4.7 6.4	 7 14
Acid (Carringer, 1995d)								
AA930210.IA	Querna 7670	5/18/93	1.1 0.58 1.7	48 49 47	5/21/93 7/8/93 10/5/93	Pre-emergence 25-40 cm Pre-harvest	 25 14	 7 14
AA930210.NC	Pioneer 3165	4/26/93	1.15 0.53 1.4 0.29	52 44 40 48	4/29/93 5/29/93 9/2/93	Pre-emergence 25-40 cm Pre-harvest	 3.3 1.6	 7 14

Table 37. Residues of 2,4-D in maize grain.

Compound (Reference) Report no. Location	Variety	Sowing date	Application	Date	Growth stage	Residue, mg/kg	PHI, days

			kg ae/ha	water l/ha				
DMA (Carringer, 1995e)								
AA930208.IA	Querna 7670	5/18/93	1.1	48	5/21/93	Pre-emergence		
			0.57	48	6/22/93	25-40 cm		
			1.7	48	10/5/93	Pre-harvest	<0.01	7
							0.01	14
AA930208.IL	Querna 7670	5/14/93	1.1	48	5/17/93	Pre-emergence		
			0.57	48	6/22/93	25-40 cm		
			1.7	48	10/4/93	Pre-harvest	0.01	7
							0.015	14
AA930208.MN	Pioneer 3861	5/21/93	1.1	47	5/26/93	Pre-emergence		
			1.1	47	7/7/93	25-40 cm		
			1.7	48	9/28/93	Pre-harvest	0.01	7
							<0.01	14
AA930208.NC	Pioneer 3165	4/23/93	1.2	58	4/26/93	Pre-emergence		
			0.5	43	5/28/93	25-40 cm		
			1.8	49	9/2/93	Pre-harvest	0.04	7
							<0.01	14
AA930208.NE	Pioneer 3162	5/3/93	1.1	47	5/4/93	Pre-emergence		
			0.56	47	6/21/93	25-40 cm		
			1.7	47	9/17/93	Pre-harvest	0.02	7
							0.01(2)	14
AA930208.OH	GL 235	5/20/93	1.2	50	5/20/93	Pre-emergence		
			0.58	49	6/23/93	25-40 cm		
			1.7	46	9/22/93	Pre-harvest	0.01	7
							0.01	14
AA930208.PA	Jacques 7710	5/14/93	1.1	50	5/17/93	Pre-emergence		
			0.58	49	6/22/93	25-40 cm		
			1.7	48	10/13/93	Pre-harvest	<0.01	7
							0.01	14
EHE (Carringer, 1995e)								
AA930209.IA	Pioneer 3861	5/21/93	1.1	47	5/21/93	Pre-emergence		
			0.58	48	6/22/93	25-40 cm		
			1.7	48	10/11/93	Pre-harvest	0.01	7
							0.01	14
AA930209.IL	Pioneer 3165	4/23/93	1.2	49	5/17/93	Pre-emergence		
			0.58	48	6/22/93	25-40 cm		
			1.7	48	10/4/93	Pre-harvest	0.01	7
							0.01	14
AA930209.MN	Pioneer 3162	5/3/93	1.1	47	5/26/93	Pre-emergence		
			1.1	48	7/7/93	25-40 cm		
			1.7	48	9/28/93	Pre-harvest	0.01	7
							<0.01	14
AA930209.NC	GL 235	5/20/93	1.2	58	4/26/93	Pre-emergence		
			0.52	45	5/28/93	25-40 cm		
			1.8	49	9/2/93	Pre-harvest	0.03	7
							0.01	14
AA930209.NE	Jacques 7710	5/14/93	1.1	47	5/4/93	Pre-emergence		
			0.56	47	6/21/93	25-40 cm		
			1.7	47	9/17/93	Pre-harvest	<0.01	7
							0.02	14
AA930209.OH	GL 235	5/20/93	1.1	49	5/20/93	Pre-emergence		
			0.58	49	6/23/93	25-40 cm		
			1.7	47	9/22/93	Pre-harvest	0.01	7
							<0.01	14

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
AA930209.PA	Jacques 7710	5/14/93	1.1	52	5/17/93	Pre-emergence		
			0.57	48	6/22/93	25-40 cm		
			1.7	68	10/13/93	Pre-harvest	<0.01	7
							0.01	14
Acid (Carringer, 1995d)								
AA930210.IA ACID	Querna 7670	5/18/93	1.1	48	5/21/93	Pre-emergence		
			0.58	49	7/8/93	25-40 cm		
			1.7	48	10/5/93	Pre-harvest	0.01	7
							0.01	14
AA930210.NC	Pioneer 3165	4/26/93	1.15	52	4/29/93	Pre-emergence		
			0.53	44	5/29/93	25-40 cm		
			1.4	40	5/29/93	25-40 cm		
			0.29	48	9/2/93	Pre-harvest	0.02	7
							0.01	14

Rice. Critical GAP (USA): 1 x 1.7 kg ae/ha, PHI 60 days. Ten trials were conducted, two in each of four states with the DMA salt, and one each in two of the states with the free acid. In each a post-emergence broadcast application was made at 1.6-1.8 kg ae/ha at tillering before first joint (Carringer, 1995p,q).

Samples of grain (without husk) and straw were collected at normal crop maturity, 61-104 days after treatment. The LODs were 0.01 mg/kg. Control samples of grain and straw from the CA trials showed residues of 0.11-0.13 mg/kg in grain and 0.03-0.04 mg/kg in straw, apparently from contamination when an adjacent field was sprayed with 2,4-D. Residues in treated samples were not corrected for apparent residues in the controls. The residues were <0.01-0.49 mg/kg in the grain and 0.06-8.8 mg/kg in the straw. The high residues at the LA2 trial may have been the result of drift from spraying 2,4-D on roadsides surrounding the trial site.

Table 38. Residues of 2,4-D in rice grain.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
DMA (Carringer, 1995p)									
AA930222.AR1	Newbonnet	5/9/93	1.8	99	7/19/93	1st joint	Treated	0.03	66
AA930222.AR2	Newbonnet	5/9/93	1.8	97	7/19/93	1st joint	Treated	0.01	66
AA930222.CA1	Cal Pearl	6/28/93	1.8	97	7/29/93	1st joint	Treated	0.07	104
							Control	0.12	104
AA930222.CA2	Cal Pearl	6/28/93	1.8	97	7/29/93	1st joint	Treated	0.08	104
							Control	0.11	104
AA930222.LA1	Lemont	4/29/93	1.7	95	6/26/93	1st joint	Treated	0.01	61
AA930222.LA2	RT 7015	5/28/93	1.8	95	6/26/93	1st joint	Treated	0.49[1]	62
AA930222.TX1	Katy	4/22/93	1.6	91	6/12/93	1st joint	Treated	<0.01	73
							Control	0.01, <0.01	73
AA930222.TX2	Lemont	4/25/93	1.8	95	6/21/93	1st joint	Treated	<0.01	64
Acid (Carringer, 1995q)									
AA930224.AR	Newbonnet	5/9/93	1.8	100	7/19/93	1st joint	Treated	0.05	66
AA930224.LA	Lemont	4/29/93	1.6	90	6/26/93	1st joint	Treated	0.01	61

[1] Outlier, result of drift from spraying of 2,4-D on roadsides surrounding the test site.

Table 39. Residues of 2,4-D in rice straw.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Commodity	Residue, mg/kg	PHI
			kg ae/ha	water l/ha					
DMA (Carringer, 1995p)									
AA930222.AR1	Newbonnet	5/9/93	1.8	99	7/19/93	1st joint	Treated	3.1	66
AA930222.AR2	Newbonnet	5/9/93	1.8	97	7/19/93	1st joint	Treated	1.5	66
AA930222.CA1	Cal Pearl	6/28/93	1.8	97	7/29/93	1st joint	Treated	0.34	104
							Control	0.04	104
AA930222.CA2	Cal Pearl	6/28/93	1.8	97	7/29/93	1st joint	Treated	0.06	104
							Control	0.03	104
AA930222.LA1	Lemont	4/29/93	1.7	95	6/26/93	1st joint	Treated	5.4	61
AA930222.LA2	RT 7015	5/28/93	1.8	95	6/26/93	1st joint	Treated	8.8	62
AA930222.TX1	Katy	4/22/93	1.6	91	6/12/93	1st joint	Treated	0.74	73
AA930222.TX2	Lemont	4/25/93	1.8	95	6/21/93	1st joint	Treated	1.1	64
Acid (Carringer, 1995q)									
AA930224.AR	Newbonnet	5/9/93	1.8	100	7/19/93	1st joint	Treated	2.1	66
AA930224.LA	Lemont	4/29/93	1.6	90	6/26/93	1st joint	Treated	6.4	61
							Control	0.01, <0.01	61

Wild rice. Critical GAP (USA): 1 x 0.28 kg ae/ha, PHI 60 days. A single trial was conducted with the DMA salt at 0.56 kg ae/ha. Three samples were collected from each plot after 53 days and one after 64 days. Samples were harvested by cutting heads, threshing out the seeds, and separating the grain and hulls. No 2,4-D was found in either grain or hulls. The LOD was 0.05 mg/kg (Kunkel, 1995f).

Table 40. Residues of 2,4-D in wild rice from treatments with DMA salt.

(Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
(Kunkel, 1995f)									
1015.92-MN01	Franklin (K2(2)c4)	5/19/92	0.56	45.96	7/9/92	Mid to Late Tillering	Seed	<0.05 (3)	53
								<0.05	64
							Hulls	<0.05 (3)	53
								<0.05	64

Sorghum. Critical GAP (USA): 1 x 0.56 kg ae/ha (esters), 1 x 1.1 kg ae/ha (other formulations), PHI for forage 30 days). Single post-emergence directed application of the EHE at 0.56 kg ae/ha and of the DMA salt at 1.1 kg ae/ha were made in separate trials in each of four US states. All applications were made using ground equipment when the plants were 20-25 cm tall. Forage samples were collected 26-31 days after treatment, and grain and fodder samples at maturity, 82-112 days after treatment (Carringer, 1995g,h,i).

The LOD for all samples was 0.01 mg/kg. The apparent residues of 2,4-D were <0.01-0.14 mg/kg in the forage samples, <0.01-0.01 mg/kg in the grain and <0.01- 0.04 mg/kg in the fodder samples. In most of the trials the residues in the control samples of grain and fodder were as high as or higher than those in the samples from treated plots suggesting that the results were invalid.

Table 41. Residues of 2,4-D in sorghum grain.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Sample	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha					
DMA (Carringer, 1995i)									
AA930212.KS	NK 2030	7/11/93	1.2	48	8/2/93	20-25 cm	Treated	<0.01	110
AA930212.MO	GK 802 G	6/2/93	1.2	48	7/2/93	20-25 cm	Treated	<0.01	89
AA930212.NE	Northrup King	5/24/93	1.1	47	6/29/93	20-25 cm	Treated	0.01	99
							Control	0.01 (2)	99
AA930212.TX	GSA 1290	5/20/93	1.1	60	6/19/93	20-25 cm	Treated	<0.01	82
EHE (Carringer, 1995g)									
AA930214.KS	NK 2030	7/11/93	0.58	48	8/2/93	20-25 cm	Treated	<0.01	110
AA930214.MO	GK 802 G	6/2/93	0.57	49	7/7/93	20-25 cm	Treated	<0.01	84
AA930214.NE	Northrup King	5/24/93	0.56	47	6/29/93	20-25 cm	Treated	0.01	99
							Control	0.01 (2)	99
AA930214.TX	GSA 1290	5/20/93	0.56	58	6/16/93	20-25 cm	Treated	<0.01	82
Acid (Carringer, 1995h)									
AA930215.KS	NK 23030	7/11/93	1.1	47	8/2/93	20-25 cm	Treated	<0.01	112
AA930215.TX	GSA 1290	5/20/93	1.1	60	6/16/93	20-25 cm	Treated	<0.01	82

Table 42. Residues of 2,4-D in sorghum forage.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha				
DMA (Carringer, 1995i)								
AA930212.KS	NK 2030	7/11/93	1.2	48	8/2/93	20-25 cm	0.14	30
AA930212.MO	GK 802 G	6/2/93	1.2	48	7/2/93	20-25 cm	0.03	31
AA930212.NE	Northrup King	5/24/93	1.1	47	6/29/93	20-25 cm	0.02	30
AA930212.TX	GSA 1290	5/20/93	1.1	60	6/19/93	20-25 cm	0.08	30
EHE (Carringer, 1995g)								
AA930214.KS	NK 2030	7/11/93	0.58	48	8/2/93	20-25 cm	0.04	30
AA930214.MO	GK 802 G	6/2/93	0.57	49	7/7/93	20-25 cm	0.02	26
AA930214.NE	Northrup King	5/24/93	0.56	47	6/29/93	20-25 cm	<0.01	30
AA930214.TX	GSA 1290	5/20/93	0.56	47	6/16/93	20-25 cm	0.03	30
Acid (Carringer, 1995h)								
AA930215.KS	NK 23030	7/11/93	1.1	47	8/2/93	20-25 cm	0.06	30
AA930215.TX	GSA 1290	5/20/93	1.1	60	6/16/93	20-25 cm	0.13	30

Table 43. Residues of 2,4-D in sorghum fodder.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Sample	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha					
DMA (Carringer, 1995i)									
AA930212.KS	NK 2030	7/11/93	1.2	48	8/2/93	20-25 cm	Treated	0.04	110
							Control	0.02, 0.03	110
AA930212.MO	GK 802 G	6/2/93	1.2	48	7/2/93	20-25 cm	Treated	0.02	89
							Control	0.02	89

AA930212.NE	Northrup King	5/24/93	1.1	47	6/29/93	20-25 cm	Treated	0.01	99
							Control	0.02	99
AA930212.TX	GSA 1290	5/20/93	1.1	60	6/19/93	20-25 cm	Treated	0.03	82
							Control	0.03	82
EHE (Carringer, 1995g)									
AA930214.KS	NK 2030	7/11/93	0.58	48	8/2/93	20-25 cm	Treated	0.02	110
							Control	0.015	110
AA930214.MO	GK 802 G	6/2/93	0.57	49	7/7/93	20-25 cm	Treated	0.01	84
AA930214.NE	Northrup King	5/24/93	0.56	47	6/29/93	20-25 cm	Treated	0.03	99
							Control	0.03	99
AA930214.TX	GSA 1290	5/20/93	0.56	47	6/16/93	20-25 cm	Treated	<0.01	82
							Control	0.03, 0.04	82
Acid (Carringer, 1995h)									
AA930215.KS	NK 23030	7/11/93	1.1	47	8/2/93	20-25 cm	Treated	0.03	112
							Control	0.02	112
AA930215.TX	GSA 1290	5/20/93	1.1	60	6/16/93	20-25 cm	Treated	0.02	82
							Control	0.04, 0.05,	82

Wheat. Critical GAP (USA): 1 x 1.4 + 1 x 0.56 kg ae/ha, PHI 14 days. In 1993 19 trials were conducted in seven US states to determine residues of 2,4-D in wheat forage, grain and straw. One or two applications of either the EHE or the DMA salt were made at 1.4 kg ae/ha/application, except in two states where two applications of 2,4-D acid were made at 1.4 kg ae/ha/application, with ground equipment at retreatment intervals from 61-90 days. In all trials, samples of forage and hay were taken 7 and 14 days after the first application, and of grain and straw 7 and 14 days after the second application (Carringer, 1995a,b,t).

In 1994 there were 16 trials in seven US states. Half of the trials were with the EHE and the other half with the DMA salt. Applications were (i) a single at-tillering at a nominal 1.4 kg ae/ha, or (ii) a single at-tillering at 1.4 kg ae/ha followed at the hard dough stage by either a nominal 0.56 or 0.84 kg ae/ha about 7 or 14 days pre-harvest. The interval between the first and second treatments was 37-98 days (Carringer, 1995y,z). Residues in the control samples ranged from <0.01 to 0.09 mg/kg in the forage and <0.01 to 0.05 mg/kg in the grain. The application of EHE and DMA salt to the GA site was made after the tillering stage which gave abnormally high residues in the grain, forage and straw and was not representative of the use pattern.

In 1996, 12 trials were carried out repeating the use pattern of 1994, with an interval between the first and second treatments of 54-101 days (Carringer, 1996a,b).

Table 44. Residues of 2,4-D in wheat forage. All single applications at tillering.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha			
EHE (Carringer, 1995b)							
AA930204.CA1	Yecora Rojo	2/12/93	1.4	47	4/10/93	33 19	7 14
AA930204.CA2	Yecora Rojo	4/8/93	1.4	45	5/18/93	18 16	7 14
AA930204.GA	Coker 9766	11/18/92	1.4	47	2/23/93	50 19	7 14
AA930204.KS	TAM 107	9/10/92	1.4	47	4/16/93	58 18	7 14
AA930204.MN	Hard Red Spring	5/13/93	1.4	47	6/19/93	23 10	7 14
AA930204.ND	Hard Red Spring	4/26/93	1.3	43	5/26/93	18 6	7 14
AA930204.OK	McNair	10/1/92	1.4	53	3/16/93	42 13	7 14
AA930204.WA	Stephens	10/11/92	1.5	50	4/27/93	41 19	7 14
Acid (Carringer, 1995t)							
AA930205.KS	TAM 107	9/10/92	1.5	49	4/16/93	35 6	7 14
AA930205.ND	Grandin	4/26/93	1.4	45	5/26/93	34 0.3	7 14
DMA (Carringer, 1995a)							
AA930207.CA1	Yecora Rojo	2/12/93	1.4	47	4/14/93	8.5 5	7 14
AA930207.CA2	Yecora Rojo	4/8/93	1.4	46	5/19/93	112 6	7 14
AA930207.GA	Coker 9766	11/18/92	1.4	47	2/23/93	16 4	7 14
AA930207.KS	TAM 107	9/10/92	1.4	48	4/16/93	26 9	7 14
AA930207.MN	Butte 86	5/13/93	1.4	48	6/29/93	17 6	7 14
AA930207.ND	Grandin	4/26/93	1.6	53	5/26/93	7 1	7 14
AA930207.OK	McNair 1003	10/1/92	1.4	53	3/16/93	6 4	7 14
AA930207.WA	Stephens	10/10/92	1.4	48	4/27/93	8 4	7 14
DMA (Carringer, 1995z)							
AA940502.CA1	Yecora Rojo	4/15/94	1.5	51	5/20/94	15 6	7 14
AA940502.CA2	Yecora Rojo	4/15/94	1.5	42	5/25/94	11 7.6	7 14
AA940502.GA	Andy	12/20/93	1.4	47	4/7/94	20 17	7 14
AA940502.KS	Karl	10/6/93	1.4	45	4/7/94	23, 30 11	7 14
AA940502.MN	Stoa	5/9/94	1.4	47	6/11/94	6	7

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha			
						2	14
AA940502.ND	Grandin	5/11/94	1.4	48	6/4/94	6 2	7 14
AA940502.OK	McNair	11/01/93	1.4	46	4/6/94	14, 22 5.5	7 14
AA940502.WA	MAC-1	10/18/93	1.4	47	4/18/94	5 3	7 14
EHE (Carringer, 1995y)							
AA940501.CA1	Yecora Rojo	4/15/94	1.4	45	5/21/94	20 11	7 14
AA940501.CA2	Yecora Rojo	4/15/94	1.4	45	5/26/94	22 17	7 14
AA940501.GA	Andy	12/20/93	1.4	47	4/7/94	9 11	7 14
AA940501.KS	Karl	10/6/93	1.4	45	4/7/94	54 22	7 14
AA940501.MN	Stoa	5/9/94	1.5	49	6/11/94	8 6	7 14
AA940501.ND	Grandin	5/11/94	1.4	48	6/4/94	19 4	7 14
AA940501.OK	McNair	11/10/93	1.4	46	4/6/94	30 17	7 14
AA940501.WA	Stephens	10/6/93	1.4	49	4/18/94	14 12	7 14
EHE (Carringer, 1996a)							
AA960501.CO	Tam 107	9/15/95	1.4	51	4/10/96	29 18	7 14
AA960501.GA	Coker 9835	12/5/95	1.4	49	3/13/96	33 21	7 14
AA960501.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	47	6/26/96	23 2.9	7 14
AA960501.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	48	6/21/96	14 1.5	7 14
AA960501.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	55 22	7 14
AA960501.WA	Madsen	11/6/95	1.4	47	4/25/96	33 17	7 14
DMA (Carringer, 1996b)							
AA960502.CO	Tam 107	9/15/95	1.4	51	4/10/96	9 3.7	7 14
AA960502.GA	Coker 9835	12/5/95	1.4	49	3/13/96	18, 24 12, 18	7 14
AA960502.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	46	6/26/96	14 7.6	7 14
AA960502.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	46	6/20/96	4.6, 6.3 0.62	7 14
AA960502.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	25 6.1, 9.4	7 14
AA960502.WA	Madsen	11/6/95	1.4	47	4/25/96	15	7
						7.7	14

Table 45. Residues of 2,4-D in wheat grain. CLICK HERE for continue

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
EHE (Carringer, 1995b)									
AA930204.CA1	Yecora Rojo	2/12/93	1.4	47	4/10/93	Tillering			
			1.4	45	6/15/93	Pre-harvest	Treated	0.85	7
							Treated	0.49	14
AA930204.CA2	Yecora Rojo	4/8/93	1.4	45	5/18/93	Tillering			
			1.45	48	7/19/93	Pre-harvest	Treated	0.87	7
							Treated	1.3	14
							Control	0.02	7
							Control	0.04	14
AA930204.GA	Coker 9766	11/18/92	1.4	47	2/23/93	Tillering			
			1.4	46	5/14/93	Pre-harvest	Treated	1.6	7
								0.69	14
AA930204.KS	TAM 107	9/10/92	1.4	47	4/16/93	Tillering			
			1.4	47	6/25/93	Pre-harvest	Treated	0.39, 0.5	7
							Treated	3.2	14
AA930204.MN	Hard Red Spring	5/13/93	1.4	47	6/19/93	Tillering			
			1.45	48	8/19/93	Pre-harvest	Treated	0.41	7
							Treated	0.29	14
AA930204.ND	Hard Red Spring	4/26/93	1.3	43	5/26/93	Tillering			
			1.4	48	8/13/93	Pre-harvest	Treated	0.68	7
							Treated	0.85	14
							Control	0.02	7
AA930204.OK	McNair	10/1/92	1.4	53	3/16/93	Tillering			
			1.45	57	5/28/93	Pre-harvest	Treated	3.4	7
							Treated	1.2 1.3	14
AA930204.WA	Stephens	10/11/92	1.45	50	4/27/93	Tillering			
			1.4	47	7/26/93	Pre-harvest	Treated	2.5	7
							Treated	0.86	14
Acid (Carringer, 1995t)									
AA930205.KS	TAM 107	9/10/92	1.5	49	4/16/93	Tillering			
			1.5	48	6/25/93	Pre-harvest	Treated	0.09	7
AA930205.ND	Grandin	4/26/93	1.4	45	5/26/93	Tillering			
			1.4	48	8/11/93	Pre-harvest	Treated	0.31	7
							Treated	0.39	14
							Control	<0.01	7
							Control	0.02	14
DMA (Carringer, 1995a)									
AA930207.CA1	Yecora Rojo	2/12/93	1.4	47	4/14/93	Tillering			
			1.4	45	6/23/93	Pre-harvest	Treated	2.9	7
							Treated	2.4	14
							Control	0.02	7
AA930207.CA2	Yecora Rojo	4/8/93	1.4	46	5/19/93	Tillering			
			1.4	48	7/21/93	Pre-harvest	Treated	1.9	7
							Treated	1.8	14
AA930207.GA	Coker 9766	11/18/92	1.4	47	2/23/93	Tillering			
			1.4	46	5/14/93	Pre-harvest	Treated	1.4	7
							Treated	0.84	14

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
AA930207.KS	TAM 107	9/10/92	1.4	48	4/16/93	Tillering			
			1.7	55	6/25/93	Pre-harvest	Treated	0.86	7
AA930207.MN	Butte 86	5/13/93	1.4	48	6/29/93	Tillering			
			1.4	55	8/19/93	Pre-harvest	Treated	0.79	7
							Treated	0.47	14
							Control	0.02	7
							Control	0.12	14
AA930207.ND	Grandin	4/26/93	1.4	48	5/26/93	Tillering			
			1.5	48	8/13/93	Pre-harvest	Treated	1.0	7
							Treated	1.2	14
							Control	0.04	14
AA930207.OK	McNair 1003	10/1/92	1.4	53	3/16/93	Tillering			
			1.4	56	5/28/93	Pre-harvest	Treated	6.2	7
							Treated	2.3	14
AA930207.WA	Stephens	10/10/92	1.4	48	4/27/93	Tillering			
			1.4	49	7/26/93	Pre-harvest	Treated	2.5	7
							Treated	1.0	14
DMA (Carringer, 1995z)									
AA940502.CA1	Yecora Rojo	4/15/94	1.5	51	5/20/94	Tillering	Treated	0.01	53
			1.4	47	5/20/94	Tillering			
			0.82	46	7/5/94	Pre-harvest	Treated	0.32	7
							Treated	0.28	15
			1.4	46	5/20/94	Tillering			
			0.54	45	7/5/94	Pre-harvest	Treated	0.18	7
							Treated	0.12	15
AA940502.CA2	Yecora Rojo	4/15/94	1.5	42	5/25/94	Tillering	Treated	0.03	45
			1.5	49	5/25/94	Tillering			
			0.87	49	7/2/94	Pre-harvest	Treated	0.71	7
							Treated	0.33	13
			1.3	48	5/25/94	Tillering			
			0.55	46	7/2/94	Pre-harvest	Treated	0.25	7
							Treated	0.31	13
AA940502.GA	Andy	12/20/93	1.4	46	4/7/94	Tillering	Treated	0.76, 0.84	46
			1.4	46	4/7/94	Tillering			
			0.84	46	5/16/94	Pre-harvest	Treated	1.4, 0.96	7
							Treated	1.1, 2.0	14
			1.4	46	4/7/94	Tillering			
			0.56	46	5/16/94	Pre-harvest	Treated	1.5, 1.3	7
							Treated	0.94, 0.69	14
AA940502.KS	Karl	10/6/93	1.4	45	4/7/94	Tillering	Treated	<0.01	69
			1.4	45	4/7/94	Tillering			
			0.87	48	6/8/94	Pre-harvest	Treated	2.5	7
							Treated	3.1, 4.3	14
			1.4	45	4/7/94	Tillering			
			0.57	48	6/8/94	Pre-harvest	Treated	0.3	7
							Treated	0.71, 0.87	14
AA940502.MN	Stoa	5/9/94	1.4	47	6/11/94	Tillering	Treated	0.03	73

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
			1.4	45	6/11/94	Tillering			
			0.85	47	8/16/94	Pre-harvest	Treated	0.72, 3.3	7
							Treated	1.2	14
			1.4	47	6/11/94	Tillering			
			0.57	48	8/16/94	Pre-harvest	Treated	1.2, 1.9	7
							Treated	0.78, 1.4	14
AA940502.ND	Grandin	5/11/94	1.4	48	6/4/94	Tillering	Treated	<0.01	82
			1.4	48	6/4/94	Tillering			
			0.84	46	8/18/94	Pre-harvest	Treated	0.41	7
							Treated	0.22	14
			1.4	48	6/4/94	Tillering			
			0.56	46	8/18/94	Pre-harvest	Treated	0.12	7
							Treated	0.22	14
AA940502.OK	McNair	11/01/93	1.4	46	4/6/94	Tillering	Treated	<0.01	72
			1.4	45	4/6/94	Tillering			
			0.84	50	6/10/94	Pre-harvest	Treated	0.31	7
			1.4	44	4/6/94	Tillering			
			0.55	49	6/10/94	Pre-harvest	Treated	0.19	7
AA940502.WA	MAC-1	10/18/93	1.4	47	4/18/94	Tillering	Treated	<0.01	106
			1.4	47	4/18/94	Tillering			
			0.86	47	7/25/94	Pre-harvest	Treated	0.38	7
							Treated	0.05	14
			1.4	47	4/18/94	Tillering			
			0.56	46	7/25/94	Pre-harvest	Treated	0.17	7
							Treated	0.11	14
							Control	0.02	7
EHE (Carringer, 1995y)									
AA940501.CA1	Yecora Rojo	4/15/94	1.4	45	5/21/94	Tillering	Treated	0.03	52
			1.4	45	5/21/94	Tillering			
			0.83	46	7/5/94	Pre-harvest	Treated	0.15	7
							Treated	0.26	15
			1.4	46	5/21/94	Tillering			
			0.56	47	7/5/94	Pre-harvest	Treated	0.13	7
							Treated	0.11	15
AA940501.CA2	Yecora Rojo	4/15/94	1.4	45	5/26/94	Tillering	Treated	0.18	44
			1.4	46	5/26/94	Tillering			
			0.83	46	7/2/94	Pre-harvest	Treated	0.33	7
							Treated	0.2, 0.56	13
			1.4	46	5/26/94	Tillering			
			0.54	45	7/2/94	Pre-harvest	Treated	0.33	7
							Treated	0.24	13
AA940501.GA	Andy	12/20/93	1.4	46	4/7/94	Tillering	Treated	0.26	46
			1.4	46	4/7/94	Tillering			
			0.84	46	5/16/94	Pre-harvest	Treated	0.28, 0.53	7
							Treated	0.76, 0.5	14
			1.4	46	4/7/94	Tillering			
			0.56	46	5/16/94	Pre-harvest	Treated	0.49	7
							Treated	0.75, 0.95	14

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
AA940501.KS	Karl	10/6/93	1.4	45	4/7/94	Tillering	Treated	0.01	69
			1.4	45	4/7/94	Tillering			
			0.83	45	6/8/94	Pre-harvest	Treated	0.38	7
							Treated	0.31	14
			1.4	45	4/7/94	Tillering			
			0.57	48	6/8/94	Pre-harvest	Treated	0.16	7
							Treated	0.17	14
AA940501.MN	Stoa	5/9/94	1.5	49	6/11/94	Tillering	Treated	0.01	94
			1.4	46	6/11/94	Tillering			
			0.85	47	9/6/94	Pre-harvest	Treated	0.78, 1.2	9
							Treated	0.46	16
			1.4	48	6/11/94	Tillering			
			0.57	48	9/6/94	Pre-harvest	Treated	0.41	8
							Treated	0.4, 0.63	14
							Control	0.015	7
AA940501.ND	Grandin	5/11/94	1.4	48	6/4/94	Tillering	Treated	<0.01	82
			1.4	48	6/4/94	Tillering			
			0.84	46	8/18/94	Pre-harvest	Treated	0.25	7
							Treated	0.27	14
			1.4	48	6/4/94	Tillering			
			0.56	47	8/18/94	Pre-harvest	Treated	0.08	7
							Treated	0.17	14
AA940501.OK	McNair	11/10/93	1.4	46	4/6/94	Tillering	Treated	<0.01	72
			1.4	46	4/6/94	Tillering			
			0.85	50	6/10/94	Pre-harvest	Treated	0.57, 0.96	7
			1.4	46	4/6/94	Tillering			
			0.56	49	6/10/94	Pre-harvest	Treated	0.23	7
							Control	0.02	7
AA940501.WA	Stephens	10/6/93	1.4	49	4/18/94	Tillering	Treated	0.02	105
			1.4	49	4/18/94	Tillering			
			0.85	47	7/25/94	Pre-harvest	Treated	0.22	7
							Treated	0.16	14
			1.4	45	4/18/94	Tillering			
			0.57	47	7/25/94	Pre-harvest	Treated	0.11	7
							Treated	0.06	14
							Control	0.03, 0.04 (2), 0.05	7
EHE (Carringer, 1996a)									
AA960501.CO	TAM 107	~9/15/95	1.4	51	4/10/96	Tillering	Treated	0.03	98
			1.4	51	4/10/96	Tillering			
			0.58	47	7/10/96	Pre-harvest	Treated	0.42	7
			1.4	51	4/10/96	Tillering			
			0.58	48	7/3/96	Pre-harvest	Treated	0.21	14
AA960501.GA	Coker 9835	12/5/95	1.4	49	3/13/96	Tillering	Treated	0.02, <0.01	75
			1.4	49	3/13/96	Tillering			
			0.57	47	5/20/96	Pre-harvest	Treated	0.05, 0.08	7
			1.4	49	3/13/96	Tillering			

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
			0.57	47	5/13/96	Pre-harvest	Treated	0.09, 0.13	14
							Control	0.01	
AA960501.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	47	6/26/96	Tillering	Treated	<0.01	69
			1.4	46	6/26/96	Tillering			
			0.56	48	8/20/96	Pre-harvest	Treated	0.19	7
			1.4	48	6/26/96	Tillering			
			0.56	48	8/13/96	Pre-harvest	Treated	0.2, 0.23	14
AA960501.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	48	6/21/96	Tillering	Treated	<0.01	68
			1.45	47	6/21/96	Tillering			
			0.57	48	8/21/96	Pre-harvest	Treated	0.03, 0.39	7
			1.4	47	6/21/96	Tillering			
			0.56	47	8/14/96	Pre-harvest	Treated	0.21, 0.22	14
AA960501.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	Tillering	Treated	<0.01, 0.03	84
			1.4	50	3/13/96	Tillering			
			0.56	50	5/25/96	Pre-harvest	Treated	0.08, 0.09	11
			1.4	50	3/13/96	Tillering			
			0.57	50	5/21/96	Pre-harvest	Treated	0.14, 0.16	15
AA960501.WA	Madsen	11/6/95	1.4	47	4/25/96	Tillering	Treated	<0.01 (2)	105
			1.4	47	4/25/96	Tillering			
			0.55	48	8/1/96	Pre-harvest	Treated	0.16, 0.17	7
			1.4	47	4/25/96	Tillering			
			0.57	47	7/25/96	Pre-harvest	Treated	0.16, 0.17	14
DMA (Carringer, 1996b)									
AA960502.CO	TAM 107	9/15/95	1.4	51	4/10/96	Tillering	Treated	<0.01 (2)	98
			1.3	51	4/10/96	Tillering			
			0.58	47	7/10/96	Pre-harvest	Treated	0.75, 0.9	7
			1.3	51	4/13/96	Tillering			
			0.58	48	7/3/96	Pre-harvest	Treated	0.01, 0.25	14
AA960502.GA	Coker 9835	12/5/95	1.4	49	3/13/96	Tillering	Treated	<0.01 (2)	75
			1.4	49	3/13/96	Tillering			
			0.57	47	5/20/96	Pre-harvest	Treated	0.14, 0.16	7
			1.4	49	3/13/96	Tillering			
			0.57	47	5/13/96	Pre-harvest	Treated	0.27, 0.34	14
AA960502.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	46	6/26/96	Tillering	Treated	<0.01 (2)	69

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
			1.4	46	6/26/96	Tillering			
			0.56	48	8/27/96	Pre-harvest	Treated	0.25, 0.36	7
			1.4	47	6/26/96	Tillering			
			0.54	46	8/20/96	Pre-harvest	Treated	0.15, 0.17	14
AA960502.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	46	6/20/96	Tillering	Treated	<0.01 (2)	69
			1.4	47	6/20/96	Tillering			
			0.56	46	8/21/96	Pre-harvest	Treated	0.57 (2)	7
			1.4	47	6/20/96	Tillering			
			0.56	47	8/14/06	Pre-harvest	Treated	0.44, 0.46	14
AA960502.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	Tillering	Treated	<0.01 (2)	84
			1.4	50	3/13/96	Tillering			
			0.57	50	5/20/96	Pre-harvest	Treated	0.08, 0.03	11
			1.4	50	3/13/96	Tillering			
			0.57	50	5/21/96	Pre-harvest	Treated	0.1, 0.24	15
AA960502.WA	Madsen	11/6/95	1.4	47	4/25/96	Tillering	Treated	<0.01	105
			1.4	47	4/25/96	Tillering			
			0.56	48	8/1/96	Pre-harvest	Treated	0.12, 0.22	7
			1.4	47	4/25/96	Tillering			
			0.56	47	7/25/96	Pre-harvest	Treated	0.08, 0.16	14

Table 46. Residues of 2,4-D in wheat straw.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
EHE (Carringer, 1995b)								
AA930204.CA1	Yecora Rojo	2/12/93	1.4	47	4/10/93	Tillering		
			1.4	46	6/15/93	Pre-harvest	73	7
							52	14
AA930204.CA2	Yecora Rojo	4/8/93	1.4	46	5/18/93	Tillering		
			1.4	48	7/19/93	Pre-harvest	76	7
							65	14
AA930204.GA	Coker 9766	11/18/92	1.4	47	2/23/93	Tillering		
			1.4	47	5/14/93	Pre-harvest	22 20	7
							17	14
AA930204.KS	TAM 107	9/10/92	1.4	47	4/16/93	Tillering		
			1.4	47	6/25/93	Pre-harvest	26	7
							17	14
AA930204.MN	Hard Red Spring	5/13/93	1.4	47	6/19/93	Tillering		
			1.5	48	8/19/93	Pre-harvest	66	7

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
							16	14
AA930204.ND	Hard Red Spring	4/26/93	1.3	43	5/26/93	Tillering		
			1.4	48	8/13/93	Pre-harvest	17	7
							17	14
AA930204.OK	McNair	10/1/92	1.4	53	3/16/93	Tillering		
			1.5	57	5/28/93	Pre-harvest	23	7
							14	14
AA930204.WA	Stephens	10/11/92	1.5	50	4/27/93	Tillering		
			1.4	47	7/26/93	Pre-harvest	19	7
							8	14
Acid (Carringer, 1995t)								
AA930205.KS	TAM 107	9/10/92	1.5	50	4/16/93	Tillering		
			1.5	49	6/25/93	Pre-harvest	7	7
AA930205.ND	Grandin	4/26/93	1.4	45	5/26/93	Tillering		
			1.4	48	8/11/93	Pre-harvest	6	7
							5	14
DMA (Carringer, 1995a)								
AA930207.CA1	Yecora Rojo	2/12/93	1.4	47	4/14/93	Tillering		
			1.4	46	6/23/93	Pre-harvest	80	7
							65	14
AA930207.CA2	Yecora Rojo	4/8/93	1.4	46	5/19/93	Tillering		
			1.4	48	7/21/93	Pre-harvest	94	7
							102	14
AA930207.GA	Coker 9766	11/18/92	1.4	47	2/23/93	Tillering		
			1.4	47	5/14/93	Pre-harvest	53	7
							5	14
AA930207.KS	TAM 107	9/10/92	1.4	55	4/16/93	Tillering		
			1.7	48	6/25/93	Pre-harvest	8	7
AA930207.MN	Butte 86	5/13/93	1.4	47	6/29/93	Tillering		
			1.4	48	8/19/93	Pre-harvest	77	7
							34	14
AA930207.ND	Grandin	4/26/93	1.4	47	5/26/93	Tillering		
			1.4	53	8/13/93	Pre-harvest	30	7
							21	14
AA930207.OK	McNair 1003	10/1/92	1.4	53	3/16/93	Tillering		
			1.4	56	5/28/93	Pre-harvest	11	7
							12	14
AA930207.WA	Stephens	10/10/92	1.4	48	4/27/93	Tillering		
			1.4	49	7/26/93	Pre-harvest	60, 63	7
							33	14
DMA (Carringer, 1995z)								
AA940502.CA1	Yecora Rojo	4/15/94	1.5	51	5/20/94	Tillering	8	53
			1.4	47	5/20/94	Tillering		
			0.82	46	7/5/94	Pre-harvest	17	7
							12	15
			1.4	46	5/20/94	Tillering		
			0.54	45	7/5/94	Pre-harvest	14	7
							15	15
AA940502.CA2	Yecora Rojo	4/15/94	1.5	42	5/25/94	Tillering	8	45

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
			1.5	49	5/25/94	Tillering		
			0.87	49	7/2/94	Pre-harvest	36	7
							51	13
			1.3	49	5/25/94	Tillering		
			0.55	46	7/2/94	Pre-harvest	6	7
							41	13
AA940502.GA	Andy	12/20/93	1.4	47	4/7/94	Tillering	51	46
			1.4	47	4/7/94	Tillering		
			0.84	47	5/16/94	Pre-harvest	84	7
							91	14
			1.4	47	4/7/94	Tillering		
			0.56	47	5/16/94	Pre-harvest	82	7
							85	14
AA940502.KS	Karl	10/6/93	1.4	45	4/7/94	Tillering	1	69
			1.4	45	4/7/94	Tillering		
			0.87	48	6/8/94	Pre-harvest	32	7
							27	14
			1.4	45	4/7/94	Tillering		
			0.57	48	6/8/94	Pre-harvest	32	7
							15	14
AA940502.MN	Stoa	5/9/94	1.4	47	6/11/94	Tillering	0.2	73
			1.4	45	6/11/94	Tillering		
			0.85	48	8/16/94	Pre-harvest	5	7
							11	14
			1.4	48	6/11/94	Tillering		
			0.57	48	8/16/94	Pre-harvest	5	7
							5	14
AA940502.ND	Grandin	5/11/94	1.4	48	6/4/94	Tillering	0.01	82
			1.4	48	6/4/94	Tillering		
			0.84	47	8/18/94	Pre-harvest	8	7
							4	14
			1.4	48	6/4/94	Tillering		
			0.56	47	8/18/94	Pre-harvest	4	7
							4	14
AA940502.OK	McNair	11/01/93	1.4	46	4/6/94	Tillering	0.32	72
			1.4	45	4/6/94	Tillering		
			0.84	50	6/10/94	Pre-harvest	23	7
			1.4	44	4/6/94	Tillering		
			0.55	49	6/10/94	Pre-harvest	14	7
AA940502.WA	MAC-1	10/18/93	1.4	47	4/18/94	Tillering	0.02	106
			1.4	48	4/18/94	Tillering		
			0.86	48	7/25/94	Pre-harvest	8	7
							7	14
			1.4	47	4/18/94	Tillering		
			0.56	46	7/25/94	Pre-harvest	11	7
							6	14
EHE (Carringer, 1995y)								
AA940501.CA1	Yecora Rojo	4/15/94	1.4	45	5/21/94	Tillering	21	52
			1.4	45	5/21/94	Tillering		

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
			0.83	46	7/5/94	Pre-harvest	32	7
							25	15
			1.4	46	5/21/94	Tillering		
			0.56	47	7/5/94	Pre-harvest	15	7
							15	15
AA940501.CA2	Yecora Rojo	4/15/94	1.4	46	5/26/94	Tillering	21	44
			1.4	46	5/26/94	Tillering		
			0.83	46	7/2/94	Pre-harvest	19	7
							22	13
			1.4	47	5/26/94	Tillering		
			0.54	45	7/2/94	Pre-harvest	18	7
							18	13
AA940501.GA	Andy	12/20/93	1.4	47	4/7/94	Tillering	24	46
			1.4	47	4/7/94	Tillering		
			0.84	47	5/16/94	Pre-harvest	30	7
							25	14
			1.4	47	4/7/94	Tillering		
			0.56	47	5/16/94	Pre-harvest	26	7
							22	14
AA940501.KS	Karl	10/6/93	1.4	45	4/7/94	Tillering	1	69
			1.4	45	4/7/94	Tillering		
			0.83	45	6/8/94	Pre-harvest	18	7
							12	14
			1.4	45	4/7/94	Tillering		
			0.57	48	6/8/94	Pre-harvest	11	7
							8	14
AA940501.MN	Stoa	5/9/94	1.5	50	6/11/94	Tillering	0.28	94
			1.4	46	6/11/94	Tillering		
			0.85	47	9/6/94	Pre-harvest	15	9
							14	16
			1.4	48	6/11/94	Tillering		
			0.57	48	9/6/94	Pre-harvest	6	8
							8	14
AA940501.ND	Grandin	5/11/94	1.4	48	6/4/94	Tillering	<0.01	82
			1.4	48	6/4/94	Tillering		
			0.84	47	8/18/94	Pre-harvest	6	7
							7	14
			1.4	48	6/4/94	Tillering		
			0.56	47	8/18/94	Pre-harvest	3	7
							4	14
AA940501.OK	McNair	~11/10/93	1.4	46	4/6/94	Tillering	0.27	72
			1.4	46	4/6/94	Tillering		
			0.85	50	6/10/94	Pre-harvest	14	7
			1.4	46	4/6/94	Tillering		
			0.56	49	6/10/94	Pre-harvest	9	7
AA940501.WA	Stephens	10/6/93	1.4	49	4/18/94	Tillering	0.35	105
			1.4	49	4/18/94	Tillering		
			0.85	47	7/25/94	Tillering	8	7
							6	14

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
			1.4	45	4/18/94	Tillering		
			0.57	47	7/25/94	Pre-harvest	7	7
							2	14
EHE (Carringer, 1996a)								
AA960501.CO	TAM 107	~9/15/95	1.4	51	4/10/96	Tillering	0.07, 0.11	98
			1.4	51	4/10/96	Tillering		
			0.58	47	7/10/96	Pre-harvest	13	7
			1.4	51	4/10/96	Tillering		
			0.58	48	7/3/96	Pre-harvest	4	14
AA960501.GA	Coker 9835	12/5/95	1.4	47	3/13/96	Tillering	0.28, 0.46	75
			1.4	49	3/13/96	Tillering		
			0.57	47	5/20/96	Pre-harvest	10, 13	7
			1.4	49	3/13/96	Tillering		
			0.57	47	5/13/96	Pre-harvest	11	14
AA960501.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	47	6/26/96	Tillering	<0.01	69
			1.4	46	6/26/96	Tillering		
			0.56	48	8/20/96	Pre-harvest	7, 3	7
			1.4	46	6/26/96	Tillering		
			0.56	46	8/13/96	Pre-harvest	3	14
AA960501.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	48	6/21/96	Tillering	0.01	68
			1.5	47	6/21/96	Tillering		
			0.57	48	8/21/96	Pre-harvest	11, 14	7
			1.4	47	6/21/96	Tillering		
			0.56	47	8/14/96	Pre-harvest	6, 7	14
AA960501.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	Tillering	0.04	84
			1.4	50	3/13/96	Tillering		
			0.56	50	5/25/96	Pre-harvest	5	11
			1.4	50	3/13/96	Tillering		
			0.57	50	5/21/96	Pre-harvest	5	15
AA960501.WA	Madsen	11/6/95	1.4	47	4/25/96	Tillering	0.05	105
			1.4	47	4/25/96	Tillering		
			0.55	48	8/1/96	Pre-harvest	2, 6	7
			1.4	47	4/25/96	Tillering		
			0.57	47	7/25/96	Pre-harvest	17 (2)	14
DMA (Carringer, 1996b)								
AA960502.CO	TAM 107	9/15/95	1.4	51	4/10/96	Tillering	0.1, 3	98
			1.3	51	4/10/96	Tillering		
			0.58	47	7/10/96	Pre-harvest	14, 23	7
			1.3	51	4/13/96	Tillering		
			0.58	48	7/3/96	Pre-harvest	3, 4	14
AA960502.GA	Coker 9835	12/5/95	1.4	49	3/13/96	Tillering	0.52, 0.58	75
			1.4	49	3/13/96	Tillering		
			0.57	47	5/20/96	Pre-harvest	15, 21	7

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
			1.4	49	3/13/96	Tillering		
			0.57	46	5/13/96	Pre-harvest	11, 15	14
AA960502.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	46	6/26/96	Tillering	<0.01, 0.01	69
			1.4	46	6/26/96	Tillering		
			0.56	48	8/27/96	Pre-harvest	10, 15	7
			1.4	47	6/26/96	Tillering		
			0.54	46	8/20/96	Pre-harvest	3, 4	14
AA960502.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	46	6/20/96	Tillering	<0.01	69
			1.4	47	6/20/96	Tillering		
			0.56	46	8/21/96	Pre-harvest	21, 23	7
			1.4	47	6/20/96			
			0.56	47	8/14/06	Pre-harvest	5, 6	14
AA960502.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	Tillering	0.05	84
			1.4	50	3/13/96	Tillering		
			0.57	50	5/20/96	Pre-harvest	2	7
			1.4	50	3/13/96	Tillering		
			0.57	50	5/21/96	Pre-harvest	5, 7	14
AA960502.WA	Madsen	11/6/95	1.4	47	4/25/96	Tillering	<0.01	105
			1.4	47	4/25/96	Tillering		
			0.56	48	8/1/96	Pre-harvest	2	7
			1.4	47	4/25/96	Tillering		
			0.56	47	7/25/96	Pre-harvest	6, 7	14

Use as herbicide on grasses for sugar or syrup production

Residues of 2,4-D in sugar cane are shown in Tables 47 (forage) and 48 (cane).

Sugar cane. Critical GAP (USA): 2 x 2.2 kg ae/ha, PHI not defined. Two trials each were conducted in Florida, Hawaii and Louisiana with the DMA salt and two additional trials in Florida and Louisiana with the acid. In all the trials the applications were broadcast with ground equipment at 2.2-2.6 kg ae/ha, pre-emergence and post-emergence 106-175 days later, at a total seasonal rate of 4.4-4.8 kg ae/ha (Carringer, 1995r,s).

Forage samples were collected 88-92 days after the second application and cane samples at maturity after 137-214 days. The LOD for cane and forage was 0.01 mg/kg. Residues of 2,4-D were undetectable (<0.01 mg/kg) in seven forage controls and eight cane controls; one forage control showed residues of 0.12 mg/kg. Residues in treated forage and cane samples were not corrected against the controls.

Table 47. Residues of 2,4-D in sugar cane forage.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
DMA (Carringer, 1995s)								
AA930201.FL1	CP-78-2114	12/4/92	2.3	91	12/9/93	Pre-emergence		

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
			2.4	102	6/3/93	Post-emergence	0.03	90
AA930201.FL2	CP-70-1133	2/6/93	2.2 2.3	94 100	2/4/93 7/2/93	Pre-emergence Post-emergence	 0.08	 90
AA930201.HI1	73-6110	3/25/93-4/25/93	2.2 2.6	93 108	4/22/93 9/13/93	Pre-emergence Post-emergence	 0.04	 88
AA930201.HI2	73-6110	4/8/93-4/16/93	2.2 2.3	93 96	4/22/93 2/24/93	Pre-emergence Post-emergence	 0.14	 88
AA930201.LA1	321	9/30/92	2.3 2.2	94 93	2/24/93 6/10/93	Pre-emergence Post-emergence	 <0.01	 92
AA930201.LA2	321	9/10/92	2.2 2.2	93 92	2/24/93 6/10/93	Pre-emergence Post-emergence	 0.01	 92
Acid (Carringer, 1995r)								
AA930202.FL	CP70-1133	2/6/93	2.3 2.2	93 93	2/10/93 7/2/93	Pre-emergence Post-emergence (Control)	 <0.01 0.12	 90 90
AA930202.LA	321	9/30/92	2.2 2.2	93 93	2/24/93 6/25/93	Pre-emergence Post-emergence	 <0.01	 92

Table 48. Residues of 2,4-D in mature cane.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
DMA (Carringer, 1995s)								
AA930201.FL1	CP-78-2114	12/4/92	2.3 2.4	91 102	12/9/92 6/3/93	Pre-emergence Post-emergence	 <0.01	 188
AA930201.FL2	CP-70-1133	2/6/93	2.2 2.3	94 100	2/4/93 7/2/93	Pre-emergence Post-emergence	 <0.01	 140
AA930201.HI1	73-6110	3/25/93-4/25/93	2.2 2.6	93 108	4/22/93 9/13/93	Pre-emergence Post-emergence	 <0.01	 214
AA930201.HI2	73-6110	4/8/93-4/16/93	2.2	93	4/22/93	Pre-emergence		
			2.3	96	2/24/93	Post-emergence	<0.01	214
AA930201.LA1	321	9/30/92	2.3 2.2	94 93	2/24/93 6/10/93	Pre-emergence Post-emergence	 <0.01	 151
AA930201.LA2	321	9/10/92	2.2 2.2	93 92	2/24/93 6/10/93	Pre-emergence Post-emergence	 <0.01	 151
DMA (Carringer, 1995s)								
AA930202.FL	CP70-1133	2/6/93	2.3 2.2	93 93	2/10/93 7/2/93	Pre-emergence Post-emergence	 0.02	 140
AA930202.LA	321	9/30/92	2.2 2.2	93 93	2/24/93 6/25/93	Pre-emergence Post-emergence	 <0.01	 137

Use as herbicide on nut trees

2,4-D is directed to the ground around trees. Residue trials were carried out on almonds, hazelnuts, pecans and pistachio nuts (Table 49).

Critical GAP for tree nuts (USA): 2 x 1.6 kg ae/ha, PHI 60 days (pistachio nuts 50 days). In hazelnuts, 4 x 0.12 kg ae/hl are used as spray to wet leaves and stems of suckers that are 15 to 20 cm in height (PHI 45 days).

Almonds. The LOD for 2,4-D residues in almonds is 0.05 mg/kg. No 2,4-D was detectable in the almond kernels except in one of the five trials in which a mechanical rake was used to gather the nuts from the orchard floor. Residues of 2,4-D in these samples ranged from <0.05 to 0.16 mg/kg (Kunkel, 1997a).

Hazelnuts. Three trials were conducted in Oregon to determine the residues of 2,4-D in hazelnuts harvested 49 days after four directed applications of 2,4-D. Each trial involved a control and side-by-side treatments of 2,4-D formulated as the DMA salt and the EHE to suckers at a rate of 0.11 kg ae/hl at retreatment intervals of 28-31 days. Solutions were applied until run-off and included a sticker/spreader (Kunkel, 1996a).

Nut samples were stored at 4°C for 4-9 days before oven drying at 40-65°C for 18 hours as in commercial practice, then hulled and shelled. The residues of 2,4-D were below the LOD (<0.05 mg/kg) in four control samples; two control samples contained 0.06 and 0.07 mg/kg. The residues in 12 treated samples were <0.05-0.1 mg/kg.

Pecans. In five trials in four states side-by-side treatments with the DMA salt and EHE were applied twice at intervals of 27-34 days (Kunkel, 1996c).

Samples were collected after about 60 days and shelled immediately. The residues were below the LOD (<0.05 mg/kg) in all samples.

Pistachio nuts. In two trials in California, the DMA salt was applied twice as a directed application at 1.6 kg ae/ha, using ground equipment, at a 22-day interval (Barney, 1995e).

Treated and control nut samples were collected 50 days after the second application and shelled. The residues of 2,4-D were below the LOD (<0.05 mg/kg) in all the samples.

Table 49. Residues in almonds, hazelnuts, pecans and pistachio nuts treated with 2,4-D.

Crop/ Reference Report no. Location	Variety	Application rate[1]	Application water l/ha	Date	Sample	Residues, mg/kg	PHI, days
Almonds (Kunkel, 1997a)							
4306.96-CA16	Nonpareil	1.6 + 1.6 DMA	51	5/21/96 + 6/20/96	Kernels	<0.05 (2)	57
		EHE			Kernels	<0.05 (2)	57
		DMA			Hulls	<0.05 (2)	57
		EHE			Hulls	<0.05 (2)	57
4306.96-CA17	Carmel	1.6 + 1.6 DMA	51	5/21/96 + 6/20/96	Kernels	<0.05 (2)	57
		EHE			Kernels	<0.05 (2)	57
		DMA			Hulls	<0.05 (2)	57
		EHE			Hulls	<0.05 (2)	57
4306.96-CA18	Carmel	1.6 + 1.6 DMA	51	5/21/96 + 6/20/96	Kernels	<0.05 (2)	57
		EHE			Kernels	<0.05 (2)	57
		DMA			Hulls	<0.05 (2)	57
		EHE			Hulls	<0.05 (2)	57
4306.96-CA19	Nonpareil	1.8 + 1.6 DMA	61	5/14/96 + 6/7/96	Kernels	0.11, 0.16	57
		EHE			Kernels	<0.05, 0.08	57
		1.8 + 1.6 DMA	61	5/14/96 + 6/7/96	Hulls	0.05, 0.1	57
		EHE			Hulls	<0.05, 0.07	57
4306.96-CA20	Nonpareil	1.8 + 1.6 DMA	61	5/14/96 + 6/7/96	Kernels	<0.05 (2)	57
		EHE			Kernels	<0.05 (2)	57
		1.8 + 1.6 DMA	61	5/14/96 + 6/7/96	Hulls	<0.05 (2)	57
		EHE			Hulls	<0.05 (2)	57
Hazelnuts (Kunkel, 1996a)							
6106.95-OR16	Barcelona	0.11 kg ea/hl DMA		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels	<0.05, 0.1	49
		0.11 kg ea/hl EHE		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels	<0.05 (2)	49
6106.95-OR17	Barcelona	0.11 kg ea/hl DMA		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels Control	<0.05 (2) 0.07	49
		0.11 kg ea/hl EHE		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels	<0.05, 0.05	49
6106.95-OR18	Barcelona	0.11 kg ea/hl DMA		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels	<0.05 (2)	49
		0.11 kg ea/hl EHE		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels Control	<0.05 (2) 0.06	49
Pecans (Kunkel, 1996c)							
6125.95-NC11	Unknown	1.6 + 1.6 amine	31	9/12/95 + 10/10/95	Kernels	<0.05 (2)	52

Crop/ Reference Report no. Location	Variety	Application		Date	Sample	Residues, mg/kg	PHI, days
		rate[1]	water l/ha				
		1.6 + 1.6 ester	31	9/12/95 + 10/10/95	Kernels	<0.05 (2)	52
6125.95-NC12	Unknown	1.6 + 1.6 amine	31	9/15/95 + 10/12/95	Kernels	<0.05 (2)	56
		1.6 + 1.6 ester	31	9/15/95 + 10/12/95	Kernels	<0.05 (2)	56
6125.95-NM03	Western Scitley	1.6 + 1.6 amine	23	9/1/95 + 9/29/95	Kernels	<0.05 (2)	59
		1.6 + 1.6 ester	23	9/1/95 + 9/29/95	Kernels	<0.05 (2)	59
6125.95-AR04	Moore	1.6 + 1.6 amine	12	8/10/95 + 9/7/95	Kernels	<0.05 (2)	65
		1.6 + 1.6 ester	12	8/10/95 + 9/7/95	Kernels	<0.05 (2)	65
6125.95-TX32	55-17-3 and Cheyenne	1.6 + 1.6 amine	46	7/13/95 + 8/16/95	Kernels	<0.05 (2)	61
		1.6 + 1.6 ester	46	7/13/95 + 8/16/95	Kernels	<0.05 (2)	61
Pistachio (Barney, 1995e)							
4301.94-CA99	Kerman	1.6 + 1.6	49	7/12/94 + 8/3/94	Kernels	<0.05 (2)	50
4301.94-CA08	Kerman	1.6 + 1.6	57	7/12/94 + 8/3/94	Kernels	<0.05 (2)	50

[1] kg ae/ha unless otherwise stated

Use as herbicide on soya beans

2,4-D is applied in the field not less than 7 days (esters) or 15 days (other formulations) before planting. The results are summarized in Tables 50-52. Critical GAP (USA): 1 x 0.56 (esters) or 1 x 1.1 (others) kg ae/ha.

In trials in five US states single applications of the EHE were made 7-9 days before planting at 0.56-0.57, 1.4-1.5 and 3-3.2 kg ae/ha. In two of the states the DMA and the free acid were also applied at the same rates (Carringer, 1994a-d).

Fresh forage and hay samples were collected 67 to 85 days after treatment. Hay samples were air-dried for 1.5 to 7 days after cutting. Seed samples were collected at maturity 124-157 days after treatment.

The LOD for all analyses was 0.01 mg/kg.

Table 50. Residues of 2,4-D in soya bean forage from pre-plant applications.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
DMA (Carringer, 1994d)							
AA930225.IL	Kennedy IV	6/10/93	0.56	140	5/25/93	<0.01	76
			1.4	143	5/25/93	<0.01	76
			3.1	149	5/25/93	<0.01	76
AA930225.LA	Hartz 6200	6/8/93	0.56	95	5/24/93	<0.01	85
			1.4	97	5/24/93	<0.01	85
			3.1	93	5/24/93	<0.01	85

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
EHE (Carringer, 1994b)							
AA930226.AR	Tracy M	7/9/93	0.57	94	7/2/93	<0.01	73
			1.4	94	7/2/93	<0.01	73
			3.1	93	7/2/93	<0.01	73
AA930226.IL	Kennedy IV	6/10/93	0.57	96	6/3/93	<0.01	67
			1.4	93	6/3/93	<0.01	67
			3.1	96	6/3/93	<0.01	67
AA930226.LA	Hartz 6200	5/31/93	0.56	93	5/24/93	<0.01	74
			1.4	94	5/24/93	<0.01	74
			3.1	94	5/24/93	<0.01	74
AA930226.MO	Avery	7/2/93	0.56	94	6/23/93	<0.01	69
			1.4	94	6/23/93	<0.01	69
			3.1	94	6/23/93	<0.01	69
AA930226.TN	Avery	6/29/93	0.57	95	6/22/93	<0.01	70
			1.5	99	6/22/93	<0.01	70
			3.2	99	6/22/93	<0.01	70
Acid (Carringer, 1994c)							
AA930227.IL	Kennedy IV	6/10/93	0.57	95	6/3/93	<0.01	67
			1.4	94	6/3/93	<0.01	67
			3	90	6/3/93	<0.01	67
AA930227.LA	Hartz 6200	5/31/93	0.56	94	5/24/93	<0.01	74
			1.4	93	5/24/93	<0.01	74
			3.1	94	5/24/93	<0.01	74

Table 51. Residues of 2,4-D in soya bean hay from pre-plant applications.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
DMA (Carringer, 1994d)							
AA930225.IL	Kennedy IV	6/10/93	0.56	140	5/25/93	<0.01	76
			1.4	143	5/25/93	<0.01	76
			3.1	149	5/25/93	<0.01	76
AA930225.LA	Hartz 6200	6/8/93	0.56	95	5/24/93	<0.01	85
			1.4	97	5/24/93	<0.01	85
			3.1	93	5/24/93	<0.01	85
EHE (Carringer, 1994b)							
AA930226.AR	Tracy M	7/9/93	0.57	94	7/2/93	<0.01	74
			1.4	94	7/2/93	0.01	74
			3.1	93	7/2/93	0.01	74
AA930226.IL	Kennedy IV	6/10/93	0.57	96	6/3/93	<0.01	69
			1.4	93	6/3/93	0.04	69
			3.2	96	6/3/93	<0.01	69
AA930226.LA	Hartz 6200	5/31/93	0.56	93	5/24/93	<0.01	81
			1.4	94	5/24/93	<0.01	81
			3.1	94	5/24/93	<0.01	81
AA930226.MO	Avery	7/2/93	0.56	94	6/23/93	<0.01, (0.77,1.1)[1]	71
			1.4	94	6/23/93	<0.01	69

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
			3.1	94	6/23/93	<0.01, (0.25, 0.26)[1]	71
AA930226.TN	Avery	6/29/93	0.57	95	6/22/93	<0.01	72
			1.5	99	6/22/93	<0.01	72
			3.3	99	6/22/93	0.02	72
Acid (Carringer, 1994c)							
AA930227.IL	Kennedy IV	6/10/93	0.57	95	6/3/93	<0.01	69
			1.4	94	6/3/93	<0.01	69
			3	90	6/3/93	<0.01	69
AA930227.LA	Hartz 6200	5/31/93	0.56	94	5/24/93	<0.01	81
			1.4	93	5/24/93	<0.01	81
			3.1	94	5/24/93	<0.01	81

[1] Contaminated sample, analysed twice. Analysis of a further sample showed residues <0.01 mg/kg.

Table 52. Residues of 2,4-D in soya bean seed from pre-plant applications.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
DMA (Carringer, 1994d)							
AA930225.IL	Kennedy IV	6/10/93	0.56	140	5/25/93	<0.01	149
			1.4	143	5/25/93	<0.01	149
			3.1	149	5/25/93	<0.01	149
AA930225.LA	Hartz 6200	6/8/93	0.56	95	5/24/93	<0.01	157
			1.4	97	5/24/93	<0.01	157
			3.1	93	5/24/93	<0.01	157
EHE (Carringer, 1994b)							
AA930226.AR	Tracy M	7/9/93	0.57	94	7/2/93	<0.01	129
			1.4	94	7/2/93	<0.01	129
			3.1	93	7/2/93	<0.01	129
AA930226.IL	Kennedy IV	6/10/93	0.57	96	6/3/93	<0.01	140
			1.4	93	6/3/93	<0.01	140
			3.2	96	6/3/93	<0.01	140
AA930226.LA	Hartz 6200	5/31/93	0.56	93	5/24/93	<0.01	144
			1.4	94	5/24/93	<0.01	144
			3.1	94	5/24/93	<0.01	144
AA930226.MO	Avery	7/2/93	0.56	94	6/23/93	<0.01	124
			1.4	94	6/23/93	<0.01	124
			3.1	94	6/23/93	<0.01	124
AA930226.TN	Avery	6/29/93	0.57	95	6/22/93	<0.01	129
			1.5	99	6/22/93	<0.01	129
			3.3	99	6/22/93	<0.01	129
Acid (Carringer, 1994c)							
AA930227.IL	Kennedy IV	6/10/93	0.57	95	6/3/93	<0.01	140
			1.4	94	6/3/93	<0.01	140
			3	90	6/3/93	<0.01	140
AA930227.LA	Hartz 6200	5/31/93	0.56	94	5/24/93	<0.01	144
			1.4	93	5/24/93	<0.01	144

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
			3.1	94	5/24/93	<0.01	144

Use as herbicide on animal feed commodities

2,4-D is used world-wide to control broad-leaved weeds in grass and pastures.

Grass and hay. Critical GAP (USA): 2 x 2.2 kg ae/ha, PHI not defined. 32 trials were conducted in 16 US states. Two post-emergence broadcast applications of the free acid, the DMA salt or the EHE were made with ground equipment at intervals of 29-33 days at about 2.2 kg ae/ha, giving a total of 4.3-4.7 kg ae/ha. Cut hay was dried for periods ranging from 10 hours to 7 days before sampling (Carringer, 1995j,k,o,u,v,w,x; Rosemond, 1995a,b,c).

The LOD for all analyses was 1 mg/kg. Residues of 2,4-D were undetectable (<1 mg/kg) in 69 forage and 70 hay controls. One forage control showed residues of 1.1 mg/kg.

Table 53. Residues of 2,4-D in rangeland and pasture grass (forage and hay). Growth stage at first treatment 20-25 cm in all trials.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg		PHI, days
			kg ae/ha	water l/ha		Hay	Forage	
DMA (Carringer, 1995k)								
AA930216.AR	Common Bermuda grass	~ 25 years	2.2	47	7/29/93			
			2.2	45	8/22/93	501 109	173 87	0 7
AA930216.KS	Tall grass prairie		2.3	49	5/25/93			
			2.3	48	6/25/93	402 155	169 117	0 7
AA930216.MO	Fescue	~1970	2.3	48	6/16/93			
			2.2	47	7/16/93	378 236	172 122	0 7
AA930216.NY	Pasture grasses	4 years old	2.3	48	5/6/93			
			2.3	49	6/6/93	111 149	92 61	0 7
AA930216.OK	Bermuda grass	5 years old	2.3	49	6/3/93			
			2.3	51	7/5/93	388 94	236 46	0 8
AA930216.PA	Kentucky bluegrass	10/8/91	2.2	50	5/17/93			
			2.3	50	6/17/93	451 145	233 41	0 7
AA930216.TN	Fescue	~1973	2.3	47	6/1/93			
			2.3	48	7/1/93	719 279	198 107	0 7
EHE (Rosemond, 1995b)								
AA930217.KS	Mixed grass	Unknown	2.3	48	5/25/93			
			2.2	46	6/25/93	142 330	223 103	0 7
AA930217.KY	Fescue/bluegrass	1978	2.3	48	6/16/93			

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg		PHI, days
			kg ae/ha	water l/ha		Hay	Forage	
			2.3	48	7/16/93	575 216	90 103	0 7
AA930217.OK	Unknown	5 years old	2.3	50	6/3/93			
			2.3	51	7/5/93	526 126	311 41	0 7
AA930217.PA	Kentucky bluegrass	10/8/91	2.2	49	5/17/93			
			2.3	50	6/17/93	457 182	358 125	0 7
AA930217.TX	Native	Native	2.3	54	1/1/00			
			2.2	46	6/27/93	477 147	192 82	0 7
AA930217.VA	Tall Fescue - Kentucky 31	~ 20 years	2.1	50	5/12/93			
			2.3	50	6/11/93	365 231	183 120	0 7
Acid (Carringer, 1995j)								
AA930218.KS	Native grass	Native	2.3	49	5/25/93			
			2.3	49	6/25/93	478 218	135 93	0 7
AA930218.PA	Tall Fescue	10/8/91	2.2	49	5/17/93			
			2.3	51	6/17/93	572 74	153 39	0 7
DMA (Rosemond, 1995c)								
AA930219.KS	Mixed grass	April 1989	2.2	47	5/15/93			
			2.5	52	6/14/93	183 61	241 23	0 7
AA930219.ND	Mixed grass	May 1957	2.3	47	5/18/93			
			2.3	46	6/17/93	402 39	314 34	0 7
AA930219.OK	Rangeland grass	> 10 years	2.3	49	5/15/93			
			2.3	50	6/15/93	229 101	280 49	0 7
AA930219.WY	Rangeland grass	Native	2.1	50	5/12/93			
			2.2	48	6/11/93	161 19	194 20	0 7
EHE (Rosemond, 1995a)								
AA930220.KS	Mixed grass	April 1989	2.4	49	5/15/93			
			2.2	47	6/14/93	114 68	177 45	0 7
AA930220.MT	Native	Native	2.2	47	5/17/93			
			2.2	49	6/19/93	244 180	285 170	0 7
AA930220.NE	Tall Fescue - Kentucky 31		2.2	48	4/17/93			
			2.2	48	5/17/93	275 65	154 20	0 7
AA930220.OK	Native Range	> 10 years	2.2	49	5/15/93			
			2.2	49	6/15/93	153 86	258 74	0 7
AA930220.SD	Western wheat grass	1987	2.2	49	5/12/93			
			2.2	44	6/11/93	239	182	0

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg		PHI, days
			kg ae/ha	water l/ha		Hay	Forage	
						96	32	7
Acid (Carringer, 1995o)								
AA930221.KS	Mixed Perennial	April 1989	2.2	47	5/15/93			
			2.3	48	6/14/93	170 40	162 19	0 7
AA930221.OK	Native stand	> 10 years	2.4	50	5/15/93			
			2.3	49	6/15/93	176 68	271 41	0 7
EHE (Carringer, 1995u)								
AA940503.MI	Perennial Ryegrass	5/93	2.3	48	6/16/94			
			2.3	46	7/15/94	103 65 47	155 116 74	14 21 30
AA940503.MO	Timothy	5 years	2.2	47	6/27/94			
			2.2	47	7/27/94	142 96 61	87 85 45	14 21 30
EHE (Carringer, 1995w)								
AA940505.OK	Native Rangelands	~ 10 years	2.3	53	6/8/94			
			2.2	47	7/8/94	115 124 150	62 71 44	14 21 30
DMA (Carringer, 1995v)								
AA940504.MI	Perennial Ryegrass	8/91	2.3	48	6/16/94			
			2.3	47	7/15/94	50 45 50	53 25 34	14 21 30
AA940504.MO	Timothy	5 years	2.2	47	6/27/94			
			2.2	47	7/27/94	206 156 107	121 139 68	14 21 30
DMA (Carringer, 1995x)								
AA940506.OK	Native Rangelands	~ 10 years	2.3	53	6/8/94			
			2.2	47	7/8/94	43 82 68	36 46 42	14 21 30

Mammalian products

(Krautter and Downs, 1996). Groups of 3 Holstein dairy cows were dosed twice daily with gelatine capsules containing 2,4-D for 28 to 30 consecutive days at levels equivalent to 1446, 2890, 5779 and 8585 ppm in the diet (dry-weight basis) with a single control. These doses corresponded to mean rates of about 50.6, 100, 190 and 280 mg 2,4-D/kg body weight/day. The cows were slaughtered over a 3-day period, within 12-18 hours after their last doses.

Two further groups of 3 cows were treated at the high-dose level for 28 consecutive days and slaughtered 3 or 7 days after their last doses. The cows were milked twice daily in the mornings and evenings. Proportional daily composites were prepared for individual cows in the four dose groups from milk taken on dose days 0 (pre-dose), 1, 3, 7, 11, 14, 18, 21, 24 and 28. Samples from cows in the recovery groups were prepared from milk taken on days 0, 24 and 28, and 3 or 7 days after the last dose.

During necropsy, animals were examined for gross tissue abnormalities. Samples of liver, kidneys, composite muscle (round and tenderloin) and composite fat (perirenal and omental) were homogenized in a frozen state with dry ice and stored frozen until analysis.

Mean daily feed consumption and milk production levels during the acclimatization period were similar to those during treatment in all groups. Mean body weight changes during the treatment period were also comparable among the groups. Since there were no unusual or adverse treatment-related effects, it is concluded that the tissue and milk samples were appropriate for analysis.

Residue samples were analysed according to the methods described in Howard, 1996a. The LODs were 0.05 mg/kg for liver, kidney, muscle and fat, and 0.01 mg/kg for milk. The results are shown in Table 54.

Table 54. The mean and range of 2,4-D residues in milk and tissues from dosed cows (Krautter, 1996).

Dose, mg/kg bw	Residue, mg/kg, mean and (range)				
	Milk	Liver	Kidney	Muscle	Fat
0	<0.01	<0.05	<0.05	<0.05	<0.05
50	0.04 (0.02-0.07) [1]	0.12 (0.07-0.20)	3.8 (1.6-6.5)	0.21 (0.16-0.24)	0.42 (0.33-0.51)
100	0.12 (0.05-0.18) [2]	1.9 (1.2-2.4)	14 (8.8-18)	0.41 (0.28-0.51)	0.59 (0.45-0.75)
190	0.29 (0.08-0.59) [1]	3.0 (2.1-3.5)	17 (9.7-29)	0.76 (0.49-1.1)	2.5 (1.3-3.6)
280	0.47 (0.15-0.87) [1]	3.1 (2.3-3.8)	24 (24-24)	1.0 (0.98-1.0)	2.2 (2.0-2.3)
3-day recovery	0.01 (0.01-0.02) [3]	0.45 (0.12-0.67)	0.06 (<0.05-0.10)	0.06 (0.05-0.06)	0.07 (<0.05-0.12)
7-day recovery	0.01 (<0.01-0.02) [4]	0.39 (0.26-0.51)	<0.05	<0.05	<0.05

[1] Samples collected from day 7 to day 28
[2] Samples collected from day 1 to day 28
[3] Samples collected 3 days after the last dose
[4] Samples collected 7 days after the last dose

Fish and shellfish

(Biever, 1996). Channel catfish, bluegill sunfish, northern crayfish and freshwater clams were exposed to 6 mg 2,4-D ae/l as the DMA salt in static aquatic systems with a soil substrate for periods of 3 hours to 15 days. The edible tissues of the bluegills, crayfish and clams were collected after 3, 6 and 12 hours, and 1, 2, 8 and 15 days, and those of the channel catfish at the same intervals up to 8 days only, owing to mortality in both treated and control systems (cause unknown).

The results are shown in Table 55. The maximum mean 2,4-D concentration in the catfish edible tissue was 0.07 mg/kg, 6 hours after exposure and decreased to day 8. The maximum mean residue in bluegill sunfish edible tissue was 0.06 mg/kg after 6 hours, and decreased to near the LOD (0.01 mg/kg) on days 8 and 15. The maximum residue in crayfish edible tissue was 1.1 mg/kg after 8 days and did not decrease appreciably between days 8 and 15. The 2,4-D concentration in the edible tissue from the freshwater clams was not reported because the quality control sample recoveries run with the initial sample analyses were outside the recovery range of 70 to 120% and repeat analyses were impracticable because there was not sufficient tissue remaining in some samples to achieve an LOD of 0.01 mg/kg.

Table 55. 2,4-D residues in edible tissues of channel catfish, bluegill sunfish and crayfish (Biever, 1996).

Species	Residue, mg/kg							
	3 h	6 h	12 h	Day 1	Day 2	Day 8	Day 15	Control
Catfish	0.045 [1]	0.063 [1]	0.056 [1]	0.036	0.027	0.02	[2]	[2]
	0.039	0.07	0.049	0.058	0.051	[3]	[2]	[2]
Mean	0.04	0.07	0.05	0.05	0.04			
Bluegill	0.043 [1]	0.067 [1]	0.055 [1]	0.048	0.028	0.012	0.017	<0.01
	0.045	0.054	0.029	0.052	0.042	0.01	0.013	[4]
Mean	0.04	0.06	0.04	0.05	0.04	0.01	0.02	
Crayfish	0.12 [1]	0.072 [1]	0.23 [1]	0.47	0.35	1.1	1.00	<0.01
	0.061	0.06	0.077	[3]	[3]	[3]	[3]	[3]
Mean	0.09	0.07	0.15					

[1] The tissue sample was not composited before the initial analysis, the remaining tissue was composited before the second analysis
[2] No tissue was available for analysis owing to death of the catfish
[3] Analytical recoveries outside the 70% to 120% acceptance limits and results not reported
[4] No duplicate analysis of control tissue

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

(Johnson and Strickland, 1995a). In two trials in California on lemons treated pre- and post-harvest with 2,4-D IPE, lemon samples were stored at a commercial storage facility at 6-16°C for 28-112 days. The results are shown in Table 28.

In processing

Lemons (Johnson and Strickland, 1995b). Whole lemons from the above trials were processed into juice, wet and dry pulp, molasses, and oil using simulated commercial procedures. A single sample of each processed fraction was collected from each sample of whole fruit.

The LOD was 0.05 mg/kg for juice and wet pulp, 0.2 mg/kg for dry pulp and molasses and 0.5 mg/kg for oil. The residues of 2,4-D were below the LODs in two control samples of each processed fraction.

The processing study was adequate and indicates that residues of 2,4-D are concentrated in molasses and dry pulp, but not in juice, wet pulp or oil. The average concentration factors were 4.3 in molasses and 4.6 in dried pulp.

Table 56. Residues of 2,4-D in lemons and their processed commodities (Johnson and Strickland, 1995b).

Location	Storage, days	Residues, mg/kg/processing factor (PF)										
		RAC	Juice	PF	Wet pulp	PF	Dry pulp	PF	Molasses	PF	Oil	PF
Tulare County, CA	0	0.42	<0.05	(<0.12) [1]	0.42	1	1.8	4.3	1.9	4.5	<0.5	<1.2
	56	0.61	0.05	0.08	0.47	0.77	1.8	3	3	4.9	<0.5	<0.82
	112	0.41	0.05	0.12	0.5	1.2	3.2	7.8	2.1	5.1	<0.5	<1.2
Ventura County, CA	0	0.54	<0.05	(<0.09) [1]	0.37	0.69	2	3.7	1.6	3	<0.5	<0.93
	56	0.52	0.05	0.1	0.34	0.65	1.8	3.5	2.5	4.8	<0.5	<0.96
	112	0.5	0.05	0.1	0.49	0.98	2.8	5.6	1.8	3.6	<0.5	<1
Mean				0.1		0.88		4.7		4.3		<1
Median		0.51	0.05		0.45	0.875	1.9	4	2.0	4.7	<0.5	<1

[1] Not included in calculation of the mean

Maize (Carringer, 1995c). In two trials in Iowa and Nebraska, maize was treated three times with 2,4-D EHE as a pre-emergence application at 1.7 kg ae/ha, a post-emergence directed application at 0.83 kg ae/ha and a broadcast pre-harvest application 2.5 kg ae/ha, with ground equipment at intervals of 32- 49 days between the first and second applications and 88-111 days between the second and third applications. Grain samples were collected 7 and 14 days after the final (pre-harvest) application (Table 57).

Two treated and control samples of grain were collected from each trial at each PHI but only single samples collected at the 7-day PHI in Nebraska were processed, by simulated commercial procedures, into starch, grits, meal, flour, crude oil (wet and dry milling) and refined oil (wet and dry milling).

The LOD for all samples was 0.01 mg/kg. Residues of 2,4-D were undetectable in all the control samples.

Table 57. Residues of 2,4-D in commodities processed from maize grain (Carringer, 1995c).

Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
		kg ae/ha	water l/ha					
Quena 7670	5/18/93	1.7	47	5/21/93	Pre-emergence			
		0.83	48	6/22/93	10-16 in.			
		2.5	47	10/11/93	Pre-harvest	grain	0.03	7
Pioneer 3162	5/3/93	1.7	47	5/3/93	Pre-emergence			
		0.83	47	6/21/93	10-16 in.			

Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
		kg ae/ha	water l/ha					
		2.5	47	9/17/93	Pre-harvest	grain	0.06	7
						starch	<0.01	
						grits	0.04	
						meal	0.05	
						flour	0.05	
						crude oil - wet milling	<0.01	
						crude oil - dry milling	<0.01	
						refined oil - wet milling	<0.01	
						refined oil - dry milling	<0.01	
						Aspirated grain fractions	2.2	

Rice (Carringer, 1995n). In two trials in Arkansas and Louisiana, 2,4-D DMA was applied to rice at about 2.5 kg ae/ha (1.5 times the GAP rate) at late tillering using ground equipment (Table 58).

Two grain samples were collected 61-66 days after treatment from treated and control plots at each site and processed into hulls, bran and milled white rice by simulated commercial procedures. Only the processed samples from Arkansas were analysed. The residues of 2,4-D were below the LOD (<0.01 mg/kg) in all the control samples.

Table 58. Residues of 2,4-D in rice and its processed fractions (Carringer, 1995n).

Sample	Location	Application, kg ae/ha	Residues, mg/kg	Processing factor
Rice, husked	AR LA	2.4 2.5	0.03 0.02	
Hulls	AR	-	0.09	3
Bran	AR	-	0.01	0.33
Milled white rice	AR	-	<0.01	indeterminate

Sorghum (Carringer, 1995m). In trials in Kansas and Texas, two sorghum grain samples were collected 81-112 days after single applications of 2,4-D DMA at 1.7 kg ae/ha with ground equipment (Table 59).

Samples from Texas were processed by simulated commercial procedures into starch and flour. The residues of 2,4-D were undetectable (<0.01 mg/kg) in the grain from both trial sites and in processed commodities from the Texas trial.

Table 59. Residues of 2,4-D in sorghum and its processed fractions (Carringer, 1995 m).

Sample	Location	Application, kg ae/ha	Residues, mg/kg	Processing factor
Sorghum	KS TX	1.8 1.7	<0.01 <0.01	
Starch	TX	-	<0.01	indeterminate
Flour	TX	-	<0.01	indeterminate

Wheat (Carringer, 1995a). In two trials each in North Dakota and Kansas, two broadcast applications of 2,4-D EHE were made at either 1.4 or 2.1 kg ae/ha, totalling 1.4 or 2.1 times the seasonal GAP rate using ground equipment with an 82-day retreatment interval. Samples were collected after 7 and 14 days in North Dakota but only after 7 days in Kansas as the 14-day sample plots were inadvertently destroyed. The Kansas grain samples were not processed.

Two treated and control grain samples were collected at each PHI in North Dakota. The 7-day samples were processed by simulated commercial procedures into bran, low grade wheat flour, patent flour, middlings, shorts and aspirated grain fractions, and the 14-day samples into aspirated grain fractions. The LOD was 0.01 mg/kg for all samples except aspirated grain fractions which had an LOD of 0.1 mg/kg. One grain control had apparent residues of 2,4-D of 0.01 mg/kg. The results are shown in Table 60.

Table 60. Residues of 2,4-D in wheat and its processed fractions (Carringer, 1995aa).

Variety	Planting date	Application		Date	Growth Stage	Sample	Residue, mg/kg	PF[1]	PHI, days
		kg ae/ha	water l/ha						
TAM 107	9/10/92	1.4	45	4/16/93	Tillering				
		1.4	47	6/25/93	Pre-harvest	Grain	0.26		7
		2.2	48	4/16/93	Tillering				
		2.1	47	6/25/93	Pre-harvest	Grain	0.56		7
Grandin	4/26/93	1.4	48	5/26/93	Tillering				
		1.4	47	8/16/93	Pre-harvest	Grain	1.5		7
						Bran	5.7	3.8	
						Low grade flour	0.21	0.14	
						Patent flour	0.19	0.13	
						Middlings	0.63	0.42	
						Shorts	0.81	0.54	
						Dust	47	31	
		2.1	47	5/26/93	Tillering				
		2.1	47	8/16/93	Pre-harvest	Grain	2.4		7
						Bran	8.3	3.5	
						Low grade flour	0.23	0.096	
						Patent flour	0.16	0.067	
						Middlings	1.1	0.46	
						Shorts	3.7	1.5	
						Dust	80	33	
		1.4	48	5/26/93	Tillering				
		1.4	47	8/16/93	Pre-harvest	Grain	0.41		14
						Dust	3.8	9.3	
		2.1	47	5/26/93	Tillering				
		2.1	47	8/16/93	Pre-harvest	Grain	0.76		14
						Dust	10	13	

[1] Processing factor

Sugar cane (Carringer, 1995l). In two trials in Florida and Louisiana, 2,4-D DMA was applied to sugar cane at 4.5 kg ae/ha with ground equipment at pre-emergence and again 110-176 days later at layby, giving a total of 9 kg ae/ha/season (4 times the GAP rate).

Single samples of cane were collected 166 or 188 days after the second application and processed into bagasse, molasses (first and final strike) and sugar by simulated commercial procedures but only the samples from Florida were analysed. The residues of 2,4-D were below the

LOD (<0.01 mg/kg) in two control cane samples and in one control sample of each processed commodity. The residues were also <0.01 mg/kg in cane samples from Florida and Louisiana and in bagasse, molasses (first strike) and sugar. The residue was 0.01 mg/kg in one sample of molasses (final strike) but a duplicate re-analysis showed <0.01 ,g/kg. The results are shown in Table 61.

Table 61. Residues of 2,4-D in sugar cane and its processed fractions (Carringer, 1995l).

Sample	Location	Total application, kg ae/ha	Residues, mg/kg
Sugar cane	FL LA	9.1 9	<0.01 <0.01
Bagasse	FL	-	<0.01
Molasses (first strike)	FL	-	<0.01
Molasses (final strike)	FL	-	0.01 <0.01
Sugar	Fl	-	<0.01

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

In a review of the US Food and Drug Administration Pesticide Monitoring Database for Fiscal Years 1992, 1993, 1994 and 1995 the only reported residues were from four samples of lemons obtained in California in 1992. The residues were 0.05, 0.06, 0.06 and 0.11 mg/kg. Table 62 shows the results from the USDA Pesticide Data Program for 1992, 1993 and 1994.

Table 62. Summary of US monitoring data for 2,4-D residues in 1992-1995.

Crop Year	Samples analysed	Samples with residues	Residues <LOD	Number of samples in residue range, mg/kg										
				≤0.01	>0.01, ≤0.02	>0.02, ≤0.03	>0.03, ≤0.04	>0.04, ≤0.05	>0.05, ≤0.06	>0.06, ≤0.07	>0.06, ≤0.07	>0.08, ≤0.09	>0.09, ≤0.10	>0.10, ≤0.15
Apples														
1992	252	0												
1993	622	7	4	4	1			1					1	
1994	683	683	239	646	36		1							
Bananas														
1992	2	0												
1993	1	1	1	1										
1994	17	17	16	17										
Broccoli														
1994	29	29	16	29										
Carrots														
1994	13	13	12	13										
Celery														
1994	17	17	17	17										

Crop Year	Samples analysed	Samples with residues	Residues <LOD	Number of samples in residue range, mg/kg										
				≤0.01	>0.01, ≤0.02	>0.02, ≤0.03	>0.03, ≤0.04	>0.04, ≤0.05	>0.05, ≤0.06	>0.06, ≤0.07	>0.06, ≤0.07	>0.08, ≤0.09	>0.09, ≤0.10	>0.10, ≤0.15
Grapefruit														
1992	256	5	5	5										
1993	630	12	2	8	2	1	1							
Grapes														
1992	261	0												
1993	621	2		1			1							
1994	658	658	202	589	69									
Green beans														
1993	1	0												
1994	3	3	3	3										
Lettuce														
1994	30	30	20	23	7									
Oranges														
1992	266	2		2										
1993	634	23		19	2	1	1							
1994	682	682	227	636	46									
Peaches														
1993	132	4		4										
1994	396	396	168	369	27									
Potatoes														
1992	243	6				2		2	2					
1993	636	28	1	9		7	2	4	2	1	1	1	1	
1994	677	677	186	583	80	5	2	2	2			1	1	1
Sweet corn														
1994	459	459	99	389	70									
Sweet peas														
1994	431	431	139	395	35	1								

NATIONAL MAXIMUM RESIDUE LIMITS

The following is a list of the national MRLs obtained from the internet site in Canada (http://www.hc-sc.gc.ca/pmra/indimrle.html).

Country	Commodity	MRL, mg/kg
Australia	citrus	5
	sugar cane	5
	edible offal (mammalian)	2
	cereal grains	0.2
	meat (mammalian)	0.2
	potato	0.1
	eggs	0.05*
	milk	0.05*
	legume vegetables	0.05*
	lupin (dry)	0.05*
	oilseed	0.05*
	poultry	0.05*
	edible offal of poultry meat	0.05*
	pulses	0.05*
Austria	all foods of vegetable origin	0.1
Belgium	citrus fruit	2
	others	0.05*
Brazil	rice, oats, rye, corn, sorghum, wheat, barley (all unprocessed)	0.2
	citrus fruits	2
	meat, milk and milk products, eggs	0.05
	grasses	P 1000
	apples, pears, quince	P 5
	sugar cane	P 2
	flax	P 1
	coffee	0.1
	soya beans	0.1
Canada	asparagus	5
	citrus fruit	2
Chile	citrus fruit	2
	potatoes	0.2
	raw cereals	0.2
	milk and dairy products, carcases, eggs	0.05*
Czech Republic	maize	0.05
	cereals (except oat)	0.1
	sorghum	0.05

Country	Commodity	MRL, mg/kg
	maize	0.05
	rice	0.05
	butcher’s meat, milk, dairy products, eggs	0.05
	baccate fruits	0.1
	potatoes	0.2
	cereals	0.5
	citrus fruits	2
Finland	citrus	2
	others	0.1
Germany	citrus fruit	2
	citrus juices	0.1
	other foods of plant origin	0.1
Hungary	all food crops (a 14 day ban on grazing)	0.1
Israel	citrus fruit	2
	eggplant	0.2
Italy	citrus fruit	0.1
	hazelnuts	0.1
	potatoes	0.1
	cereals	0.1
	forage, clover	0.1
	milk, egg, meat	0.05
Japan	rice	0.2
Kenya	citrus fruits	2
	barley, oats, rye. wheat	0.5
	potato	0.2
	blackberries, raspberries, red-black, vaccinium berries, including bearberry	0.1
	maize, rice, sorghum	0.05
	eggs, meat, milk products, milks	0.05
Korea	grapefruit	0.5
	oranges, lemons	2
	other citrus fruits	0.1
	radishes (roots)	0.1
	eggplant	0.1
	celery	0.1
	cherries	0.1

Country	Commodity	MRL, mg/kg
	cotton seed	0.1
	soya beans	0.1
	carrots	0.1
	tomatoes	0.1
	asparagus	0.1
	spinach	0.1
	red peppers	0.1
	iceberg lettuce	0.1
	ginger	0.1
	Korean plums	0.1
	wheat, oats, barley, rye	0.5
	grapes	0.5
	apples, pears	2
	apricots	2
	corn (maize), African millet, rice	0.05
	strawberries	0.05
	chestnuts, walnuts, almonds, pecans	0.2
	potatoes	0.2
	beef, goat meat, pork, horsemeat, mutton or lamb	0.05
Malaysia	meat, egg, milk and milk products	0.05
	potatoes	0.2
	cereal grains	0.2
	fruits	2
	sugar cane	3
Mexico	rice (straw), wheat (forage), sugar cane (forage), corn (forage), sorghum (forage)	20
	sugar cane (pomace and molasses)	5 FA
	citrus fruit	5 PH
	asparagus	5
	apples, pears	5
	sugar cane	2
	corn (fresh & grain), sorghum, wheat (grain)	0.5
	grapes	0.5
	potatoes	0.2
	nuts	0.1*
	melon	0.1*

Country	Commodity	MRL, mg/kg
	tomato	0.1*
	chilli pepper	0.1*
	avocado	0.1*
	cotton (seed)	0.1*
	cucumber	0.1*
	watermelon	0.1*
	citrus fruit	0.1*
	pecans	0.1*
	strawberries	0.1*
	eggplant	0.1*
	squash	0.1*
	rice	0.1
	strawberries	0.05
Netherlands	citrus fruit	2
	blueberry, blackberry, raspberry	0.1
	other fruit	0.05*
	vegetables	0.05*
	cereal	0.05*
	others	0.05*
New Zealand	stone fruit	1
	citrus fruit	5
Romania	eggs without shell, whole milk and milk products, meat	0.05
Republic of Singapore	citrus fruit	2
	edible offal of cattle, pigs, sheep and goats	2
	barley, rye, wheat	0.5
	other cereal grains	0.2
	potatoes	0.2
	blackberries, raspberries and other berries	0.1
	eggs, meat, milk and milk products	0.05
Slovak Republic	maize, rye	0.05
	raw meat, milk products, milk, eggs	0.05
	blackberries, blueberries, raspberries	0.1
	cereal	0.2
	potatoes	0.2
	citrus fruit	2

Country	Commodity	MRL, mg/kg
South Africa	citrus	2
	barley, mealies, rye, sorghum, wheat	0.5
	sugar cane	0.5
	potatoes	0.1
Spain	citrus fruits	0.1
	fruits with or without shell	0.1
	seed fruits	0.1
	stone fruits	0.1
	berries and small fruits	0.1
	other fruits	0.1
	root and tuber vegetables	0.1
	bulb vegetables	0.1
	fruits and peponides	0.1
	vegetables of the genus Brassica	0.1
	fresh aromatic herbs and leaf vegetables	0.1
	young stalks	0.1
	fungi	0.1
	legumes	0.1
	oilseeds	0.1
	other edible seeds	0.1
	potatoes	0.1
	tea and other infusions	0.1
	hops	0.1
	spices	0.1
	grains	0.1
	other products for consumption (tobacco, sugar beets, sugar cane other)	0.1
	hay and forage crops except Gramineae forage and cereal straw	0.1
	dried products	0.1
	Gramineae forage	0.2
	cereal straw	0.2
Sweden	citrus fruits	2
	fruits and vegetables (fresh and dried fruits, fresh and deep-frozen berries and green vegetables and also root vegetables)	0.1
	cereals (ripe fruits of wheat, rye, barley, oats, rice, maize, millet and buckwheat) and hulled grain, flakes and flour made from cereals	0.1
Switzerland	cereal	0.05

Country	Commodity	MRL, mg/kg
	stone fruit	0.05
	pip fruit	0.05
Taiwan	sugar cane	0.05
	citrus fruits	2
USA	asparagus	5
	apples	5
	apricots	5
	barley, grain	0.5
	barley, forage	20
	blueberries	0.1
	citrus fruit	5
	corn, grain	0.5
	corn, fresh (sweet)	0.5
	corn, fodder	20
	corn, forage	20
	cranberries	0.5
	grapes	0.5
	grass, hay	300
	grass, pasture	1000
	grass, rangeland	1000
	milled fractions (except flour) derived from barley, oats, rye and wheat	2
	millet, grain	0.5
	millet, fodder	20
	millet, forage	20
	nuts	0.2
	oats, grain	0.5
	oats, forage	20
	pears	5
	pistachios	0.2
	potable water	0.1
	potatoes	0.2
	quinces	5
	rice, grain	0.1
	rice, straw	20
	rye, grain	0.5

Country	Commodity	MRL, mg/kg
	rye, forage	20
	sorghum, grain	0.5
	sorghum, fodder	20
	sorghum, forage	20
	soya bean, grain	0.1
	stone fruits	0.2
	strawberries	0.05
	sugar cane	2
	sugar cane, forage	20
	sugar cane molasses	5
	wheat, forage	20
	wheat, grain	0.5
	raspberries	0.1
	fish	1
	shellfish	1
	cattle, fat	0.2
	cattle, kidney	2
	cattle, meat	0.2
	cattle, meat by-products (except kidney)	0.2
	eggs	0.05
	goats, fat	0.2
	goats, kidney	2
	goats, meat	0.2
	goats, meat by-products (except kidney)	0.2
	hogs, fat	0.2
	hogs, kidney	2
	hogs, meat	0.2
	hogs, meat by-products (except kidney)	0.2
	horses, fat	0.2
	horses, kidney	2
	horses, meat	0.2
	horses, meat by-products (except kidney)	0.2
	milk	0.1
	poultry	0.05
	sheep, fat	0.2

Country	Commodity	MRL, mg/kg
	sheep, kidney	2
	sheep, meat	0.2
	sheep, meat by-products (except kidney)	0.2

* MRL at the LOD P: provisional tolerance FA: tolerance for processed food PH: post harvest application

APPRAISAL

2,4-D, 2,4-dichlorophenoxyacetic acid was evaluated for residues at several Joint Meetings between 1970 and 1987, when MRLs were recommended for a number of commodities, and for its effects on the environment in 1997. The compound was evaluated by the present Meeting in the CCPR Periodic Review Programme.

The Meeting received information on animal and plant metabolism, environmental fate, analytical methods, updated GAP, supervised residue trials on crops, animal feeding studies, and residues after processing.

2,4-D is formulated as salts (diethanolamine, DEA; dimethylamine, DMA; tri-isopropanolamine, TIPA; isopropylamine, IPA) or esters (2-butoxyethyl, BEE; isopropyl, IPE; 2-ethylhexyl, EHE). It is a selective, systemic foliar-applied hormone herbicide, readily absorbed by leaves and roots, which acts as a growth regulator to control broad-leaved weeds.

The absorption, distribution, metabolism and excretion of [^{14}C]2,4-D have been studied in mice, rats, a goat, hens and fish.

Studies on rats and mice show that the absorption of 2,4-D after oral administration is rapid and almost complete: peak plasma levels were reached about 4 hours after dosing.

After oral administration of the 2-ethylhexyl ester to rats the test substance could not be detected in blood, indicating that it was rapidly hydrolyzed to 2,4-D acid whose concentration peaked in plasma 2 to 4 hours after administration and then decreased with an apparent half-life of about 9 hours.

When rats were dosed orally with 1 or 100 mg/kg bw of [^{14}C]2,4-D the excretion of radioactivity was rapid: over 94% of the administered dose was recovered by 48 hours after dosing and the half-life for urinary excretion was about 5 hours. Urine was the main route of excretion (85-94%), while faeces represented a minor excretory pathway (2-11%). At the high dose of 100 mg/kg bw 2,4-D elimination was saturated during the first hours after dosing. Its rapid clearance from plasma and rapid excretion in the urine show that its potential to accumulate is low.

In rats, [^{14}C]2,4-D was eliminated primarily unchanged in the urine (>97%). Two minor metabolites, probably 2,4-D conjugates, were detected.

The 2-ethylhexyl ester was rapidly absorbed and hydrolysed to 2,4-D and 2-ethylhexanol. No 2,4-D 2-ethylhexyl ester was found in the blood, urine or faeces 72 hours after oral administration. The 2,4-D acid produced was rapidly excreted unchanged in the urine, and the 2-ethylhexanol was further metabolized to 2-ethyl-hexanoic acid, 2-ethyl-1,6-hexanedioic acid, 2-ethyl-5-oxohexanoic acid, 2-ethyl-5-hydroxyhexanoic acid, 2-heptanone and 4-heptanone, which were and rapidly excreted in the urine, faeces and expired air. CLICK HERE for continue

The distribution pattern of the ^{14}C in the organs, tissues milk and urine of a lactating goat dosed orally with [^{14}C]2,4-D showed that the kidney (which contained 0.45% of the dose) is the main target organ. Lower proportions were found in the liver (0.07 %), milk (0.06%), fat (0.03 %) and muscle (0.01 %), whereas the total ^{14}C in the urine was 99.4 % (97.9% identified as 2,4-D). The metabolites found at lower levels were 2- or 4-chlorophenoxyacetic acid (2- or 4-CPAA) and 2,4-dichlorophenol (2,4-DCP).

In hens dosed orally with [^{14}C]2,4-D, about 90% of the dose was recovered from the excreta. The edible tissues and eggs each contained <0.1% of the total dose.

Bluegill sunfish were exposed to 11 mg/l [^{14}C]2,4-D in their water under static conditions for four consecutive days. The total ^{14}C (as 2,4-D) in the day-4 viscera (inedible) and fillet (edible) represented 1.9 and 0.41 mg/kg respectively. 2,4-D (80% of the ^{14}C, 0.33 mg/kg) and 2,4-DCP (7.9% of the total ^{14}C, 0.03 mg/kg) were present in the edible portion.

Information on the metabolism of 2,4-D in plants was provided for apples, lemons, potatoes and wheat.

After application of the 2-ethylhexyl ester to a potato crop at a rate of 0.35 kg acid equivalent per hectare (ae/ha), the residues in the tubers were 0.24 mg/kg 2,4-D (42% of the total ^{14}C), 0.15 mg/kg 4-CPAA (26% of the total ^{14}C) and 0.09 mg/kg 4-hydroxy-2,5-D (15.5% of the total ^{14}C).

In apples after the spray application of [^{14}C]2,4-D to the turf beneath the canopy of a dwarf apple tree according to label instructions, the residues were too low to be identified (total ^{14}C 0.009 mg/kg as 2,4-D).

In the forage and straw of wheat treated with 2,4-D-EME 74 and 70% of the total ^{14}C was recovered as free or conjugated 2,4-D. The rest consisted of a large number of distinct metabolites, of which 4-hydroxy-2,5-D was the major compound (8% of the total ^{14}C). In wheat grain about half the total ^{14}C was associated with natural products (protein, starch and cellulose). The remainder consisted mainly of unidentified polar and unextractable compounds. 2,4-D accounted for 6% of the total ^{14}C and was the only component identified.

[^{14}C]2,4-D IPE applied to lemons post-harvest resulted in residues of 2.4 mg/kg as 2,4-D. The fruits were stored at 5-6°C up to 16 weeks. Most of the total ^{14}C was found in the peel, with very small amounts in the pulp and juice. Lemon peel at 20 weeks contained 93.5% of the total ^{14}C (2.1 mg/kg). These residues were mainly free and conjugated forms of 2,4-D (64% of the total ^{14}C, 1.5 mg/kg). Other compounds found in minor quantities were free and bound 2,4-D IPE (0.73 % of the total ^{14}C, 0.017 mg/kg), 4-hydroxy-2,3-D or 5-hydroxy-2,4-D (0.58%, 0.013 mg/kg), 4-hydroxy-2,5-D (0.44%, 0.01 mg/kg) and 2,4-DCP (0.72%, 0.016 mg/kg). The main metabolites found in the pulp and juice were also free and conjugated 2,4-D (2.9% of the total ^{14}C, 0.07 mg/kg in the pulp; 0.99% of the total ^{14}C, 0.023 mg/kg in the juice).

The degradation of 2,4-D does not lead to environmentally significant levels of degradation products in soil or water.

Under aerobic incubation conditions, 2,4-D is rapidly degraded in soil (half-life in silty clay soil 1.7 days at 25°C). The final degradation products are CO_2 and soil-bound residues, which are mostly distributed in the fulvic acid and huminic acid fractions of the soil.

Further information was received on the fate of the 2-ethylhexyl and isopropyl moieties of the 2,4-D esters and the dimethylamine and diethanolamine of the salts.

The K_{OC} values of [^{14}C]2,4-D ranged from 59 to 117, indicating a fairly high potential for 2,4-D to be leached through the tested soils (Arizona clay loam, Mississippi loam, California sandy loam, Plainfield sand), whereas the leaching potential of the degradation products 2,4-dichloroanisole (K_{OC}: 436-1442) and 2,4-dichlorophenol (K_{OC}: 368-1204) is medium to low. In contrast to that, the results of two field lysimeter studies show that 2,4-D and its degradation products are not mobile in sandy soils (pH 5.7 in the first 30 cm, 4.8-5.0 in the next soil horizons). This indicates that 2,4-D, in spite of its high potential to be leached, is not expected to be found in groundwater (owing to its rapid degradation in the soil) when the product has been used in compliance with GAP.

Terrestrial field dissipation studies with the dimethylamine salt and 2-ethylhexyl ester over a 2-year period showed similar rates of dissipation of 2,4-D when applied as either the salt or ester because both formulations are converted rapidly to the same anionic form.

Residues in rotational crops were determined in radishes, lettuce and wheat planted 30 and 139 days after the treatment of the soil with [^{14}C]2,4-D at a rate of 2.2 kg ae/ha (acid equivalent/ha). The total radioactive residues in the 30-day crops were <0.001 mg/kg in wheat forage, 0.01 mg/kg in radish roots and 0.06 mg/kg in wheat straw. No ether-soluble residues from free or conjugated 2,4-D or its metabolites were present at levels above 0.01 mg/kg after a 30-day planting interval. The ^{14}C residues observed in the rotational crops planted after both 30 and 139 days were due to incorporation into natural products.

An aerobic aquatic degradation study of [^{14}C]2,4-D was conducted at a concentration of 5 mg/l for up to 46 days. 2,4-D acid was degraded slowly at first and represented ≤75% of the applied dose after 25 days. The rate of degradation then increased sharply and at day 46 2,4-D represented only 0.5% of the applied radioactivity. The major product was CO_2, which accounted for 64% of the applied ^{14}C at the end of the study period. The highest levels of the other identified residues (expressed as % of applied ^{14}C) were 1.1% 2,4-dichlorophenol at day 35, 1.1% 4-chlorophenoxyacetic acid at day 14 and 1.4 % 4-chlorophenol at day 20.

2,4-D is not likely to remain long in the environment under anaerobic aquatic conditions, in which it was degraded with a half-life of 41 days.

Further information was received on the aquatic field and pond dissipation of the dimethylamine salt and its major degradation products 2,4-D, 2,4-dichlorophenol, 2,4-dichloroanisole, 4-chlorophenoxyacetic acid and 4-chlorophenol.

The current residue analytical methods are based on extraction with a basic aqueous solution before clean-up by solid phase extraction on a C18-bonded silica cartridge and solvent partitioning. After methylation and further clean-up of the ester, the 2,4-D residues are determined as 2,4-D methyl ester by GLC with an ECD. The method was validated for plant and animal commodities with recoveries above 70%. The typical limits of determination in plant materials, milk and animal tissues are 0.01- 0.05 mg/kg. For most of the supervised trials the reported LOD was 0.01 mg/kg. Residues were determined in water, soil and sediment by GLC with mass-selective detection with LODs of 0.001 mg/l in water and 0.01 mg/kg in soil and sediment.

The analytical method provided by The Netherlands is based on similar extraction and clean-up procedures but the SPE extracts are further processed by column-switched HPLC on a pre-column packed with internal surface reversed-phase (ISRP) material and a bonded C-18 analytical column with UV detection at 118 nm. The LOD was reported to be 0.02 mg/kg for meat and 0.05-0.1 mg/kg for cereals and vegetables.

Information was submitted on the stability of 2,4-D residues in various stored analytical samples. The Meeting concluded that the compound was stable for the duration of the studies (at least two years in potatoes, cherries and cranberries and for one year in the raw agricultural

commodities and processed products of cereal grains, fodder and forage, oil seed, sugar cane, grapes and pears, and for seven months in citrus fruits, plums and peaches).

The nature of the 2,4-D residues in plants is adequately understood from the apple, lemon, potato and wheat metabolism studies, and the residues in animals are known from the mouse, rat, goat, poultry and fish metabolism studies.

The Meeting concluded that the definition of the residue in plants and animals should be defined as 2,4-D *per se* for compliance with MRLs and for the estimation of the dietary intake.

The value of the partition coefficient of 2,4-D at natural pH values (log P_{OW} = 0.18 and –0.83 at pH 5 and 7 respectively) indicates that the compound is not fat-soluble.

Plant metabolism studies on wheat and potatoes treated with the 2-ethylhexyl ester and on lemon treated with the isopropyl ester indicate nearly complete hydrolysis of the esters by about 10 days after treatment with 2,4-D as the terminal residue of importance. Mammalian pharmacokinetic and metabolism studies in rats and mice indicate that the 2-ethylhexyl ester is rapidly converted to 2,4-D acid and its metabolism can be considered to be equivalent to that of 2,4-D. For these reasons, the definition of the residue arising from the application of the ethylhexyl ester or other esters should be the same as that for the residue from the free acid.

Supervised residue trials on numerous crops were carried out all in the USA and evaluated against US GAP. Because no significant difference was observed between the residues left by the acid, esters and salts, the trials in which 2,4-D acid, the ethylhexyl ester and 2,4-D dimethylamine salt were applied were combined for evaluation.

Citrus fruits. 2,4-D is used as a plant growth regulator pre-harvest on grapefruit and oranges (US GAP 1 x 0.0024 kg ae/hl, PHI 7 days), and post-harvest on lemons (US GAP 1 x 0.05 kg ae/hl). The Meeting was informed that foliar spraying of grapefruit and oranges with 2,4-D is a minor use.

Two trials according to US GAP were carried out on grapefruit. Because one year passed between the first and the last application, the samples of mature fruits from 1994 and 1995 are used for evaluation. The residues in the whole fruit were <0.05 (2), 0.07 and 0.08 mg/kg. Two further trials complying with GAP on oranges both resulted in residues in the whole fruit below the LOD: <0.05 mg/kg. All the residues in rank order were <0.05 (4), 0.07 and 0.08 mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg for grapefruit and oranges, and recommended withdrawal of the current CXL of 2 mg/kg for citrus fruit. As no residue data were submitted for the edible pulp the Meeting estimated an STMR of 0.05 mg/kg, based on the residues in the whole fruit.

Two supervised residue trials of post-harvest use on lemons were carried out in California. No decrease of the residue level during storage (0-112 days at 6-16°C) was observed (range from 0.29 to 0.61 mg/kg). The Meeting could not estimate a maximum residue level owing to the small number of trials.

Use as herbicide in orchards and vineyards

A further use of 2,4-D in fruits is for weed control with applications directed to the orchard or vineyard floor. The apple metabolism study indicates that no residues are to be expected in the fruits after application directed to the orchard floor and is supporting the interpretation of the supervised trial residue data.

Pome fruits. A number of trials on apples and pears in the USA complied with current GAP (2 x 2.2 kg ae/ha, directed application, PHI 14 days). The residues in the fruits from all the 10 trials available were below the LOD of 0.01 mg/kg at 13-15 days PHI. The Meeting estimated a maximum residue level for pome fruits of 0.01* mg/kg as being a practical limit of determination. Because the residues

were below the LOD in all samples, including fruit from one trial at a fivefold rate, an STMR level of 0 was estimated.

Stone fruits. Three trials each on cherries, peaches and plums (one on fresh prunes) treated at rates up to the maximum US GAP (2 x 1.6 kg ae/ha, directed application, PHI 14 days) resulted in residues below the LODs of 0.05 mg/kg (cherries) or 0.01 mg/kg (peaches and plums) at 14 days PHI. The Meeting estimated a maximum residue level for stone fruits of 0.05* mg/kg as being a practical limit of determination. Because the residues were below the LOD in all samples including fruit from one trial at a fourfold rate an STMR level of 0 was estimated.

Berries and other small fruits. In four blueberry trials at rates of 2 x 1.6 kg ae/ha as a directed application which complies with GAP in the USA, residues up to 0.01 mg/kg were found about 30 days after the last application. The residues were <0.01 (2) and 0.01 (2) mg/kg.

In six residue trials on strawberries according to US GAP (1 x 1.7 kg ae/ha, before blossom), no residues (<0.05 mg/kg) were found 59-129 days after treatment.

Two US trials on cranberries with 3 x 4.5 kg ae/ha were reported. US GAP specifies 2 x 4.5 kg ae/ha, directed application. At a PHI of 30 days, no residues above the LOD of 0.02 mg/kg were found in samples from the first trial but up to 0.11 mg/kg in those from the second trial.

Only one trial was carried out on raspberries (1 x 1.6 + 1 x 3.1 kg ae/ha). No residues above the LOD of 0.05 mg/kg were found. No residue data were reported for blackberries.

Two residue trials were carried out on grapes according to current US GAP (1 x 1.6 kg ae/ha, directed application). No residues above the LOD of 0.05 mg/kg were found at the recommended PHI of 100 days.

All the residues from trials complying with US GAP for berries in rank order were <0.01 (2), 0.01 (2), <0.05 (9) and 0.11 mg/kg.

The Meeting estimated a maximum residue level of 0.1 mg/kg for berries and other small fruits (including grapes) and recommended withdrawal of the CXLs for blackberries, raspberries, and vaccinium berries (including bearberry).

The Meeting estimated an STMR of 0.05 mg/kg for berries except grapes, and an STMR of 0 mg/kg for grapes because of their special use pattern (100 days PHI and high phytotoxicity).

Use as herbicide on vegetables

2,4-D is directed to the ground for weed control in vegetables. Supervised trials on sweet corn, potatoes and asparagus were reported.

Sweet corn (corn-on-the-cob). Nine supervised trials at US application rates were reported. Only two of them included the recommended PHI of 21 days but the treatment in all the trials was carried out at the registered plant growth stage. The residues were at or below the LOD of 0.05 mg/kg in all samples of kernels plus cob with husks removed. The Meeting estimated a maximum residue level for sweet corn of 0.05* mg/kg as being a practical limit of determination, and an STMR of 0.05 mg/kg.

Potatoes. Eight of ten trials in the USA complied with US GAP (2 x 0.078 kg ae/ha). The treatments were carried out at the registered plant growth stage. At harvest, the residues were <0.05 (5), 0.08 (2) and 0.13 mg/kg. The Meeting confirmed the current CXL of 0.2 mg/kg and estimated an STMR of 0.05 mg/kg.

Asparagus. Four trials covering the US application rate were reported but only two included the specified PHI of 3 days (the residues were 0.1 and 3 mg/kg). Two trials are not enough to estimate a maximum residue level.

Use as herbicide on cereals

2,4-D is used world-wide for the pre- or post-emergence or pre-harvest treatment of winter and summer cereals.

Maize. After three applications of the dimethylamine salt (7 trials), 2-ethylhexyl ester (6 trials), or free acid (1 trial) totalling 3.4 kg ae/ha, the residues of 2,4-D in grain after 7 days (US GAP) or 14 days were <0.01, 0.01 (8), 0.015, 0.02 (2), 0.03 and 0.04 mg/kg (4 residues at 14 days were higher than the corresponding 7-day residues). The Meeting estimated a maximum residue level of 0.05 mg/kg to replace the current CXL (0.05* mg/kg) and an STMR of 0.01 mg/kg.

Rice. Seven of ten supervised US trials complied with GAP (1 x 1.7 kg ae/ha, PHI 60 days). The residues in the rice grain without husk in rank order were <0.01(2), 0.01 (3), 0.03 and 0.05 mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg for husked rice to replace the current CXL of 0.05* mg/kg for rice and an STMR of 0.01 mg/kg.

Wild rice. Only one overdosed trial (4 replicates) was reported. No residues were found after treatment with 0.56 kg ae/ha at day 53 or 64. One trial is not enough to estimate a maximum residue level.

Sorghum. 2,4-D is registered in the USA for applications of 0.56 kg ae/ha of esters or 1.1 kg ae/ha of the acid or salts. In a total of ten trials in four US states the recommended rates were applied at the registered plant growth stage.

No residues above the LOD of 0.01 mg/kg were found in the grain at harvest. The Meeting estimated a maximum residue level for sorghum of 0.01* mg/kg as being a practical limit of determination to replace the current CXL of 0.05* mg/kg, and an STMR of 0.01 mg/kg.

Wheat and rye. Many field trials were carried out on wheat in the USA, 24 of them according to US GAP (1.4 + 0.56 kg ae/ha, PHI 14 days). The residues in wheat grain in rank order were 0.11 (2), 0.12, 0.13, 0.16 (2), 0.17 (4), 0.21, 0.22 (2), 0.23, 0.24 (2), 0.31, 0.34, 0.46, 0.63, 0.87, 0.94, 0.95 and 1.4 mg/kg. The Meeting agreed to extrapolate the residue data from wheat to rye because GAP is identical and estimated maximum residue levels of 2 mg/kg to replace the current CXLs of 0.5 mg/kg with STMRs of 0.22 mg/kg.

Other cereals. 2,4-D is registered world-wide for use on barley, millet, oats and triticale. Although the US GAP for barley, oats and millet is the same as for wheat the Meeting agreed that extrapolation from wheat to barley, oats and millet could be recommended because the residue could be considerably higher from the use after blossom at the dough stage.

2,4-D is registered on triticale in Australia (1 x 1.6 kg ae/ha, PHI 7 days). Many US trials on wheat complied with Australian GAP but the Meeting did not support extrapolation of the US data as the climatic conditions are different.

The Meeting agreed to recommend the withdrawal of the current CXLs for barley and oats of 0.5 mg/kg and could not estimate a maximum residue level for millet or triticale.

Sugar cane. Eight US supervised trials according to GAP with one pre-emergence and one post-emergence treatment of 2.2 kg ae/ha were reported. The residues in mature cane at PHIs of 137-214 days were <0.01 (7) and 0.02 mg/kg. The Meeting estimated a maximum residue level of 0.05 mg/kg and an STMR of 0.01 mg/kg.

Tree nuts. Ten trials each on almonds and pecans were carried out in the USA, five with directed applications of the dimethylamine salt and five with the 2-ethylhexyl ester, according to US GAP (2 x 1.6 kg ae/ha, PHI 60 days).

Two trials with directed applications on pistachio nuts were also according to US GAP (2 x 1.6 kg ae/ha, PHI 50 days).

Three trials each with the dimethylamine salt and the 2-ethylhexyl ester complied with the critical US GAP on hazelnuts, where 4 x 0.12 kg ae/hl are used as a spray to the stems of suckers with a PHI of 45 days.

The residues were <0.05 (8), 0.08 and 0.16 mg/kg in almond kernels, below the LOD of 0.05 mg/kg in all the samples of pecans and pistachio nuts and <0.05 (2), 0.05 and 0.1 mg/kg in hazelnuts. All residues in rank order were <0.05 (22), 0.05, 0.08, 0.1 and 0.16 mg/kg.

The Meeting estimated a maximum residue level for tree nuts of 0.2 mg/kg and an STMR of 0.05 mg/kg.

Soya bean seed, fodder and forage. The use of 2,4-D is registered in the USA for pre-planting applications of 1 x 0.56 kg ae/ha of esters or 1 x 1.1 kg ae/ha of free acid or salts. Twenty seven supervised trials were reported, with treatments of 0.56, 1.4 or 3.2 kg ae/ha. The residues in all samples of beans were lower than the LOD of 0.01 mg/kg. The Meeting concluded that no detectable residue is likely to occur in soya beans, and estimated a maximum residue level of 0.01* mg/kg and an STMR of 0 mg/kg.

No residues were detected in any of the 27 samples of fresh forage.

The fodder samples were analysed after air-drying forage for 1.5-7 days after cutting. No residues above the LOD of 0.01 mg/kg were found in the nine trials according to GAP. Residues up to 0.04 mg/kg were found after the treatments at higher rates.

The Meeting concluded that no detectable residue is to be expected in soya bean forage (green) or fodder, and estimated maximum residue levels of 0.01* mg/kg as a practical limit of determination. STMRs of 0 for soya bean forage (green) and 0.01 mg/kg for fodder were estimated.

Animal feedstuffs

Forage, hay or fodder of grasses. Supervised trials according to US GAP (2 x 2.2 kg ae/ha) were reported on rangeland and pasture grass used for animal feed. The Meeting was informed that a PHI of 0 days has to taken into account for the estimation of a maximum residue level for rangeland. The residues in the forage on the day of treatment in rank order were 90, 92, 135, 153, 154, 162, 169, 172, 173, 177, 182, 183, 192, 194, 198, 223, 233, 236, 241, 258, 271, 280, 285, 31, 314 and 358 mg/kg. The Meeting estimated an STMR of 193 mg/kg for grass forage.

The highest residues from each trial on hay (PHI of fresh forage 7-30 days) were 19, 39, 40, 50, 61, 65, 68 (2), 74, 82, 86, 94, 96, 101, 103, 109, 126, 142, 145, 147, 149, 150, 155, 180, 182, 206, 216, 218, 231, 236, 279 and 330 mg/kg. The Meeting estimated a maximum residue level of 400 mg/kg and an STMR of 117.5 mg/kg for the hay or fodder (dry) of grasses.

Maize forage and fodder. US GAP allows pre-emergence application at 1.1 kg ae/ha, a directed post-emergence application at 0.56 kg ae/ha when the maize is 25-41 cm high, and a pre-harvest application at 1.7 kg ae/ha (PHI for grain 7 days).

After two applications of 2,4-D at rates totalling 1.7-2.2 kg ae/ha, the residues in rank order were 0.01, 0.03, 0.09, 0.25 (2), 0.33, 0.46, 0.61, 0.69, 0.88, 1.0 (2), 1.1, 2.7, 3.0 and 5.2 mg/kg in 16 forage samples collected at a 7-day PHI and <0.01 (14), 0.01, 0.03 mg/kg in 16 samples for silage use collected after 54-89 days.

After three applications of 2,4-D totalling approximately 3.4 kg ae/ha, the residues in fodder were 3.6, 4.2, 4.4 (2), 5.7, 6.4 (2), 9.1, 9.9, 15, 20, 25 and 30 mg/kg at 7 or 14 days after treatment.

The Meeting estimated a maximum residue level of 10 mg/kg for maize forage and 40 mg/kg for maize fodder. STMRs of 0.65 and 6.4 mg/kg were estimated for maize forage and fodder respectively.

Rice straw and fodder. The residues of 2,4-D after treatments according to GAP at 61-66 days were 1.1, 1.5, 2.1, 3.1, 5.4, 6.4 and 8.8 mg/kg. The Meeting estimated a maximum residue level of 10 mg/kg and an STMR of 3.1 mg/kg for rice straw and fodder, dry.

Sorghum, straw and fodder. The residues in the green forage in the 10 US trials described above in rank order were <0.01, 0.02 (2), 0.03 (2), 0.04, 0.06, 0.08, 0.13 and 0.14 mg/kg 30 days after treatment. The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.035 mg/kg for sorghum forage (green).

Fodder samples were harvested at maturity, approximately 82-112 days after treatment. The residues in the untreated control samples were of the same order as those in the supervised trials. The Meeting therefore concluded that the submitted data could not be used to estimate a maximum residue level for sorghum straw and fodder.

Wheat forage, straw and fodder. In the USA the first application of 2,4-D is recommended after the plant is fully tillered but before joints are formed in the stems, and the second when the grain is at the dough stage.

The wheat can be cut before the pre-harvest application and used as forage, so the forage samples were taken 7 days after the first treatment. The residues in rank order were 5, 6 (3), 6.3, 7, 8 (2), 8.5, 9 (2), 11, 14 (3), 15 (2), 16, 17, 18 (2), 19, 20 (2), 22 (2), 23 (2), 24, 25, 26, 29, 30 (2), 33 (3), 34, 35, 41, 42, 50, 54, 55, 58 and 112 mg/kg.

The residues in straw from treatments according to GAP were 2, 3, 4 (5), 5 (3), 6 (2), 7 (3), 8 (2), 11, 15 (4), 17, 18, 22, 41 and 85 mg/kg 13-15 days after pre-harvest treatment.

The Meeting estimated a maximum residue level of 100 mg/kg and an STMR of 7 mg/kg for wheat straw and fodder, dry, and an STMR of 20 mg/kg for wheat forage.

Sugar cane forage. After applying 2,4-D pre-emergence and post-emergence (at layby) to sugar cane at 2.2 kg ae/ha, the residues were <0.01(2), 0.01, 0.03, 0.04, 0.08 and 0.14 mg/kg in forage samples collected 88-92 days after the second application. The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.03 mg/kg.

Animal transfer studies

Groups of 3 cows were dosed at four dose levels equal to 1446, 2890, 5779 and 8585 ppm 2,4-D ae in the diet on a dry weight basis for 28 to 30 consecutive days. Two further groups were treated at the high dose level for 28 days and slaughtered 3 or 7 days after the last dose.

Residues of 2,4-D were detected in most of the milk samples analysed. The mean residue levels in the samples from the high-dose group reached a plateau after 7 days of treatment, showing a residue level of 0.47 mg/l throughout the remaining treatment period. The mean residues in the

groups allowed 3 and 7 days of recovery decreased from the levels of 0.46 and 0.47 mg/kg at 28 days to 0.01 mg/l.

The residues in the milk from the medium-high dose groups also reached a plateau after 7 days at mean levels of 0.29 and 0.04 mg/kg respectively. The residues from the medium-low dose group became steady after the first day of treatment, having a mean level of 0.12 mg/kg throughout the remaining treatment period.

Residues of 2,4-D were also detected in most of the tissue samples analysed. The mean liver residue levels in the high, medium-high, medium-low and low dose groups were 3.1, 3.0, 1.9 and 0.12 mg/kg respectively, decreasing to 0.45 and 0.39 mg/kg after 3 and 7 days recovery respectively.

The mean residues in the kidneys from the four groups were 24, 17, 14 and 3.8 mg/kg respectively, decreasing to 0.06 and <0.05 mg/kg after 3 and 7 days recovery. The mean residues in the muscles from the four groups were 1.0, 0.76, 0.41 and 0.21 mg/kg, decreasing to 0.06 and <0.05 mg/kg after 3 and 7 days recovery, and those in the fat were 2.2, 2.5, 0.59 and 0.42 (those in the medium-high group being highest), and were 0.07 and <0.05 mg/kg after 3- and 7-day recovery periods.

Thus the highest residues were in the kidneys, followed in decreasing order by liver, fat, muscle and milk. This relationship was generally consistent in all four dose groups. The residue levels were generally dose-dependent, except in fat where the mean residue in the high dose group was slightly lower than that in the medium-high group, indicating that a plateau level had been reached in fat.

The highest exposure to 2,4-D residues will arise from the use of the herbicide on pasture, where the highest residues were 358 mg/kg in grass forage. With the assumption that the maximum daily feed consumption of a dairy cow (body weight 550 kg) is 20 kg on a dry matter basis, of which 60% is grass forage containing 25% dry matter, the intake may be calculated as follows.

358 mg/kg on a wet weight basis is equivalent to 1432 mg/kg on a dry matter basis (358 + 0.25).

Grass forage forms 60% of the diet and therefore contributes 859.2 ppm total feed on dry matter basis (1432 x 0.6).

Hence the dietary intake is 859.2 x 20 / 550 = 31 mg/kg bw/day.

The lowest dose in the feeding study was 50.6 mg/kg bw/day but, as a nearly linear relation between dose and residue level with its graph passing through the origin was established, the Meeting concluded that an extrapolation downwards to the estimated actual intake was justified in this case. The following Table shows the highest and the mean measured and extrapolated residues. Maximum residue levels were estimated from the highest extrapolated residue, and STMRs from the medians of the mean extrapolated residues for estimation of the maximum residue level and the STMR respectively.

Dose, group	Residues, mg/kg									
mg/kg bw/day	Milk		Liver		Kidney		Muscle		Fat	
	highest	mean	highest	mean	highest	mean	highest	mean	highest	mean
(50.6) Actual	(0.07)	(0.04)	(0.2)	(0.12)	(6.5)	(3.8)	(0.24)	(0.21)	(0.51)	(0.42)
31 Extrapolated	0.043	0.025	0.12	0.074	3.98	2.33	0.15	0.13	0.31	0.26
(99) Actual	(0.18)	(0.12)	(2.4)	(1.9)	(18)	(14)	(0.51)	(0.41)	(0.75)	(0.59)
31 Extrapolated	0.056	0.038	0.75	0.59	5.64	4.38	0.16	0.13	0.23	0.18
(189) Actual	(0.59)	(0.29)	(3.5)	(3.0)	(29)	(17)	(1.1)	(0.76)	(3.6)	(2.5)
31 Extrapolated	0.097	0.048	0.57	0.49	4.76	2.79	0.18	0.12	0.59	0.41
(276) Actual	(0.87)	(0.47)	(3.8)	(3.1)	(24)	(24)	(1.0)	(1.0)	(2.3)	(2.2)
31 Extrapolated	0.098	0.053	0.43	0.35	2.7	2.7	0.11	0.11	0.26	0.25

[1]Residues found in the feeding study are in parentheses

The Meeting considered that liver and kidney should by combined as "edible offal", with the residues found in kidney, and estimated maximum residue levels of 0.1 mg/kg for milk, 5 mg/kg for edible offal and 0.2 mg/kg for meat and STMRs of 0.043 mg/kg for milk, 2.745 mg/kg for edible offal and 0.125 mg/kg for meat, and recommended the withdrawal of the CXLs for milks and milk products (0.05* mg/kg). No maximum residue level or STMR was estimated for fat as the results appeared to be atypical.

A metabolism study in hens showed that about 90% of the dose was recovered in the excreta. The edible tissues and eggs contained <0.1% of the total dose. The highest exposure to 2,4-D residues will arise from wheat and rye grain in which the highest residue found in the supervised trials was 1.4 mg/kg and maximum residue levels of 2 mg/kg and STMRs of 0.22 mg/kg were estimated. With the assumption that the daily maximum feed consumption of a chicken (bw 1.9 kg) is 0.12 kg on a dry matter basis, consisting of 80% wheat grain (89% dry matter) and 20% rye grain (88% dry matter), an intake of 2.25 ppm can be calculated from the maximum residue level. Therefore, no residues higher than 0.002 mg/kg (0.1%) could be expected theoretically in edible tissues and eggs. The Meeting estimated STMRs of 0 for poultry meat, edible offal and eggs, and maximum residue levels for poultry meat and edible offal of 0.05* mg/kg as a practical limit of determination. The Meeting estimated a maximum residue level for eggs at the LOD of 0.01* mg/kg to replace the CXL of 0.05* mg/kg.

Processing

Studies have been carried out to determine the effect of processing on residues of 2,4-D in lemons, maize, rice, sorghum, wheat and sugar cane.

Lemons containing 0.51 mg/kg 2,4-D (median) were processed to juice, wet and dry pulp, molasses and oil, which contained median residues of 0.05, 0.45, 1.9, 2.0 and <0.5 mg/kg respectively. The corresponding mean processing factors were 0.1, 0.88, 4.7, 4.3 and <1. The Meeting applied these factors to the STMRs of 0.05 mg/kg for oranges and grapefruit, and estimated STMR-Ps of 0.005 mg/kg for juice, 0.044 mg/kg for wet pulp, 0.235 mg/kg for dried pulp, 0.215 mg/kg for molasses and 0.05 mg/kg for oil.

The processing data on maize indicate that residues of 2,4-D do not concentrate in any of its processed commodities used for food or feed. In grits, meal and flour, the 2,4-D residues (0.04, 0.05 and 0.05 mg/kg respectively) were of the same order as in the grain (0.06 mg/kg). In aspirated maize grain fractions the residues of 2,4-D were approximately 37 times those in the grain. In view of the chemical nature of the compound, the residues in maize oil would be lower than the LOD of 0.01 mg/kg.

Because an STMR of 0.01 mg/kg was estimated for maize grain and the residues in the processed commodities were similar to those in the raw commodity, the Meeting estimated STMR-Ps of 0.01 mg/kg for maize grits, meal and flour.

One processing study on rice was reported. Residues of 2,4-D were not concentrated in rice bran or milled white rice but were concentrated by a factor of 3 in rice hulls. No STMR-P could be estimated for milled white rice because no data were reported for the unprocessed commodity (rice with husk).

As residues of 2,4-D were not detectable in sorghum grain or its processed commodities the processing trials could not be evaluated.

Wheat was treated with excessive amounts of 2,4-D to obtain high residues (1.5 and 2.4 mg/kg) and processed to produce bran, flour, middlings and shorts. The residues were concentrated in the bran and reduced in the flour by mean processing factors of 3.65 and 0.11 respectively. From

the STMR for wheat grain of 0.22 mg/kg and these factors the Meeting estimated STMR-Ps of 0.803 mg/kg and 0.024 mg/kg for wheat bran and flour respectively.

Residues from two supervised trials on sugar cane with treatment at four times the GAP rate were below the limit of determination (0.01 mg/kg). The cane from one trial was processed into molasses and sugar with residues of ≤0.01 mg/kg in molasses and <0.01 mg/kg in sugar. No STMR-Ps were estimated.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and for the estimation dietary intake: 2,4-D.

Commodity		Recommendation		
		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
GC 0640	Barley	W	0.5	
FB 0018	Berries and other small fruits	0.1	-	
	Berries, except grapes			0.05
FB 0264	Blackberries	W[1]	0.1	
FC 0001	Citrus fruits	W	2	
MO 0105	Edible offal (Mammalian)	5	-	2.745
PE 0112	Eggs	0.01*	0.05*	0
FC 0203	Grapefruit	0.1	2[2]	0.05
JF 0203	Grapefruit juice			0.005
	Grapefruit molasses			0.215
	Grapefruit oil			0.05
	Grapefruit pulp, dry			0.235
	Grapefruit pulp, wet			0.044
FB 0269	Grapes			0
	Grass forage (green)			193
AS 0162	Hay or fodder (dry) of grasses	400	-	117.5
GC 0645	Maize	0.05	0.05*	0.01
CF 1255	Maize flour			0.01
AS 0645	Maize fodder	40	-	6.4
AF 0645	Maize forage	10	-	0.65
	Maize grits			0.01
CF 0645	Maize meal			0.01
MM 0095	Meat (from mammals other than marine mammals)	0.2	0.05*	0.125
	Milk products	W	0.05*	
ML 0106	Milks	0.1	0.05*	0.043
GC 0647	Oats	W	0.5	
JF 0004	Orange juice			0.005
	Orange molasses			0.215
	Orange oil			0.05
	Orange pulp, dry			0.235
	Oranges pulp, wet			0.044
FC 0004	Oranges, Sweet, Sour	0.1	2[2]	0.05
FP 0009	Pome fruits	0.01*	-	0
VR 0589	Potato	0.2	0.2	0.05
PM 0110	Poultry meat	0.05*	-	0
PO 0111	Poultry, Edible offal of	0.05*	-	0
FB 0272	Raspberries, Red, Black	W[1]	0.1	
GC 0649	Rice	W[3]	0.05*	
CM 0649	Rice, husked	0.1	-	0.01
AS 0649	Rice straw and fodder, dry	10	-	3.1
GC 0650	Rye	2	0.5	0.22

Commodity		Recommendation		
		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
GC 0651	Sorghum	0.01*	0.05*	0.01
AF 0651	Sorghum forage (green)	0.2	-	0.035
VD 0541	Soya bean (dry)	0.01*	-	0
AL 0541	Soya bean fodder	0.01*	-	0.01
AL 1265	Soya bean forage (green)	0.01*	-	0
FS 0012	Stone fruits	0.05*	-	0
GS 0659	Sugar cane	0.05	-	0.01
AV 0659	Sugar cane forage	0.2	-	0.03
VO 0447	Sweet corn (corn-on-the-cob)	0.05*	-	0.05
TN 0085	Tree nuts	0.2	-	0.05
FB 0019	Vaccinium berries, including Bearberry	W[1]	0.1	
GC 0654	Wheat	2	0.5	0.22
CF 0654	Wheat bran, processed	-	-	0.803
CF 1211	Wheat flour	-	-	0.024
	Wheat forage			20
AS 0654	Wheat straw and fodder, dry	100	-	7

[1]Replaced by recommendation for berries and other small fruits

[2]Included in MRL for Citrus fruits

[3]Replaced by recommendation for Rice, husked

DIETARY RISK ASSESSMENT

The International Estimated Daily Intakes of 2,4-D, based on the STMRs estimated for 26 commodities, for the five GEMS/Food regional diets were in the range of 3 to 10% of the ADI. The Meeting concluded that the intake of residues of 2,4-D resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

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DICLORAN (83)

EXPLANATION

Dicloran was evaluated for toxicology and residues in 1974 and 1977. An ADI was established in 1977.

Dicloran is a protective fungicide used to control *Botrytis, Monilinia, Rhizopus, Sclerotinia and Sclerotium* spp. on fruits and vegetables during the growing stages and/or post-harvest. The compound was evaluated at the present Meeting within the CCPR Periodic Review Programme.

The Meeting received data on residues and information on GAP from the manufacturers and the governments of The Netherlands, Poland and Germany.

IDENTITY

ISO common name: dicloran

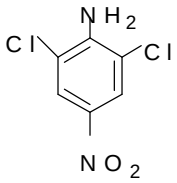
Chemical name
IUPAC: 2,6-dichloro-4-nitroaniline
CA: 2,6-dichloro-4-nitrobenzeneamine

CAS No: 99-30-9

Synonyms: DCNA, ditranil, RD 6584, U-2069, SN 107682

Trade names: Botran, Allisan, Fubotran, Fusan, Fubotec
Deccotrazil, Deccotran, Fumite

Structural formula:



Molecular formula: $C_6H_4Cl_2N_2O_2$

Molecular weight: 207.0 g/mol

Physical and chemical properties

Pure active ingredient

Colour: bright yellow

Bulk density: 0.277 g/cm^3

Melting point: 192-194 °C

Vapour pressure:	2.61×10^{-4} Pa at 25 °C (Bright, 1987)	
Solubility(g/l):	water:	0.0063
	cyclohexane:	0.06
	carbon tetrachloride:	0.6
	xylene:	3.6
	trichloroethylene:	3.8
	toluene:	4.5
	diethyl ether:	5.5
	methanol:	6.6
	chloroform:	12
	dioxane:	40
Octanol/water partition coefficient:	log P_{ow} 2.8 at 25°C (Knuth, 1984)	
Hydrolysis:	stable in buffer and solutions in the range pH5-9 at 25°C for at least 72 days (Jaglan, 1983c)	

Technical material

Guaranteed minimum purity:	95%
Typical purity:	≈98%
Melting range:	188-190°C
Storage stability:	stable at least three years under ambient conditions

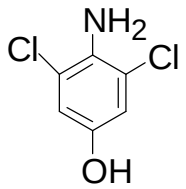
Formulations

The following formulations are commercially available
Wettable powder (75%): used for more than 80% of all pre- and post-harvest applications
Suspension concentrate (46%): used mainly for application to row crops by chemigation
Dust (6%): used mainly on vines
Premix (20% containing 20% dicloran and 7.5% imazalil): used for post-harvest use
Smoke generator formulations: used for glasshouse applications

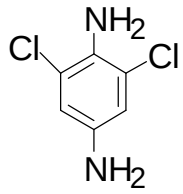
METABOLISM AND ENVIRONMENTAL FATE

The following abbreviations are used for dicloran metabolites and degradation products.

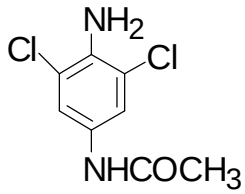
DCHA: 4-amino-3,5-dichlorophenol



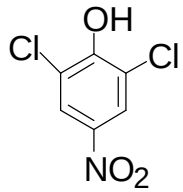
DCPD: 4-amino-2,6-dichloroaniline



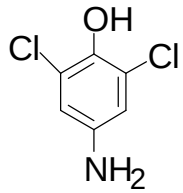
DCAA: 4-amino-3,5-dichloroacetoanilide



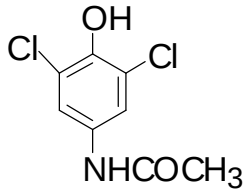
DCNP: 2,6-dicloro-4-nitrophenol



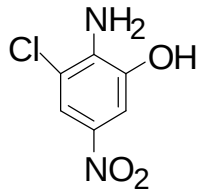
DCAP: 4-amino-2,6-dichlorophenol



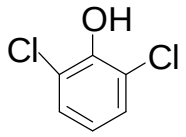
DCNAP: 3,5-dicloro-4-hydroxyacetanilide



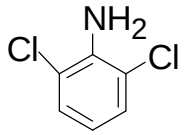
HNCA: 2-chloro-6-hydroxy-4-nitroaniline



2,6-DCP: 2,6-diclorophenol



2,6-DCA: 2,6-dicloroaniline



Animal metabolism

Metabolism has been studied in rats, goats and hens with [^{14}C]dicloran. Dicloran metabolism in animals involves reduction of the nitro group to amino, deamination and hydroxylation to phenolic derivatives, and acetylation at the amino group to form acetanilides.

Conjugation as glucuronate and/or sulfate at the N or O position and glutathione conjugation at the Cl position also apparently occurs.

The contribution of each of the metabolic reactions differs among the species examined. While DCHA and its conjugates were the predominant metabolites in rats, DCAA and DCNP were at higher levels than DCHA in goats and hens respectively.

Rats. Several metabolism studies were carried out with [^{14}C]dicloran.

(1) Single oral doses of [^{14}C]dicloran at nominal rates of 1.5 and 10 mg/kg bw were given to female Sprague-Dawley rat for 72 hours (Jaglan *et al*., 1985a; Jaglan and Arnold, 1985a)
(2) Single oral doses of [^{14}C]dicloran at 5 and 500 mg/kg bw were given to male and female Sprague-Dawley rat for 96 hours (O'Boyle and Challis, 1991a,b)
(3)Male and female Sprague-Dawley rats were given single doses of 500 mg/kg [^{14}C]dicloran or repeated doses of 5 mg/kg bw/day of the unlabelled compound for 14 days followed by single doses of 5 mg/kg of labelled material (Cheng, 1996a)

The total recovery of radioactivity was >94% in all the studies and >90% was excreted within 48 hours after dosing. In all cases the major route of excretion was the urine (72.3% to 90.2%). The faeces contained 7.97% to 22.4% of the radioactivity.

In experiment (2) the radioactivity in the expired air was monitored in the group dosed once with 5 mg/kg bw and no significant amounts of ^{14}C were detected, indicating that the molecule was not completely broken down (O'Boyle and Challis, 1991a). In experiment (3) residues in the tissues from the low dose after 7 days were highest in the liver (0.06 and 0.049 mg/kg in males and females respectively) and kidneys (0.016 and 0.015 mg/kg in males and females). All other tissue residues were at or below the limit of determination of 0.01 mg/kg (Cheng, 1996a).

The tissue residues 96 hours after single doses of 5 and 500 mg/kg bw (experiment 2) are shown in Table 1.

Table 1. ^{14}C residues in rats following single oral doses of [^{14}C]dicloran (O'Boyle and Challis, 1991a,b).

Sample	^{14}C, mg/kg as dicloran			
	5 mg/kg bw dose		500 mg/kg bw dose	
	Male	Female	Male	Female
Blood	<0.01	<0.01	2.84	4.06
Plasma	<0.02	<0.02	2.11	2.56
Liver	0.10	0.08	13.24	14.58
Kidney	<0.02	<0.02	3.28	3.98
Carcase	0.06	0.41[1]	1.10	1.20

[1]Thought to be contamination from urine

The major urinary metabolites from the repeated doses of 5 mg/kg and the single dose of 500 mg/kg were DCHA sulfate and DCHA glucuronide, together accounting for up to 79% of the total administered radioactivity. The metabolites DCHA, DCAP and DCNAP were also observed. The faeces from the rats dosed with 500 mg/kg contained a small amount of dicloran and many minor metabolites. Much of the radioactivity in the faeces was released only by acid hydrolysis and was thought to be from glutathione conjugates. In summary, similar metabolites were observed from repeated low doses and single high doses of dicloran. Table 2 shows the compounds detected in the urine and faeces (Cheng, 1996a).

Table 2. Compounds detected in rat urine and faeces after oral administration of [^{14}C]dicloran.

Compound	Urine, % of ^{14}C in dose				Faeces, % of ^{14}C in dose			
	Repeated low dose		Single high dose		Repeated low dose		Single high dose	
	Male	Female	Male	Female	Male	Female	Male	Female
dicloran	<0.1	<0.1	0.3	0.5	<0.1	<0.1	1.5	4.7
DCHA	3.3	22.8	4.6	6.8	0.6	1.2	0.3	1.1
DCPD	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DCAA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DCNP	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
DCAP	0.3	0.47	8.5	6.1	<0.1	<0.1	0.5	<0.1
DCNAP	<0.1	1.9	0.6	0.2	<0.1	0.1	<0.1	<0.1
HNCA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DCHA sulfate	63.4	32.8	21.9	21.5	0.6	0.1	2.9	0.6
DCHA glucuronide	15.6	22.2	23.6	28.6	<0.1	<0.2	<0.1	<0.1
A-1 [1]	1.1	1.0	<0.1	0.1	1.2	1.2	3.3	2.3
A-2 [1] HNCA	<0.1	1.7	<0.1	<0.1	0.1	<0.1	<0.1	<0.1
A-3 [1]	0.5	2.4	1.4	2.1	2.3	1.6	6.2	4.8
PES [3]	<0.1	<0.1	<0.1	<0.1	3.5	3.0	6.7	7.6
Total	84.2	85.3	61.1	65.4	8.3	7.4	21.4	21.1

[1]A-1- A-3: components derived from glutathione conjugates
[2]PES = Post-extraction solid. Radioactivity released by acid hydrolysis. Hydrolyates contained A-1, A-2 and A-3.

The study by Jaglan *et al*. (1985a) also indicated that the metabolite DCHA and its sulfate or glucuronide conjugates were found in urine from the 1.5 mg/kg bw and 10 mg/kg bw doses with a range of 58.8% to 70.4%. (The original report did not refer to the presence of the glucuronide conjugate, but hydrolysis was carried out with aryl sulfatase which would have glucuronidase activity.)

The nature of the residues in the liver was examined 72 hours after dosing at 10 mg/kg bw (Jaglan and Arnold, 1985a). Most of the radioactivity (>90%) was extracted from the liver with a

mixture of chloroform and methanol. TLC analysis showed that 5% of the liver residue was DCHA. Other polar metabolites were assumed to be its conjugates.

The metabolism of dicloran involved reduction, deamination and hydroxylation of the nitro group to yield the metabolite DCHA, then conjugation to form the major metabolites DCHA sulfate and DCHA glucuronide. DCAP was produced by reduction of the nitro group with deamination and hydroxylation of the original amino group, and *N*-acetylation of DCAP yielded DCNAP. A minor metabolic pathway involved dechlorination and hydroxylation to form HNCA. It appeared that the glutathione conjugation pathway was involved in forming minor metabolites. Proposed metabolic pathways are shown in Figure 1.

Goats. Jaglan *et al*. (1985a) dosed female goats with single 1.5 or 10 mg/kg bw doses of [^{14}C]dicloran and studied excretion and tissue distribution. In another study (Cheng, 1996b) a lactating goat received [^{14}C]dicloran for 5 consecutive days at an average level of 613 mg/day (12 mg/kg bw), equivalent to 359 ppm in the diet based on the actual feed consumption during the treatment period.

The total recoveries of radioactivity were 77.9% and 113.6% 72 hours after dosing from the single 1.5 mg/kg bw and 10 mg/kg bw doses respectively, and 88.7% 22 hours after the final dose from the lactating goat. The radioactivity excreted in the urine ranged from 33.0% to 68.9% and in the faeces from 43.3 to 44.9% in the three studies. The highest tissue residues were observed in the liver, 72 hours after the single doses and 22 hours after the last of the repeated doses. The concentrations of radioactivity in the blood and tissues are shown in Table 3.

Table 3. Concentrations of radioactivity in the blood and tissues after administration of [^{14}C]dicloran to goats (Jaglan *et al*., 1985a; Cheng, 1996b).

Sample	^{14}C, mg/kg as dicloran		
	Single dose, 1.5 mg/kg	Single dose, 10 mg/kg	Repeated doses
Blood	NA	NA	0.36
Liver	0.83	4.37	17.7
Kidney	0.03	0.17	1.39
Muscle	<0.01	0.01	0.111
Fat	<0.01	0.01	1.24
Milk (day 3)	-	-	3.57

NA: not analysed

The urine from the goats receiving single doses was extracted with ether. The aqueous fraction was hydrolyzed with aryl sulfatase, then again extracted with ether. Both ether fractions were co-chromatographed by TLC with authentic DCAA, DCPD and DCHA. DCAA and its conjugates in the urine from the high- and low-dose goats accounted for 3.3 to 5.6% of the urinary metabolites, but DCPD was not detected. After the enzymic hydrolysis, only 1.6% of the ^{14}C in the urine from the low-dose goat was from DCHA.

The nature of the residues in the liver and muscle of the goat dosed at 10 mg/kg bw was examined (Jaglan and Arnold, 1985a,b). A mixture of chloroform and methanol extracted almost all the radioactivity from muscle but only about 1% of it from the liver. The metabolite DCAA was isolated from the muscle extract (Jaglan and Arnold, 1985b).

In a study of the bio-availability of the bound residues in goat livers to rats about 8% of the administered radioactivity was found in rat urine and about 20% was extracted from the faeces, indicating that part of the bound residue in the goat liver was solubilized by the flora or environment of the rat gut (Jaglan *et al*., 1985b).

A detailed study of the metabolites in tissues and milk was conducted with the lactating goat after repeated doses of [^{14}C]dicloran (Cheng, 1996b). The extraction of ^{14}C from milk, liver, kidney, muscle and fat ranged from 65.2% in muscle to 93.6% in fat and milk. Dicloran accounted for 80.7% of the total radioactive residues in fat, 19.6% in milk and 15.7% in muscle. DCAA was found in muscle (35.0%), kidney (13.9%) and liver (11.9%). DCAP was found in milk (25.7%). DCHA, DCPD and DCNP individually constituted less than 5% of the radioactivity in the tissues and milk. Two metabolites (37% together) were isolated from the liver extract and identified as methylated 2,6-dichloro-4-nitro-3-glutathionylaniline and 4-amino-3-chloro-5-glutathionylacetanilide. The radioactivity in the post-extractions solids of liver and muscle were not sulfate or glucuronide conjugates. Most of the remaining radioactivity in the liver and muscle was released by protease hydrolysis. DCHA, DCNP, DCAA, and the glutathione conjugates were detected. Less than 10% of the radioactivity in the tissues and milk remained unidentified. The results are shown in Table 4.

Table 4. Compounds detected in goat tissues and milk collected 22 hours after the last of 5 daily oral doses of [^{14}C]dicloran (Cheng, 1996b).

Compound	^{14}C, % of TRR and (mg/kg as dicloran)				
	Liver	Kidney	Fat	Muscle	Milk
dicloran	<0.1 (<0.01)	<0.1 (<0.01)	80.7 (1.00)	15.7 (0.017)	19.6 (0.701)
DCHA	a	4.7 (0.062)	4.3 (0.053)	1.1 (<0.01)	1.1 (0.039)
DCPD	3.8 (0.677) b	4.9 (0.068)	<0.1 (<0.01)	3.0 (<0.01)	1.7 (0.062)
DCAA	11.9 (2.10)a	13.9 (0.193)	2.3 (0.028)	35.0 (0.039)	<0.1 (<0.01)
DCNP	1.6 (0.277)	3.4 (0.048)	<0.1 (<0.01)	1.1 (<0.01)	1.0 (0.036)
DCAP	b	3.4 (0.048)	<0.1 (<0.01)	<0.1 (<0.01)	25.7 (0.916)
DCNAP	<0.1 (<0.01)	<0.1 (<0.01)	<0.1 (<0.01)	<0.1 (<0.01)	<0.1 (<0.01)
A-1 [1]	37.0 (6.44)	35.3 (0.491)	1.0 (0.013)	3.0 (<0.01)	31.5 (1.12)
A-2	6.5 (1.15)	9.4 (0.131)	<0.1 (<0.01)	6.9 (<0.01)	3.6 (0.13)
A-3	a	<0.1 (<0.01)	<0.1 (<0.01)	<0.1 (<0.01)	<0.1 (<0.01)
PES [2]	30.5 (5.40)	23.6 (0.328)	<0.1 (<0.01)	35.7 (0.04)	4.9 (0.176)
Total	91.3	98.6	88.3	101.5	89.1

a: DCHA, DCAA and A-3 were co-eluted; DCAA was the major component
b: DCPD and DCAP were co-eluted; DCPD was the major component
[1] 4-amino-3-chloro-5-glutathionylacetanilide and methylated 2,6-dichloro-4-nitro-3-glutathionylaniline were isolated from the fraction.
[2] Radioactivity in PES was from the metabolites associated with protein. Of the 14% of the radioactivity in liver released by protease 10.4% was A-1, 24.1% DCPD/DCAP, 16.6% A-2, and 4.4% DCHA/DCAP/A-3. The remaining radioactivity was probably A-1.

In summary, the metabolism of dicloran in goats involves reduction of the nitro group to yield DCPD which is acetylated to DCAA. Deamination and hydroxylation of the amino group in DCPD yield DCHA or DCAP. Glutathione conjugation of dicloran can occur at either a chlorine substituent or ring hydrogen. Other minor polar metabolites are thought to be derived from the glutathione conjugation pathway. Proposed metabolic pathways are shown in Figure 1.

Laying hens. Dawson (1988) dosed hens for 3 days at 0.15 mg/bird/day (0.075 mg/kg bw/day) and killed them 24 hours after the last dose. Lipid-rich tissues such as egg yolk and fat contained mainly parent dicloran with no detectable metabolites. Egg white contained approximately equal amounts of dicloran and DCNP. Residues in the liver consisted essentially of dicloran (54.8%), DCAA (24.2%) and DCNP (21.0%).

In a further study (Cheng, 1996c) laying hens were dosed by capsule for 5 consecutive days at 0.24 and 3.8 mg/kg bw/day, equivalent to 3.1 and 50 ppm in the diet, and killed 22 hours after the last dose. The total recovery of radioactivity was 84.5% and 91.6% in the low- and high-dose groups respectively. Over 80% of the administered radioactivity was eliminated in the excreta, of

which 311% was parent compound. The entire egg production contained less than 0.6% of the total radioactivity. Less than 2% of the total dose was retained in all the tissues combined. The total distribution of radioactivity is shown in Table 5.

Table 5. Distribution of radioactivity in laying hens (Cheng, 1996c).

Sample	% of total radioactivity	
	Low dose	High dose
Blood	0.15	0.14
Skin with fat	0.23	0.35
Fat (abdominal)	0.71	0.80
Liver	0.60	0.49
Muscle (breast and thigh)	0.11	0.19
Subtotal	1.80	1.97
Egg whites	0.06	0.07
Egg yolks	0.48	0.24
Excreta	80.4	87.8
GI tract and wash	1.18	0.92
Paper wipe	0.60	0.57
Subtotal	82.7	89.6
Total	84.5	91.6

In the high-dose group, the level of radioactivity expressed as dicloran was 6.64 mg/kg in the abdominal fat, 2.98 mg/kg in the liver and 0.36 mg/kg in muscle. The egg yolks contained up to 2.38 mg/kg and egg whites up to 0.19 mg/kg. Dicloran was the major component in fat (94%), egg yolk (>80%) and egg white (up to 72%). DCNP was prominent in the liver (45-58%), egg white (28-33%) and muscle (11-14%) but constituted less than 3% of the residue in egg yolk and fat. DCAA constituted up to 29% of the residue in the muscle and 12% in liver, and DCNAP up to 33% and 2% respectively. Minor metabolites (each less than 10% of the residue in individual tissues and eggs) were DCHA, DCPD, DCAP, dicloran sulfate, dicloran *N*-acetylcysteine conjugate and 2-acetylthio-6-chloro-4-nitroaniline. The compounds detected are shown in Tables 6 and 7 (Cheng, 1996c).

Table 6. Compounds detected in hen tissues, low dose (Cheng, 1996c).

Compound	% of total ^{14}C in sample					
	Liver	Muscle	Fat	Egg white (Day 5)	Egg yolk (Day 6)	Excreta
Dicloran	5.1	8.0	93.8	59.7	87.5	3.0
DCHA	<0.1	<0.1	<0.1	<0.1	<0.1	17.9
DCPD	1.8	9.7	0.2	1.6	<0.1	16.4
DCAA	8.2	11.6	0.6	<0.1	<0.1	<0.1
DCNP	58.2	13.9	0.1	28.3	2.4	4.6
DCAP	<0.1	<0.1	<0.1	0.9	<0.1	3.8
DCNAP	1.1	33.4	<0.1	<0.1	<0.1	2.2
M-1 [1]	5.0	<0.1	<0.1	<0.1	<0.1	25.7
M-2 [2]	<0.1	<0.1	<0.1	<0.1	<0.1	4.6
Subtotal [3]	78.6	76.6	94.7	90.5	89.9	78.2
PES [4]	12.2	9.95	0.42	1.40	3.76	25.6
Total [3]	90.8	86.6	95.1	91.9	93.7	103

[1] Contained DCHA sulfate and 2-acetylthio-6-chloro-4-nitroaniline
[2] Contained dicloran *N*-acetyl cysteine conjugate
[3] Values listed as <0.1 taken as 0
[4] Post-extraction solid. After acid hydrolysis, the radioactivity was detected in the polar region (M-1)

Table 7. Compounds detected in hen tissues, high dose (Cheng, 1996c).

Compound	% of total ^{14}C in sample					
	Liver	Muscle	Fat	Egg white (Day 5)	Egg yolk (Day 6)	Excreta
dicloran	10.5	16.1	94.2	72.1	81.0	10.7
DCHA	1.3	<0.1	<0.1	<0.1	<0.1	13.8
DCPD	1.6	1.5	0.3	1.9	<0.1	7.6
DCAA	12.3	29.1	0.6	0.5	<0.1	<0.1
DCNP	44.9	11.0	0.2	32.6	2.4	5.3
DCAP	<0.1	<0.1	<0.1	1.1	<0.1	17.8
DCNAP	1.6	15.5	<0.1	<0.1	<0.1	1.2
M-1 [1]	4.3	<0.1	<0.1	<0.1	<0.1	17.8
M-2 [2]	0.3	<0.1	<0.1	<0.1	<0.1	6.1
Subtotal [3]	76.5	72.2	95.3	108.2	83.4	80.7
PES [4]	14.5	11.4	0.23	1.31	1.39	22.7
Total [3]	91.0	83.6	95.5	110.0	84.8	103

[1] Contained DCHA sulfate and 2-acetylthio-6-chloro-4-nitroaniline.
[2] Contained dicloran *N*-acetyl cysteine conjugate
[3] Values listed as <0.1 taken as 0
[4] Post-extraction solid. After acid hydrolysis, the radioactivity was detected in the polar region (M-1)

In summary, the metabolism of dicloran in hens involves deamination and hydroxylation of the amino group to yield DCNP; subsequent reduction and *N*-acetylation of the nitro group yields the minor metabolites DCAP and DCNAP. Reduction and *N*-acetylation of nitro group in dicloran yields DCPD and DCAA, and deamination and hydroxylation of DCPD gives DCHA. Sulfate conjugation occurs to form DCHA sulfate, and glutathione conjugation at a chlorine substitution site to form dicloran *N*-acetylcysteine conjugate. This is degraded to 2-acetylthio-6-chloro-4-nitroaniline. Proposed metabolic pathways are shown in Figure 1.

Plant metabolism

Metabolism studies were carried out with peaches, potatoes and lettuce; all showed similar metabolic profiles. In summary, the metabolism of dicloran in plants involves reduction and acetylation of the nitro group, with deamination and hydroxylation of the amino group. Glutathione conjugation with simultaneous removal of one or both chlorine atoms was shown to occur.

Peaches. Metabolism was investigated under field and glasshouse conditions (Smith, 1989). Peaches were treated 3 times at 7 day intervals with [^{14}C]dicloran formulated as a WP at the maximum field concentration of 130 g ai/hl with simulated commercial application. The field-grown peaches were treated with a total of 0.54 mg ai/fruit and the glasshouse peaches with 0.77 mg ai/fruit in an attempt to maximize residue levels for identification (Smith, 1989). The field peaches harvested 14 days after the third application contained a total radioactive residue of 1.65 mg/kg dicloran equivalents, of which 71.7% was extractable with solvent (hexane/acetone, acetonitrile, acetonitrile/water).

The glasshouse peaches harvested 18 days after the third treatment contained 14.07 mg/kg dicloran equivalents, 56.6% of which was solvent-extractable. The peach fibre (43.4%) was processed by hydrolysis with 6M sodium hydroxide, followed by Soxhlet extraction with acetonitrile, ethyl acetate and water, and finally hydrolysis with 4M hydrochloric acid to leave only 5.9% of the residue still bound to the fibre. After extensive treatment by TLC, HPLC and LCMS over 50% of the residue in the glasshouse peach fibre was identified. The low residue levels in the field-grown peach fibre precluded such detailed analysis.

The principal component in the residue was dicloran with its conjugate, 31.7% in glasshouse peaches and 51.3% in field peaches. The remainder comprised DCHA and conjugates

(10.9% glasshouse, 4.1% field), DCAA with its conjugate (7.9% glasshouse, 1.2% field), and conjugated DCPD (6.5% glasshouse, 2.2% field). In addition, DCAP (5.5%), 2,6-DCP (2.8%) and DCNP (1.2%) were isolated after hydrolysis of the glasshouse peach fibre. The remainder of the residue in both the field and glasshouse peaches comprised many minor components, none of which constituted more than 3.6% of the total residue. The results are shown in Table 8.

Table 8. Residues in glasshouse- and field-grown peaches.

Compound or fraction	% of total ^{14}C	
	Glasshouse	Field
dicloran	28.5	50.1
dicloran conjugate	3.2 [1]	1.2
DCHA	0.2	0.2
DCHA conjugate	10.7 [1]	3.9
DCPD	-	-
DCPD conjugate	6.5 [1]	2.2
DCAA	4.9	1.2
DCAA conjugate	3.0 [1]	-
DCNP	-	-
DCNP conjugate	1.2 [1]	-
2,6-DCP	-	-
2,6-DCP conjugate	2.8 [1]	-
DCAP	-	-
DCAP conjugate	5.5 [1]	-
Fibre-bound	43.4	23.2
Fibre-bound after hydrolysis and extraction	5.9	

[1] Includes metabolites derived from fibre as well as from hydrolysis of conjugates

It was noted however that some of the identified and unidentified residue recovered from the fibre may have been derived from the breakdown of dicloran under the extremely vigorous conditions required to release it. In control experiments, although base hydrolysis of [^{14}C]dicloran gave only DCNP, addition of untreated ‘control’ fibre to the hydrolysis resulted in entirely different products. The principal product was DCPD, with smaller amounts of all the 6 compounds isolated from the hydrolysis of treated fibre. There were in addition several components which had identical chromatographic properties to minor compounds found in the treated fibre which remained unidentified. No significant differences were observed between the metabolic profile of field and glasshouse peaches. Another metabolic study with glasshouse-grown peaches (Hawkins *et al*.,1988) under identical conditions gave similar results.

Potatoes. Seed pieces were planted under field conditions and treated with 8 broadcast applications of [^{14}C]dicloran approximately every two weeks at 1.8 kg ai/ha, just over the maximum label use rate, at a typical stage of growth. Mature tubers were harvested, with vines and roots, 14 days after the final application (O’Neal, 1997a). The total radioactive residue was determined by combustion and liquid scintillation counting. The radioactive residues were isolated by extracting with polar and non-polar solvents, acetonitrile and methylene chloride, and the extracts were hydrolysed with hydrochloric acid followed by sodium hydroxide. The hydrolysates were partitioned with methylene chloride and the unextracted plant solids were combusted to determine the total recovery of ^{14}C. From 26.9 to 37% of the radioactive residue in the tubers, vines and roots was extracted into acetonitrile and separated by high-performance liquid chromatography. Much of the radiocarbon was released by acidic and basic hydrolysis and the remaining bound radioactivity found in the fibre of the tubers, vines and roots was 2.7, 10.8 and 16.2% respectively. The distribution of the radioactivity is shown in Table 9.

Table 9. Distribution of radioactivity in potatoes treated with [^{14}C]dicloran.

Fraction	Root TRR = 6.79 mg/kg		Vine TRR = 74.52 mg/kg		Tuber TRR = 0.60 mg/kg	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Extracts:						
Acetonitrile	26.9	1.82	37.0	27.56	31.9	0.19
Dichloromethane	0.8	0.05	1.6	1.22	0.9	<0.01
Hydrolysates:						
Acid	13.7	0.93	13.4	9.95	41.7	0.25
Basic	24.7	1.68	26.1	19.42	9.3	0.06
Bound	16.2	1.10	10.8	8.03	2.7	0.02
Total recovery	82.3	5.58	88.8	66.18	86.6	0.52

The radioactive extracts were concentrated and analysed by high-performance liquid chromatography, the retention times of radioactive peaks being compared with those of authentic labelled and unlabelled standards. The ^{14}C in the peaks was measured by liquid scintillation counting. Identifications were confirmed by thin-layer chromatography. Dicloran was found in all the samples, and DCNAP, DCAA, DCHA and 2,6-DCA in some of them. Unknown 1, a polar component in the acid and/or base hydrolysates, accounted for 30-50% of the total ^{14}C. It was characterized as a mixture of glutathione conjugates. Six other unidentified components were present, each [0.03 mg/kg. The composition of the residues is shown in Table 10.

Table 10. Residues in potatoes after application of [^{14}C]dicloran.

Compound or fraction	Root		Vine		Tuber	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
dicloran	25.68	1.74	39.17	29.19	10.81	0.06
DCAA	ND	ND	0.16	0.12	0.76	<0.01
DCNAP	ND	ND	0.80	0.60	ND	ND
DCHA	ND	ND	0.64	0.48	14.91	0.09
2,6-DCA	0.38	0.03	ND	ND	ND	ND
Unknown 1	35.45	2.42	30.22	22.52	49.55	0.30
Unknown 2	0.24	0.02	ND	ND	ND	ND
Unknown 3	1.46	0.10	ND	ND	NA	NA
Unknown 4	ND	ND	ND	ND	0.15	<0.01
Unknown 5	ND	ND	ND	ND	1.49	0.01
Unknown 6	ND	ND	ND	ND	4.18	0.03
Unknown 7	ND	ND	ND	ND	0.28	<0.01
Unextractable	16.20	1.10	10.80	8.03	2.70	0.02
Total	79.41	5.41	81.79	60.94	84.83	0.51

ND: not detected
NA: not analysed

The metabolism of dicloran involved reduction and acetylation of the nitro group and deamination and hydroxylation of the amino group(s). Glutathione conjugation at one or both of the chlorine atoms also appears to occur. The minor metabolites are likely to be derived from the glutathione conjugation pathway.

Lettuce. Seeds were planted under field conditions and [^{14}C]dicloran was applied broadcast at 4.9 kg ai/ha, slightly over the maximum label use rate, according to typical agricultural field practices (O'Neal, 1997b). Mature lettuce were harvested after twenty days. The total radioactive residue was

determined by combustion and liquid scintillation counting. The radioactive residues were isolated by extracting with acetonitrile, acetonitrile/water, water, methanol and methylene chloride, and the extracts were hydrolysed with hydrochloric acid followed by sodium hydroxide. The hydrolysates were partitioned with methylene chloride and the unextracted plant solids were combusted to determine the total ^{14}C. The results are shown in Table 11.

Table 11. Distribution of radioactivity in lettuce treated with [^{14}C]dicloran.

Fraction	TRR = 13.31 mg/kg as dicloran	
	% of TRR	mg/kg
Extracts:		
Acetonitrile	73.2	9.75
Acetonitrile/water (1:1)	2.5	0.33
Water	1.5	0.20
Dichloromethane	0.5	0.06
Methanol	0.4	0.05
Hydrolysates:		
Acid	8.9	1.19
Basic	8.6	1.15
Bound	8.4	1.12
Total recovery	104.0	13.85

Seventy-three per cent of the radioactive residue was extracted into acetonitrile and analysed by HPLC. About 9% of the radiocarbon was in the acid and base fractions, and about 8% remained as bound material. The radioactive extracts were concentrated and analysed by high-performance liquid chromatography, the retention times of radioactive peaks being compared with those of authentic labelled and unlabelled standards. The ^{14}C in the peaks was measured by liquid scintillation counting. Identifications were confirmed by thin-layer chromatography. The results are shown in Table 12.

Table 12. Residues in lettuce after application of [^{14}C]dicloran.

Compound or fraction	^{14}C	
	% of TRR	mg/kg as dicloran
Dicloran	73.91	9.84
DCAP	0.28	0.03
DCPD	0.04	<0.01
DCNAP	0.37	0.05
DCAA	0.06	0.01
DCHA	0.04	0.01
DCNP	0.02	<0.01
2,6-DCP	0.02	<0.01
2,6-DCA	0.28	0.04
Unknown 1	6.48	0.86
Unknown 2	2.28	0.30
Unknown 3	0.03	<0.01
Unknown 4	2.84	0.38
Unknown 5	0.01	<0.01
Unknown 6	0.06	0.01
Unknown 7	0.11	0.01
Unknown 8	0.01	<0.01
Unknown 9	0.03	<0.01
Unknown 10	0.02	<0.01
Bound	8.4	1.12
Total	95.29	12.66

Dicloran was the major component of the extractable residues. A small amount of DCAP was also observed. All the identified metabolites listed in Table 12 were observed in the organic fraction from the acid hydrolysate, and the ten unidentified components were detected in the aqueous and organic phases after partitioning the acid and base hydrolysates. None of these ten exceeded 5% of the TRR in an individual hydrolysate; their total in all the hydrolysates accounted for about 12% of the TRR. Unknown 1 was the main component at 6.48% of the TRR and was later shown to be a mixture. The residues were too low to characterize unknown 1 further but it showed the same characteristics as the corresponding unknown 1 from potatoes and was therefore likely again to be a mixture of glutathione conjugates. The pattern of metabolism was similar to that in potatoes.

Environmental fate in soil

Photodegradation

In a study of photolysis on a microbially active sandy loam soil (Misra, 1995b) [^{14}C]dicloran was applied at the rate of 5.0 µg/g and the soil was maintained at or near 75% field moisture capacity at 1/3 bar and 25 ± 1°C for 15 days under xenon light which simulated the solar spectrum at a constant intensity with an output of 279 W/m^2 at 440 nm. Samples taken at 0, 24, 64, 136, 236 and 360 hours were extracted and analysed by LSC and HPLC. Volatile compounds were trapped and analysed similarly. The recovery of radiocarbon was 91.5 ± 5.5%. After 360 hours of continuous irradiation, 88% of the applied dicloran had been lost from the soil by a combination of degradation and volatilization. About 37% of the applied radioactivity was associated with volatile compounds, 23% with carbon dioxide. The remaining volatile radioactivity was due to a mixture of at least four components. About 18% of the applied radioactivity remained unextracted. None of the photoproducts in the soil extracts accounted for more than 10% of the applied radioactivity. After 360 hours in the dark control, 83.93%, 4.26% and 0.55% of the applied radioactivity was found in the extracted, bound and volatile fractions respectively. The estimated half-life of the irradiated dicloran based on first-order kinetics was 123 hours, and that of dicloran in the dark control 1932 hours. The half-life estimated from the net photolysis rate constant was 132 hours. The distribution of the radioactivity is shown in Tables 13 and 14 and the results of the HPLC analysis of the irradiated soil extracts in Table 15.

Table 13. Distribution of radioactivity in fractions from irradiated and unirradiated soil treated with dicloran.

Fraction	% of applied radioactivity					
	0 h	24 h	64 h	136 h	236 h	360 h
Extracted I	97.38	76.93	60.19	45.64	35.59	27.40
D	97.38	91.73	89.89	91.37	84.30	83.93
Bound I	0.27	10.10	16.68	14.78	19.47	18.09
D	0.27	1.32	2.85	2.97	4.80	4.26
Volatile I	NA	1.31	6.26	13.47	23.10	36.68
D	NA	0.19	0.27	0.35	0.43	0.55
Total I	97.65	88.34	83.12	73.89	78.15	82.17
D	97.65	93.23	93.00	94.70	89.53	88.73

NA: not analysed
I: irradiated
D: dark control

Table 14. Distribution of volatile radioactivity from irradiated dicloran.

Location	% of applied radioactivity					
	0 h	24 h	64 h	136 h	236 h	360 h
NaOH trap	NA	0.81	4.83	10.52	15.51	23.33
Ethylene glycol trap	NA	0.20	0.41	0.56	4.02	4.07
Test vessel	NA	0.31	1.02	2.39	3.56	9.28
Total	NA	1.31	6.26	13.47	23.10	36.68

NA: not analysed

Table 15. Results of HPLC analysis of extracts of irradiated soil.

Compounds	% of applied radioactivity					
	0 h	24 h	64 h	136 h	236 h	360 h
Dicloran	97.38	73.25	55.53	41.70	21.57	12.10
Unknown 1	ND	1.57	4.65	2.49	9.32	9.30
Unknown 2	ND	2.11	ND	1.44	4.69	6.00
Total	97.38	76.93	60.18	45.63	35.58	27.40

ND: Not detected

Degradation under aerobic and anaerobic conditions

The degradation of dicloran in Cambridge sandy loam and Suffolk sand was examined under aerobic and anaerobic conditions in the laboratory (Arnold and Allen, 1988). The moist soils, equivalent to 100g of air-dried soil, in 250 ml Erlenmeyer flasks were treated with [^{14}C]dicloran in acetone at a concentration equivalent to a field application rate of 4.5 kg ai/ha.

For the aerobic study, the soils were adjusted to 40% moisture holding capacity with distilled water and incubated at 25ºC in the dark for 12 months. Throughout the incubation period, a continuous stream of carbon dioxide-free air was supplied to the flasks and evolved $^{14}CO_2$ was trapped in ethanolamine.

In one study of anaerobic degradation, the soils were treated with [^{14}C]dicloran and after 2 hours flooded with distilled water to a level of about 2 cm above the soil surface, then incubated at

25ºC in the dark for up to 60 days. The flasks were supplied with air and connected to ethanolamine traps.

In a second anaerobic experiment the soil was treated with [^{14}C]dicloran and maintained under aerobic conditions as above for 30 days before flooding and incubation as before for 6 months. Radioactivity in the trapping solutions was quantified at intervals by liquid scintillation counting (LSC), and soil samples were Soxhlet-extracted with dichloromethane followed by the more polar acetonitrile/water (8:2). The flooded soils were filtered before Soxhlet extraction.

The bound residues were investigated in four flooded soil samples after incubation for 2-4 months. The Soxhlet-extracted soils were dried, milled and re-extracted by Soxhlet with dichloromethane followed by acetonitrile/water. The soils were transferred to Erlenmeyer flasks and extracted under nitrogen with 0.1M sodium hydroxide for 18 hours at room temperature. The extracts were centrifuged and filtered, and the caustic solutions acidified with concentrated hydrochloric acid to pH 1. The acid extracts were filtered to separate the filtrate (fulvic acid fraction) from the insoluble humic acid fraction. The acid-insoluble residue was then methylated with diazomethane or extracted with methanol. Portions of the original dichloromethane and acetonitrile/water extracts and the methanol extracts of the humic acid fraction were concentrated to near dryness and redissolved in dichloromethane or acetonitrile/water for analysis by TLC and HPLC against authentic reference standards.

The recoveries of the applied radioactivity averaged 93 and 90% for the aerobically incubated sandy loam and sand respectively, 89 and 80% for the unaged anaerobic soils and 89 and 86% for the aged anaerobic. Radioactivity was detected in the ethanolamine traps from all the soils. In general, the evolution of volatile radioactivity from sand was slightly faster than from sandy loam and that from flooded soil slightly faster than from soil under aerobic conditions after the same incubation period. The radioactivity trapped in ethanolamine was assumed to be from $^{14}CO_2$.

In aerobically incubated soils most of the radioactivity was extracted with dichloromethane initially but the proportion decreased with time. There were concomitant increases in the acetonitrile/water-extractable and unextractable radioactivity. The extractable radioactivity decreased from approximately 90% at zero time to 64% and 26% after 12 months in sandy loam and sand respectively, with approximately 20% and 50% unextractable. The distribution of the radioactivity in the aerobic soils is shown in Table 16.

The major radiolabelled component in the aerobic soil extracts was unchanged dicloran. Small quantities (<1%) of DCPD, DCAA and DCHA were observed. Other products and polar radioactivity retained at the origin of the TLC plate accounted for 3% or less of the applied radioactivity. Assuming first-order degradation kinetics the half-life of dicloran was approximately 6 months in the sand and 18 months in the sandy loam. The compounds identified under aerobic conditions are shown in Table 17.

Table 16. Distribution of radioactivity from soil treated with [^{14}C]dicloran under aerobic conditions.

Fraction	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)								
	2 h	7 days	14 days	30 days	2 m	3 m	6 m	9 m	12 m
CH_2Cl_2 extract	89.5 87.2	87.8 92.5	92.7 89.6	86.8 83.5	95.1 76.9	78.9 63.1	63.6 42.2	67.6 33.4	56.1 20.3
Acetonitrile/ water extract	0.5 0.3	1.2 0.7	1.6 1.1	2.6 1.6	3.9 4.2	4.5 3.4	7.4 2.7	10.3 6.5	7.9 5.3
Unextracted	1.0 0.6	1.4 1.3	2.2 2.2	3.0 4.2	5.4 12.4	9.7 22.0	13.8 36.9	16.9 43.7	19.4 50.7
Carbon dioxide	NA NA	0.1 0.1	0.1 0.2	0.2 0.2	0.4 0.7	0.8 1.5	1.9 2.8	2.3 5.4	2.8 7.6
Total recovered	91.0 88.1	90.5 94.6	96.6 93.1	92.6 89.5	104.8 94.2	93.9 90.0	86.7 84.6	97.1 89.0	86.2 83.9

NA: not analysed

Table 17. Residues in soil treated with [^{14}C]dicloran under aerobic conditions.

Compound	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)								
	2 h	7 days	14 days	30 days	2 m	3 m	6 m	9 m	12 m
Dicloran	89.8 83.9	89.7 89.9	93.9 88.3	82.9 81.0	94.6 73.7	78.6 64.7	63.1 41.6	75.9 36.8	58.3 21.8
DCPD	ND ND	ND <0.1	ND 0.1	ND 0.1	0.1 0.2	0.2 0.1	ND 0.4	ND 0.1	ND ND
DCAA	ND ND	ND 0.1	ND <0.1	ND ND	0.1 0.2	ND ND	ND 0.1	ND 0.3	ND ND
DCHA	ND ND	ND ND	ND ND	ND ND	ND ND	0.2 ND	ND ND	ND 0.1	ND 0.1
Other products	ND <0.1	0.2 1.7	0.1 2.2	1.5 0.2	0.1 0.4	0.8 0.1	0.2 0.2	0.5 1.0	1.4 0.5
Origin, TLC	0.3 0.9	0.7 0.7	0.6 0.7	1.1 1.1	0.9 0.5	2.2 1.0	0.2 0.5	0.6 0.6	1.1 2.2
Total	90.1 84.8	90.6 92.4	94.6 91.3	85.5 82.4	95.8 75.0	82.0 65.9	63.5 42.8	77.0 38.9	60.8 24.6

ND: not detected

In anaerobically incubated soils more radioactivity was extracted with the polar solvent mixture and the rate of increase of bound residues was much greater than in the aerobic experiments. Degradation of dicloran in the flooded soils was also much faster. First-order half-lives were approximately 5 days for sand and 10 days for sandy loam without aerobic pre-incubation and 30 days for both types of soil with aerobic pre-incubation. Less than 11% of the applied radioactivity was present in the surface water of the flooded soils, in most samples less than 5%. Examination of the soil extracts by TLC showed the radioactive degradation products to include DCPD (5% and 12% in sandy loam and sand respectively) and DCAA and/or DCHA (up to 6% and 8%). These products were degraded to more polar products, including material remaining at the origin of the TLC plates, which accounted for up to 18% and 15% of the applied radioactivity in sandy loam and sand respectively. The distribution of the radioactivity from the two anaerobic studies is shown in Tables 18 and 19, and identification of the residues in Tables 20 and 21.

Table 18. Distribution of radioactivity from soil treated with [^{14}C]dicloran under anaerobic conditions without aerobic ageing.

Fraction	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)				
	2 hours	7 days	14 days	30 days	60 days
Surface water	9.7 8.0	4.3 2.6	5.4 2.6	0.9 4.5	0.7 1.5
CH_2Cl_2 extract	37.3 44.2	32.0 32.7	23.3 17.8	14.4 7.3	7.8 4.6
Acetonitrile/ water extract	39.5 21.8	48.7 30.4	33.7 29.1	25.2 16.2	25.0 17.1
Unextracted	2.5 3.6	9.7 17.9	29.3 31.4	45.1 48.9	51.2 55.7
Carbon dioxide	NA NA	0.1 0.1	0.1 0.2	0.4 0.8	0.9 1.1
Total recovered	98.0 77.6	94.8 83.7	91.8 81.1	86.0 77.7	85.6 80.0

Times are after flooding.
N.S.: no sample
NA: not analysed

Table 19. Distribution of radioactivity from soil treated with [^{14}C]dicloran under anaerobic conditions with aerobic pre-ageing.

Fraction	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)					
	2 hours	30 days	2 m	3 m	4 m	6 m
Surface water	5.8 5.9	2.3 6.1	1.3 2.0	0.8 1.2	0.5 0.6	0.3 N.S.
CH_2Cl_2 extract	42.8 42.9	24.7 26.4	16.9 10.9	11.3 3.9	4.0 2.2	3.4 1.9
Acetonitrile/ water extract	34.9 28.9	37.2 20.8	34.0 7.7	20.6 9.3	20.7 6.9	15.1 7.0
Unextracted	3.8 4.9	22.9 35.0	39.8 58.2	54.0 67.3	63.8 70.8	65.4 78.5
Carbon dioxide	0.2 0.3	0.3 0.6	0.6 2.0	1.2 3.3	1.7 5.1	2.5 6.3
Total recovered	87.5 82.9	87.4 88.9	92.6 80.8	87.9 85.0	90.7 85.6	86.7 93.7

Times are after flooding.
N.S.: no sample

Table 20. Residues in soil treated with [^{14}C]dicloran under the anaerobic conditions without aerobic ageing.

Compound	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)				
	2 h	7 days	14 days	30 days	60 days
Dicloran	71.8 73.4	73.6 50.5	35.3 12.0	6.8 2.2	1.6 2.7
DCPD	4.4 0.9	0.5 11.9	2.1 11.9	2.9 1.1	3.8 6.5
DCAA	2.4 1.8	1.2 0.9	4.0 7.4 (a)	4.9 6.0 (b)	3.8 1.3
DCHA	ND ND	ND ND	ND (a)	<0.1 (b)	1.7 ND
Other products	0.5 ND	1.1 2.4	9.2 8.2	13.6 11.5	10.4 4.6
Origin, TLC	2.2 1.0	4.2 3.0	1.2 4.2	4.3 3.0	7.5 5.9
Total	81.3 77.1	80.6 68.7	51.8 43.7	32.5 23.8	28.8 21.0

Times are after flooding
ND: not detected
(a) and (b): regions of radioactivity not clearly separated on TLC

Table 21. Residues in soil treated with [^{14}C]dicloran under anaerobic conditions with aerobic pre-ageing.

Compounds	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)					
	2 h	30 days	2 m	3 m	4 m	6 m
Dicloran	75.2 71.4	54.4 29.8	28.6 7.7	12.1 5.9	4.5 2.2	4.1 1.6
DCPD	0.2 0.2	0.2 7.5	1.1 2.4	1.4 2.2	1.1 ND	1.0 1.2
DCAA	0.2 0.3	0.9 1.3	3.7 (a) 0.4	4.6 (b) 0.2	2.3 (c) ND	0.3 (d) 0.1
DCHA	ND ND	ND 0.2	(a) ND	(b) ND	(c) ND	(d) ND
Other products	0.2 2.2	4.1 2.8	5.4 2.8	4.6 3.2	7.1 4.2	6.0 1.8
Origin, TLC	3.9 2.6	5.4 8.3	4.9 1.8	7.0 1.7	5.9 2.0	5.7 3.8
Total	79.7 76.7	65.1 49.9	43.7 15.1	29.7 13.2	20.9 8.4	17.1 8.5

Times are after flooding
ND: not detected
(a), (b), (c) and (d): regions of radioactivity not clearly separated on TLC

Re-extraction of the dried and milled soils with dichloromethane followed by acetonitrile/water released a further 0.4-4.8% of the applied radioactivity, and up to 19% was extracted with sodium hydroxide (0.1M). The radioactivity present in this extract was considered to be associated with the humic and fulvic acid fractions of the soil organic matter. Acidification of this extract left between 2% and 4% in the fulvic acid supernatant, the remainder being associated with the precipitated humic acid fraction. Extraction of the humic acids with methanol released up to 4% of the applied radioactivity, partially resolved by reversed-phase TLC. Small quantities (<0.2% of the applied radioactivity) of dicloran, DCPD, DCAA and DCHA were observed but most of radioactivity (up to 2.8%) was characterized as polar. Most of the soil-bound residue (about 25% and 40% of the applied radioactivity in sandy loam and sand respectively) was still retained in the

soil even after caustic extraction, and this material was not extracted by a 2% aqueous solution of hydrofluoric and hydrochloric acids. The results of basic and acidic treatments are shown in Table 22.

Table 22. Fractionation of bound soil residues.

Fraction	^{14}C, % of applied			
	Sandy loam		Sand	
	Flooded, unaged	Flooded with aerobic ageing	Flooded, unaged	Flooded with aerobic ageing
	2 m	3 m	2 m	4 m
CH_2Cl_2 extract after milling	0.2	0.5	0.2	0.5
Acetonitrile/ water extract	3.6	1.9	0.2	4.3
NaOH extract	19.0	12.9	11.8	16.1
Fulvic acid	2.9	2.1	2.7	3.6
Humic acid extract	0.4	ND	3.1	3.8
Humic acid residue	NA	5.8	NA	NA
Soil residue	24.2	24.9	35.0	41.9
Total	47.0	40.2	47.2	62.8

NA: not analysed ND: not detected

Field dissipation. The degradation of dicloran was examined in bare Foster fine sandy loam soil in the San Joaquin Valley of central California (Kliskey, 1997). Formulated dicloran (WP) was applied to the plot at the maximum use rate of 4.5 kg ai/ha with a boom sprayer using 960 l/ha spray volume. Core samples from control and treated plots were taken to a depth of 120 cm one day before application, immediately after application, and then at intervals of 1, 7, 14 and 20 days and 1, 2, 3, 4, 5, 6, 9, 12, 15 and 18 months. The cores were subdivided into 15 cm segments and analysed for residues of the parent compound, DCAA and DCHA.

Dicloran was dissipated with a half-life of 32.8 days and was not detected 15 months after application. Dicloran *per se* showed little tendency to leach below 15 cm even when exposed to at least 110% of the 10-year mean precipitation and otherwise typical weather conditions. No degradation products were detected in any of the samples throughout the study, except DCHA on day 0. The results are shown in Table 23.

Table 23. Residues in soil after dicloran application.

Period after treatment	Depth, cm	Dicloran, mg/kg	DCHA, mg/kg	DCAA, mg/kg
0 day	0-15	1.90	0.26	<0.05
	15-30	<0.05	<0.25	<0.05
1 day	0-15	1.64	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
7 days	0-15	0.84	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
14 days	0-15	1.25	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
20 days	0-15	0.89	<0.25	<0.05
	15-30	0.08	<0.25	<0.05
1 m	0-15	1.06	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
2 m	0-15	0.40	<0.25	<0.05

Period after treatment	Depth, cm	Dicloran, mg/kg	DCHA, mg/kg	DCAA, mg/kg
	15-30	<0.05	<0.25	<0.05
6 m	0-15	0.26	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
12 m	0-15	0.15	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
18 m	0-15	<0.05	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05

Environmental fate in water and water/sediment systems

Hydrolysis

The hydrolysis of dicloran in aqueous buffer solutions at 25°C was measured by Jaglan and Arnold (1983). Approximately 1 mg of [^{14}C]dicloran was added to 500 ml of sterilized 0.01 and 0.05 M solutions of phthalate buffer (pH 5), phosphate buffer (pH 7) and borate buffer (pH 9). The solutions were maintained at 25 ± 1.0°C in darkness. Twenty five ml aliquots in duplicate from each solution were taken at 0, 3, 7, 14, 21, 37 and 72 days and extracted with dichloromethane. The radioactivity in the aqueous and dichloromethane phases was determined by LSC, and dicloran in the dichloromethane phase by GLC. There were no significant changes in any of these throughout the experimental period at any pH.

Photolysis.

Brehm (1987) irradiated aqueous 10 mg/l solutions of [^{14}C]dicloran in pH 7, 0.02M, phosphate buffer containing 1% of acetonitrile with filtered light from a mercury arc lamp in a carousel photoreactor for approximately 120 hours. The light intensity in the 290-430 nm region where dicloran absorbs, measured by chemical actinometry, was of the same order as that of natural sunlight in summer at moderate northern latitudes. The half-life of dicloran under these conditions according to first-order kinetics was 41.0 hours. Estimation of the quantum yield for the photodegradation of dicloran gave a value of 2.58 x 10^{-5} molecules degraded/photon absorbed. Using this value and solar intensity data, extrapolation to environmental conditions with the computer programme GCSOLAR gave half-lives of 1.6-8.0 days depending on season and latitude. Reverse-phase HPLC-chromatograms of the photolysis solutions showed only one peak for dicloran and one broad peak at the front of the chromatograms indicating polar or polymer products whose amounts were too small for isolation and identification.

In a study with filtered light from a xenon arc lamp (Misra, 1995) aqueous solutions of [^{14}C]dicloran (approximately 3 mg/l) in pH 7, 0.01M, phosphate buffer containing 0.4% of acetonitrile were irradiated and the head-space of the reaction vessel purged with carbon dioxide-free air. Volatile radioactivity was trapped in ethanolamine. The sampling intervals were 0, 20, 30, 40, 65, 90, 185 and 360 hours. The irradiation source simulated the solar spectrum at a constant intensity. The radioactivity in the test and ethanolamine solutions at each sampling was determined by LSC and the concentrations of dicloran and its degradation products in the test solutions by HPLC.

Dicloran in the test solution was degraded completely in 90 hours to a mixture of products which were characterized by HPLC and mass spectrometry. HPLC analysis suggested at least six oxygenated aromatic compounds in the irradiated solution and mass spectrometry further indicated the presence of five or six chlorine atoms. The compounds were apparently from polymeric materials generated by reactions of dicloran and its primary degradation products. The exact

number of products was uncertain because their HPLC peaks overlapped, but most of them accounted for less than 10% of the applied radioactivity. The results are shown in Table 24. The half-life of dicloran was calculated by first-order regression analysis to be 23.6 hours under continuous irradiation. Dicloran in the dark controls was not degraded during the study.

Table 24. Distribution and characterization of radioactivity in irradiated solutions of dicloran.

Fraction	% of applied radioactivity							
	0 h	20 h	30 h	40 h	65 h	90 h	185 h	360 h
Test solution	100	100	98.43	95.53	88.99	83.37	71.79	63.28
Dicloran	100	58.48	46.17	31.96	14.99	Trace	ND	ND
Unknown 1	ND	20.78	35.41	46.46	67.73	83.37	71.79	63.28
Unknown 2	ND	14.13	15.42	13.12	4.64	ND	ND	ND
Unknown 3	ND	6.61	1.43	3.99	1.63	ND	ND	ND
Volatile	NA	0.28	0.54	1.37	3.22	4.18	5.06	7.28
Total	100	100.28	98.97	96.90	92.21	87.55	76.85	70.56

Fate in water/sediment systems

The degradation of dicloran in a water/sediment system was examined in the laboratory under anaerobic conditions for 59 days (Wisocky, 1995). Approximately 24 g of pond sediment (equivalent to 10 g dry weight) and 60 ml of pond water obtained from Delton Davis farm pond were taken into flasks. Approximately 1% (0.7g) glucose was added to each flask, and the flasks purged with nitrogen. The prepared flasks were incubated at 25°C in the dark for at least 30 days to ensure anaerobic conditions. One day into the incubation period polyurethane plugs were connected to the flasks and the flasks re-purged with nitrogen. After ageing for about 30 days, the water layers were spiked with [^{14}C]dicloran at a rate of 2.25 mg/kg, and traps containing 10 ml of 1N potassium hydroxide were immediately connected in series with the foam plugs. The flasks were again purged with nitrogen, stoppered and incubated at 25°C. Samples were taken after 0, 2, 4, 8 and 12 hours and 1, 2, 3, 7, 14, 30 and 59 days.

The contents of the flasks were filtered, the supernatant was partitioned with dichloromethane and the sediment extracted with a mixture of acetonitrile and 0.01N hydrochloric acid followed by methanol. The remaining solid residue was designated as post-extraction solids (PES). The acidic acetonitrile extracts were partitioned with dichloromethane to yield organic and aqueous fractions. The organosoluble extracts were then concentrated for chromatographic analysis. The PES fraction from day 59 was refluxed with methanol for 24 hours, then with 0.25 N hydrochloric acid for 1 hour. The hydrochloric acid fraction was partitioned with ethyl acetate. The remaining solids were extracted with 0.5 N sodium hydroxide for 24 hours at room temperature. The sodium hydroxide extract was acidified with concentrated hydrochloric acid and centrifuged to separate the supernatant fulvic acid fraction from the precipitated humic acids.

The average percentage of radioactivity in the original pond supernatant fraction decreased from 23.26% to 1.31% of the total applied radioactivity during the period from 0 to 59 days, and the proportion of radioactivity that could be extracted from the sediment into acidic acetonitrile decreased from 71.70% to 4.68%. The radioactivity in the methanol fraction remained approximately constant however, ranging from 1.51% (59 days) to 4.83% (8 hours). The percentage of the radioactivity in the PES fraction increased sharply from 0.62% to 86.21%. The evolved volatiles trapped in the potassium hydroxide and the foam plug remained fairly constant: the total trapped never exceeded 0.37% of the applied radioactivity found at 59 days. Total recoveries of the

applied radioactivity ranged from an average of 94.70% to 100.5%. The distribution of radioactivity is shown in Table 25.

Table 25. Distribution of radioactivity in a water/sediment system after incubation.

Fraction	% of applied radioactivity											
	0 time	2 h	4 h	8 h	12 h	24 h	2 days	3 days	7 days	14 days	30 days	59 days
Supernatant	23.26	14.75	13.08	12.37	11.35	8.04	6.15	5.94	3.04	2.84	2.81	1.31
CH_2Cl_2 phase	23.13	14.62	12.77	12.13	11.05	7.84	5.78	5.55	2.77	2.40	1.58	0.40
Aqueous phase	0.13	0.14	0.32	0.24	0.30	0.20	0.38	0.39	0.27	0.44	1.23	0.82
CH_3CN and water extract	71.70	73.97	62.46	59.15	49.05	44.43	38.45	30.37	19.23	11.21	9.91	4.68
CH_3CN/CH_2Cl_2 phase	71.69	73.94	62.30	59.01	48.84	44.29	38.28	30.21	19.07	10.97	9.72	4.51
Aqueous phase	0.01	0.04	0.16	0.15	0.22	0.15	0.17	0.16	0.17	0.24	0.19	0.17
Methanol extract	3.90	4.40	4.31	4.83	4.21	4.39	4.66	3.99	3.51	2.58	2.25	1.51
PES	0.62	4.65	18.59	24.14	34.78	39.87	47.51	55.41	70.68	81.13	80.59	86.21
Volatiles in KOH	NA	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.02	0.14	0.11	0.31
Volatiles in foam plug	NA	0.02	0.02	0.03	0.04	0.07	0.05	0.17	0.05	0.22	0.09	0.06
Total	99.47	97.79	98.46	100.5	99.43	96.80	96.84	95.90	96.52	98.11	95.74	94.07

NA: not analysed

TLC of the organosoluble extracts of the water and sediments showed that the parent compound decreased from 98.0% at time 0 to 45.7% at 12 hours and less than 1% at 59 days. In addition to the parent compound a total of 9 degradation products were detected. These were designated as Met-1 to Met-9. Met-3, Met-5, Met-6 and Met-7 were identified as DCNAP, DCHA, DCAA and DCPD respectively by TLC and/or HPLC co-chromatography. They reached their maximum respective levels of 0.4% at 14 days, 5.1% at 3 days, 6.2% at 14 days and 7.4% at 12 hours. Met-1, Met-2, Met-4, Met-8 and Met-9 could not be identified but they did not individually exceed about 5% of the applied radioactivity during the experimental period.

The characterization of the radioactive residues in the organosoluble fractions from the supernatant and sediment are shown in Table 26. Acidic followed by basic hydrolysis of the PES from the 59-day sample released 11% and 37% of the radioactivity. The remaining 32% of the applied radioactivity was still bound to the sediment. The distribution of the radioactivity in the fractions from the PES are shown in Table 27. The degradation of dicloran appears to be biphasic, with a calculated half-life during the first 12 hours of 0.45 days and from 1 to 14 days of 3.03 days.

Table 26. Characterization of radioactive residues in dicloromethane extract of supernatant and organic solvent extract of sediment after treatment with [^{14}C]dicloran.

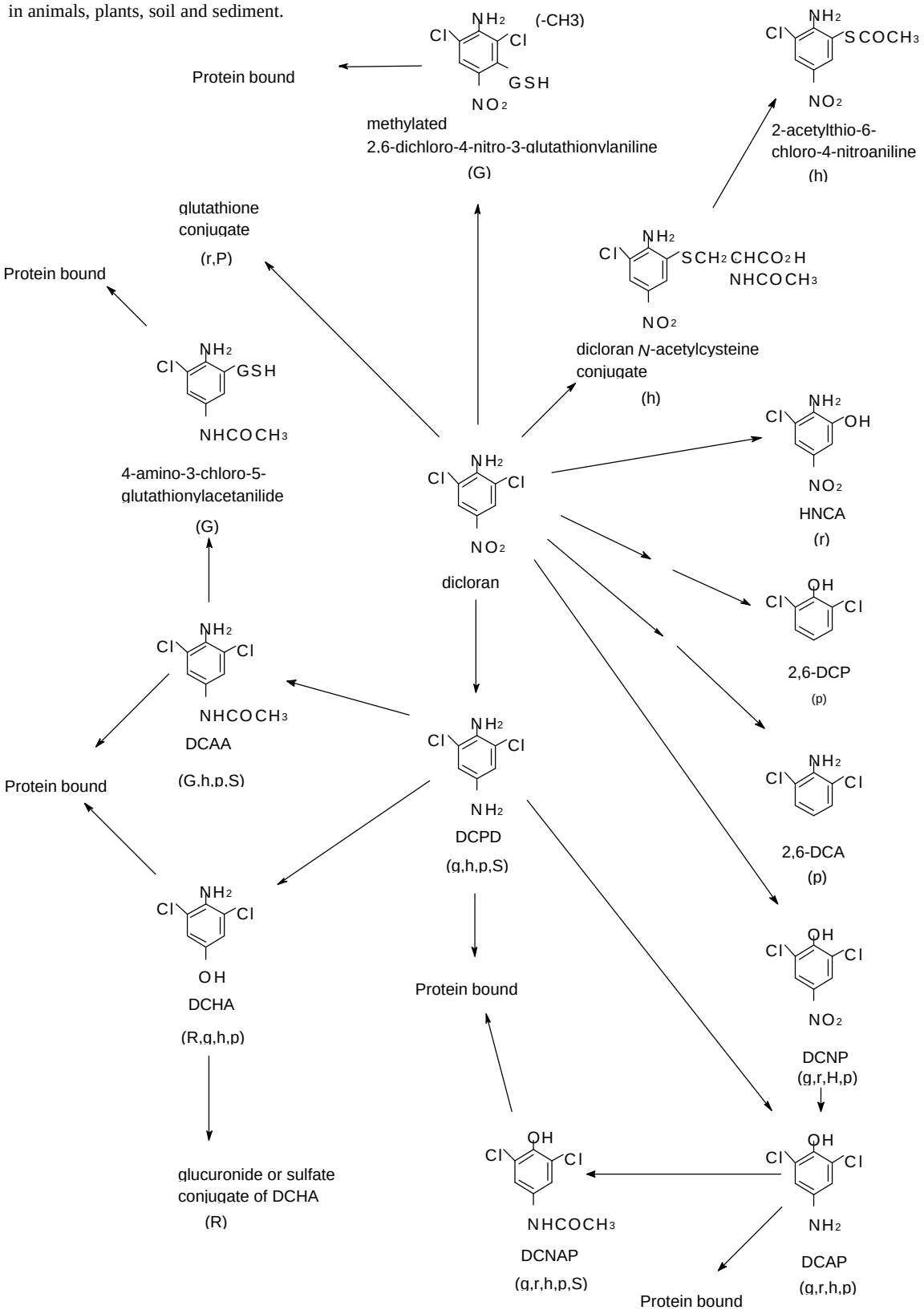
Compound	% of applied radioactivity											
	0 time	2 h	4 h	8 h	12 h	24 h	2 days	3 days	7 days	14 days	30 days	59 days
Dicloran	98.0	91.4	66.0	58.2	45.7	42.6	34.1	23.5	13.8	2.0	1.0	0.9
Met - 1	0.2	0.6	3.1	5.8	5.0	0.8	4.2	3.6	3.9	3.2	4.4	2.2
Met - 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.8	0.3	0.5
Met - 3 (DCNAP)	ND	ND	ND	ND	ND	0.2	ND	0.1	ND	0.4	0.3	0.2
Met - 4	0.1	ND	ND	0.1	ND	0.2	0.2	0.2	0.3	0.1	0.5	ND
Met - 5 (DCHA)	ND	0.1	2.5	ND	ND	0.2	3.0	5.1	3.0	ND	ND	ND
Met - 6 (DCAA)	ND	ND	ND	4.0	2.5	1.9	ND	ND	ND	6.2	3.0	1.1
Met - 7 (DCPD)	0.4	1.0	6.7	4.5	7.4	4.5	4.0	4.3	0.9	1.9	1.1	0.7
Met - 8	ND	ND	0.8	1.6	1.3	4.5	1.3	1.0	1.1	0.6	0.8	ND
Met - 9	ND	ND	0.5	1.9	2.4	2.0	2.1	2.0	2.5	1.1	2.3	0.8
Total	98.6	93.0	79.4	76.1	64.2	56.7	48.8	39.7	25.4	16.1	13.5	6.3

ND: not detected

Table 27. Distribution of radioactivity in fractions from analysis of post-extraction solids at 59 days.

Fraction	^{14}C, % of applied
Methanol extract	6.05
Acid hydrolysate of PES	11.18
Ethyl acetate phase	4.41
Aqueous phase	6.78
Basic hydrolysate of PES	36.91
Fulvic acid fraction	11.23
Ethyl acetate phase	4.41
Aqueous phase	6.82
Humic acid fraction	25.68
Bound to sediment (humins)	32.07
Total (PES)	86.21

Figure 1. Proposed metabolic and degradation pathways in animals, plants, soil and sediment.



G, R, H, P, S in parentheses indicate metabolism by goats, rats, hens and plants, and degradation in soil or sediment. Upper and lower case show major and minor products.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Historically residues of dicloran in food commodities were determined by colorimetric methods, which were mainly used in the supervised trials carried out in the early 1960s. After the mid-1960s, dicloran residues were determined by GLC, usually with microcoulometric detection. Current GLC methods commonly use capillary columns with an ECD.

Colorimetric methods

Plant samples are macerated with benzene and filtered. The extract is evaporated to dryness, and if necessary lipid is removed by partitioning with acetonitrile and hexane. The residue is dissolved in benzene and cleaned up on a Florisil column eluted with benzene. The eluate is evaporated to dryness and the residue dissolved in acetone. Aqueous KOH is added and the residual dicloran determined by measuring the optical density against a control sample solution at 464 nm. The detection limits were about 0.05 mg/kg with general recoveries of about 75%. The methods can be applied to fruits and vegetables.

Information on the selectivity of the colorimetric determination of dicloran and its metabolites was not available, but the Meeting concluded that the colorimetric method used in the supervised trials was acceptable since the sample extracts were cleaned up by column chromatography and the predominant plant metabolites lacked the nitro group which may affect the absorbence significantly.

Early GLC methods

Sample preparation was similar to that in the colorimetric methods described above. The detection limit was about 0.01-0.5 mg/kg, with recoveries generally above 70%.

Current GLC methods

Analytical methods have been developed to determine dicloran in plant material, eggs, milk and animal tissues.

Plant residues are extracted with acetone or chloroform and isolated by partition between acetonitrile and hexane or petroleum ether. If necessary, further clean-up can be achieved by evaporating the acetonitrile layer to dryness, dissolving the resulting residue in acetone, adding an excess of water and sorbing the dicloran on a solid-phase disposable C-18 column which is eluted with toluene. Capillary gas chromatography with electron capture detection can be used for quantitative determination of the analyte. Limits of determination are in the range 0.02-0.05 mg/kg. Recoveries exceed 79%.

Residues in milk and animal tissues are extracted by steam distillation with hexane from acidified samples. The hexane extract is evaporated to dryness and the residue dissolved in petroleum ether. Capillary gas chromatography with electron capture detection is used for quantitative determination. The limit of determination is 0.03 mg/kg with recoveries above 73%.

Sample preparation is modified for eggs and fat. Eggs are blended with acetonitrile and the acetonitrile is partitioned with hexane. The acetonitrile layer is taken to dryness, then steam-distilled from an acid solution. Fat is dissolved in hexane and partitioned with acetonitrile. The acetonitrile

layer is evaporated to dryness, the residue is dissolved in hexane and cleaned up on a Florisil column eluted with hexane before capillary column chromatography. The limit of determination is 0.03 mg/kg. Recoveries are more than 90%.

Multi-residue methods

Dicloran residues in food commodities can be determined by multi-residue methods. A sophisticated method developed in The Netherlands depends upon a modular arrangement to cover a wide range of pesticide-sample combinations. Recoveries were satisfactory in various types of sample. Determination limits depend on the clean-up procedure. The method is suitable for monitoring dicloran residues in a range of food commodities.

Stability of pesticide residues in stored analytical samples

Storage stability studies with fruits, vegetables and animal products (Boyack, 1963; Upjohn, 1964a,b; Kemman, 1997; Bright, 1989) showed that residues of dicloran in macerated fruits and vegetables were stable for the duration of storage, usually about one year. Dicloran was shown to be stable for 18 months in bovine muscle and eggs, and for 25 months in fat, but in fortified liver only 55% of the added amount was found after 18 months. The results of the studies are shown in Tables 28-32.

Table 28. Stability of dicloran in frozen macerated cherries (Boyack, 1963).

Sample treatment	Storage period (m)	Initial residue, mg/kg	Residue after storage, mg/kg	% remaining after storage
1000 mg/kg dipping	11	11.5	11.2	97
500 mg/kg dipping	11	2.3	2.8	122
1000 mg/kg dipping (washed cherries)	11	2.3	3.0	130
500 mg/kg dipping (washed cherries)	11	3.4	2.7	79

Table 29. Storage stability of dicloran in the macerated lettuce and carrots (Kemman, 1997).

Storage period (m)	Lettuce, % remaining after storage		Carrots, % remaining after storage	
	–15°C	–5°C to –15°C	–15°C	–5°C to –15°C
0	100.1	89.5	89.8	88.3
1	95.3	90.9	93.8	81.8
2	83.2	84.5	90.1	62.0
3		91.3		71.3
4	80.5		79.3	
6	92.7		81.5	
9	86.3		81.0	
12			94.8	
15			74.4	
18			64.2	

Samples were fortified with dicloran at 2.0 mg/kg

Table 30. Storage stability of dicloran in macerated fruits (Upjohn, 1964a).

Sample (Range of initial residue, mg/kg)	Storage period, days	% remaining after storage
Cherry (1.75-1.80)	146	101
Peach (1.58-2.78)	128	97.0
Strawberry (5.76-8.76)	121	105.9
Apricot (6.57-6.78)	106	94.1
	153	87.2
Apple (1.18)	223	145.2
Nectarine (0.93)	77	102.1
Grape (5.28)	18	81.3

Samples were taken from treated fields and stored frozen

Table 31. Storage stability of dicloran in macerated onions, snap beans and grapes (Upjohn, 1964b).

Sample (initial residue, mg/kg)	Storage period, days	% remaining after storage
Onion (2.1)	125	119.0
Snap bean (8.1)	83	129.6
Grape (3.6)	27	102.8

Samples were taken from treated fields and stored frozen

Table 32. Storage stability of dicloran in animal products (Bright, 1989).

Sample	Storage period (m)	% remaining after storage
Cow liver	18	55
Cow muscle	18	149
Cow fat	25	85
Egg	18	71

Samples were fortified at 0.33-1 mg/kg with dicloran and stored at -20°C

Definition of the residue

The plant metabolism studies showed that dicloran will be degraded gradually by reduction and acetylation of the nitro group, and deamination and hydroxylation of the amino group. Glutathione conjugation at the chlorine atoms may also occur. However, 14-20 days after the final application, dicloran was still the main residue in all the crops examined except potato tubers.

The rate of decrease of dicloran was slower after post-harvest than after pre-harvest treatment. The Meeting took into consideration the rate of decrease of dicloran in or on crops and concluded that the present definition of the residue as dicloran was appropriate both for enforcement and the estimation of dietary intake. The animal metabolism studies showed dicloran to be concentrated in lipid-rich tissues or products. Taking into consideration the residues found in animals and the octanol/water partition coefficient log P_{ow} = 2.8, the Meeting concluded that residues of dicloran should be categorized as fat-soluble.

USE PATTERN

Dicloran is a protective fungicide used on fruit and vegetables pre- and/or post-harvest. The registered uses are shown in Table 33.

Table 33. Registered uses of dicloran.

Crop	Country	From.	Application				PHI, days, or application timing
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Almonds	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Apple (Po)	Spain	SC	Drencher/ Dip	0.03-0.1		1	
Apricot	Israel	WP	Spray	0.098	1.5-2.0	1	
Apricot	USA	WP, SC	Spray	0.12	1.1-4.5	1	10
Apricot	USA	D	Dust		3.4	1	10
Apricot (Po)	USA	SC	Spray (a)	0.09		1	
Basil	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Basil	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Beans	Australia	WP	Spray	0.075	>0.9	(j)	
Beans (Po)	Australia	WP	Dip	0.075		1	
Beans broad (G)	Netherlands	FU	Fumigation		1.4	5	3
Beans dry	Canada	WP	Spray		2.4		2
Beans dry	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	
Beans fava (G)	Netherlands	FU	Fumigation		1.4	5	3
Beans green (G)	Netherlands	FU	Fumigation		1.4	5	3
Beans mung (G)	Netherlands	FU	Fumigation		1.4	5	3
Beans pole	Canada	WP	Spray		3.4	(d)	2
Beans snap	Canada	WP	Spray		2.4		2
Beans snap	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	
Beans snap (bush varieties)	USA	WP, SC	Spray	0.27	1.9	(d)	2
Beans snap (bush varieties)	USA	D	Dust		2.7	(d)	2
Beans snap (pole varieties)	USA	WP, SC	Spray	0.36	3.4	(d)	2
Beans snap (pole varieties)	USA	D	Dust		3.4	(d)	2
Berries	Chile	WP	Spray	0.23-0.26	2.6	4	1
Bulbs	Australia	WP	Spray to soil	0.75	1L/4.5 m of row	1	ap
Bulbs	Australia	WP	Spray	0.075		(g)	
Bulbs (seed)	Australia	WP	Dip	0.098		1	ap
Carrot	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	
Carrot	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Carrot	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Carrot (Po)	Israel	WP	Dip	0.053		1	
Carrot (Po)	USA	SC	Dip	0.09		1	
Celery	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	7
Celery	USA	WP, SC	Spray to soil		4.5	1	28
Celery	USA	WP, SC	Spray	0.18	2.8	(h)	7
Cherries	Argentina	WP	Spray	0.15		3	1
Cherries	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Cherries (Po)	Argentina	WP	Dip/ Spray	0.09-0.11		1	
Cherries (Po)	Chile	WP	Dip	0.13		1	
Cherries (Po)	USA	SC	Spray	0.12		1	
Cherries sweet	USA	WP, SC	Spray	0.12	1.1-4.5	5	10
Citrus fruits (Po)	Spain	SC	Drencher/ Dip	0.03-0.1		1	

Crop	Country	From.	Application				PHI, days, or application timing
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Corms	Australia	WP	Spray to soil	0.75	1L/4.5 m of row	1	ap
Corms	Australia	WP	Spray	0.075		(g)	
Corms (seed)	Australia	WP	Dip	0.098		1	ap
Cucumber (G)	Netherlands	FU	Fumigation		1.4	5	3
Cucumber (G)	UK	FU	Fumigation		2.3	(d)	2
Cucumber (G)	USA	WP, SC	Spray	0.12	1.1	(c)	1
Endive (escarole)	USA	WP, SC	Spray	0.24	2.2	2	14
Endive (G)	Netherlands	FU	Fumigation		1.4	5	14 or 28 (i)
Garlic (fall planting)	Canada	WP	Spray to soil		27-33	1	ap
Garlic (spring planting)	Canada	WP	Spray to soil		5.1-8.3	1	ap
Garlic	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	
Garlic	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Garlic	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Garlic	USA	WP	Spray	0.24-0.48		1	ap
Garlic	USA	SC	Spray to soil		2.8	1	ap
Garlic	USA	SC	Spray		1.3-2.2	(c) (m)	14
Garlic	USA	D	Dust		2.0-3.4	1	ap
Gherkin (G)	Netherlands	FU	Fumigation		1.4	5	3
Grapes	Argentina	WP	Spray	0.19			7
Grapes	Chile	WP	Spray	0.19-0.26	2.3		1
Grapes	Israel	WP	Spray	0.053-0.075	0.42-0.75	(c)	10
Grapes	USA	D	Dust		2.0	(c)	1
Grapes	USA (o)	WP, SC	Spray	0.12	1.7-3.9	(d) (k)	
Lettuce	Argentina	WP	Spray	0.28			10
Lettuce	Australia	WP	Spray to seed beds	0.075	5.6	1	ap
Lettuce	Australia	WP	Spray	0.075	>0.9	(j)	21
Lettuce	Canada	WP	Spray		1.7-2.8	2	14
Lettuce	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	14
Lettuce	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Lettuce	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Lettuce (G)	UK	FU	Fumigation		2.3	(c)	14
Lettuce crisphead (G)	Netherlands	FU	Fumigation		1.4	5	14 or 28 (i)
Lettuce head (G)	Netherlands	FU	Fumigation		1.4	5	14 or 28 (i)
Lettuce leaf	USA	D	Dust		2.0		14
Lettuce leaf (G)	USA	WP, SC	Spray	0.24	2.2		14
Lettuce leaf (G)	USA	D	Dust		2.0		14
Lettuce leaf and head	USA	WP, SC	Spray		0.84-1.7 2.2-4.5	(k)	ap 14
Melon	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Melon	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Melon (G)	Netherlands	FU	Fumigation		1.4	5	3
Melon (Po)	Spain	SC	Dip/ Spray	0.1		1	
Nectarine	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Nectarine	USA	WP, SC	Spray	0.12	1.1-4.5	4	10
Nectarine (Po)	Chile	WP	Dip	0.09		1	
Nectarine (Po)	USA	WP, SC	Spray (a)	0.24		1	
Onion (fall planting)	Canada	WP	Spray to soil		27-33	1	ap
Onion (spring planting)	Canada	WP	Spray to soil		5.1-8.3	1	ap
Onion	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	

Crop	Country	From.	Application				PHI, days, or application timing
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Onion	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Onion	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Onion	Thailand	WP	Spray	0.064		1	14
Onion	USA	WP	Spray	0.24-0.48		1	ap
Onion	USA	SC	Spray to soil		2.8	1	ap
Onion	USA	SC	Spray		1.3-2.2	(c) (m)	14
Onion	USA	D	Dust		2.0-3.4	1	ap
Peach	Argentina	WP	Spray	0.15		3	1
Peach	Canada	WP	Spray	0.13		2	10
Peach	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Peach	Israel	WP	Spray	0.098	1.5-2.0	2	5
Peach (for canning only)	South Africa	WP	Spray	0.075		2	2
Peach (for canning only)(Po)	South Africa	WP	Dip for at least 2 min.	0.1		1	
Peach	USA	WP, SC	Spray	0.12	1.1-4.5	4	10
Peach (Po)	Argentina	WP	Dip/ Spray	0.09-0.11		1	
Peach (Po)	Chile	WP	Dip	0.09		1	
Peach (Po)	Israel	WP	Dip/ Spray	0.023		1	
Peach (Po)	USA	SC	Spray/ Dip/ Brusher	0.09 or 0.24 (e)		1	
Pear (Po)	Spain	SC	Drencher/ Dip	0.03-0.1		1	
Pepper	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	
Pepper	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Pepper	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Pepper sweet (G)	Netherlands	FU	Fumigation		1.4	5	3
Plums	Argentina	WP	Spray	0.15		3	1
Plums	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Plums	USA	WP, SC	Spray	0.12	1.1-4.5	2	up to full bloom
Plums (Po)	Argentina	WP	Dip/ Spray	0.09-0.11		1	
Plums (Po)	USA	SC	conventional or low volume applicator	0.24 or 0.9-1.1 (f)		1	
Potato	Argentina	WP	Spray	0.23-0.26		1	ap
Potato	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	14
Potato	USA	WP, SC	Spray	0.18	1.7	(g)	14
Potato (seed)	Argentina	WP	Dip	0.39		1	ap
Prunes	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Prunes	USA	WP, SC	Spray	0.12	1.1-4.5	2	up to full bloom
Raspberries	Chile	WP	Spray	0.23-0.26	2.6	4	1
Rhubarb (G)	USA	WP, SC	Spray	0.12	1.1	(d)	3
Shallot	USA	WP	Spray	0.24-0.48		1	ap
Shallot	USA	SC	Spray to soil		2.8	1	ap
Shallot	USA	SC	Spray		1.3-2.2	(c)(m)	14
Shallot	USA	D	Dust		2.0-3.4	1	ap
Stone fruit (Po)	Australia	WP	Dip/ Spray	0.075		1	
Strawberries	Chile	WP	Spray	0.23-0.26	2.6	4	1
Strawberries	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Strawberries	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Strawberries	Spain	SC	Spray	0.02		3	7
Strawberries (G)	Netherlands	FU	Fumigation		1.4	5	3
Sweet potato	USA	SC	Spray to seed beds		2.5-3.2	1	ap

Crop	Country	From.	Application				PHI, days, or application timing
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Sweet potato (Po)	Australia	WP	Dip	0.098		1	
Sweet potato (seed)	USA	SC	Dip	4.5		1	ap
Sweet potato (set)	Australia	WP	Dip	0.075		1	ap
Tomato	Australia	WP	Spray	0.075		(j)	
Tomato	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Tomato	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Tomato (G)	Canada	WP	Spray	0.13		(d)	1
Tomato (G)	Netherlands	FU	Fumigation		1.4	5	3
Tomato (G)	UK	FU	Fumigation		2.3	(d)	2
Tomato (G)	USA	WP, SC	Spray	0.09	0.84	4 (d)	10 or 14 (n)
Tomato (G)	USA	D	Dust		2.0	4	10
Tomato (Po)	Australia	WP	Dip	0.06		1	
Tree fruits (Po)	Netherlands	FU	Fumigation		1.4g/250 m3		

(a): with wax
(b): at 8-10-day intervals for flowering period and 15-day intervals for pre-harvest period
(c): at 14 day intervals
(d): at 7-day intervals
(e): 0.24 kg/hl for freezing or canning
(f): 0.24 kg/ha for conventional application at 113-190 l/ha, 1 kg ai/25,000 kg of fruit
0.9-1.1 kg/hl for low-volume application at 19-30 l/ha, 1 kg ai/56,000-67,000 kg of fruit
(g): 10-14-day intervals
(h): 7-day intervals in summer and 14-day intervals in autumn and winter
(i): 14 days from March to October and 28 days from November to February
(j): 7-10-day interval
(k): up to 4.5 kg/ha per season.
(m): up to 2.8 kg/ha per season
(n): 10 days for WP and 14 days for SC
(o) limited to grapes grown west of the Rocky Mountains
(Po): Post-harvest application
(G): Glasshouse use
ap: treatment before, during or immediately after planting or transplanting

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of supervised trials on crops are shown in Tables 34-51.

Most of the old trials were reported in summary form and sometimes without necessary information such as recovery data. The trials which lack critical information are shown shaded in the Tables.

The residues derived from trials under maximum GAP conditions and those from trials according to GAP but not at the maximum allowed are doubly and singly underlined respectively.

Table 34. Apples (post-harvest)
Table 35. Pears (post-harvest)
Table 36. Apricots
Table 37. Cherries
Table 38. Cherries (post-harvest)
Table 39. Citrus fruits (post-harvest)
Table 40. Grapes
Table 41. Kiwifruit
Table 42. Nectarines

Table 43. Peaches
Table 44. Plums
Table 45. Strawberries
Table 46. Carrots
Table 47. Cucumbers and gherkins
Table 48. Lettuce
Table 49. Onions
Table 50. Tomatoes
Table 51. Common beans (immature)

Table 34. Residues of dicloran in apples after post-harvest application, Spain.

Year (Variety)	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No. (Method)	kg ai/ha	kg ai/hl			
1990 (Golden Delicious)	SC (10%)	1(drench)		0.035	1	1.8, 2.0, 1.8, 1.8, 2.3, 1.8, 1.9, 2.2, 2.2, 2.4 (10 trials)	Seu, Lleida 1990[1]
					29	1.0, 1.1, 1.3, 1.2, 1.9, 0.5, 0.9, 0.9, 0.6, 1.2 (10 trials)	
					86	0.7, 0.3, 0.8, 1.0, 0.9, 0.2, 0.2, 0.3, 0.2, 0.2 (10 trials)	
					118	0.3, 0.1, 0.3, 0.6, 0.6, <0.1, 0.1, 0.1, <0.1, <0.1 (10 trials)	
					147	0.3, 0.2, 0.3, 0.4, 0.3, 0.2, 0.2, 0.1, 0.2, 0.1 (10 trials)	
					177	0.3, 0.1, 0.1, 0.2, 0.3, 0.2, 0.2, 0.1, 0.1, <0.1 (10 trials)	
					202	0.1, 0.1, 0.1, 0.2, 0.2, 0.1, 0.1, 0.1, 0.1, <0.1 (10 trials)	
					238	0.1, <0.1, 0.1, 0.3, 0.2, <0.1, <0.1, <0.1, <0.1, <0.1 (10 trials)	
1990 (Belleza de Rome)	SC (10%)	1 (drench)		0.035	1	1.5, 2.5, 1.9, 1.6 (4 trials)	
					29	0.9, 1.2, 1.1, 1.0 (4 trials)	
					86	0.4, 0.6, 0.8, 0.3 (4 trials)	
					118	0.2, 0.3, 0.4, 0.1 (4 trials)	
					147	0.3, 0.2, 0.3, 0.3 (4 trials)	
					177	0.1, 0.1, 0.3, 0.1 (4 trials)	
					202	0.1, <0.1, 0.1, <0.1 (4 trials)	
					238	<0.1, <0.1, 0.1, 0.1 (4 trials)	
1990 (Granny Smith)	SC (10%)	1 (drench)		0.035	1	2.0, 2.4, 2.0, 2.5 (4 trials)	
					29	2.7, 0.9, 1.7, 0.8 (4 trials)	
					86	1.0, 0.5, 1.4, 0.3 (4 trials)	
					118	0.4, 0.4, 0.8, 0.1 (4 trials)	
					147	0.2, 0.3, 0.5, 0.2 (4 trials)	
					177	0.2, 0.3, 0.3, 0.1 (4 trials)	
					202	0.3, 0.1, 0.2, <0.1 (4 trials)	
					238	0.1, 0.2, 0.1, <0.1 (4 trials)	
1991 (Golden Delicious)	SC (10%)	1 (drench)		0.04	0	0.04, 0.04 (2 trials)	Seu, Lleida 1991[1]
					18	0.23, 0.03 (2 trials)	
					32	0.67, 0.45 (2 trials)	
					61	0.69, 0.64 (2 trials)	
					147	0.34, 0.43 (2 trials)	
1995	SC (20%)	1 (drench)		0.08	0	1.05, 1.16 (2 trials) 0.97, 1.37 (replicates)	Gomez 1995[1]
(Golden)					30	1.03, 1.26 (2 trials) 0.91, 1.25 (replicates)	
					60	0.58, 1.13 (2 trials)	

Year (Variety)	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No. (Method)	kg ai/ha	kg ai/hl			
						0.71, 1.05 (replicates)	
					90	0.41, 0.67 (2 trials) 0.48, 0.66 (replicates)	
1995 (Gloster)	SC (20%)	1 (drench)		0.08	0	0.34, 0.39 (2 trials) 0.23, 0.64 (replicates)	
					30	0.47, 0.33 (2 trials) 0.47, 0.48 (replicates)	
					60	0.28, 0.29 (2 trials) 0.22, 0.21 (replicates)	
					90	0.22, 0.19 (2 trials) 0.13, 0.10 (replicates)	

[1] Recovery data and concentration of dicloran in treatment solution not reported

Table 35. Residues of dicloran in pears after post-harvest application, Spain.

Year (Variety)	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No (Method)	kg ai/ha	kg ai/hl			
1990 (Blanquilla)	SC (10%)	1 (drench)		0.035	1	1.6, 1.7, 2.8, 2.0, 1.7, 1.8, 1.1, 1.7, 1.9, (9 trials)	Seu, Lleida 1990[1]
					29	0.8, 1.1, 1.2, 1.7, 1.0, 1.0, 0.6, 1.4, 1.1 (9 trials)	
					86	0.5, 0.7, ----, 1.0, 0.6, 0.6, 0.3, 0.9, 0.4 (8 trials)	
					118	0.2, 0.4, 0.5, 0.3, 0.4, 0.4, 0.1, 0.7, 0.3 (9 trials)	
					155	0.2, 0.3, 0.1, 0.3, 0.2, 0.2, 0.1, 0.4, 0.2 (9 trials)	
1990 (Flor de Invierno)	SC (10%)	1 (drench)		0.035	1	2.3	
					29	1.7	
					86	1.2	
					118	0.7	
					147	0.3	
1990 (Passa Crassana)	SC (10%)	1 (drench)		0.035	1	1.6, 1.7, 1.5 (3 trials)	
					29	0.9, 0.9, 0.7 (3 trials)	
					86	1.1, 0.5, 0.6 (3 trials)	
					118	0.4, 0.1, 0.2 (3 trials)	
					147	<0.1, 0.2, 0.1 (3 trials)	
					177	0.1, 0.1, <0.1 (3 trials)	
1991 (Blanquilla)	SC (10%)	1 (drench)		0.04	0	0.15, 0.16 (2 trials)	Seu, Lleida 1990[1]
					14	0.03, 0.02 (2 trials)	
					32	0.02, 0.02 (2 trials)	
					75	0.71, 0.29 (2 trials)	
					160	0.56, 0.88 (2 trials)	
1992 (Blanquilla)	SC (10%)	1 (drench)		0.04	0	0.22, 0.13, 0.20 (3 trials)	Seu, Lleida 1992[1]
					7	0.25, 0.30, 0.17 (3 trials)	
					18	0.30, 0.36, 0.25 (3 trials)	
					34	<0.01, 0.25, 0.17 (3 trials)	
1995 (Conference)	SC (20%)	1 (drench)		0.08	0	1.14, 1.42, 0.46, 0.60 (4 trials) 0.95, 1.09, 0.62, 0.49 (replicates)	Gomez 1995[1]
					30	1.21, 0.41, 0.60, 0.50 (4 trials)	
						0.65, 0.69, 0.39, 0.60 (replicates)	
					60	0.73, 0.81, 0.37, 0.45 (4 trials) 0.85, 0.97, 0.44, 0.39 (replicates)	

Year (Variety)	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No (Method)	kg ai/ha	kg ai/hl			
					90	0.49, 0.71, 0.32, 0.32 (4 trials) 0.57, 0.72, 0.28, 0.33 (replicates)	

[1] Recovery data and concentration of dicloran in treatment solution not reported

Table 36. Residues of dicloran in apricots, USA.

Year	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No	kg ai/ha	kg ai/hl			
1964	WP (50%)	1	3.3	0.09	0 11	5.41 0.59	R49
		1	3.3	0.09	0 4	5.59 2.12	
		2	3.3	0.09	4	3.21	
	WP (75%)	1	3.3	0.09	0 11	4.53 0.05	
		1	3.3	0.09	0 4	6.46 1.17	
		2	3.3	0.09	4	1.76	
	WP (50%)	1	2.9	0.078	0	3.19, 3.39, 3.44[1]	
	WP (75%)	1	3.3	0.09	0	3.69, 3.86, 4.19[1]	
1963	WP (50%)	1	2.3-2.9	0.09	0	1.58	R50
		3	2.3-2.9	0.09	2	0.74	
	WP (75%)	1 3	2.3-2.9 2.3-2.9	0.09 0.09	0 2	1.98 1.23	
1961	WP (50%)	1		0.06	1 4 7	3.1 1.4 <1.4	R354[2]
		1		0.12	1 4 7	10 4.1 2.4	

[1] Replicate samples
[2] Recovery data not reported

Table 37. Residues of dicloran in cherries.

Country Year	Application Form.	No	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg[1]	Reference
USA 1963	WP (50%)	1		0.09	1	0.50, 0.81, 0.82 0.23, 0.28, 0.28 (light wash) 0.26, 0.28, 0.46 (vigorous wash)	R65
	WP	1		0.09	0	2.10, 2.35 (2 trials)	
	(75%)						
USA 1964	WP (75%)	1		0.12	1	7.20, 12.2	R95
		1		0.12	1	12.2, 12.4	
Canada 1964	WP (50%)	5	3.4		1	2.6, 3.0	R108
Canada 1964	WP (50%)	3		0.24	1 7	0.7, 10.9 2.8	R109[2]

[1] Multiple values are from replicate samples
[2] The samples were thawed and juice had separated from thawed fruit

Table 38. Residues of dicloran in cherries after post-harvest application, USA, 1964. All single treatments with Gotelli sorting machine (Upjohn, 1964c).

Application Form.	kg ai/ha	kg ai/hl	Days after treatment	Residues, mg/kg[1]	Reference
WP		0.12	0	8.8, 10.3 (include stems)	R83
(50%)		0.12	0	11.8 (include stems)	
		0.12	0	11.1 (include stems)	
		0.09	0	0.74, 1.3	R66
		0.09	0	1.4	
		0.12	0	3.37, 5.90 (include stems)	R86
		0.12	0	1.34, 4.98, 4.9 (3 trials) (include stems)	
		0.09	0	0.06 (include stems)	
		0.12	0	4.4, 4.7 (include stems)	R87
			1	4.6, 4.8 (include stems)	
			5	3.3, 3.4 (include stems)	
			7	2.9, 3.4 (include stems)	

[1] Multiple values are from replicate samples

Table 39. Residues of dicloran in citrus fruit after post-harvest application, Spain.

Crop Year	Application Form.	No (Method)	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference
1987-88	WP (75%)	1 (drench)		0.075		0.01, 0.02, 0.05, 0.06 (orange, 4 trials)	R435[1]
		1 (drench)		0.075		0.12, 0.13 (mandarin, 2 trials)	
1990-91	SC (10%)	1 (drench)		0.03	8-12	0.29, 0.35, 0.90 (orange, 3 trials)	de la Cuadra 1991[1]
		1 (drench)		0.03	20-42	0.01, 0.05, 3.10 (orange, 3 trials)	
		1 (drench)		0.03	8-12	0.52, 1.01 (mandarin, 2 trials)	
		1 (drench)		0.03	20-42	0.01, 0.08, 0.22 (mandarin, 3 trials)	
		1 (drench)		0.04	8-12	0.48, 0.70, 0.72 (orange, 3 trials)	
		1 (drench)		0.04	20-42	0.01, 0.06, 1.47 (orange, 3 trials)	

Crop Year	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No (Method)	kg ai/ha	kg ai/hl			
		1 (drench)		0.04	8-12	0.28, 0.36, 0.69 (mandarin, 3 trials)	
		1 (drench)		0.04	20-42	0.01, 0.10, 0.26 (mandarin, 3 trials)	
Orange 1996	SC (20%)	1 (drench)		0.08	0	0.44, 1.29, 1.63, 1.77 (4 trials) 0.41, 0.83, 1.35, 1.31 (replicates)	Gomez 1996[1]
					7	0.66, 1.13, 1.02, 1.91 (4 trials) 0.68, 1.15, 1.17, 1.98 (replicates)	
					14	0.84, 1.48, 1.02, 1.80 (4 trials) 0.70, 1.46, 1.23, 1.45 (replicates)	
					30	0.85, 0.80, 1.48, 1.91 (4 trials) 0.86, 0.97, 1.26, 1.46 (replicates)	
					45	0.68, 1.69, 1.43, 1.30 (4 trials) 1.18, 1.72, 1.17, 1.65 (replicates)	
					60	0.72, 0.80, 1.44, 1.57 (4 trials) 1.26, 1.61, 1.46, 1.83 (replicates)	
Mandarin 1996	SC (20%)	1 (drench)		0.08	0	1.15, 0.93, 0.74, 2.05 (4 trials) 1.31, 0.88, 1.12, 1.36 (replicates)	
					7	1.23, 1.23, 1.15, 1.32 (4 trials) 1.12, 1.59, 0.85, 1.27 (replicates)	
					14	1.02, 1.35, 1.22, 1.55 (4 trials) 1.29, 1.21, 0.86, 1.48 (replicates)	
					30	0.97, 1.03, 1.37, 1.16 (4 trials) 1.38, 1.13, 1.64, 1.36 (replicates)	
					45	1.48, 1.15, 1.40, 1.56 (4 trials) 1.36, 1.31, 1.20, 1.60 (replicates)	
					60	1.86, 1.19, 1.42, 1.59 (4 trials) 1.12, 1.75, 1.32, 1.66 (replicates)	

[1] Recovery data and concentration of dicloran in treatment solution not reported

Table 40. Residues of dicloran in grapes.

Country Year	Application				PHI, days	Residues, mg/kg[1]	Reference
	Form.	No	kg ai/ha (Form.)	kg ai/hl			
Italy 1982	WP (75%)	4		0.25	3 7 14 21	1.31 1.20 0.83 0.06	R405[2]
USA (California) 1967	WP (75%) D (6%)	3	2.2 x 1 (WP) 2.0 x 2 (D)		2	N.D, N.D	R180[3]
		2	2.2 x 1 (WP) 2.0 x 1 (D)		12	N.D, N.D	
		3	2.2 x 1 (WP) 2.0 x 2 (D)		1	4.65, 7.34	
		1	2.2 (WP)		92	N.D x3 (three trials)	
		1 1	2.2 (WP) 2.0 (D)		142 15	N.D, 0.22 N.D, 0.70	
USA (California) 1980	WP (75%) D (6%)	3	2.2 x 2 (WP) 1.7 x (D)		76	<0.1, <0.1	R339[4]
		1	1.7 (D)		76	<0.1, <0.1	
		5	2.2 x 2 (WP) 1.7 x 3 (D)		19	0.2, 0.3	
		3	1.7 (D)		19	0.2, 0.3	
		4	2.2 x 2 (WP)		10	<0.1, <0.1	

Country Year	Application				PHI, days	Residues, mg/kg[1]	Reference
	Form.	No	kg ai/ha (Form.)	kg ai/hl			
			2.4, 1.0 (D)				
		2	2.4, 1.0 (D)		10	<0.1, <0.1	
		2	2.2 (WP) 1.7 (D)		76	<0.1, <0.1	
		3	2.2 x 2 (WP) 2.0 x 1 (D)		42	0.1, 0.1	
		1	2.0 (D)		42	<0.1, <0.1	
		3	2.2 x 2 (WP) 2.0 x 1 (D)		68	<0.1, <0.1	
		3	2.2 x 1 (WP) 1.7 x 2 (D)		15	<0.1, <0.1	
		1	1.7 (D)		15	<0.1, <0.1	
		3	2.2 x 1 (WP) 1.7 x 2 (D)		20	<0.1, <0.1	
		1	1.7 (D)		20	<0.1, <0.1	
USA (California) 1984	WP 75%	4	2.2 x 1 (WP) 2.0 x 3 (D)		1	0.29	#6607
	D 6%	10	2.2 x 2 (WP) 0.2 x 1 (D) 2.0 x (D)		1	0.62	
USA (California) 1995	WP 75%	2	4.5		3	0.83, 1.23	#95012

[1] Multiple values are from replicate samples
[2] Recovery data not reported
[3] Limit of detection not reported
[4] Samples rotten because freezer broke down

Table 41. Residues of dicloran in kiwifruit after post-harvest application, USA, 1979.

Application				Days after application	Residues, mg/kg[1]	Reference
Form.	No	kg ai/ha	kg ai/hl			
WP (75%)	1		0.10 0.15 0.20	1 1 1	1.0, 1.0 1.8, 2.1 2.8, 3.2	R231
	1 (spray)		0.20	1	5.5, 6.0 (with wax)	
	1 (dip)		0.20	1	23.8, 45.9 (with wax)	

[1] Duplicate samples

Table 42. Residues of dicloran in nectarines.

Country Year	Application				Days after application[1]	Residues, mg/kg[2]	Reference
	Form.	No. (pre or post)	kg ai/ha (Form.)	kg ai/hl			
USA 1968	WP (50%)	1 (post)[3]		0.24	0	1.4, 2.5	R185[3]
		1 (post)[3]		0.24	0	0.84, 0.92	
		1 (post)[3]		0.24	0	0.48, 0.51	
USA 1968	WP (75% or 50%)	1 (pre)		0.12	1	0.3	R204[3,4]
		1 (pre) 1 (post)[3]		0.12 0.24	(1) 0	4.4 (with wax)	
		1 (pre) 1 (post)[3]		0.12 0.24	(1) 0	3.3, 6.2 (with wax)	
		1 (pre) 1 (post)[3]		0.12 0.34	(1) 0	5.1 (with wax)	
		1 (pre)		0.12	1	N.D, 0.6	
		1 (pre) 1 (post)[3]		0.12 0.24	(1) 0	0.4 (with wax)	
		1 (pre) 1 (post)[3]		0.12 0.24	(1) 0	0.4, 0.5 (with wax)	
	WP (50%)	1 (post)[3]		0.24	0	1.7, 2.3	
		1 (post)[3]		0.24	0	0.8, 1.1	
	D (6%)	3 (pre)	3.4 (D)		1	N.D	
	WP (75%)	3 (pre) 1 (post)[3]	3.4 (D)	0.24	(1) 0	1.5	
Australia 1973	SC (50%)	1 (post) (dip)		0.075	1 2 4 6 8 10 12 14	2.3 (surface wash) 4.0 (surface wash) 3.3 (surface wash) 2.0 (surface wash) 4.6 (surface wash) 2.8 (surface wash) 4.6 (surface wash) 2.5 (surface wash)	R422

[1] Where both pre- and post-harvest treatments were applied the pre-harvest intervals (invariably 1 day) are shown in parentheses
[2] Multiple values are from replicate samples
[3] Treated with Decco wax applicator
[4] Limit of detection not reported

Table 43. Residues of dicloran in peaches.

Country Year	Application				Days after application[1]	Residues, mg/kg[2]	Reference
	Form.	No. (pre or post) (Method)	kg ai/ha	kg ai/hl			
Canada 1964	WP (50%)	7	6.7		0	2.69, 5.14	R107
USA 1966	WP (75%)	2 (pre) 1 (post)[3]	1.1	0.12 0.045	(1) 0	1.21, 1.76	R174-1[6]
		2 (pre) 1 (post)[3]	1.1	0.12 0.09	(1) 0	3.41, 3.90	
		2 (pre) 1 (post)[3]	1.1	0.12 0.13	(1) 0	5.54, 5.57	

Country Year	Application				Days after application[1]	Residues, mg/kg[2]	Reference
	Form.	No. (pre or post) (Method)	kg ai/ha	kg ai/hl			
		2 (pre) 1 (post)[3]	1.1	0.12 0.18	(1) 0	6.51, 7.66	
		1 (post)[3]		0.036	0	1.48	R174-2
		1 (post)[3]		0.054	0	1.93	
		1 (post)[3]		0.06	0	1.25, 2.18, 2.41, 2.71	R174-3
		1 (post)[4]		0.09	0	2.5, 3.2, 3.2, 3.6, 3.7	R174-4[6]
		1 (post)[5]		0.09	0	2.1, 4.0, 5.7, 6.3	
		1 (post)[4]		0.18	0	4.0	
		1 (post)[5] 2 (pre) 1 (post)[3]		0.09 0.16 0.046 0.09	0 (1) 0 0	1.5 3.60, 6.16 6.05, 7.34	R174-5[6]
				0.14 0.18	0 0	7.63, 10.1 13.5, 19.1	
		2 (pre) 1 (post)[3]		0.16 0.046 0.09 0.14 0.18	(1) 0 0 0 0	 12.87, 21.45 (with antifoam) 19.88, 23.76 (with antifoam) 30.52, 41.25 (with antifoam) 36.63, 45.92 (with antifoam)	
	WP (50%)	1 (post)[5]		0.15	0	1.25, 3.55	R174-6
	WP (75%)	2 (pre)		0.12	4	0.08, 0.10	R174-7
		2 (pre) 1 (post)[3]		0.12 0.018	(4) 0	0.7, 0.8	
						2.1, 2.8 (after cold water dump tank)	
						0.7, 0.9 (after wet brush defuzzing)	
						0.4, 0.4, 0.6, 0.9 (after grading and packing)	
						0.7, 0.7 (after chlorine wash)	
		2 (pre) 2 (post)[3]		0.12 0.018, 0.015	(4) 0	0.9, 1.0	
Canada 1966	WP (75%)	1 (post)[5]		0.36	0	1.88, 2.29	R174-8
USA 1988	WP (75%)	3 (pre) 1 (post)	4.5	0.09	(1), 0	16.3 (dip)	R414
					(1), 0	15.4 (hydrocooler + antifoam)	
					(1), 0	11.9 (hydrocooler)	
		3 (pre) 1 (post)	3.4	0.09	(1), 0	11.1 (dip)	
					(1), 0	18.7 (hydrocooler + antifoam)	
					(1), 0	8.3 (hydrocooler)	
USA	WP	4 (pre)	4.5		(10)	4.6, 6.1, 6.5	95007
1996	(75%)	1 (post) (dip)		0.09	0		

Country Year	Application				Days after application[1]	Residues, mg/kg[2]	Reference
	Form.	No. (pre or post) (Method)	kg ai/ha	kg ai/hl			
		5 (pre)	4.5		(10)	4.3, 5.5, 6.7	
		1 (post) (dip)		0.09	0		
USA 1975	WP (75%)	1 (post)[3]		0.09	0	4.8, 5.0, 5.2, 5.8 (4 trials, unwaxed)	R276[7]
					0	2.7, 2.8, 2.8, 3.0, 3.3, 3.3, 3.4, 3.5 4.2, 4.6, 5.3, 5.4, 6.8 (13 trials) (waxed)	
USA 1976	WP (75%)	1 (post)[3]		0.5		2.8, 4.2 (waxed)	R279[7]
Australia 1971	WP (75%)	1 (post) (dip)		0.18	1	3.0	R205[8]
					2	2.4	
					4	1.9	
					5	1.3	
Australia 1973	WP (75%)	1 (post) (dip)		0.075	1	5.44, 5.62 (surface wash)	R420
					3	3.45, 4.75 (surface wash)	
					6	2.35, 4.55 (surface wash)	
					9	1.92, 3.46 (surface wash)	
Australia 1973	SC (50%)	1 (post) (dip)		0.075	1	6.3, 6.0 (2 trials) (surface wash)	R422
					2	7.5, 8.2 (2 trials) (surface wash)	
					4	8.7, 6.2 (2 trials) (surface wash)	
					6	4.9, 3.9 (2 trials) (surface wash)	
					8	4.6, 6.4 (2 trials) (surface wash)	
					10	2.3, 2.3 (2 trials) (surface wash)	
					12	8.1, 8.8 (2 trials) (surface wash)	
					14	4.1, 9.7 (2 trials) (surface wash)	
Spain 1995	SC (10%)	1 (post) (drench)		0.04	0	2.36, 3.40, 3.22, 3.04 (4 trials) 4.27, 3.78, 3.00, 3.68 (replicates)	de la Cuadra[7]
					7	4.20, 1.85, 2.98, 3.40 (4 trials) 5.00, 3.36, 1.34, 3.60 (replicates)	
					14	5.03, 3.42, 2.10, 5.61 (4 trials) 6.63, 1.56, 1.87, 6.75 (replicates)	
					21	5.53, 2.48, 2.27, 5.56 (4 trials) 5.92, 3.45, 1.96, 4.38 (replicates)	
					28	----, 3.79, 2.96, ---- (2 trials) ----, 2.42, 3.07, ---- (replicates)	

[1] Where both pre- and post-harvest treatments were applied, the pre-harvest intervals are shown in parentheses
[2] Multiple values are from replicate samples unless otherwise stated
[3] Treated with hydrocooler
[4] Treated with FMC brusher
[5] Sprayed
[6] Untreated samples contained high residues
[7] Recovery data not reported
[8] Only summary data submitted

Table 44. Residues of dicloran in plums.

Country Year	Application				PHI days[1]	Residues, mg/kg[2]	Reference
	Form.	No	kg ai/ha	kg ai/hl			

		(pre or post) (Method)					
Spain 1995	SC (10%)	1 (post) (drench)		0.04	0	0.35, 0.39, 0.32, 0.36 (4 trials) 0.34, 0.37, 0.35, 0.31 (replicates)	Gomez 1995[3]
					7	0.31, 0.29, 0.37, 0.28 (4 trials) 0.45, 0.32, 0.32, 0.32 (replicates)	
					14	0.33, 0.23, 0.27, 0.26 (4 trials) 0.31, 0.25, 0.32, 0.23 (replicates)	
					21	0.27, 0.25, 0.30, 0.29 (4 trials) 0.26, 0.29, 0.24, 0.32 (replicates)	
					28	0.31, 0.35, 0.22, 0.34 (4 trials) 0.33, 0.30, 0.24, 0.31 (replicates)	
USA	WP	2 (pre)	2.8		(112)	14.0 (2.3 l/hr spray)	R415
1986	(75%)	1 (post)[4]		8.7	0	(with wax)	
		2 (pre) 1 (post)[5]	2.8	0.24	(88) 0	6.1 (110 l/hr spray) (with wax)	
USA 1995	WP (75%)	2 (pre) 1 (post)[5]	4.5	0.24	(154) 0	1.1, 2.1, 2.4 (replicates with wax) (1 kg ai/25000 kg of fruit)	95008
		2 (pre) 1 (post)[4]	4.5	1.1	(154) 0	1.9, 2.1 2.4 (replicates with wax) (1 kg ai/56000 kg of fruit)	
USA 1995	WP 75%	4	4.5		10	0.17	#95011

[1] Where both pre- and post-harvest treatments were applied, the pre-harvest intervals are shown in parentheses
[2] Multiple values are from replicate samples unless otherwise stated
[3] Recovery data not reported
[4] Low-volume applicator
[5] Conventional applicator

Table 45. Residues of dicloran in strawberries.

Country Year	Application Form.	No	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg[1]	Reference
Spain 1995	SC (10%)	1		0.015	0	1.29, 0.91, 0.99, 0.95 (4 trials)	Gomez 1995[2]
					3	0.43, 0.46, 0.45, 0.43 (4 trials) 0.47, 0.46, 0.63, 0.50 (replicates)	
					5	0.66, 0.12, 0.35, 0.46 (4 trials) 0.45, 0.25, 0.37, 1.94 (replicates)	
					7	0.31, 0.16, 0.25, 0.12 (4 trials) 0.18, 0.10, 0.26, 0.27 (replicates)	
					14	0.04, 0.06, 0.07, 0.05 (4 trials) 0.05, 0.09, 0.05, 0.07 (replicates)	
		1		0.02	0	0.99, 1.25, 1.95, 1.54 (4 trials)	
					3	0.86, 0.97, 1.66, 1.30 (4 trials) 0.68, 1.67, 1.64, 1.46 (replicates)	
					5	0.37, 0.74, 1.23, 0.75 (4 trials) 0.67, 1.08, 0.79, 2.64 (replicates)	
					7	0.44, 0.15, 0.23, 0.28 (4 trials) 0.28, 0.18, 0.32, 0.38 (replicates)	
					14	0.10, 0.10, 0.14, 0.09 (4 trials) 0.09, 0.08, 0.09, 0.09 (replicates)	
USA	WP	9		0.12	1	2.2, 2.8, 2.8	R52
1963	(50%)	10		0.12	5	0.88, 1.3, 1.8, 2.3	
		9		0.12	1	2.5, 2.9, 3.0, 3.0	
		10		0.12	5	0.93, 1.6, 2.1, 2.8	
	WP (75%)	1		0.09	1	3.8, 5.0, 5.1, 7.9 (with cap)	
USA	WP	1		0.04	2	1.2	R54

Country Year	Application Form.	No	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg[1]	Reference
1963	(50%)	2		0.09	1	0.50, 0.70	
						0.65, 1.10 (with cap)	
	WP (75%)	1		0.09	0	5.8, 6.7	
					1	5.0, 5.4	
					3	5.3, 5.9	
					5	4.5, 5.4	
USA	WP	4	1.7		11	0.2	R151
1963	(75%)	3	1.7		9	0.77, 1.71	
		4	1.7		0	0.45	
		4		0.16	11	0.13	

[1] Multiple values are from replicate samples unless otherwise stated
[2] Recovery data not reported

Table 46. Residues of dicloran in carrots.

Country Year	Application Form.	No (pre or post) (method)	kg ai/ha	kg ai/hl	PHI, days[1]	Residues, mg/kg[2]	Reference
USA 1995	WP (75%)	1	5.0		7	1.50, 2.03, 2.10	95031
		1	5.0		7	0.37, 0.65, 0.71	
		1	5.0		7	<0.05 x 3	
		2	2.5		7	0.47, 0.88, 0.97	
		1	5.0		7	0.69, 0.69, 0.80	
		2	2.5		7	0.78, 1.01, 1.34	
		1	5.0		7	0.97, 1.04, 1.71	
		2	2.5		7	1.60, 1.63, 1.89	
USA 1965	WP (75%)	1 (post) (dip)		0.10	0	3.07, 3.85, 7.87, ---- (3 trials)	R138
					1	4.04, 4.81, 7.32, 4.70 (4 trials)	
					3	5.94, 4.95, 7.10, 4.59 (4 trials)	
					7	5.67, 6.11, 8.97, 10.84 (4 trials)	
					14	3.99, 5.03, 10.84, 10.73 (4 trials)	
		1 (post) (dip)		0.09	0	4.82	
					1	4.92	
					4	4.04	
					7	4.32	
					14	3.67	
USA 1983	WP (75%)	3 (pre)	3.4		11	2.60	R254[3]
		3 (pre) 1 (post) (dip)	3.4	0.075	(11) 0	4.95	
		2 (pre)	6.7, 3.4		25	2.50	
		2 (pre) 1 (post) (dip)	6.7, 3.4	0.075	(25) 0	5.96	
		3 (pre)	3.4		24	1.03	
		3 (pre)	3.4		(24)	6.80	
		1 (post) (dip)		0.075	0		
		2 (pre)	6.7, 3.4		38	1.53	
		2 (pre) 1 (post) (dip)	6.7, 3.4	0.075	(38) 0	9.20	

Country Year	Application				PHI, days[1]	Residues, mg/kg[2]	Reference
	Form.	No (pre or post) (method)	kg ai/ha	kg ai/hl			
		3 (pre)	3.4		18	0.54	
		3 (pre) 1 (post) (dip)	3.4	0.075	(18) 0	4.95	
		2 (pre)	6.7, 3.4		32	2.55	
		2 (pre)	6.7, 3.4		(32)	5.45	
		1 (post) (dip)		0.075	0		
Israel 1968	WP (50%)	1 (post) (dip)		0.05	1 14 24	2.6 4.4 3.6	R264[4]
		1 (post) (dip)		0.10	1 14	7.0 6.1	

[1] Where both pre- and post-harvest treatments were applied the pre-harvest intervals (invariably 1 day) are shown in parentheses
[2] Multiple values are from replicate samples unless otherwise stated
[3] Untreated samples contained high residues
[4] Recovery data not reported

Table 47. Residues of dicloran in cucumbers and gherkins.

Crop Country Year	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No	kg ai/ha	kg ai/hl			
Cucumber (Glasshouse) USA 1965	WP (75%)	1 2		0.09 0.15	8 1	0.13, 0.18 (duplicates) 0.99, 1.79 (duplicates)	R139
		1		0.14	14 21	0.07 0.22	R140
		1 (soil) 1 (foliar)	13	0.14	21	0.23	
		1 (soil)	13		30	0.10	
Gherkin (Glasshouse) Netherlands 1972	FU	1	1.6-1.8		1 3	0.59, 0.62 (2 trials) 0.09, 0.10 (2 trials)	R270

Table 48. Residues of dicloran in lettuce (next page).

Country Year	Application				PHI, days[1]	Residues, mg/kg[2]	Reference
	Form.	No	kg ai/ha	kg ai/hl			
USA 1971 (Glasshouse)	Not stated	1 (soil)	10		bp	0.135, 0.165	R207[3]
		1 (soil)	10		bp	0.03, 0.07, 0.10	
		1 (soil)	20		bp	0.125, 0.315	
		1 (soil)	20		bp	0.10, 0.11, 0.215	

Country Year	Application				PHI, days[1]	Residues, mg/kg[2]	Reference
	Form.	No	kg ai/ha	kg ai/hl			
		1 (foliar)	1		ap-4	<0.01, <0.01, 0.04, 0.06	
		1 (foliar)	1		ap-4	0.02, 0.04	
		2 (foliar)	1		ap-18	0.04, 0.245 (2 trials)	
		3 (foliar)	1		ap-32	0.45, 1.41 (2 trials)	
		1 (soil) 1 (foliar)	10 1		ap-4	0.03, 0.16	
		1 (soil)	10		ap-4	0.19	
		1 (foliar)	1				
		1 (soil) 2 (foliar)	10 1		ap-18	0.16, 0.23 (2 trials)	
		1 (soil) 1 (foliar)	20 1		ap-4	0.115, 0.20	
		1 (soil) 1 (foliar)	20 1		ap-4	0.30	
		1 (soil) 2 (foliar)	20 1		ap-32	0.54, 1.83 (2 trials)	
UK 1972 (Glasshouse) (season was not reported)	FU	1	1.6		0.5 1 2 3 4	12.0, 12.0, 12.0, 13.5 16.5, 16.5, 19.5, 31.5 13.5, 13.5, 39.0 12.0, 15.0 <6.0, 12.0, 13.5 <6.0, <6.0, 12.0	R268
Belgium 1977 (Glasshouse) (January or November)	FU	1	1.6		10 17	0.66, 0.67, 3.07 0.24, 0.33, 1.98	R287[3]
		1	1.6		10 17 25	1.32, 1.38, 2.15 1.06, 1.15, 1.25 0.17, 0.21, 0.42	
		2	1.6		14 21	1.59, 2.10, 2.29 0.73, 0.82, 1.05	
Belgium 1975 (Glasshouse) (season not reported)	FU	1	1.5		2 9 16 27	25.7, 31.1 2.90, 3.19 2.77, 2.43 <0.01, 0.01	R274[3]
The Netherlands 1970-71 (Glasshouse)	FU	2	2.9		14 21 26	3.9 5.0 2.9	707/71[3]
(November - February)		2	2.9		18 22 28	2.1 3.1 0.7	
		2	2.9		29	0.5	
		1	1.5		15 17 29	1.0 4.7 0.2	
(March)	FU	2	2.9		23	0.2	
		1	1.5		21	0.25	
USA 1964	WP (75%)	2		0.18	25	N.D, 0.08	R112
		2		0.36	25	0.04, 0.05	
		1	3.4		26	0.13	R113

[1] bp: before planting; ap-4, -18, -32: applied 4, 18 or 32 days after planting;
[2] Multiple values are from replicate samples
[3] Recovery data not reported

Table 48. Residues of dicloran in onions. CLICK HERE for continue

Country Year	Application				PHI, days[1]	Residues, mg/kg[2]	Reference
	Form.	No	kg ai/ha	kg ai/hl			
USA	G	1[3]	11		111	0.03, 0.06, 0.07, 0.07 (broadcast treatment)	R70
1962	(5%)	1[3]	11		111	N.D, 0.02 (band treatment)	
(Spring planting)	WP	1[3]	11		111	0.05, 0.09, 0.11, 0.11	
	(50%						
USA	WP	1 (dusted)[3]	28		225	N.D, N.D, 0.01, 0.06	
1963	(50%)	1 (dusted)[3]	35		225	N.D x 4, 0.05, 0.11	
(Fall planting)							
USA	WP	9	2.2		7	<0.1	R248
1983	(75%)	9	2.2		8	<0.1	
(Fall planting)							
USA	WP	1[3]	34		84	0.47 (Spring planting)	R416
1986	(75%)	1[3]	34		182	0.19 (Fall planting)	
		1[3]	34		194	<0.05 (Fall planting)	
Finland	WP	1 (dip)[4]		0.1	99	<0.03, <0.03 (2 trials)	R281
1976	(75%)					(washed)	[5]
USA	D	1 (post)	1 lb./bin[6]		100	8.46, 9.59, 10.2	R421
1973	(8%)	1 (post)	2 lb./bin[6]		100	18.25, 20.93, 21.00	
		(dressing)				9.56, 9.53 (after sorting and packing)	

[1] In the case of post-harvest treatment, figure are days after application
[2] Multiple values are from replicate samples
[3] Treatment at planting
[4] Sets were dipped
[5] Recovery data not reported
[6] Bin size not reported

Table 50. Residues of dicloran in tomatoes.

Crop Country Year	Application				Days after application	Residues, mg/kg[1]	Reference
	Form.	No	kg ai/ha	kg ai/hl			
USA	WP	1		0.07	0	0.67, 0.83, 1.05, 1.07	R24
1962	(75%)				5	0.55, 0.72, 0.76, 0.77 0.03, 0.20, 0.26, 0.32 (washed)	
(Glasshouse)					10	0.22, 0.29, 0.51, 0.62 0.06, 0.11, 0.24, 0.29 (washed)	
		1		0.13	0	0.87, 1.30, 1.63, 1.77	
					5	0.66, 0.71, 0.86, 0.89 0.08, 0.13, 0.33, 0.49 (washed)	
					10	0.28, 0.41, 0.64, 0.69 0.15, 0.18, 0.22, 0.36 (washed)	
		1		0.27	0	1.82, 2.29, 3.66, 4.29	
					5	1.59, 3.15, 3.28, 4.96 0.26, 0.49, 0.67, 0.72 (washed)	
					10	1.33, 1.65, 2.12, 2.81	
						0.58, 0.74, 0.88, 1.14 (washed)	
UK	FU	1	1.3		4 h	0.45, 0.89 (surface wash)	R269
1972					6 h	0.33, 0.72 (surface wash)	
(Glasshouse)					8 h	0.13, 0.71 (surface wash)	
					10 h	0.09, 0.50 (surface wash)	
					12 h	0.08, 0.43 (surface wash)	

Crop Country Year	Application				Days after application 1 2 - 10	Residues, mg/kg[1] <0.05, 0.09 (surface wash) <0.05 x 13 (surface wash)	Reference
	Form.	No	kg ai/ha	kg ai/hl			
USA	WP	2	1.1		15	0.96, 0.99, 1.12, 2.17	R71
1963	(50%)	2	1.7		0	0.47	
		2	1.1, 2.2		0	0.31	
		1	2.7		5	0.64	
		1	5.4		14	0.59	
	D (8%)	2	4.5		0	0.12, 0.19, 0.25, 0.34, 0.34	
	D (4%)	1	1.6		0	0.35, 0.43	
USA 1963	WP (50%)	3	1.1		8	0.12, 0.22	R73
		4	1.1		0	0.99, 1.39	
		5	1.1		4	0.78, 2.15	
		6	1.1		0 15	2.28, 2.52 0.72, 1.99	
		7	1.1		0	1.88, 2.01	
USA 1995	WP 75%	4	0.84		3	0.2	#95010
USA 1963	WP (75%)	1 (post)		0.9[2]	0	1.12, 1.56, 2.23, 2.74 2.83, 2.84, 3.39 (7 trials) (1l of solution/2400 kg of fruit)	TOM 95
		1 (post)		0.9[2]	0	2.48, 2.76, 2.81, 2.93, 4.24, 4.35 (6 trials) (1l of solution/1800 kg of fruit)	
		1 (post)		1.2[2]	0	2.8, 4.5 (2 trials) (1l of solution/2400 kg of fruit)	
		1 (post)		1.8[2]	0	3.68, 4.11, 4.49, 5.73 (4 trials) (1l of solution/2400 kg of fruit)	

[1] Multiple values are from replicate samples
[2] Application by controlled droplet applicator (CDA). Solution included wax.

Table 51. Residues of dicloran in common beans (immature).

Country Year (Variety)	Application Form.	No (pre or post) (Method)	kg ai/ha	kg ai/hl	Days after application[1]	Residues, mg/kg[2]	References Remarks
USA	WP	2	3.4, 6.7		12	0.05, 0.06	R115
1964	(75%)	3	3.4, 3.4, 6.7		12	0.09, 0.12	
(Pole)							
USA	WP	3	3.4		0	20.0, 29.2 (early planted)	R116
1964	(75%)	3	3.4		0	23.2, 25.2 (late planted)	
(Pole)		2	3.4		4	4.4, 7.9 (early planted)	
					7	10.2, 11.5 (early planted)	
		2	3.4		4	13.2, 14.5 (late planted)	
					7	17.0, 17.1 (late planted)	
		2	3.4, 6.7		15	9.27	
		3	3.4, 3.4, 6.7		15	7.27, 10.8	
		1	3.6		4	9.45, 9.67 (early planted)	
					7	3.47, 4.86 (early planted)	
		1	3.6		4	12.64, 14.01 (late planted)	
					7	4.37, 7.53 (late planted)	
USA	D	4	3.4		2	0.45	P R167
1965	(6%)	4	3.4		4	0.61	B
(P: pole and	WP	4	1.1		2	1.40	P
B: bush in the	(75%)	4	1.7		4	1.44	B
last column)		1	3.4		4	2.50	B
		4	3.4		2	4.80, 1.90, 9.80	P
		4	3.4		4	4.20, 1.05, 5.20	B
		6	3.4		2	4.90	P
		6	3.4		4	4.30	B
		1	6.7		2	16.1	P
		1	6.7		4	6.10	B
					9	1.30, 1.50	
		2	6.7		2	5.90	P
		2	6.7		4	10.50	B
		4	6.7		2	15.5	P
		4	6.7		4	11.40	B
USA	WP	1 (soil)	6.7		54	0.10	R168
1965	(75%)	2 (foliar)	3.4		13	9.00	
(Bush)		4 (foliar)	3.4		0	11.75	
					3	6.90	
					7	4.80	
		1 (soil) 3 (foliar)	6.7 3.4		1	8.55	
		1 (soil) 4 (foliar)	6.7 3.4		3 7	5.30 5.20	
Australia	WP	1 (post) (dip)		0.06	0	17, 18	R419[2]
1963	(50%)	1 (post) (dip)		0.12	0	26, 27	
Australia	WP	1 (post)		0.06	0	6.4	R205[3]
1971	(50%)	(dip)			1	7.8	

Country Year (Variety)	Application				Days after application[1]	Residues, mg/kg[2]	References Remarks
	Form.	No (pre or post) (Method)	kg ai/ha	kg ai/hl			
					2	5.3	
					3	5.2	
					13	1.3	
		1 (post) (dip)		0.12	0	12.0	
					1	11.0	
					2	11.0	
					3	7.2	
					13	5.3	

[1] Multiple values are from replicates
[2] Recovery data not reported
[3] Only summary data submitted

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Grapes. Field-treated grapes were processed to juice, wet pomace, raisins and raisin waste in two trials at California State University according to commercial practice (Brown, 1987).

Fresh grapes were harvested, stemmed and pressed to give juice and wet pomace. Grapes for raisins were further treated with 2.0 kg ai/ha of dust formulation on the drying trays and sun-dried for 21 days on the trays to give unprocessed raisins. These were separated mechanically into raisin waste, midget raisins and C grade raisins, and the separated raisins washed to yield A and B grade raisins. The results are shown in Table 52.

Table 52. Residues of dicloran in grapes and processed fractions, USA, 1984 (Brown, 1987).

Application	Sample	Residues, mg/kg	Processing factor
Trial A	Raw fruit	0.29	-
2.2 kg/ha x 1 (WP)	Juice	0.39	1.34
2.0 kg/ha x 3 (D)	Wet pomace	0.61	2.10
1 day PHI	Unprocessed raisins	<0.1	<0.3
2.0 kg/ha (D, on drying tray)	Raisin waste	<0.1	<0.3
	Midget and C grade raisins	<0.1	<0.3
	A and B grade raisins	<0.1	<0.3
Trial B	Raw fruit	0.62	-
2.2 kg/ha x 2 (WP)	Juice	0.70	1.13
0.2 kg/ha x 1 (D)	Wet pomace	0.61	0.98
2.0 kg/ha x 7 (D)	Unprocessed raisins	<0.1	<0.2
1 PHI day	Raisin waste	<0.1	<0.2
2.0 kg/ha (D, on drying tray)	Midget and C grade raisins	<0.1	<0.2
	A and B grade raisins	<0.1	<0.2

Residues immediately after post-harvest treatment were not reported

A trial by Kliskey (1996a) simulated commercial juice and raisin production as closely as possible. To produce juice the fresh grapes were hand-fed into a Cantinetta crusher/stemmer and

the stems and pulp were collected separately. The pulp was pressed in a Suntech fruit press to separate the juice. The fresh juice was filtered through a standard milk filter.

For processing to raisins the fresh grapes were sun-dried in a greenhouse for about one month, then sifted on a Sweco sifter to remove loose dirt, field debris and panicles. A representative sample of the screened raisins was hand-sorted to remove cap stems, smaller panicles and undesirable raisins. The sorted raisins were batch-washed with cold water for 15 seconds in a high-pressure spray washer and allowed to drain to remove excess water. The finished moisture content was 13.4%. The results are shown in Table 53.

Table 53. Residues of dicloran in grapes and processed fractions, USA, 1995 (Kliskey, 1996a).

Application	Sample	Residues, mg/kg	Processing factor
4.5 kg/ha x 2	Raw grapes	1.23	-
3 days PHI	Juice	0.91	0.74
	Dried grapes	0.83	0.67
	Raisins	<0.05	<0.04

Plums. Dried prunes were produced by a process which simulated commercial production as closely as possible (Kliskey, 1996b). The fresh plums were sorted and any rotten or otherwise damaged plums removed, and the sorted plums washed in cold water for 5 minutes. The plums were dried in trays in a laboratory tray air dryer at 68-79 °C for 24-36 hours to reduce the moisture content to the desired range of 19-29%. The dried prunes were left to cool for approximately 20 minutes, inspected and any remaining stems removed. The results are shown in Table 54.

Table 54. Residues of dicloran in plums and dried prunes, USA, 1995 (Kliskey, 1996b).

Application	Sample	Residues, mg/kg	Processing factor
4.5 kg/ha x 4	Plums	0.17	-
10 days PHI	Dried Prunes	0.31	1.8

Tomatoes. Paste and purée were produced by a process which simulated commercial operation as closely as possible. (Kliskey, 1996c). Fresh tomatoes were sorted by hand and soaked in 0.5% lye solution for 3 minutes at 52-60°C, then batch rinsed with a high pressure spray for 30 seconds at 68-74°C and steamed in an atmospheric steam cabinet for 30 seconds. The tomatoes were crushed in a hammermill chopper, heated rapidly in a steam-jacketed kettle to 79-85°C and held for 15-30 seconds. The hot juice was fed into a pulper finisher machine with a 0.05-0.08 cm mesh screen to separate the seeds, skin and stems, was then frozen for evaporation at a later date. The frozen juice was thawed and concentrated in a Groen batch vacuum pan evaporator until it reached a concentration of 12.0-12.5 Brix at which time a purée fraction was removed. The remaining purée was then transferred to a 7.5 l scrape surface vacuum evaporator and further evaporated to 26.0-33.0 Brix to give finished paste.

Both the purée and finished paste were treated with 1% of salt, heated to a temperature of 82-88°C and sealed in cans with an electric can sealer. The sealed cans were heated in an open atmospheric water batch kettle for 15-20 minutes at 98-100°C and cooled under running tap water. The results are shown in Table 55.

Table 55. Residues of dicloran in tomatoes and processed fractions, USA, 1995 (Kliskey, 1996c).

Application	Sample	Residues, mg/kg	Processing factor
0.84 kg/ha x 4	Tomatoes	0.20	-
3 days PHI	Paste	0.38	1.9
	Purée	0.22	1.1

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The government of The Netherlands reported the results of monitoring crops for dicloran shown in Table 56.

Table 56. Monitoring data for dicloran in crops in The Netherlands, 1994-96.

Commodity	Samples analysed	Samples containing residues[1]	Detection frequency, %	Mean residues, mg/kg[2]
Tangerines	623	5	0.80	<0.01
Oranges	982	2	0.20	<0.01
Apples	1654	2	0.12	<0.01
Nectarines	247	1	0.40	0.01
Plums	467	3	0.64	<0.01
Grapes	765	1	0.13	<0.01
Strawberries	2743	3	0.11	<0.01
Raspberries	269	16	5.94	0.02
Currants(red, black, white)	481	1	0.21	<0.01
Kiwifruit	260	1	0.38	<0.01
Other fruits and products	469	1	0.21	<0.01
Radishes	1050	2	0.19	<0.01
Tomatoes	1242	3	0.24	<0.01
Peppers	1655	6	0.36	<0.01
Cucumbers	1089	2	0.18	<0.01
Kohlrabi	41	1	2.44	0.01
Lettuce	3834	6	0.16	<0.01
Endive	1297	1	0.08	<0.01
Witloof	549	2	0.36	<0.01
Other leafy vegetables	230	1	0.43	<0.01

[1] LOD = 0.01 mg/kg
[2] For samples with residues below the LOD half the LOD is taken for the calculation of the mean

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported to the Meeting.

Crop	Country	MRL
All edible crops[1]	Finland	5
All edible crops[1]	Germany	0.1
All edible crops[1]	Netherlands	0.01
All edible crops[1]	Spain	0.01
Anguria	Slovak Republic	0.5
Apricot	Brazil, USA	20
Apricot	Canada, Israel, Korea, Malaysia, Netherlands, Slovak Republic	10
Artichoke	Italy	10
Asparagus	Italy	10
Beans, dry (field)	Australia, Brazil	20
Beans, dry	Netherlands, Slovak Republic	2
Beans, dry	Taiwan	0.1
Beans, green (snap, common, French)	Australia, Brazil, Canada	20
Beans, green (snap, common, French)	Kenya, Malaysia, Netherlands, Slovak Republic	2
Beans, green (snap, common, French)	Spain	5
Beans, green (snap, common, French)	USA	20
Berry fruits	Australia	20
Berry fruits	Spain	5
Blackberry	Canada	10
Blackberry	Kenya, Malaysia, Netherlands, Slovak Republic	5
Blackberry	USA	15
Boysenberry	USA	15
Bulb vegetables	Italy	10
Cabbage	Italy	10
Carrot	Australia	15
Carrot	Canada, Denmark	5
Carrot	Chile, Israel, Italy, Kenya, Korea, Malaysia, Netherlands, Slovak Republic, USA	10
Celery	Canada, Korea	10
Celery	USA	15
Cherry, sour	Brazil	20
Cherry, sour	Chile, Kenya, Malaysia, Netherlands, Slovak Republic	15
Cherry, sour	Korea	10
Cherry, sweet	Brazil	20
Cherry, sweet	Canada, Chile, Kenya, Malaysia, Netherlands, Slovak Republic	15
Cherry, sweet	Korea	10
Cherry, sweet	USA	20
Citrus fruits	Spain	0.5
Cotton seed	Korea, USA	0.1
Cucurbits	Malaysia	0.5
Cucurbits	Spain	5
Currant	Kenya, Malaysia, Netherlands, Slovak Republic	5
Egg plant, aubergine	Spain	5
Endive, escarole	Belgium	3
Endive, escarole	USA	10
Fruiting vegetables	Belgium	0.3
Fruiting vegetables	Finland	1
Fruiting vegetables	Italy	10
Fruiting vegetables[1]	Netherlands	0.3
Fruits[1]	Belgium	0.1
Fruits[1]	Denmark	10

Crop	Country	MRL
Fruits[1]	Slovak Republic	10
Garlic	Brazil, Canada	0.5
Garlic	USA	5
Gherkin, cucumber	Canada, Israel, Kenya, Netherlands	0.5
Grape	Brazil, Canada, Chile, Israel, Kenya, Korea, Malaysia, Netherlands, USA	10
Grape	Czech Republic	5
Kiwifruit	Korea, Netherlands	10
Kiwifruit	USA	20
Leafy vegetables	Denmark	5
Leafy vegetables	Italy	10
Leafy vegetables	Netherlands	3
Leafy vegetables[2]	Taiwan	2
Legumes	Korea	20
Lettuce	Australia	20
Lettuce	Belgium	3
Lettuce	Brazil, Canada, Chile, Slovak Republic, USA	10
Lettuce, head	Kenya, Korea, Malaysia	10
Lettuce	Spain	5
Meat, milk	Netherlands	0.01
Mushroom	Taiwan	2
Nectarine	Brazil	20
Nectarine	Kenya, Malaysia, Netherlands, Slovak Republic	10
Nectarine	USA	20
Onion	Australia	20
Onion	Brazil	10
Onion	Canada, USA	5
Onion	Korea	10
Peach	Brazil	20
Peach	Canada, Chile, Israel, Kenya, Malaysia, Netherlands, Slovak Republic	15
Peach	Finland, Korea	10
Peach	South Africa	1
Peach	USA	20
Plum	Canada	5
Plum	Chile, Kenya, Korea, Malaysia, Netherlands, Slovak Republic	10
Plum	USA	15
Pome fruits	Denmark	10
Pome fruits	Taiwan	5
Potato	Canada	5
Potato	Italy	10
Potato	Korea, USA	0.25
Raspberry	Canada, Kenya, Malaysia, Netherlands, Slovak Republic	10
Raspberry	USA	15
Rhubarb	Canada	5
Rhubarb	USA	10
Seed fruits	Spain	2
Small fruits	Australia	20
Small fruits	Denmark, New Zealand	10
Soya beans	Korea	20
Stone fruits	Australia	15
Stone fruits	New Zealand	10
Stone fruits	Taiwan	5
Strawberry	Belgium	0.3
Strawberry	Brazil	15
Strawberry	Canada, Denmark, Italy, Kenya, Korea, Malaysia, Netherlands, Slovak Republic	10
Strawberry	Spain	5
Sweet potato, kumera	Australia	20
Sweet potato, kumera	Brazil, Korea, USA	10
Sweet potato, kumera	Canada, New Zealand	5

Crop	Country	MRL
Tomato	Australia	20
Tomato	Belgium	3
Tomato	Brazil, Canada, Spain, USA	5
Tomato	Chile, Kenya, Korea, Malaysia, Netherlands, Slovak Republic	0.5
Vegetables[1]	Belgium	0.01
Witloof	Belgium, Netherlands	1
Witloof	Malaysia	15

[1] Except as specifically listed
[2] Leafy vegetables with small leaves

APPRAISAL

Dicloran was evaluated for toxicology and residues in 1974 and 1977. An ADI was established in 1977.

Dicloran is a protective fungicide used to control *Botrytis, Monilinia, Rhizopus, Sclerotinia and Sclerotium* spp. on fruits and vegetables during the growing stages and/or post-harvest. The compound was evaluated at the present Meeting within the CCPR Periodic Review Programme.

The Meeting received data on residues and information on GAP from the manufacturer and the governments of The Netherlands, Poland and Germany.

Animal metabolism

The following abbreviations for dicloran metabolites are used.

DCHA: 4-amino-3,5-dichlorophenol
DCAA: 4-amino-3,5-dichloroacetoanilide
DCAP: 4-amino-2,6-dichlorophenol
HNCA: 2-chloro-6-hydroxy-4-nitroaniline
2,6-DCA: 2,6-dichloroaniline
DCPD: 4-amino-2,6-dichloroaniline
DCNP: 2,6-dichloro-4-nitrophenol
DCNAP:3,5-dichloro-4-hydroxyacetanilide
2,6-DCP: 2,6-dichlorophenol

Animal metabolism was studied in rats, goats and hens with [^{14}C]dicloran. Dicloran metabolism in animals involves reduction of the nitro group to amino, deamination and hydroxylation to phenolic derivatives, and acetylation to form acetanilides.

Conjugation to form the glucuronide and/or sulfate at the *N* or *O* position and glutathione conjugation at the Cl position also apparently occurred.

The contribution of each of the metabolic reactions differs among the species examined. While DCHA and its conjugates were the predominant metabolites in rats, DCAA and DCNP were at higher levels than DCHA in goats and hens respectively.

Rat metabolism has been studied with [^{14}C]dicloran in several experiments (single doses of 1.5-500 mg/kg bw, repeated doses of 5 mg/kg bw). The total recoveries of radioactivity were >94% in the studies, and >90% of the radioactivity was excreted within 48 hours after dosing. Irrespective of the dosing regimen, most of the radioactivity (72.3-90.2%) was excreted in the urine. The faeces contained 7.9-22.4%.

The radioactivity in the expired air was monitored in the group dosed once with 5 mg/kg bw and no significant amounts of ^{14}C were detected in the carbon dioxide traps, indicating that the molecule was not completely broken down.

After repeated doses of 5 mg/kg bw for 7 days the tissue residues were highest in the liver (0.06 and 0.049 mg/kg as dicloran in males and females respectively) and kidneys (0.016 and 0.015 mg/kg in males and females respectively). All other residues in the tissues were at or below the limit of determination (0.01 mg/kg).

The major urinary metabolites were DCHA sulfate and DCHA glucuronide, together accounting for up to 79% of the total administered radioactivity. The metabolites DCHA, DCAP and DCNAP were also found.

The faeces from the animals dosed at 500 mg/kg contained a small amount of dicloran and many minor metabolites. Much of the radioactivity in the faeces was released only by acid hydrolysis and was thought to be from glutathione conjugates of several metabolites. Similar metabolic pathways were found after repeated low doses and single high doses of dicloran.

Metabolism in goats was studied in two experiments. In one, female goats were given single doses of 1.5 or 10 mg/kg bw of [^{14}C]dicloran and slaughtered after 72 hours. In the other study a lactating goat was dosed with [^{14}C]dicloran for 5 consecutive days at an average level of 613 mg/day (12 mg/kg bw), equivalent to 359 ppm of dicloran in the diet based on the measured feed consumption during the treatment period. The goat was killed 22 hours after the final dose. The total recoveries of radioactivity were 77.9% after the single dose of 1.5 mg/kg bw, 113.6% after the single 10 mg/kg bw dose, and 88.7% after the last of the repeated doses of 12 mg/kg bw/day. Overall, the radioactivity excreted in the urine ranged from 33.0% to 68.9% and the faeces contained 43.3-44.9% of the dose. The highest tissue residues in all the animals were found in the livers.

Examination of the urine from the singly-dosed goats showed the metabolite DCAA and its conjugates after both high and low doses, with a range from 3.3% to 5.6% of the urinary radioactivity, but DCPD was not detected. After enzymatic hydrolysis, a small amount of DCHA (1.6% of the urinary ^{14}C) was detected in the urine from the low-dose goat.

The residues in the tissues and milk of the lactating goat given repeated doses of [^{14}C]dicloran were examined in detail. The extraction of ^{14}C from milk, liver, kidney, muscle and fat ranged from 65.2% from muscle to 93.6% from fat and milk. Dicloran accounted for 80.7% of the total radioactive residues in fat, 19.6% in milk and 15.7% in muscle. DCAA was found in muscle (35.0% of the TRR), kidney (13.9%) and liver (11.9%). The metabolite DCAP was found in milk (25.7%). DCHA, DCPD and DCNP each constituted less than 5% of the radioactivity in the tissues or milk.

Two metabolites totalling 37% of the TRR were isolated from liver extracts and identified as methylated 2,6-dichloro-4-nitro-3-glutathionylaniline and 4-amino-3-chloro-5-glutathionylacetanilide. The radioactivity in the post-extraction solids from liver and muscle was not due to sulfate or glucuronide conjugates. Most of the remaining radioactivity in the liver and muscle was released by protease hydrolysis. DCHA, DCNP, DCAA, and the glutathione conjugates were detected. Less than 10% of the radioactivity in the tissues and milk remained unidentified.

Laying hens were dosed for 3 days at a level of 0.15 mg/bird/day (0.075 mg/kg bw/day) and killed 24 hours after the last dose. Lipid-rich tissues such as egg yolk and fat contained almost exclusively dicloran with no detectable metabolites. Egg white contained approximately equal

amounts of dicloran and DCNP. Residues in the livers consisted mainly of dicloran (54.8% of the ^{14}C), DCAA (24.2%) and DCNP (21.0%).

In a further study laying hens were dosed by capsule for 5 consecutive days at levels equivalent to 3.1 and 50 ppm in the diet (0.24 and 3.8 mg/kg bw) and killed 22 hours after the last dose. The total recovery of radioactivity was 84.5% and 91.6% for the low-dose and high-dose groups respectively. Over 80% of the administered radioactivity was eliminated in the excreta, of which 3-11% was from the parent compound. The entire egg production contained less than 0.6% of the total radioactivity. Less than 2% of the total ^{14}C was retained in all the other tissues combined. In the high-dose group the concentration of radioactivity as dicloran was 6.64 mg/kg in abdominal fat, 2.98 mg/kg in liver and 0.36 mg/kg in muscle. Egg yolks contained up to 2.38 mg/kg and egg whites up to 0.19 mg/kg.

Dicloran was the major component in the fat (94%), egg yolk (>80%) and egg white (up to 72%). DCNP was found in liver (45-58%), egg white (28-33%) and muscle (11-14%) but constituted less than 3% of the residue in egg yolk and fat. DCAA constituted up to 29% of the residue in muscle and 12% in liver, and DCNAP up to 33% and 2% respectively. Minor metabolites (individually less than 10% of the residues in tissues and eggs) were DCHA, DCPD, DCAP, dicloran sulfate, dicloran *N*-acetylcysteine conjugate and 2-acetylthio-6-chloro-4-nitroaniline.

Plant metabolism

Studies were carried out with peaches, potatoes and lettuce. There were no significant differences between the metabolic profiles of these crops. In summary, the metabolism of dicloran in plants involves reduction and acetylation of the nitro group, and deamination and hydroxylation of the amino group. Glutathione conjugation with simultaneous removal of one or both chlorine atoms was also shown to occur.

The metabolism of dicloran in peaches was investigated under field and glasshouse conditions. The peaches were treated with [^{14}C]dicloran formulated as a WP at the GAP concentration of 130 g ai/hl with simulated commercial application. The fruit were treated 3 times at 7-day intervals. The field-grown peaches were treated with a total of 0.54 mg ai/peach and the glasshouse peaches at the higher level of 0.77 mg/peach to aid identification.

At the final-harvest, 14 days after the third application, a total residue of 1.65 mg/kg dicloran equivalents was found in the field-grown peaches, of which 71.7% was extractable with solvent (hexane/acetone, acetonitrile, or acetonitrile/water). The glasshouse peaches at the final harvest 18 days after the third treatment contained 14.07 mg/kg dicloran equivalents of which 56.6% was solvent-extractable. A further 37.5% was recovered by processing the peach fibre, which contained 43.4% of the ^{14}C. The fibre was treated with 6M sodium hydroxide, then soxhlet-extracted successively with acetonitrile, ethyl acetate, and water, and finally hydrolysed with 4M hydrochloric acid to leave only 5.9% of the residue still bound to the fibre. After extensive clean-up and purification over 50% of the residue in the glasshouse peach fibre was identified using TLC, HPLC and LC-MS.

Free and conjugated dicloran with its conjugate formed the principal component in the residue (31.7% for glasshouse peaches and 51.3% for field peaches). The remainder comprised free and conjugated DCHA (10.9% glasshouse, 4.1% field) and DCAA with its conjugate (7.9% glasshouse, 1.2% field), and conjugated DCPD (6.5% glasshouse, 2.2% field). In addition, DCAP (5.5%), 2,6-DCP (2.8%) and DCNP (1.2%) were isolated after hydrolysis of the glasshouse peach fibre. The remainder of the residue in both the field and glasshouse peaches comprised many minor components, none of which constituted more than 3.6% of the total residue. There was no significant difference between the metabolic profiles of the field and glasshouse peaches.

Potato seed pieces were planted under field conditions and broadcast-treated with eight applications of [^{14}C]dicloran at approximately 1.8 kg ai/ha, slightly above the maximum US label rate. Mature tubers, vines and roots were harvested 14 days after the final application at a typical stage for dicloran treatment. The radioactive residues were isolated by extracting with polar and non-polar solvents. Extracted samples were hydrolysed with hydrochloric acid followed by sodium hydroxide. The hydrolysates were partitioned with methylene chloride. A range from 26.9 to 37% of the radioactive residue in the tubers, vines and roots was extracted with acetonitrile. Most of the unextracted radiocarbon was released by acid and basic hydrolysis and the remaining bound radioactivity found in the fibre was 2.7, 10.8 and 16.2% for tubers, vines and roots respectively.

Dicloran was found in all the samples. The metabolites DCNAP, DCAA, DCHA and 2,6-DCA were also present in some fractions. Unknown 1, a polar component found in the acid and/or base hydrolysates, accounted for 30-40% of the TRR. Unknown 1 is a mixture and appeared to consist of the glutathione conjugates of several dicloran metabolites. Five other unidentified components were detected at levels of 0.03 mg/kg as dicloran.

Lettuce seeds were planted under field conditions and broadcast-treated with [^{14}C]dicloran at 4.9 kg ai/ha, 10% above the maximum US label use rate, at a typical stage for dicloran application. The plants were grown according to typical agricultural field practices. Mature lettuce were harvested 20 days after the final application, and the radioactive residues isolated by extracting with polar and non-polar solvents. Extracted samples were hydrolysed with hydrochloric acid followed by sodium hydroxide, and the hydrolysates were partitioned with methylene chloride.

Seventy three per cent of the radioactive residue was extracted by acetonitrile, about 9% of the radiocarbon was contained in each of the acid and base hydrolysates, and about 8% of the TRR remained bound.

Dicloran was the main residue in the solvent extracts; a small amount of DCAP was also present. None of the residue in the aqueous phases resulting from the partitioning the acid and base hydrolysates was identified. All of the identified metabolites were in the organic extract of the acid hydrolysate: DCAP, DCPD, DCNAP, DCAA, 2,6-DCP and 2,6-DCA. Ten unidentified components were detected in the aqueous and organic phases after partitioning of the acid and base hydrolysates. None of these individually represented more than 5% of the TRR in the hydrolysate, and their total in all the hydrolysate fractions accounted for 12% of the TRR. Of these, unknown 1 represented 6.48% of the TRR and was later determined to be a mixture.

Environmental fate

In a study of aerobic degradation in soil the main residue in the soil extracts was the parent compound, with <1% of DCAA and DCPD also present. Other unidentified polar compounds constituted less than 3% of the applied radioactivity.

These results were confirmed in a field soil dissipation study in California, USA. Dicloran was applied at the rate of 4.5 kg/ha and the soil was analysed for residues of the parent compound, DCAA, DCHA and DCPD for a period of 18 months. Dicloran dissipated rapidly during the first two months of the study and the half-life then stabilized at approximately 35 days. No degradation products were detected.

Dicloran is degraded rapidly in flooded soils. In laboratory studies with [^{14}C]dicloran the half-life was less than 30 days under flooded conditions. The principal degradation product, arising from reduction of the parent compound, was DCPD. This did not accumulate but was further degraded to unextractable bound residues and CO_2.

In another study [^{14}C]dicloran was incubated in flooded sediment under anaerobic conditions. The decline of dicloran was biphasic with half-lives of 0.45 days in the initial fast phase (0-12 hours) and 3 days in the following slow phase (up to 14 days). Small amounts of nine products, including DCHA, DCPD, DCAA, DCNAP and a polymeric material, were detected. The radioactivity became progressively more bound and was associated with the humic and fulvic acid fractions of the sediment.

Photolysis studies were conducted on soil and in aqueous solutions and half-lives were calculated as 132 hours on soil and 24-41 hours in aqueous solution.

Analytical methods

Historically residues of dicloran in food commodities were determined by colorimetric methods, which were mainly used in the supervised trials carried out in the early 1960s. After the mid-1960s, dicloran residues were determined by GLC, usually with microcoulometric detection. Current GLC methods commonly use capillary columns with an ECD.

Colorimetric methods

Plant samples are macerated with benzene and filtered. The extract is evaporated to dryness, and if necessary lipid is removed by partitioning with acetonitrile and hexane. The residue is dissolved in benzene and cleaned up on a Florisil column eluted with benzene. The eluate is evaporated to dryness and the residue dissolved in acetone. Aqueous KOH is added and the residual dicloran determined by measuring the optical density against a control sample solution at 464 nm. The detection limits were about 0.05 mg/kg with general recoveries of about 75%. The methods can be applied to fruits and vegetables.

Information on the selectivity of the colorimetric determination of dicloran and its metabolites was not available, but the Meeting concluded that the colorimetric method used in the supervised trials was acceptable since the sample extracts were cleaned up by column chromatography and the predominant plant metabolites lacked the nitro group which may affect the absorbance significantly.

Early GLC methods

Sample preparation was similar to that in the colorimetric methods described above. The detection limit was about 0.01-0.5 mg/kg, with recoveries generally above 70%.

Current GLC methods

Analytical methods have been developed to determine dicloran in plant material, eggs, milk and animal tissues.

Plant residues are extracted with acetone or chloroform and isolated by partition between acetonitrile and hexane or petroleum ether. If necessary, further clean-up can be achieved by evaporating the acetonitrile layer to dryness, dissolving the resulting residue in acetone, adding an excess of water and sorbing the dicloran on a solid-phase disposable C-18 column which is eluted with toluene. Capillary gas chromatography with electron capture detection can be used for quantitative determination of the analyte. Limits of determination are in the range 0.02-0.05 mg/kg. Recoveries exceed 79%.

Residues in milk and animal tissues are extracted by steam distillation with hexane from acidified samples. The hexane extract is evaporated to dryness and the residue dissolved in

petroleum ether. Capillary gas chromatography with electron capture detection is used for quantitative determination. The limit of determination is 0.03 mg/kg with recoveries above 73%.

Sample preparation is modified for eggs and fat. Eggs are blended with acetonitrile and the acetonitrile is partitioned with hexane. The acetonitrile layer is taken to dryness, then steam-distilled from an acid solution. Fat is dissolved in hexane and partitioned with acetonitrile. The acetonitrile layer is evaporated to dryness, the residue is dissolved in hexane and cleaned up on a Florisil column eluted with hexane before capillary column chromatography. The limit of determination is 0.03 mg/kg. Recoveries are more than 90%.

Multi-residue methods

Dicloran residues in food commodities can be determined by multi-residue methods. A sophisticated method developed in The Netherlands depends upon a modular arrangement to cover a wide range of pesticide-sample combinations. Recoveries were satisfactory in various types of sample. Determination limits depend on the clean-up procedure. The method is suitable for monitoring dicloran residues in a range of food commodities.

Stability of pesticide residues in stored analytical samples

Storage stability studies were carried out with fruit, vegetables and animal products. Residues of dicloran in macerated fruits and vegetables were stable for the duration of storage, about 1 year. Dicloran was shown to be stable for eighteen months in bovine muscle and eggs, and for 25 months in fat, but in fortified liver only 55% of the added amount was found after eighteen months.

Definition of the residue

The plant metabolism studies showed that dicloran will be degraded gradually by reduction and acetylation of the nitro group, and deamination and hydroxylation of the amino group. Glutathione conjugation at the chlorine atoms may also occur. However, 14-20 days after the final application, dicloran was still the main residue in all the crops examined except potato tubers.

The rate of decrease of dicloran was slower after post-harvest than after pre-harvest treatment. The Meeting took into consideration the rate of decrease of dicloran in or on crops and concluded that the present definition of the residue as dicloran was appropriate both for enforcement and the estimation of dietary intake. The animal metabolism studies showed dicloran to be concentrated in lipid-rich tissues or products. Taking into consideration the residues found in animals and the octanol/water partition coefficient log P_{ow} = 2.8, the Meeting concluded that residues of dicloran should be categorized as fat-soluble.

Residues from supervised trials

Most of the old trials data were provided in summary form and sometimes without necessary information such as data on recoveries. The Meeting agreed not to use trials data which did not include information on recoveries unless recovery data were reported for other trials from which samples were analysed in the same laboratory at about the same time.

Apple and pears. Twenty four post-harvest trials on apples and 22 on pears were carried out in Spain (1990-95), at nominal concentrations of 0.035, 0.04 and 0.08 kg/hl. The residues were not proportional to the intended concentration however. Because the information on recoveries and the actual concentration of dicloran in the treatment solution was not available the Meeting could not estimate maximum residue levels.

Apricots. Fourteen supervised trials were carried out in the USA (1961-64). Two supervised trials with an application rate of 0.09 kg/hl and a PHI of 11 days were comparable to US GAP (0.12 kg/hl, 10 days PHI). The residues were 0.05 and 0.59 mg/kg. Another trial with an application rate of 0.12 kg/hl and PHI of 7 days also approximated US GAP, but there were no recovery data. The other eleven trials were not according to any reported GAP. There were too few trials to estimate a maximum residue level.

Cherries. Five pre-harvest trials were carried out in the USA (1963-64) and two in Canada (1964) but no relevant GAP was reported and the analysis of the sample in one Canadian trial was unsatisfactory.

Eleven post-harvest trials were carried out in the USA (1964), but the sample in nine trials were analysed with stems. The Meeting agreed not to use these results for the evaluation.

Two adequately conducted trials at 0.09 kg/hl were comparable with Argentinian, US and Australian GAP. The residues were 1.3 and 1.4 mg/kg. There were too few adequate trials to estimate a maximum residue level for cherries.

Citrus fruits. Twenty post-harvest trials on oranges and 17 on mandarins were carried out in Spain (1987-1996) at treatment concentrations of 0.03-0.08 kg/hl. Four of the trials, at 0.075 kg/hl (1990-91) and 0.08 kg/hl (1996), complied with Spanish post-harvest GAP (0.03-0.1 kg/hl, dipping or drenching), but the residues from the two groups were in different populations although the treatments by drenching were essentially the same. Because information on recoveries and the actual concentrations of dicloran in the treatment solution was not available the Meeting could not estimate a maximum residue level.

Grapes. One Italian and 25 US trials were reported.

The Italian trial carried out in 1982 did not comply with any reported GAP and there were no recovery data.

Two US trials in 1967 and two in 1984 with a WP application at 2.2 kg/ha followed by 1-3 dust applications at 2.0 kg/ha with 1-2 days PHI were comparable with US GAP (1.7-3.9 kg/ha for WP/SC or 2.0 kg/ha for D, 1 day PHI). The residues were undetectable, 0.29, 0.62 and 7.34 mg/kg at 1 or 2 days PHI.

One US trial in 1995 with a WP application at 4.5 kg/ha approximated US GAP (1.7-3.9 kg/ha for WP/SC): the residue was 1.23 mg/kg.

Six US trials in 1967 with a WP or D application at 2.0-2.2 kg/ha and 12-142 days PHI complied with US application rates. The residues ranged from undetectable to 0.70 mg/kg.

The samples from 14 US trials in 1980 rotted because the freezer broke down. The results could not be used for evaluation.

The Meeting concluded that there were too few satisfactory trials and recommended withdrawal of the existing CXL (10 mg/kg Po).

Kiwifruit. Three supervised trials were carried out in the USA (1979), but no relevant GAP was reported. The Meeting could not estimate a maximum residue level.

Nectarines. Three pre-harvest trials were carried out in the USA (1968), but the conditions (0.12 kg/hl with WP or 3.4 kg/ha with D, 1-day PHI) were not comparable with any reported GAP.

Five post-harvest and five combined pre- and post-harvest trials were carried out in the USA (1968) with a post-harvest application rate of 0.24 kg/hl. The concentration in the treatment solution accorded with US post-harvest GAP but in six trials the treatment solution did not contain wax, whereas US GAP specifies the use of wax. The Meeting considered that these trials were not according to GAP since the use of wax could have a significant influence on the residue level.

The pre-harvest conditions in the combined trials (0.12 kg/hl of WP or 3.4 kg/ha of D, 1 day PHI) did not comply with US pre-harvest GAP (0.12 kg/hl, 4 applications, 10 days PHI) but the Meeting considered that as the residue levels would depend mainly on the post-harvest treatments the deviation of the pre-harvest treatments from GAP could be ignored. The residues in the four valid trials were 0.4, 0.5, 4.4 and 6.2 mg/kg.

One combined pre- and post-harvest trial with a 0.34 kg/hl post-harvest application did not comply with any reported GAP.

One Australian post-harvest trial complied with Australian post-harvest GAP (0.075 kg/hl dip or spray for stone fruit) but only the surface residue was measured. The Meeting concluded that there were too few trials to estimate a maximum residue level.

Peaches. One trial in Canada (1964) and one the USA (1966) were reported but there was no information on relevant GAP.

Twenty six post-harvest and 22 combined pre- and post-harvest trials were carried out in the USA (1966, 1975, 1976, 1988 and 1996), but there were very high residues in several untreated samples (maximum 11 mg/kg) and many reports were summaries without recovery data. The Meeting concluded that the trials could not be evaluated.

Two US (1966) post-harvest trials at application rates of 0.054-0.06 kg/hl approximated Australian post-harvest GAP for stone fruit (0.075 kg/hl dip or spray). The residues were 1.93 and 2.71 mg/kg.

In eight US combined post- and pre-harvest trials (1988, 1996) the post-harvest rate of 0.09 kg/hl complied with post-harvest GAP in Argentina (0.09-0.11 kg/hl dip or spray), Chile (0.09 kg/hl dip), the USA (0.09 kg/hl) and Australia but in six trials the pre-harvest applications were made one day before harvest whereas US pre-harvest GAP requires 10 days. The Meeting concluded that these trials were not according to GAP. The residues from the two trials which complied with pre- and post-harvest US GAP were 6.5 and 6.7 mg/kg.

One US pre- and post-harvest trial at the post-harvest rate of 0.018 kg/hl was comparable with Israel post-harvest GAP (0.023 kg/hl dip or spray), but not pre-harvest. The Meeting concluded that the data could be used for the estimation of a maximum residue level, since the residue from the pre-harvest application was much lower than from the post-harvest treatment. The residue was 2.8 mg/kg. Other US post-harvest trials at 0.036 and 0.15 kg/hl were not according to reported GAP.

One Canadian post-harvest trial (1966) at 0.36 kg/hl did not comply with any reported GAP. Four post-harvest supervised trials in Australia (1971, 1973) were not adequately reported or not properly conducted. Four Spanish post-harvest trials (1995) were reported without recovery data and no relevant GAP was available.

The Meeting concluded that there were too few trials to estimate a maximum residue level and recommended the withdrawal of the CXL for peach (15 mg/kg).

Plums. One pre-harvest trial in the USA (1995) was not according to any reported GAP.

Three of four post-harvest trials in the USA (1986, 1995) at 0.24 kg/hl or 1.1 kg/hl complied with US post-harvest GAP (0.24 kg/hl, 113-190l/h, 1 kg ai/25000 kg of fruit, or 0.9-1.1 kg/hl, 19-30 l/h, 1 kg/56000-67000 kg of fruit). The residues were 2.4, 2.4 and 6.1 mg/kg.

Four post-harvest trials in Spain (1995) were not according to any reported GAP and recovery data were not reported.

There were too few trials to estimate a maximum residue level. The Meeting recommended the withdrawal of the existing CXL for plums (including prunes) of 10 mg/kg.

Strawberries. Eight supervised trials in Spain (1995) lacked recovery data. Twelve trials in the USA (1963) did not comply with reported GAP.

The Meeting could not estimate a maximum residue level and recommended withdrawal of the existing CXL for strawberry (10 mg/kg).

Carrots. Eight pre-harvest trials in the USA (1995) were not comparable with any reported GAP. Five post-harvest trials in the USA (1965) at 0.09 and 0.10 kg/hl complied with US post-harvest GAP (0.09 kg/hl dip). The residues were 4.92, 5.94, 6.11 and 10.84 (2) mg/kg.

In six pre- and six pre- and post-harvest trials in the USA (1983) the residues in untreated samples were unreasonably high. The Meeting concluded that they could not be evaluated.

Two Israel post-harvest trials were reported without recovery data and could not be used for evaluation.

The residues in the five relevant trials were 4.92, 5.94, 6.11 and 10.84 (2) mg/kg.

The Meeting estimated a maximum residue level of 15 mg/kg and an STMR of 6.11 mg/kg for carrot.

Cucumbers and gherkins. The conditions in three of five indoor trials on cucumbers in the USA in 1965 (0.09-0.15 kg/ha, 1 and 8-21 days PHI) were according to US GAP (0.12 kg/ha, 1 day PHI). The residue at the GAP PHI was 1.79 mg/kg and at 8-21 days 0.18 and 0.22 mg/kg.

Two supervised trials on gherkins in The Netherlands (1972) at 1.6 and 1.8 kg/ha, 3 days PHI complied with GAP (1.4 kg/ha, 5 applications, 3 days PHI) except in the number of applications. The Meeting concluded that the trials could be used for evaluation because the effect of repeated application would be offset by growth dilution.

The Meeting could not estimate a maximum residue level for cucumbers or gherkins because there were too few trials.

Lettuce. Eighteen glasshouse trials with foliar and/or soil treatments in the USA (1971) lacked necessary information such as formulation type and recovery data. The Meeting could not evaluate them.

One of three field trials in the USA (1964) at 3.4 kg/ha, 26 days PHI, complied with US GAP (0.84-4.5 kg/ha, 14 days PHI) and the residue was 0.13 mg/kg. The other two trials were not comparable with any reported GAP.

One trial was carried out in the UK (1972) but no relevant GAP was reported.

Four trials in Belgium (1975, 1977) and six in The Netherlands (1970-71) were reported without recovery data and could not be used for evaluation.

The Meeting could not estimate a maximum residue level as there was only one satisfactory trial, and recommended withdrawal of the CXL for head lettuce (10 mg/kg).

Onions. Four trials with spring planting and six with autumn planting were carried out in the USA (1962, 1963, 1983 and 1986). The application rate in three of the spring trials (11 kg/ha at planting) was slightly higher than Canadian GAP (5.1-8.3 kg/ha for spring planting) but the Meeting agreed that the data could be used for estimation of a maximum residue level because the residues were low: 0.02, 0.07 and 0.11 mg/kg. The other spring trial was at the excessive application rate of 34 kg/ha.

Four of the autumn trials (28-35 kg/ha at planting) complied with Canadian GAP (27-33 kg/ha at planting). The residues were <0.05, 0.06, 0.11 and 0.19 mg/kg. The other two autumn planting trials with 9 applications of 2.2 kg/ha, 7-8 days PHI, exceeded the total application limit of US GAP (1.3-2.2 kg/ha, up to 2.8 kg/ha per season, 14 days PHI) and the PHI was too short, but the Meeting concluded that the trials could be evaluated because the residues in both were below the limit of determination, <0.1 mg/kg.

One trial in Finland and two US post-harvest trials were reported but without relevant GAP.

The residues from the nine relevant trials were 0.02, <0.05, 0.06, 0.07,<0.1 (2) 0.11 (2) and 0.19 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.1 mg/kg for bulb onion.

Tomatoes. Three glasshouse trials were carried out in the USA (1962). One at 0.07 kg/hl, 10 days PHI, with a residue of 0.62 mg/kg complied with US glasshouse GAP (0.09 kg/hl, 0.84 kg/ha, 10 days PHI and another with a residue of 0.89 mg/kg (0.13 kg/hl, 5 days PHI) approximated Canadian glasshouse GAP (0.13 kg/hl, 1 day PHI).

One glasshouse fumigation trial in the UK in 1972 (1.3 kg/ha, 2 days PHI) complied with GAP in The Netherlands (1.4 kg/ha, 5 applications, 3 days PHI). The Meeting could only regard the trial as supplementary because only the surface residue was determined.

Twelve field trials and four post-harvest trials were carried out in the USA (1963) but no relevant GAP was reported.

There were too few suitable trials to estimate a maximum residue level and the Meeting recommended withdrawal of the CXL for tomato (0.5 mg/kg)

Common beans. Thirty supervised trials were carried out in the USA (1964, 1965). Four trials in 1964 at application rates of 3.4 and 3.6 kg/ha and 4-7 days PHI accorded with US GAP (3.4 kg/ha, 2 days PHI). The residues were 9.67-17.1 mg/kg.

Three of the trials in 1965 at 3.4 kg/ha and 2 days PHI which also complied with US GAP gave residues of 0.45, 4.90 and 9.8 mg/kg.

One trial with a bush variety at 3.4 kg/ha with a dust formulation and another at 1.7 kg/ha with a WP formulation accorded with US GAP for the bush variety (2.7 kg/ha for dust, 1.9 kg/ha for WP, 2 days PHI). The residues were 0.61-1.44 mg/kg.

Twenty one other trials were not in accord with reported GAP.

Four trials in Australia (1963,1971) were reported only in summary form without necessary information, and could not be used for the estimation of a maximum residue level.

The Meeting concluded that there were too few satisfactory trials to estimate a maximum residue level.

Processing studies

Processing studies were carried out on grapes, plums and tomatoes. Processing factors for grapes were 1.34, 1.1 and 0.47 to juice, 2.10 and 0.98 to wet pomace, <0.1 and <0.2 to raisin waste and <0.1, <0.2 and <0.04 to raisins.

The raisins in the processing trials were sun-dried. In view of the photodegradability of dicloran, it was assumed that the very low residue of dicloran in the raisin waste and raisins was mainly due to photodegradation. The Meeting considered that a processing factor of zero for raisin waste and raisins could apply only to sun-dried raisins.

The mean processing factors were 1.1 to juice, 1.5 to wet pomace and zero to sun-dried raisin waste and raisins.

The processing factor from plums to dried prunes was 1.8 and the processing factors for tomatoes were 1.9 to paste and 1.1 to purée.

RECOMMENDATIONS

On the basis of the residues found in supervised trials, the Meeting concluded that the residues listed below are suitable for establishing MRLs and STMRs. The Meeting could not confirm many current CXLs and recommended their withdrawal. These recommendations are also indicated below.

Definition of the residue for compliance with MRLs and for estimation of dietary intake: dicloran

The residue is fat-soluble.

Commodity		Maximum residue level, mg/kg		Estimated STMR, for dietary intake estimation, mg/kg
CCN	Name	New	Previous	
VR 0577	Carrot	15, Po	10, Po	6.11
FB 0269	Grapes	W	10, Po	
VL 0482	Lettuce, Head	W	10	
VA 0385	Onion, Bulb	0.2	10, Po	0.1
FS 0247	Peach	W	15, Po	
FS 0014	Plums (including Prunes)	W	10, Po	
FB 0275	Strawberry	W	10	
VO 0448	Tomato	W	0.5	

DIETARY RISK ASSESSMENT

STMRs have been estimated for 2 commodities. The International Estimated Daily Intakes for the five GEMS/Food regional diets were in the range 0-20% of the ADI. The Meeting concluded that the intake of residues of dicloran resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

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DIMETHOATE (27)

OMETHOATE (55)

FORMOTHION (42)

EXPLANATION

Dimethoate was evaluated for residues by the JMPR in 1965–1967, 1970, 1973, 1977, 1978, 1983, 1984, 1986–1988, and 1990. The 1986 JMPR recommended separate MRLs for dimethoate and its metabolite omethoate to replace the previous limits for the combined residue. The 1988 JMPR reviewed substantial quantities of new field trial data, but most of the trials were in two countries in Europe. The 1990 JMPR reviewed additional data on two commodities.

The toxicology of dimethoate was reviewed by the 1996 JMPR within the CCPR periodic review programme. The Meeting allocated an ADI for the sum of dimethoate and omethoate expressed as dimethoate, although it was noted that omethoate was considerably more toxic. The 1996 Meeting noted that a re-evaluation of the toxicity of dimethoate might be required if the periodic review of its residue chemistry showed omethoate to be a major part of the residue.

Dimethoate was scheduled by the 1992 CCPR (ALINORM 93/24) for a periodic review of its residue chemistry by the 1993 JMPR. The schedule was changed in subsequent years, and the 1996 CCPR scheduled dimethoate, omethoate and formothion for periodic review in 1998 (ALINORM 97/24).

Data and information have been submitted by the Dimethoate Task Force (BASF, Cheminova, and Isagro, via Scientific Consulting Co., Woellstein, Germany), Cheminova, and the governments of Australia, Germany, The Netherlands, Thailand, and the UK.

Omethoate is a metabolite of dimethoate and was a marketed pesticide. Australia submitted product labels for omethoate and The Netherlands also submitted information on GAP as well as summaries of supervised field trials on apples and plums and monitoring data on food in commerce. No additional trial data were submitted for the use of omethoate *per se* on any agricultural commodity. The CCPR agreed that the MRLs for omethoate should reflect residues arising from the use of dimethoate.

Formothion has no extant MRLs. No data or information were submitted.

The following evaluation, within the CCPR Periodic Review Programme, is essentially restricted to dimethoate.

IDENTITY

Chemical name:

IUPAC: *O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate

CA: *O,O*-dimethyl *S*-[2-(methylamino)-2-oxoethyl] phosphorodithioate

CAS No.: 60-51-5

CIPAC No.:

Synonyms: cygon, cekuthoate, daphene, devigon, dimet, dimethogen, trimetion

Structural formula: $(CH_3O)_2P(=S)SCH_2CONHCH_3$

Molecular formula: $C_5H_{12}NO_3PS_2$

Molecular weight: 229.2 g/mol

Physical and Chemical Properties

Pure active ingredient

Appearance: white crystalline solid

Vapour pressure: 1.85×10^{-6} mm Hg at 25°C
1.18×10^{-6} mm Hg at 35°C (Teeter, 1988)

Melting point: 51–52°C

Octanol/Water Partition coefficient: 5.06 (log K_{ow} = 0.775) (Mangels, 1987)

Solubility:
Water, mg/ml: 39.8 at 25°C (Mangels, 1987)
23.3 at pH 5
23.8 at pH 7
25.0 at pH 9 (20°C) (Robson, *et al.*, 1991)
Other solvents: 140 g/100 ml acetone
140 g/100 ml acetonitrile
120 g/100 ml cyclohexanone
0.043 g/100 ml dodecane
150 g/100 ml ethanol
120 g/100 ml ethyl acetate
0.030 g/100 ml hexane
120 g/100 ml 2-propanol
160 g/100 ml methanol
150 g/100 ml dichloromethane
52 g/100 ml 1-octanol
100 g/100 ml toluene
31 g/100 ml xylenes
120 g/100 ml 1,2-dichloroethane
0.024 g/100 ml n-heptane
(25°C; Madsen, 1994)

Specific gravity: 1.277 g/ml at 65°C

Hydrolysis: Half-lives at 25°C: 68 days at pH 7
: 156 days at pH 5
: 4.4 days at pH 9

The main degradation products are *O*-demethyl-dimethoate and *O,O*-dimethyl hydrogen phosphorothioate acid at pH 9; *O*-demethyl-dimethoate at pH 5 and pH 7 (Hawkins, *et al*, 1986)

Photolysis: Stable under artificial sunlight (15 days continuous exposure) in acetate buffer solution at 25°C (Hawkins, *et al.*, 1986).
Decomposed on sandy loam soil thin-layer plates under artificial sunlight (15 days continuous exposure). Half-lives 7–16 days, control 40 days. Major degradation products were volatiles (9%), dimethyl hydrogen phosphate (15%), and dimethoxon (7%) (Hawkins, *et al.*, 1986)

Thermal stability: Stable up to 35°C. Isomerization to *O,S*-dimethyl *O*-methylcarbamoylmethyl phosphorodithioate occurs at higher temperatures. Rapid decomposition when heated.

Technical material

Minimum purity: 96%

Main impurities: Methyl (dimethoxyphosphinothioyl)thioacetate (CAS 757-86-8), 1.5% w/w, *O,O,S*-trimethyl phosphorodithioate (CAS 2953-29-9) 1.5% w/w

Melting range: 45–47°C

Stability: as pure active ingredient

formulations

The following formulations are available: Cygon, Clean Crop Dimethoate, Perfekthion, BI 58, Danadim 40, Roxion, Rogor. All are emulsifiable concentrates (EC), typically 400 g/l.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Rats (Dimethoate Task Force, 1995). Dimethoate, labelled with carbon-14 in the two *O*-methyl groups and having a specific activity of 32300 dpm/µg, was administered to Wistar rats, 7–10 weeks of age, at 10 and 100 mg/kg bw in a single dose in three separate experiments (1) orally, in water solution; (2) intravenously, in isotonic saline; and (3) dermally, in 1% aqueous sodium carboxymethylcellulose solution. A separate group of 18 rats was dosed orally at 10 mg/kg bw for seven consecutive days. The radiolabelled material was diluted with natural abundance dimethoate to obtain the desired specific activity.

Urine and faeces samples were collected from each of the single orally dosed animals at intervals for five days after dosing. Expired air was passed through traps of 2-ethoxyethanol/ethanolamine. At slaughter, the stomach and gi tract, adrenal glands, brain, heart, kidneys, liver, lungs, ovaries, testes,

pancreas, spleen, thyroid gland, uterus, muscle, fat, bone, bone marrow, and skin were taken for measurement of the ^{14}C balance. Additional groups of six rats each were killed at 0.5, 2, 6, and 25 hours after dosing, and tissues were taken for quantitative determinations. Rats from the dermal treatment were killed after 120 hours.

The excretion of radioactivity from the various forms of administration is shown in Table 1. After oral and intravenous administration about 80% of radioactivity was excreted within 24 hours, almost all in the urine. Although not indicated in Table 1, no differences were observed between males and females.

Table 1. Elimination of radioactivity from rats after a single dose of [^{14}C]dimethoate.

Dose, mg/kg bw	Route	Sample	Elapsed time (h)	Incremental % of dose
10	Oral	Urine	0–6	71 ± 1.2
			6–12	12 ± 4.7
			12–24	3.0 ± 0.60
			24–120	2.4 ± 1.0
		Expired air	0–72	2.2 ± 0.09
		Faeces	0–72	1.3 ± 0.16
		Carcase (incl. gi, kidney, liver, etc)	-	1.5 ± 0.52
		Total		93
100	Oral	Urine	0–6	56
			6–12	22
			12–24	9.9
			24–120	3.4
		Expired air	0 - 72	2.5
		Faeces	0–120	1.4
		Carcase (incl. gi, kidney, liver, etc)	-	1.7
		Total		97
10	Intravenous	Urine	0–6	81
			6–12	4.4
			12–24	2.1
			24 - 120	1.8
		Expired air	0–72	1.7
		Faeces	0–120	1.2
		Carcase (incl. gi, kidney, liver, etc)	-	0.88
		Total		93
10	Dermal	Urine	0–6	5.0
			6–24	2.5
			24–120	0.52
		Faeces	0–120	0.40
		Carcase (incl gi, kidney, liver, etc)	-	0.76
		Skin wash	6	62
		Treated skin		15
		Total		86
100	Dermal	Urine	0 - 6	0.66
			6 - 24	0.32
			24–120	0.15
		Faeces	0–120	0.09
		Carcase (incl gi, kidney, liver, etc)	-	0.16
		Skin wash	6	84
		Treated skin		2.9
		Total		88

The mean concentrations of triplicate determinations of radioactivity in male and female rat plasma after single oral doses at 10 and 100 mg/kg bw reached maxima in about 0.5 hours in both sexes dosed at 10 mg/kg bw and in females at 100 mg/kg bw. In males at 100 mg/kg bw the time was 0.25 hours. The mean maxima were similar in the two sexes dosed at 10 mg/kg bw, 8.62 mg dimethoate equivalents/l in males and 7.68 mg/l in females. After the 100 mg/kg bw dose the mean maxima were 50.7 and 93.2 mg dimethoate equivalents/l in males and females respectively. The decrease in radioactivity after the peak concentration was biphasic. At 24 hours after administration of the 100 mg/kg bw dose, the plasma concentrations of dimethoate were below detectable levels (0.05 mg/l).

Urine samples collected from animals 48 hours after oral, intravenous, and dermal doses (10 and 100 mg/kg bw) were combined and analysed by HPLC and TLC. Additional aliquots were incubated with ∃-glucuronidase/sulfatase enzymes and analysed by TLC. Other extracts, e.g. kidney and liver, were analysed by HPLC and TLC and co-chromatographed with reference standards. Some urine metabolites were isolated by preparative HPLC and identified by MS or GC-MS.

Four metabolites were identified in the urine: U4, dimethyl hydrogen phosphorothioate; U7, dimethyl hydrogen phosphorodithioate; U9, dimethoate carboxylic acid, and omethoate. U4 (8% of the TRR, 0.14% of the dose), U9 (15% of the TRR, 0.26% of the dose) and U7 (40% of the TRR, 0.68% of the dose) were also found in the kidneys (by TLC and co-chromatography). U4 (12% of the TRR, 0.51% of the dose) and U 7 (22% of the TRR, 0.95% of the dose) were found in the liver. The results are shown in Table 2.

Table 2. Radioactive compounds in rat urine after single doses.

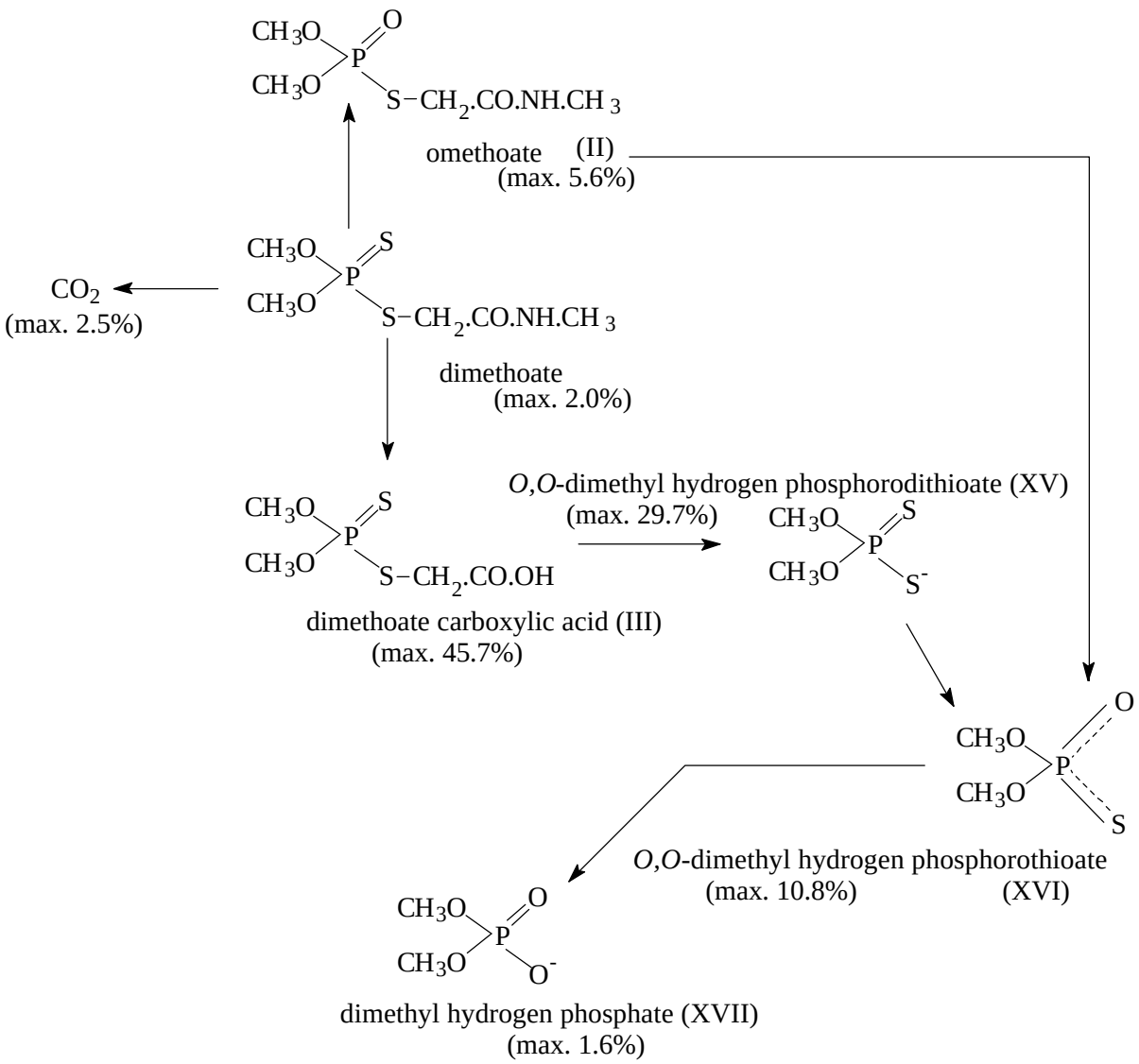
Compound	% of dose							
	Oral: 10 mg/kg bw		Oral: 100 mg/kg bw		Intravenous: 10 mg/kg bw		Dermal: 10 mg/kg bw[1]	
	Male	Female	Male	Female	Male	Female	Male	Female
U1	5.2	5.0	4.8	3.8	4.3	3.9	0.6	0.5
Omethoate	1.5	2.5	3.7	3.7	1.3	1.8	0.2	0.2
U2	0.3	0.2	0.4	0.3	-	-	-	-
U3	4.1	4.0	2.2	2.0	3.7	3.7	0.3	0.3
U4	8.3	5.7	8.7	4.7	6.5	4.0	0.8	0.6
U5	0.9	0.7	1.0	1.3	0.9	0.7	0.2	<0.1
U6	2.5	2.1	2.3	1.9	3.7	1.8		0.1
U7	26.6	25.2	20.3	22.1	22.5	24.1	2.9	3.2
Dimethoate	1.4	0.7	0.7	2.0	0.4	0.5	0.1	0.1
U9	37.8	35.1	43.2	44.4	42.7	45.7	2.5	2.8

[1] Radioactive components from the 100 mg/kg bw treatment were proportionally lower than from 10 mg/kg bw, <0.1–0.3%

The Dimethoate Task Force (DTF) proposed the biotransformation pathway shown in Figure 1.

Figure 1. Metabolism of dimethoate in rats

The values in parentheses are the maximum proportions of the administered dose found in urine. The $^{14}CO_2$ was found in expired air, and XVII was found only in tissues; its identification is tentative.



Poultry (Jalali, *et al.*, 1995). Three groups of 5 White Leghorn laying hens were dosed orally with [*methoxy*-^{14}C]dimethoate by capsule once daily for 7 consecutive days at 0.9 mg/kg bw, equivalent to 10 ppm in the diet. Eggs were collected twice daily, separated into yolks and whites, and pooled within groups. The hens were killed within 24 hours of the last dose, and tissues were composited in each group.

Sub-samples of tissues, eggs, excreta, and blood were homogenized and radio-assayed by combustion and liquid scintillation counting. The results are shown in Table 3.

Table 3. Residues in tissues, eggs, and excreta from the oral administration of [methoxy-^{14}C]dimethoate to laying hens.

Sample	Time	^{14}C, mg/kg as dimethoate			
		Group B[1]	Group C	Group D	Mean
Liver	7 days	0.615	0.621	0.687	0.641
Breast muscle	7 days	0.098	0.087	0.102	0.096
Thigh muscle	7 days	0.079	0.090	0.083	0.084
Fat	7 days	0.028	0.024	0.061	0.038
Skin	7 days	0.042	0.044	0.066	0.051
Blood	7 days	0.234	0.234	0.242	0.237
Egg yolk	0–24 hr	0.018	0.020	0.016	0.018
Egg yolk	24-48 hr	0.040	0.051	0.044	0.045
Egg yolk	4 8-72 hr	0.106	0.099	0.110	0.105
Egg yolk	96–120	0.277	0.246	0.241	0.255
Egg yolk	144 -	0.310	0.351	0.355	0.339
Egg white	0–24	0.080	0.070	0.120	0.090
Egg white	24–48	0.092	0.112	0.141	0.115
Egg white	48–72	0.090	0.120	0.202	0.137
Egg white	96–120	0.183	0.152	0.175	0.170
Egg white	144-	0.144	0.161	0.149	0.151
Excreta	75% dose				

[1] Each group (B,C,D) consisted of 5 hens. Group A was a control group of 5 hens

Homogenized tissue and egg samples were subjected to sequential solvent extraction (hexane and/or acetonitrile/water, methanol/1M ammonium hydroxide, 1:1), protease hydrolysis, 6 N HCl hydrolysis, and 3 N NaOH hydrolysis. These treatments solubilized the following percentages of the TRR: liver 90%, breast 102%, thigh 92%: egg whites 87%, egg yolks 94%, skin 70%, fat 58%, blood 34% and excreta 95%. The acetonitrile/water extracts and the methanol/ammonium hydroxide extracts were analysed by HPLC, as were some protease extracts, e.g. liver. The distribution of the radioactivity is shown in Table 4. Dimethoate was not found in any sample, and omethoate was found at low concentrations only in the liver and egg white.

Table 4. Distribution of the radiolabelled residues from the administration of dimethoate to hens.

Sample	Fraction	% of TRR	mg/kg as dimethoate	Characterization[1] or identification
Liver (0.822 mg/kg)	Hexane	3.0	0.025	
	Methanol/ammonium hydroxide	22	0.18	Phosphorylated natural products 0.16 mg/kg. No formate.
	Protease	36	0.29	0.081 mg/kg omethoate; 0.131 mg/kg dimethoate carboxylic acid. Not confirmed by 2D-TLC (interference). 0.11 mg/kg phosphorylated natural products.
	6 N HCl	27	0.22	No amino acids
	3 N NaOH	2.4	0.020	
	Total	90	0.74	
Breast muscle (0.098 mg/kg)	Acetonitrile/water (8/2)	46	0.045	Phosphorylated natural products
	Protease	34	0.034	
	Methanol/ammonium hydroxide	14	0.014	
	6 N HCl	8,4	0.008	
	Total	102	0.101	
Thigh muscle (0.079 mg/kg)	Acetonitrile/water (8/2)	36	0.028	Phosphorylated natural products
	Protease	36	0.028	
	Methanol/ammonium hydroxide	6.9	0.005	

Sample	Fraction	% of TRR	mg/kg as dimethoate	Characterization[1] or identification
	6 N HCl	6.2	0.005	
	3 N NaOH	6.2	0.005	
	Total	92	0.071	
Egg white (0.127 mg/kg; 96-120 h)	Acetonitrile/water (8/2)	50	0.064	Phosphorylated natural products. No formate.
	Protease	14	0.018	Omethoate 0.004 mg/kg. Dimethoate carboxylic acid, 0.003 mg/kg
	Methanol/ammonium hydroxide	9.5	0.012	
	6 N HCl	4.5	0.006	
	3 N NaOH	8.6	0.011	
	Total	87	0.110	
Egg yolk (0.192 mg/kg; 96-120 h)	Acetonitrile/water (8/2)	29	0.056	Phospholipids. Co-chromatography
	Protease	35	0.067	Phosphorylated natural product and many other peaks
	Methanol/ammonium hydroxide	11	0.021	
	6 N HCl	1.2	0.002	
	3 N NaOH	18	0.035	
	Total	94	0.18	
Fat (0.028 mg/kg)	Hexane	31	0.008	
	Acetonitrile/water (8/2)	9.8	0.003	
	Protease	10	0.003	
	Methanol/ammonium hydroxide	1.2	0.000	
	6 N HCl	5.4	0.001	
	Total	58	0.016	

[1] Phosphorylated natural products = 4 min HPLC peak + ^{14}C not recovered from HPLC +^{14}C solubilized by HCl and/or NaOH

Goats (Jalali *et al*, 1995; Jalali and Hiler, 1995). Dimethoate radiolabelled on the methoxy carbons was orally administered by capsule once daily for 3 consecutive days to two lactating goats at a level of 1.6 mg/kg bw/day. On the basis of the mean feed consumption for three days before the test, this was equivalent to 30 ppm dimethoate in the diet. During the treatment period, milk was collected twice daily. Urine and faeces were also collected, and the goats were slaughtered within 24 hours of the third dose. Total radioactive levels in the milk were determined by direct radio-assay and in the tissues by combustion and liquid scintillation counting. The results are shown in Table 5.

Table 5. Radioactivity in the tissues, milk, and excreta from goats dosed with 1.6 mg [^{14}C]dimethoate/kg bw/day for three consecutive days.

Sample	Collection time	Total radioactive residue, mg/kg, as dimethoate	
		Goat 1	Goat 2
Liver	Slaughter	1.22	1.01
Kidney	Slaughter	0.15	0.15
Muscle	Slaughter	0.070	0.047
Fat	Slaughter	0.045	0.057
Blood	Slaughter	0.076	0.079
Milk	0–12 h	0.15	0.082
	12–24 h	0.035	0.055
	24–36	0.18	0.13
	36–48	0.081	0.052
	48–60	0.23	0.14
	60 -	0.10	0.070
Urine + cage wash		91% of dose	86% of dose
Faeces		3.2% of dose	3.9% of dose

Homogenized tissue sub-samples were extracted sequentially with hexane, acetonitrile/water (8/2), and methanol/1 M ammonium hydroxide (1/1). The final post-extraction residue from the liver only was hydrolysed sequentially with protease, 6 N HCl, and 3 N NaOH. The extracts were analysed by HPLC (C-18 reverse phase) and/or TLC. Some extracts were benzylated with pentafluorobenzyl bromide (PFBB) before analysis. PFBB would benzylate dimethyl phosphate, methyl phosphate, dimethyl phosphorothioate etc.

Milk (48–60 hours) was sequentially extracted with hexane and acetonitrile/water (8/2). The acetonitrile extract was radio-assayed, concentrated, and chromatographed on an anion-exchange SAX solid-phase extraction column. The aqueous fraction from the column was benzylated and analysed by HPLC. In a separate experiment, the water eluate was lyophilized and analysed on a carbohydrate HPLC column. A sample of [^{14}C]lactose was similarly analysed, both before and after hydrolysis with 1.0 N HCl.

Dimethoate was not found in any of the tissue or milk. A low concentration of omethoate, released by protease treatment, was found in liver.

Urine (from 48 hours to slaughter) was fractionated on a QAE Sephadex A-25 column. Three major peaks were found . A separate urine fraction was fractionated on a C-18 solid phase extraction column. Combined aqueous fractions were analysed by TLC. The three fractions from the SPE column that contained the most radioactivity were prepared on a large scale, benzylated, purified, and analysed by HPLC and GC-MS.

The distribution and characterization of the radioactivity is shown in Table 6.

Table 6. Distribution and characterization of radioactivity from the administration of [^{14}C]dimethoate to lactating goats.

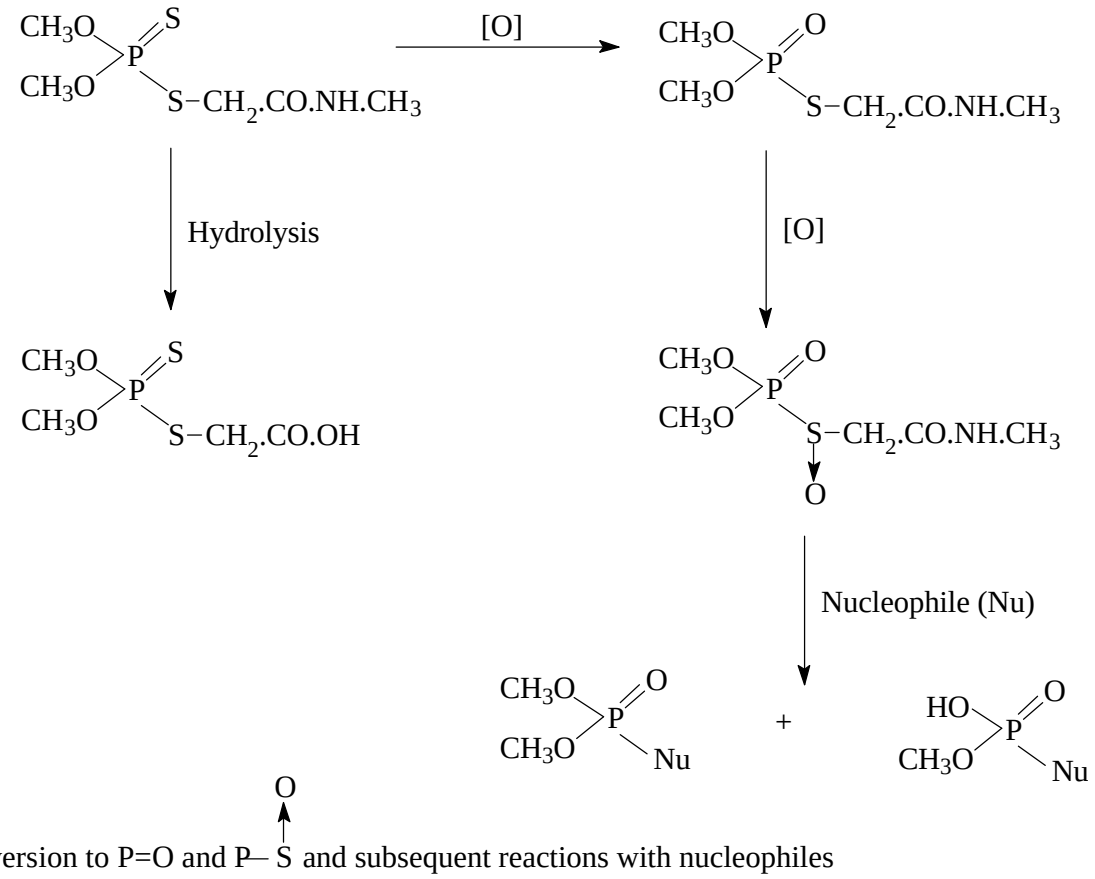
Sample	Fraction	% Total of TRR in sample	mg/kg as dimethoate	Identification or characterization[1, 2]
Liver (1.22 mg/kg)	Hexane	0.3	0.003	
	Acetonitrile/water	41	0.50	Anions 0.076 mg/kg (4 components by HPLC) . Phosphorylated natural products 0.4 mg/kg.
	Methanol/ammonium hydroxide	2.0	0.024	
	Protease	22	0.26	omethoate 0.12 mg/kg, dimethoate carboxylic acid 0.031 mg/kg by HPLC. Confirmation not successful (co-extractives). Phosphorylated natural products 0.03 mg/kg
	6 N HCl	14	0.18	No analysis
	3 N NaOH	1.8	0.022	
	Residue	19	0.23	
Liver (modified extraction)	Hexane	1.0	0.013	
	Acetonitrile/water (8/2)	21	0.26	HPLC peak at 4 min. 84% of injected ^{14}C accounted for. Phosphorylated natural products 0.20 mg/kg, 16% of TRR. No dimethoate carboxylic acid, no dimethyl phosphorothioate, no dimethyl phosphate (A-25 Sephadex). No [^{14}C]formate.
	Protease	22	0.27	Phosphorylated natural products 0.13 mg/kg (HPLC), 11% of TRR. Omethoate and dimethoate carboxylic acid present.
	Residue	11	0.13	

Sample	Fraction	% Total of TRR in sample	mg/kg as dimethoate	Identification or characterization[1, 2]
Kidney (0.149 mg/kg)	Hexane	2.0	0.003	
	Acetonitrile/water (8/2)	66	0.099	HPLC peak at 4 min., 76% of injected ^{14}C accounted for. Phosphorylated natural products 0.048 mg/kg, 32% of TRR. Anions about 0.020 mg/kg, 3 components.
	Methanol/ammonium hydroxide	5.1	0.008	
	Residue	34	0.051	
Muscle (0.070 mg/kg)	Hexane	0.5	<0.001	
	Acetonitrile/water (8/2)	57	0.040	HPLC peak at 4 min., 96% of injected ^{14}C accounted for. Poor benzylation (10%). Phosphorylated natural products 0.037 mg/kg, 53% of TRR. Anions 0.002 mg/kg.
	Residue	17	0.012	
Fat (0.045 mg/kg)	Hexane	11	0.005	
	Acetonitrile/water	12	0.005	
	Acetonitrile	4.2	0.002	
	Acetone	1.8	0.001	
	Residue	82	0.037	
Milk (48 h) (0.228 mg/kg)	Hexane	8.5	0.020	
	Acetonitrile/water (8/2)	82	0.18	HPLC peak at 4 min., 93% of injected ^{14}C accounted for. Poor benzylation, 17%. Phosphorylated natural products 0.12 mg/kg, 53% of TRR. Anions 0.005 mg/kg, 2 components. Lactose not radioactive.
Urine (48 h)	Solid phase extraction (water fractions)			Major metabolites identified by HPLC and TLC: dimethoate carboxylic acid, dimethyl phosphorothioate, dimethyl phosphate (GC-MS). Good benzylation of each metabolite: carboxylic acid 68%; phosphates 95% and 102%.

[1]Phosphorylated natural products = ^{14}C HPLC peak at 4 min minus benzylated peaks plus ^{14}C not recovered from HPLC column plus ^{14}C content of ammonium hydroxide/methanol extract (liver, kidney) plus ^{14}C residue. This represents an estimate of the maximum possible amount.
[2]Anions were assumed to be the ^{14}C peaks at about 50 min retention (C-18 HPLC) from the acetonitrile extract after benzylation

The metabolic pathways shown in Figure 2 are proposed for both poultry and ruminants. Almost all the dimethoate is eliminated in the urine as dimethyl phosphorothioate and dimethyl phosphate, products of the cleavage of the P–S–CH_2 linkage. The residues found in milk and tissues are consistent with the formation of the sulfoxides of omethoate and dimethoate carboxylic acid. The sulfoxides would combine with available nucleophiles, leading to the phosphorylation of proteins and lipids. Incorporation of -$O^{14}CH_3$ into natural products did not occur, as there was no apparent radioactive formate or lactose in milk.

Figure 2: Metabolism of dimethoate in poultry and ruminants.



NU (nucleophile) is a generic term for any electron-rich endogenous component. For example, the sulfoxide might phosphorylate proteins and lipids.

Plant metabolism

The DTF submitted summary information and literature citations on the metabolism of dimethoate in plants (Heidemann, 1995). No detailed reports were submitted.

The metabolism of [^{32}P]dimethoate in sugar beet was studied by Santi *et al* (1964). The radiolabelled dimethoate was applied to sugar beet plants 5 days after emergence, and the distribution of radioactivity was monitored by autoradiography. The metabolites identified were omethoate, de-*O*-methyl-dimethoate, *O,O*-demethyl hydrogen phosphorothiate ethyl hydrogen phosphate and phosphoric acid. Four metabolites remained unidentified. The concentration of omethoate increased to that of dimethoate after 13 to 30 days. Neither dimethoate nor omethoate could be found in the roots or leaves after day 37. The detailed report was submitted in Italian and could not be evaluated.

The metabolism of [^{32}P]dimethoate was investigated after foliar application by plant dipping to maize, cotton, peas and potatoes (Dauterman *et al.,* 1960). The plants were extracted 2 and 12 days after treatment, and metabolites were identified by paper chromatography and HPLC with co-chromatography. The proportion of the applied radioactivity on the leaf surfaces of maize, potato, and cotton decreased to

≤40% within 12 days of application. The most rapid decrease occurred with cotton, where <20% remained in 4 days, and the slowest with maize, where 40% remained at 12 days. These losses are attributed to volatilization and translocation from the surface. The surface residue on potato foliage after two days consisted of 87% dimethoate, 0.8% omethoate, and 13% water-soluble compounds, and after twelve days 17% dimethoate, 1.3% omethoate and 82% water-soluble compounds. The interval residues consisted of 40% dimethoate, 2.5% omethoate and 57% water-soluble compounds after two days, and 3.8% dimethoate, 1.1% omethoate and 95% water-soluble compounds after 12 days. The water-soluble surface and internal compounds were fractionated into four components by ion-exchange chromatography. The results are shown in Table 7.

Table 7. Composition of the water-soluble extracts of plant leaf surfaces and internal tissues after dipping in [^{32}P]dimethoate.

Interval, days	Surface H_3PO_4	Internal H_3PO	Surface $(MeO)_2P(O)OH$	Internal $(MeO)_2P(O)OH$	Surface Dimetho-ate COOH	Internal Dimetho-ate COOH	Surface De-O-methyl dime-thoate	Internal De-O-methyl dimethoate	Surface $(MeO)_2P(S)OH$	Internal $(MeO)_2P(S)OH$
Maize										
2	0.0	-	3.2	-	77	-	10	-	9.0	
12	0.0	0.0	6.3	14	88	4.1	3.5	64	2.7	18
Potato										
2	0.0	-	0.7	-	94	-	2.6	-	2.7	-
12	0.0	0.0	4.4	26	81	10	8.6	45	4.6	18
Cotton										
2	0.0	-	2.4	-	94	-	1.1	-	2.5	-
12	0.0	0.0	6.2	13	71	65.4	18	13	4.6	69
Pea										
12	52	48	7.6	12	81	5.7	8.6	45	6.0	18

The metabolism of [^{32}P] and [^{14}C]dimethoate (carbonyl label) in beans was studied by Lucier and Menzer (1968). Beans (*Phaseolus vulgaris L*) were planted in a greenhouse and treated after 18 days at the two-leaf stage with a foliar application of 5.15 mg/l [^{14}C]dimethoate to each plant. Plant samples (2 plants each) were taken on days 0, 2, 4, 6, 8 and 10 after treatment. For the [^{32}P] study plants were grown in a Percival plant growth chamber and treated 14 days after planting (1.78 mg/l). Samples taken 2 and 4 days were frozen for thirty minutes and rinsed with acetone to remove surface residues, then macerated in acetone and filtered. The filtrate was concentrated and extracted sequentially with hexane and chloroform. The hexane fraction was analysed by celite column chromatography and the chloroform and water fractions by TLC (2-dimensional, with reference compounds). The results are shown in Table 8.

Table 8. Radiolabelled compounds found from the application of [^{32}P]dimethoate or [^{14}C]dimethoate to the foliage of beans.

Compound	% of applied radioactivity at interval, days						
	2 (^{14}C)	2 (^{32}P)	4 (^{14}C)	4 (^{32}P)	6 (^{14}C)	8 (^{14}C)	10 (^{14}C)
Dimethoate	29	66	23	44	18	13	12
Omethoate	0.69	2.2	0.81	4.4	0.61	0.53	0.48
De-*N*-methyl-dimethoate	0.72		0.05		0.03	0.05	0.05
Dimethoate carboxylic acid	0.12	1.6	0.14	2.4	0.07	0.06	0.20
De-*O*-methyl carboxylic acid	0.21	0.08	0.17	0.09	0.15	0.05	0.21
De-*O*-methyl-dimethoate		0.39		0.49			
Dimethyl phosphorodithioate		2.5		4.2			
Dimethyl phophorothioate		0.43		0.76			
Dimethyl phosphate		0.38		0.74			
Unknown (2)	11		1.3				

Compound	% of applied radioactivity at interval, days						
	2 (^{14}C)	2 (^{32}P)	4 (^{14}C)	4 (^{32}P)	6 (^{14}C)	8 (^{14}C)	10 (^{14}C)
Unknown (6)		4.0		3.1			
Hexane extract (excluding dimethoate)	2.2	1.9	1.9	1.2	1.6	1.2	1.1
Post-extraction solid	8.7	2.4	8.8	7.0	12	16	16
Total recovery (% of applied dose)	53	82	36	68	32	31	30

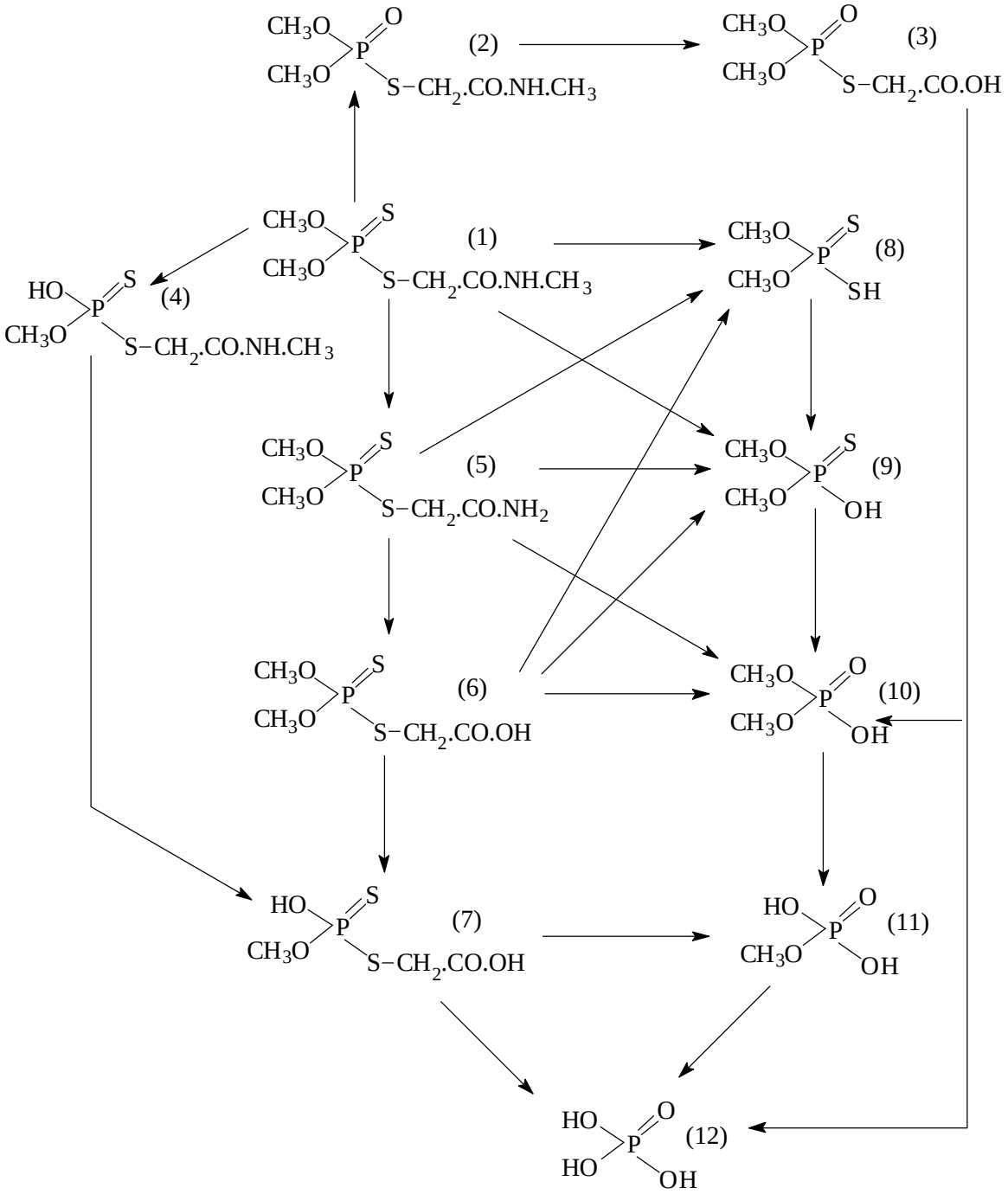
The metabolism of [^{32}P]dimethoate was studied on excised cotton leaves by Hacskaylo and Bull (1963). The third and fourth leaves from the terminal of 8-week old cotton plants removed and the basal ends of the petioles inserted into separate vials containing 100 µg of [^{32}P]dimethoate in 200 ml water. After the solutions were absorbed, the leaves were placed under fluorescent lights for 12 hours. The leaves were macerated with acetone 1, 3, 6 and 14 days after the treatment and the extracts analysed by paper chromatography. The dimethoate fell to 10% of its initial value within 6 days. Omethoate remained at about 6% of the total reactivity in the extract throughout the study. The compounds detected were phosphoric acid, de-*O*-methyl dimethoate carboxylic acid, dimethyl phosphate (2.5–11% of the total radioactivity on the chromatogram), dimethyl phosphorothioate (1.6–12%), dimethyl phosphorodithioate (4–11%), dimethoate carboxylic acid (15–50%) and omethoate. The dimethoate concentration ranged from 70% of the normalized total radioactivity on day 1 to 1.9% on day 14.

The metabolism of [^{32}P]dimethoate on lemons was reported by Santi (1961). The report was in Italian and only an English summary prepared by the Scientific Consulting Co. was available. The radioactive material applied, the method of application and the concentration were not specified. The compounds found were dimethoate, omethoate, dimethyl phosphate, phosphoric acid, *O,O*-dimethyl hydrogen phosphorothioate and de-*O*-methyl dimethoate.

Other studies on tomatoes, olives, wheat grain, sorghum grain, onions and cucumbers were reported in detail or as summaries but they provided information deemed inadequate or supplementary. Some residue dissipation studies, e.g. on spinach, with unlabelled dimethoate were also reported.

Although all the studies were deficient in the conduct of the experiments and/or the reporting of the data, taken together they defined the metabolic pathways shown in Figure 3. The metabolism follows two paths, oxidation to omethoate and hydrolysis with the formation of phosphoric acid, dimethyl phosphate, *O,O*-dimethyl hydrogen phosphorothioate and de-*O*-methyl dimethoate

Figure 3: Proposed metabolic pathways of dimethoate in plants.



1. dimethoate
2. omethoate
3. omethoate carboxylic acid
4. de-*O*-methyl-dimethoate
5. de-*N*-methyl-dimethoate
6. dimethoate carboxylic acid
7. de-*O*-methyl-dimethoate carboxylic acid
8. *O*,*O*-dimethyl hydrogen phosphorodithioate
9. *O*,*O*-dimethyl hydrogen phosphorothioate
10. dimethyl hydrogen phosphate
11. methyl dihydrogen phosphate
12. phosphoric acid

Environmental fate in soil

Residues in rotational crops

In a confined rotational crop study with lettuce, turnips and wheat as the secondary crops (Adair *et al.*, 1995) twelve plots, each consisting of a plastic-lined wooden box 90 x 75 cm x 30 cm deep were filled with Litchfield sandy loam soil in Watsonville, California, USA. Six boxes served as controls. Each of the remaining six was sprayed with an acetone solution of [^{14}C]dimethoate labelled on the methoxy carbons at a rate of 0.56 kg ai/ha which was incorporated into the soil. Before planting the boxes were moved into greenhouses. At 30 days after treatment (DAT), lettuce, wheat and turnips were planted in control and treated boxes. This procedure was repeated at 120 DAT using boxes in which nothing had been planted previously. Some boxes intended for longer planting intervals were not used after measuring the radioactivity levels in the 120 DAT crops.

Samples were collected at normal maturity, weighed and frozen. Wheat hay was dried for three days before freezing. The samples were homogenized with dry ice and returned to frozen storage. The total radioactive residue (of the TRR) in sub-samples was determined by combustion and liquid scintillation counting. Other sub-samples were extracted with solvent, typically acetonitrile or acetonitrile/0.1 N HCl (1:1). Wheat forage extracts (30 DAT) were hydrolysed with hydrochloric acid (6 N, 4 h reflux) to determine conjugates. Other fractions of the wheat forage acetonitrile extracts were acetylated with acetic anhydride in pyridine to determine hydroxy compounds. Wheat forage extracts from the 30 DAT planting were benzylated to determine acidic compounds. The ^{14}C in the post-extraction solids was measured by combustion and LSC.

The final extracts were analysed by HPLC with a C-18 column and UV detector. Fractions were collected at half-minute intervals and analysed by LSC. Extracts were also analysed by TLC on silica gel F254 plates. Compounds were identified by co-chromatography with unlabelled reference standards. All analyses were within 30 days of harvest. The results are shown in Table 9.

Table 9. ^{14}C residues in crops grown in sandy loam soil treated with [^{14}C]dimethoate at 0.56 kg ai/ha.

Crop	Planting DAT	Harvest DAT	TRR, mg/kg as dimethoate	Extracted residue, % of TRR	Unextracted residue, % of TRR	Extract characterization or identification[1]	
						% of TRR, mg/kg	Component
Lettuce	30	78	0.030	74	26	60	Polar
Turnip roots	30	97	0.008	-	-		
Turnip foliage	30	97	0.037	55	45	32	Polar
Wheat forage	30	62	0.036	63	42	50 0 0 25	Polar hydroxy compounds (no acetylation). Conjugates Acidic compounds
Wheat hay	30	97	0.037	35	84	35	Polar
Wheat straw	30	141	0.045	72	29	56	Polar
Wheat grain	30	141	0.021	62	52	57	Polar
Lettuce	120	174	0.003				
Turnip roots	120	208	0.001				
Turnip foliage	120	208	0.005				
Wheat forage	120	168	0.004				
Wheat hay	120	258	0.009				
Wheat straw	120	258	0.020	88	28	55	Polar
Wheat grain	120	258	0.012	27	82		

[1] Co-chromatography with reference standards showed the following compounds to be absent: dimethoate, omethoate, de-*N*-methyl-dimethoate, isodimethoate, de-*O*-methyl-dimethoate, de-*O*-methyl-omethoate, *O*,*O*-dimethyl hydrogen phosphorothioate, MP-1-acetic acid., demethyl-MPEM, methyl dihydrogen phosphate, de-*O*-methyl-dimethoate carboxylic acid.

Degradation

The DTF reported studies on the degradation of radiolabelled dimethoate in soil under both aerobic and anaerobic conditions (Hawkins *et al.*, 1989, 1990). In the aerobic study (in 1988), [*O-methyl-*^{14}C]dimethoate in water was applied to English sandy loam soil at a rate of 2.15 µg/g soil (dry weight). Some soil samples were fortified at the high level of 3.2 mg dimethoate/sample, the dimethoate being a mixture of radiolabelled and unlabelled material. About 80 g of treated soil was placed in each of a series of dishes which were maintained in glass columns flushed with an upward stream of humidified air which was then passed through trapping solutions for $^{14}CO_2$. The systems were maintained in the dark at 22°C. Duplicate dishes were removed at intervals of 0–181 days for analysis and the trapping solutions were sampled at the same times. The soils were extracted with acetonitrile or 1:1 acetonitrile/water at ambient temperature or under reflux. The extracts were radio-assayed and analysed by both reverse- and normal-phase TLC. Identification was based on co-chromatography with authentic standards in two solvent systems.

The [^{14}C]dimethoate was rapidly degraded under aerobic conditions in the sandy loam soil, with a half-life of 2.4 days. Dimethoate as a proportion of the applied radioactivity decreased from 96% on day 0 to 54% on day 2, 28% on day 4, 2% on day 14, 0.8% on day 30 and 0.4% on day 90. Two degradation products were identified: dimethyl phosphorothioate and de-*O*-methyl dimethoate. Neither exceeded 2% of the applied radioactivity at any time. Numerous unknown compounds were found, but none exceeded 2% of the applied radioactivity. As indicated in Table 10, the major route of degradation was volatilization, with $^{14}CO_2$ accounting for about 75% of the applied radioactivity after 181 days.

Table 10. Recovery of radioactivity from sandy loam soil treated with [^{14}C]dimethoate at 2 mg/kg under aerobic conditions.

Elapsed time, days	% of applied ^{14}C			
	Cumulative CO_2	Extractable	Unextractable	Soil total
0		96.9	0.3	97.2
1	5.2	81.0	4.6	85.6
4	15.2	66.3	9.9	76.2
7	52.2	17.3	15.7	33.0
14	61.4	8.7	19.4	28.1
30	65.1	6.6	20.8	27.4
60	67.8	4.6	19.4	24.0
90	70.2	3.7	16.0	19.7
120	72.8	3.4	15.3	18.7
181	74.6	2.2	16.2	18.4

In the anaerobic study [*O-methyl-*^{14}C]dimethoate in water was applied to English sandy loam soil at a rate of 2.06 µg/g soil (dry weight). 100 g portions of treated soil in Buchner flasks equipped with CO_2 traps were maintained at 25°C in darkness and a stream of air was passed through each system for two days at a rate of 30 ml/minute. After two days of aerobic incubation the soil in each flask was flooded to a depth of 2 cm with distilled, degassed water and the gas purge was changed to nitrogen. Flasks were removed at intervals and the soils extracted as in the aerobic study after removal of the supernatant water. Some soil sub-samples were also extracted with 0.5 M aqueous sodium hydroxide, either at ambient temperature or by reflux, for 24 hours. Supernatants and extracts were radio-assayed and analysed by TLC and HPLC. Autoradiographs of the TLC plates were taken and the HPLC was equipped with both UV and radioactivity detectors. The half-life of dimethoate was calculated to be 4 days from the start of anaerobic conditions with biphasic exponential decay. Two degradation products were identified from the anaerobic period as de-*O*-methyl-dimethoate (10% of the applied radioactivity) and *O,O*-dimethyl phosphorothioate (5%). About 15% of the applied radioactivity was lost as $^{14}CO_2$ during the 60-day anaerobic phase, in addition to a 27% loss during the

initial 2 days of aerobic incubation. The degradation of dimethoate was slower under anaerobic than aerobic conditions. The results are shown in Table 11.

Table 11. Distribution of radioactivity in sandy loam soil after application of [^{14}C]dimethoate at 2 mg/kg under aerobic and anaerobic conditions.

Elapsed time, days	^{14}C, % of applied								
	Cumula-tive CO_z	Super-natant water	Solvent extract	NaOH Extract	Unextract-able	Soil total[1]	Dime-thoate	Dimethyl phosphoro thionate	De-*O*-methyl-dimethoate
Aerobic phase (days 0–2)									
0		N/A	96		0.3	96	94.7		
2	27		54	9.7	0.8	64	39.8	1.4	3.2
Anaerobic phase (days 2–62)									
9	30	28	18	13	1.0	60	19	3.4	8.6
16	32	28	15	12	0.8	56	13	4.4	9.6
34	35	24	13	14	1.0	52	8.3	4.2	6.2
62	41	16	9.0	21	2.0	48	5.5	3.6	7.1

[1] Supernatant water plus solvent extract plus NaOH extract plus unextractable

Both the DTF and Cheminova reported studies in the UK and USA on the dissipation of dimethoate in or on soil (Burden, 1991; Jacobson and Williams, 1994a,b). In the UK study Riverside clay loam, Middlefield silty clay and Somersham sandy loam were each fortified with dimethoate (60 µg per 50 g dry soil, equivalent to 1.2 kg ai/ha) and incubated aerobically in the dark at 20 ± 3°C . The soils were contained in conical flasks with cotton wool stoppers. The concentration of dimethoate was monitored from day 0 to day 16. The analysis consisted in overnight Soxhlet extraction of a 50 g sample with acetone/hexane (4/1, 200 ml) and hydrochloric acid (1 ml, 4 M). The extract was concentrated, the solvent changed to toluene and the analysis completed by GLC (25 m x 0.53 mm CP Sil-8 column, NPD). The method was validated by fortification of control samples of each of the three soil types. The overall mean recovery was 92% for a fortification range of 0.05 to 1.2 mg/kg, n = 15, range 79–126%. Concurrent recoveries were also determined.

In the New York studies, bare ground characterized as sandy loam at 0–60 cm and as loam at 60-120 cm was treated with dimethoate formulated as a 25% ai wettable powder (WP) at a rate of 4.5 kg ai/ha, in July 1993. The broadcast application was made with a tractor-mounted applicator. Soil core samples were taken immediately before and after treatment and at selected intervals up to 88 days after application. Total irrigation plus rainfall over the 88-day period totalled 28 cm. Samples (25 g frozen up to 177 days before analysis) were extracted with acetone/water (95/5, 250 ml). The filtrates were stripped of acetone and the residual water solutions partitioned with methylene chloride. The extracts were purified on Celite/charcoal columns and the hexane/acetone (1/1) eluate fractions were fortified with carbowax to 0.1%. The final extracts were analysed by GLC (30 m x 0.53 mm RTX-5 column and FPD). The method was validated with overall recoveries of 91% for dimethoate and 86% for omethoate, n = 12, fortification range 0.01–1.0 mg/kg. The recovery ranges were 82–110% for dimethoate and 80–100% for omethoate. Concurrent recoveries were also determined.

In the Texas trial, a sorghum plot was sprayed with dimethoate formulated as a 43.5% ai EC (Dimethoate 400) in July 1993. The application was broadcast, post-emergence, at 1/7 kg ai/ha top two- to four-leaf plants. The soil was characterized as silt loam at 0–120 cm. Soil core samples were taken immediately before and after treatment and at selected intervals for 90 days. The total rainfall plus irrigation over the 90-day period was 22 cm. Soil cores were stored frozen and analysed within 123 days of collection by the method used for the New York work.

The results of the three dissipation studies are shown in Table 12. The half-life of dimethoate in the UK and New York soils was 2–4 days. In Texas, where a crop was sprayed, the half-life was about 11 days. The US trials showed that the dimethoate did not migrate below the top soil layer.

Table 12. Dissipation of dimethoate in soil.

Trial/Year	Application rate, kg ai/ha	Post - treatment interval, days	Soil type/depth, cm, in US trials	Dimethoate, mg/kg	Omethoate, mg/kg	Concurrent analytical recoveries
DTF-UK/1991	1.2	0	Riverside clay loam/NA	1.0		88% at 1.2 mg/kg
		1		0.94		93% at 1.0 mg/kg
		2		0.62		97% at 0.8 mg/kg
		4		0.42		73% at 0.5 mg/kg
		5		0.13		105% at 0.8 mg/kg
		7		0.11		93% at 0.1 mg/kg
		8		0.077		87% at 0.1 mg/kg
		10		0.065		72% at 0.1 mg/kg
		12		0.041		57% at 0.1 mg/kg
	1.2	0	Middlefield silty clay	1.5		115% at 1.2 mg/kg
		1		1.0		93% at 1.0 mg/kg
		2		0.74		95% at 0.8 mg/kg
		4		0.79		57% at 0.5 mg/kg
		5		0.25		57% at 0.8 mg/kg
		7		0.070		100% at 0.1 mg/kg
		8		0.081		90% at o.1 mg/kg
		10		0.063		98% at 0.1 mg/kg
		12		0.037		56% at 0.1 mg/kg
		0	Somersham sandy loam	0.95		82% at 1.2 mg/kg
		1		0.77		82% at 1.0 mg/kg
		2		0.75		84% at 0.8 mg/kg
		4		0.52		72% at 0.5 mg/kg
		5		0.42		74% at 0.8 mg/kg
		7		0.43		87% at 0.1 mg/kg
		8		0.32		
		10		0.065		
		12		0.096		75% at 0.5 mg/kg
		16		0.10		93% at 0.1 mg/kg
Cheminova New York/ 1993	4.5	0	0–5.2	1.38	<0.01	D: 80-110%, n = 15, at 0.01 mg/kg, mean 92% O: 50-100%, n = 15, at 0.01 mg/kg, mean 81% D: 83-95%, n = 10, at 0.02-0.10 mg/kg, mean 87% O: 65-80%, n=10, at 0.02-0.10 mg/kg, mean 69% D: 91-111%, n =5, at 0.25-2.0 mg/kg, mean 92% O: 71-89%, n=5, at 0.25–2.0 mg/kg, mean 78%
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
			45.7-61	<0.01	<0.01	
		1	0-15.2	1.44	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
			45.7-61	<0.01	<0.01	
		2	0-15.2	1.52	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		3	0-15.2	1.39	0.017	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		6	0-15.2	0.59	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		10	0-15.2	0.23	<0.01	
			15.2-30.5	0.011	<0.01	
			30.5-45.7	<0.01	<0.01	
			45.7-61	<0.01	<0.01	
		14	0-15.2	0.090	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
			45.7-61	<0.01	<0.01	

Trial/Year	Application rate, kg ai/ha	Post - treatment interval, days	Soil type/depth, cm, in US trials	Dimethoate, mg/kg	Omethoate, mg/kg	Concurrent analytical recoveries
		28	0-15.2	0.012	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		60	0-15.2	<0.01	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		88	0-15.2	<0.01	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
Cheminova Texas/1993	1.7	0	0-15.2	0.48	<0.01	D: 60–100%, n = 14, at 0.01 mg/kg, mean 89% O: 70–110%, n = 14, at 0.01 mg/kg, mean 86% D: 70-106%, n = 11 at 0.05–0.25, mean 92 O: 26–80%. n = 11, at 0.05–0.25 mg/kg, mean 69 (sd 18) D: 89- 96%, n = 4 at 0.50–1.00 mg/kg, mean 93% O: 67–86%, n = 5 at 0.50–2.0 mg/kg, mean 77%
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		1	0-15.2	0.37	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		2	0-15.2	0.40	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		3	0-15.2	0.37	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		6	0-15.2	0.32	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-35.7	<0.01	<0.01	
		11	0-15.2	0.21	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		14	0-15.2	0.17	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		28	0-15.2	0.088	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		60	<0.01	<0.01	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.01	<0.01	
		90	0-15.2	<0.01	<0.01	
			15.2-30.5	<0.01	<0.01	
			30.5-45.7	<0.1	<0.01	

The DTF reported a soil dissipation study with bean, grape and bare ground plots in California (Becker, 1991). A dimethoate EC formulation was applied three times with a 7-day re-treatment interval at 0.56 kg ai/ha to green beans planted in Atwater Sandy Loam and twice at 2.8 kg ai/ha to bare ground with a 14-day re-treatment interval. The applications were at the early bloom, bloom to 5.1 cm pod and 5.1 to 7.6 cm pod stages. A WP formulation (Dimethogon 25WP, 25% ai; for apples, pears, grapes) was applied twice to the bare ground was with an overhead spray boom at 2.8 kg ai/ha with a 14-day interval The application to grape vines was by airblast spray to the foliage at the 0.75-1.5 and 1.5-2.0 cm diameter berry stages. The crops were maintained according to normal agricultural practice, including furrow irrigation. The half-lives were 9.8 days in bean soil, 6.0 days in grape soil and 7.8 days in bare soil.

Soil cores stored frozen pending analysis were segmented and analysed after acetone extraction by GLC with flame photometric detection. The method was validated with control soil samples fortified at 0.01–0.10 mg/kg with dimethoate and omethoate.

In the bean trial dimethoate and omethoate were not detected below the top core segment (0–15 cm) at any time up to 227 days after the first application. The highest dimethoate concentration was 0.19 mg/kg on the day of the third treatment and the highest omethoate concentration was 0.038 mg/kg 3 days after the third treatment.

In the grape vine plots the maximum dimethoate and omethoate concentrations in the top soil layers (0–15 cm) were 0.27 and 0.093 mg/kg respectively, both 4 days after the second application. Dimethoate only was found in the second core layer (15–30 cm) seven days after the first application at 0.014 mg/kg. Monitoring was continued for 112 days after the first application, with a nominal limit of quantification of 0.01 mg/kg.

After treating bare ground the maximum dimethoate concentration was 1.8 mg/kg in the 0–15 cm layer on the day after the second treatment, and the maximum omethoate concentration 0.56 mg/kg in the same layer three days after the second treatment. Dimethoate was found in lower soil layers up to two weeks after each treatment. The deepest apparent residue was 0.025 mg/kg in the 91–120 cm layer immediately after the second application, but this may have been spurious as no dimethoate was found in the four higher layers (15–91 cm) nor in the 91-120 cm layer in two replicate plots. Generally, dimethoate in the lower layers was highest 2–7 days after an application, with a maximum concentration of 0.022 mg/kg in the 46–61 cm segment. The maximum omethoate migration appeared to occur 3–7 days after the first application with maximum concentrations of 0.015 mg/kg in the 46–61 cm and 0.012 mg/kg in the 61–91 cm layers. No migration was observed after the second application. The bare ground was irrigated one and nine days after the first application and seven days after the second application, 15.2 cm each time.

The DTF reported a study of the mobility of [*O-methyl*-^{14}C]dimethoate in columns of four English soils: sand, sandy loam, silt loam and clay loam (Hawkins *et al.*, 1986). All four were leached after adding unaged dimethoate, and the sandy loam also after ageing. In the experiment with aged residues the sandy loam was treated with a mixture of labelled and unlabelled dimethoate equivalent to 0.15 mg dimethoate per 100 g soil (sifted and brought to 40% of maximum water holding capacity). The samples were placed in conical flasks and stored in the dark at 22ºC. After thirty days storage one sample was taken for radio-assay and a duplicate sample was subjected to column leaching. The sample for assay was extracted with 1:1 acetonitrile/water and the radioactivity in both the extract and the extracted soil was determined. For the leaching trial a column of the sandy loam soil (25 cm height) was topped with the remainder of the stored dimethoate-treated soil mixed with ^{36}Cl-sodium chloride. The radiolabelled sodium chloride was used to ascertain the void volume, defined as the volume of eluant needed to leach 50% of the recovered ^{36}Cl through the column. The column was eluted with distilled water (1 l) and fractions of 16–21 ml each were radio-assayed for ^{14}C and ^{36}Cl. The column was divided into six sections of 5 cm each and the soil from each section was air-dried and radio-assayed.

This procedure was repeated with freshly fortified samples of each of the four soils. A weighed 30 cm column of each sifted soil was covered with distilled water and 1 ml of an aqueous solution of [^{14}C]dimethoate and sodium [^{36}Cl]chloride. The application rate was 0.15 mg dimethoate per column, approximately equal to 0.75 kg ai/ha.

The eluates and soil extracts from both aged and unaged soil columns were analysed by TLC and HPLC.

The [^{14}C]dimethoate was extensively leached on columns of all four soils, both unaged and aged. The rate of leaching was inversely proportional to the loam content, being most rapid with sand. The results are shown in Table 13.

Table 13. Elution of [^{14}C]dimethoate from soil columns.

Column section	% of applied radioactivity				
	Somersham sandy loam	Gleadthorpe sand	Goole silt loam	Sandiacre clay loam	30-day aged Somersham sandy loam
1 (top)	2.9	0.3	1.6	2.0	28.4
2	1.7	0.3	2.7	2.7	6.2
3	1.4	0.3	2.7	2.5	0.1
4	1.2	0.2	3.2	2.5	0.1
5	2.1	0.3	3.6	2.5	0.2
6 (bottom)	1.9	0.3	4.0	3.4	0.1
Total retained	11.2	1.6	17.8	15.6	35.1
Total eluted	86.7	100.6	72.8	71.8	5.1
Total recovered	97.9	102.2	90.5	87.4	40.2
% Dimethoate eluted (TLC)	79	93	60	55	-
Distribution coefficient, K_d[1]	0.30	0.06	0.57	0.74	-
% organic carbon in soil	1.5	0.9	3.5	7.4	1.5

[1] K_d (ml/g) = [(vp-1)vv]/[vv/w] where vp is volume of eluant to leach 50% of applied ^{14}C through column, vv is void volume of column, and w is the weight of soil in the column

The DTF also reported a lysimeter trial (Wyss-Benz *et al.*, 1993). [*Carbonyl*-^{14}C]dimethoate was applied as a foliar spray to cabbages planted in two lysimeters embedded in the ground to soil level in 1992 in Itingen, Germany. The depth was 120 cm and the cultivated area was 1 m^2 (115 cm diameter). The amount of dimethoate applied to each lysimeter was 120 mg, corresponding to 1.2 kg ai/ha. Various crops were planted around the lysimeters. The actual applications were 112.02 mg to lysimeter 1 and 113.08 mg to lysimeter 2. Each lysimeter had a steel sieve bottom and was surrounded by a cylindrical sleeve with a vessel to collect water that had percolated through the lysimeter soil. The total precipitation and irrigation over the two-year study was 190 cm. After harvesting the cabbage, winter salad, garden salad, endive salad and winter wheat were planted sequentially. The total study period was 744 days. Some results are shown in Table 14.

The leachates were analysed by TLC after lyophilization. Dimethoate was never detected. Layers 12 and 11 from the lysimeters were extracted and 30–38% of the extractable radioactivity (<4%) was attributable to dimethoate. The unextracted radioactivity was characterized as bound to fulvic acids (20%), bound to humic acids (45%) and bound to humin (30%).

Table 14: Percolation of [^{14}C]dimethoate applied to cabbage at 1.2 kg ai/ha in lysimeters.

Sample	% of applied radioactivity	
	Lysimeter 1	Lysimeter 2
Leachate year 1	0.31	0.28
Leachate year 2	0.12	0.075
Cabbage	1.4	2.5
Winter salad	0.009	0.006
Garden salad	0.019	0.017
Endive salad	0.015	0.015
Winter wheat	0.002	0.002
Layer 12 (0-12 cm)–744 d	18	16
Layer 11 (12-21 cm)	1.3	0.85
Layer 10 (21-30 cm)	0.30	0.30
Layer 9 (30-40 cm)	0.20	0.14
Layer 8 (40-50 cm)	0.12	0.07
Layer 7 (50-60 cm)	0.05	0.04
Layer 6 (60-70 cm)	0.03	0.03
Layer 5 (70-80 cm)	0.02	0.02
Layer 4 (80-90 cm)	0.01	0.03
Layer 3 (90-100 cm)	0.01	0.01
Layer 2 (100-110 cm)	0.01	0.02
Layer 1 (110-120 cm)	0.02	0.01

[1]Unaccounted radioactivity (78–80% of that applied) was assumed to be in volatile substances

The DTF reported a study on the adsorption and desorption of dimethoate on soil (Schanne, 1981). Dimethoate, labelled on the carbonyl carbon, in 0.01 M $CaCl_2$ aqueous solution was equilibrated with various soils (5 g) by shaking at 150-200 oscillations/min for 4.5 hours. The dimethoate concentration range studied was about 0.04 to 5.2 mg/l. The mixtures were centrifuged and decanted. For desorption, the residual soils were equilibrated with $CaCl_2$ solution for 16 hours.

It was found that the amounts adsorbed increased with increasing silt content of the soils. On the basis of the linear relationship between the dimethoate solution concentration and the amount adsorbed, the sorption behaviour was described by a distribution coefficient. The results are shown in Table 15.

Table 15. Freundlich adsorption and desorption constants for dimethoate in various soils.

Soil	% silt	Adsorption k (dm^3/kg)	Desorption k (first step)
Sand/loamy sand	4.8	0.25	0.56
Sandy loam	25	0.33	1.34
Silt loam	52.2	0.42	2.38
Loam/silt loam	50.7	0.42	0.77
Sand	24.5	0.34	0.97
Loam	42.6	0.37	0.34

Environmental fate in water/sediment systems

The DTF reported a study on the degradation of dimethoate in aqueous systems (Volkl, 1993). The systems studied were Rhine river water (550 ml) + sediment (275 g) (system I) and pond water (550 ml) + sediment (190 g) (system II). The apparatus included an all-glass series of traps with an open air-flow system (60-80 ml/min) maintained in the dark at 20°C. Exactly 0.211 mg of [^{14}C]dimethoate, corresponding to a field application rate of 1.194 kg ai/ha, was added in acetone/water solution to each test system. The systems were incubated for 105 days with samples taken 0, 6, 24 and 48 hours and 7, 14, 30, 61 and 105 days. The water and sediment in each sample were separated and radioanalysed. The water phases were analysed by TLC and sediments extracted with acetonitrile or by Soxhlet with methanol. Some extracts were analysed by HPLC.

The half-lives of dimethoate were 17.2 days in system I and 13.2 days in system II estimated by non-linear regression analysis. The half-life values for the transfer of dimethoate to the sediments were 14.8 days for system I and 12.5 days for system II. The major degradation product was demethyl-dimethoate, which reached a maximum value of 22% of the applied radioactivity in the river system on day 30 and 17% in the pond system on day 7. The distribution of the dimethoate residues is shown in Table 16. Most of the ^{14}C was bound to sediment or converted to carbon dioxide.

Table 16. Distribution of ^{14}C from [^{14}C]dimethoate in water/sediment systems after 105 days.

Component	% of applied radioactivity	
	Rhine river system	Pond system
Demethyl-dimethoate	0.9	1.8
Polar metabolites	<5	<2
$^{14}CO_2$	28	24
Humin bound	16	28
Humic acid bound	4.8	11
Fulvic acid bound	21	13
Total accounted for	76	80

Cheminova reported a study of the photodegradation of dimethoate in contact with soil (Skinner and Shepler, 1994). [^{14}C]dimethoate labelled at the *O*-methyl groups was applied to sandy

loam soil at a nominal rate of 2.24 kg ai/ha. The treated soil was exposed to natural sunlight for 30 days at a controlled temperature of 25°C. A control soil in an identical apparatus was maintained in the dark. A continuous humidified air flow was maintained and volatile compounds were trapped. The soils were sampled at 0, 2, 5, 10, 20 and 30 days and extracted with acetonitrile/water (1:1, 3 x 10 ml). The extracts were radio-assayed and analysed by TLC, with radioanalytical imaging and HPLC. Residual solids were radio-assayed. Three main degradation products were indicated and two were isolated and identified by GC-MS. The third was lost during isolation and derivatization, apparently as a result of the extreme volatility of the derivative.

The half-life of dimethoate in sunlight was 10.5 days, but its half-life of the control (dark) soils was 7.9 days, showing that dimethoate on soil is not prone to photolytic degradation. On day 30 the extract of the irradiated soil contained 79% of the applied radioactivity, and that of the unexposed soil 84%. The bound soil residues accounted for 12% and 7.9% respectively. Dimethoate represented 11% of the applied radioactivity in the exposed soil and 4.9% in the unexposed (HPLC). The major degradation products identified in the 30-day extracts were dimethyl hydrogen phosphate, 28% and 13% of the applied radioactivity in the exposed and unexposed soils respectively, and dimethyl hydrogen phosphorothioate, 25% and 56% respectively (TLC). A third unidentified product accounted for about 6% of the applied radioactivity, and volatiles for about 5%.

METHODS OF RESIDUE ANALYSIS

Analytical methods

A series of related methods and validation data for them were presented for the determination of dimethoate and omethoate in or on various raw and processed agricultural commodities (ABC Laboratories, 1998). The methods are on the basis of those of Leoni (1992) and Aoki (1975). A homogenized sample, typically 50 g, is blended with acetone (100 ml). If the water content is <47%, 50 ml water is added. The slurry is filtered and the filtrate extracted with methylene chloride (3 x 100 ml). The combined methylene chloride extracts are evaporated to dryness, dissolved in hexane/acetone (1/1), and cleaned up on a column of Celite topped with Celite/charcoal (4:1). The column is eluted with hexane/acetone (200 ml, 1/1) under sufficient vacuum to obtain a 3-5 ml/min flow. Carbowax 200 is added to the eluate to give a 0.1% solution, which is concentrated in a rotary evaporator under nitrogen.

The extraction procedure is modified for oily substrates, such as corn oil and orange oil. A 10 g sample is brought to 50 ml with a methylene chloride/cyclohexane mixture (15/85), mixed thoroughly and chromatographed on a 50 g GPC column. The eluates are adjusted with Carbowax 200 solution to 0.1% and concentrated to 0–2 ml by rotary evaporation. The residue is taken up in acetone for GLC analysis.

This method, with the GPC clean-up, was used in a 1994 market basket survey in Australia (Marro, 1996).

Cotton seed (50 g) is extracted for 24 h with ethyl acetate in a Soxhlet extractor. After extraction the ethyl acetate is stripped and the residual oil is cleaned up by GPC as above. Soapstock (10 g) is mixed with galcial acetic acid (1.5 ml) and cleaned up by GPC. Potato chips (50 g) are mixed with ethyl acetate (3 x 200 ml) and sodium sulfate (~50 g). The mixture is filtered and again cleaned up by GPC.

The concentrated purified extracts are all analysed by GLC on a 30 m x 0.53 mm RTX-5 or 15 m x 0.53 mm DB-17 capillary column with an initial column temperature of 140°C, injection by flash vaporization (splitless) and flame photometric detection in the phosphorus mode. Calibration is with external standards of 0.05–1.0 µg/ml (0.01 to 0.08 mg/kg). The standards are prepared in acetone

containing 0.1% Carbowax 200. The Carbowax is needed to maintain constant sensitivity over the course of the GLC run. The limit of quantification is ≤ 0.01 mg/kg for each analyte.

The recoveries from a wide range of samples are shown in Table 17.

Table 17. Validation of the ABC/Leoni/Aoki methods for dimethoate and omethoate.

Sample	Fortification range, mg/kg	No. of analyses	Mean Recovery, %		Standard Deviation, %		Recovery Range, %	
			Dimethoate	Omethoate	Dimethoate	Omethoate	Dimethoate	Omethoate
Sorghum grain	0.01–0.50	7	83	85	4	4	80–90	80–90
Sorghum forage	0.01–0.50	7	86	91	3	5	80–90	87–100
Sorghum hay	0.01–0.50	7	85	93	8	7	75–100	83–100
Wheat grain	0.01–0.50	7	92	110	3	7	90–96	104–120
Wheat bran	0.01–0.50	7	93	103	3	5	90–98	96–109
Wheat middlings	0.01–0.50	7	93	97	6	3	80–99	91–100
Wheat shorts	0.01–0.50	7	95	106	5	11	90–102	92–120
Wheat flour	0.01–0.50	7	92	93	23	17	70–140	73 - 124
Maize grain	0.01–0.50	7	87	86	5	10	80–92	71–100
Maize grits	0.01–0.50	7	90	92	2	9	87–92	83–110
Maize meal	0.01–0.50	7	88	88	8	8	76–100	74–100
Maize flour	0.01–0.50	7	96	101	4	15	91–100	82–120
Maize starch	0.01–0.50	7	86	86	4	6	80–90	80–100
Maize oil	0.01–0.50	7	87	78	5	13	78–91	66–100
Cotton seed	0.01–0.50	5	98	65	8	14	90–110	49–80
Cotton seed meal	0.01–0.50	7	83	82	4	8	78–90	66–90
Cotton seed hulls	0.01–0.50	7	87	90	3	8	83–90	81–100
Cotton seed oil (crude)	0.01–0.50	7	105	116	13	17	90–120	99–140
Cotton seed soapstock	0.01–0.05	4	76	31	6	7	70–82	28–40
Oranges (whole)	0.01–0.50	8	101	100	5	12	95–110	82–120
Orange juice	0.01–0.50	7	107	99	4	5	102 –110	90–107
Orange pulp (dry)	0.01–0.50	7	79	72	5	6	69–84	63 - 80
Orange molasses	0.01–0.50	7	87	90	12	12	70–100	66–101
Orange oil	0.01–0.50	7	93	79	7	21	80–100	65–120
Potato	0.01–0.50	7	93	114	3	10	90–98	100–130
Potato granules	0.01–1.0	9	98	112	6	9	90–106	101–130
Potato chips	0.01–0.50	7	100	96	11	21	91–120	77–130
Potato peel (wet)	0.01–1.0	9	89	101	5	13	80–97	80 –120
Potato peel (dry)	0.01–0.50	7	83	87	5	8	80–93	76–100
Tomatoes (whole)	0.01–0.50	7	89	110	7	5	80–96	100–116
Tomato pomace (dry)	0.01–0.50	7	87	97	11	17	70–104	70–114
Tomato paste	0.01–0.50	7	98	88	7	18	90–110	60–107
Beans (succulent)	0.01–0.50	7	92	111	3	6	90–98	105–120
Bean forage	0.01–0.50	7	89	100	5	4	80–95	94–108
Bean straw	0.01–0.50	7	92	96	4	11	86–100	80 - 110
Peas (peas + pods)	0.01–0.50	7	99	104	8	12	90–110	91–120
Pea vines	0.01–0.50	7	88	98	9	16	79–100	83–120
Pea hay	0.01–0.50	7	75	83	5	9	70–82	74–100

The DTF reported a series of validations of Deutsche Forshungsgemeinschaft (DFG) method 236 (Lieferung, 1989). The method involves macerating a homogenized sample (typically 20-25 g) with acetone (2 x 100 ml) and water (2 x 50 ml), filtering, purifying by partition with methylene chloride (100 ml + 3 x 50 ml) followed by activated charcoal (2 g) after drying with sodium sulfate or by gel permeation or Florisil chromatography. The initial extraction solvent mixture may also contain ethyl acetate (e.g. for peas) or may be methanol/water rather than acetone, e.g. for barley. Residues in the concentrated extract are determined by GLC with a flame photometric detector and a 10 m x 530 µm HP-17 or 30 m x 530 µm HP-5 capillary column in the splitless mode, or equivalent. The limit of determination was 0.01 mg/kg, with recoveries of 70–110% and a relative standard deviation of ≤20%. Calibration was by external standards with a typical linear calibration range of 0.02 to 1.0 µg/ml. Recoveries are shown in Table 18.

Table 18. Recoveries from various samples fortified with dimethoate and omethoate and analysed by DFG method 236.

Sample	Omethoate		Dimethoate		Reference
	Fortifications, mg/kg/number	Recovery, %, range/mean [! SD]	Fortifications, mg/kg/number	Recovery, %, range/mean [! SD]	
Potato	0.010 n = 6	79–103 92 ± 8.8	0.010 n = 6	87–107 95 ± 8.3	Flatt, 1996
	0.20 n = 6	80–107 94 ± 11	0.20 n = 6	96–112 104 ± 7.0	
Sugar beet, leaf	0.010 n = 6	79–108 94 ± 10	0.010 n = 6	94–116 106 ± 8.2	Flatt, 1995
	0.20 n = 6	81–107 97 ± 11	0.20 n = 6	96–116 107 ± 7.2	
	5.0 n = 6	86–99 94 ± 5.2	5.0 n = 6	98–106 102 ± 2.7	
Sugar beet, root	0.010 n = 6	79–104 91 ± 8.7	0.010 n = 6	69 – 108 94 ± 16	
	0.20 n = 6	77–104 90 ± 11	0.20 n = 6	88–113 102 ± 9.6	
Peas (with pod)	0.01 n = 3	70 – 100 83	0.01 n = 3	71 – 90 80	Heyer and Schreitmuller, 1996
	0.5 n = 3	67–72 69	0.5 n = 3	74–77 75	
	3.0 n = 3	72 – 78 73 76	20. n = 3	55–72 64	
Peas (seeds)	0.01 n = 3	78–90 86	0.01 n = 3	90–100 93	
	0.5 n = 3	96–100 98	0.5 n = 3	65–75 69	
			1.0 n = 3	69–87 78	
Peas (straw)	0.01 n = 3	60–80 73	0.01 n = 3	90–130 113	
	0.20 n = 4	43–56 47	0.20 n = 4	70–73 72	
	5.0 n = 3	42–66 52	0.20 n = 3	75–79 78	
Barley (grain)	0.01 n = 3	60–80 70	0.01 n = 3	89–109 96	Melkebeke, 1996
	0.2 n = 3	77–86 82	0.2 n = 3	91–97 95	
Barley (straw)	0.01 n = 3	61-66 63	0.01 n = 3	93–115 103	
	0.5 n = 3	59–76 66	2. n = 3	79–88 84	
Maize (grain)	0.01 n = 6	90 90	0.01 n = 6	100–110 102 ± 4.0	Heyer, 1995
	0.2 n = 6	69 – 110 88 ± 16	0.2	81–108 95 ± 11	
Maize (cob)	0.01 n = 6	70 – 120 87 ± 18	0.01 n = 6	80–100 88 ± 7.5	
	0.2 n = 6	66–96 83 ± 12	0.2 n = 6	87–95 91 ± 4.0	
Maize (plant, green)	0.01 n = 6	50–70 62 ±7.5	0.01 n = 6	90–130 105 ± 14	
	0.2 n = 6	50–66 59 ± 7.2	0.2 n = 6	91–100 95 ± 3.7	
			5.0 n = 6	66–96 84 ± 10	
Wheat (whole plant)	0.01 n = 6	85–102 94 ± 6.3	0.01 n = 6	96–115 107 ± 7.7	Flatt, 1995
	0.20 n = 6	73-83 78 ± 4.5	0.20 n = 6	84–95 91 ± 4.2	

Sample	Omethoate		Dimethoate		Reference
	Fortifications, mg/kg/number	Recovery, %, range/mean [! SD]	Fortifications, mg/kg/number	Recovery, %, range/mean [! SD]	
			5.2 n = 6	81–89 85 ± 2.9	
Wheat (grain)	0.01 n = 6	70-94 84 ± 9.9	0.01 n = 6	81–95 89 ± 5.4	
	0.20 n = 6	70–81 75 ± 3.9	0.21 n = 6	87–96 93 ± 3.4	
Wheat (straw)	0.01 n = 6	53–72 61 ± 6.4	0.01 n = 6	64–84 76 ± 7.7	
	0.50 n = 6	58–74 66 ± 7.1	0.52 n = 6	88–94 91 ± 2.3	

The Netherlands submitted their official method for the determination of dimethoate (Ministry of Health, Welfare and Sport, 1996). It is a multi-residue method for compounds amenable to determination by GLC. Information was also supplied on methods used for field trials, but it was in Dutch. The official method contains extraction schemes for oily and non-fatty samples, meat, eggs and milk. Extracts are purified by gel permeation chromatography or liquid-liquid partitioning (milk, meat). For organophosphorus pesticides, the recovery is >80% for non-fatty foods, with a limit of determination of 0.01–0.05 mg/kg, and 65–105% for fatty foods, with a limit of determination of 0.01–0.04 mg/kg.

Australia provided information on several methods used with market basket surveys and field trials. method M16.01 (Melksham and Hargreaves, 1981) specifies extraction of the sample (50 g) with acetone (200 ml), evaporation, filtration and washing with water, extraction of the aqueous solution with chloroform, evaporation to dryness and sweep co-distillation (200°C) with ethyl acetate. The distillation step destroys omethoate. The distillate is analysed by GLC with a flame photometric detector. The recommended column is 1800 x 6 mm 3% OV101, operated isothermally at 196°C. The detector response is linear over a range of 20–120 ng dimethoate. The recoveries are shown in Table 19.

Table 19. Recoveries of dimethoate by method M16.01.

Commodity	Dimethoate fortification, mg/kg	Recovery, %	Reference
Avocado peel	2.2	86.5; 78.3; 72.3; 78.3; 78.9	Hargreaves *et al.*, 1982
Avocado pulp	0.48	118.9; 109.1	
	0.39	94.1	
Tomatoes	1	117; 92.4	Hamilton *et al.*, 1980
	0.5	95	
	0.4	95	Hargreaves and Jackson, 1988
Zucchini	0.4	94	

A method was described for the extraction and analysis, without clean-up, of rockmelons and cucumbers (Hargreaves and Heather, 1989). A sample (50 g) is macerated with acetone (3 x 150 ml) and filtered. The final volume is adjusted to 500 ml with acetone. An aliquot (20 ml) is mixed with water (30 ml), stripped of acetone and extracted with chloroform (1 x 100 ml, 2 x 50 ml). The combined organic extracts are concentrated to dryness and dissolved in ethyl acetate (1 ml). This extract is analysed by GLC with a 10 m HP-5 column and a flame photometric detector. The nominal limit of detection is 0.01 mg/kg. The method was validated for rockmelons at 1.5 and 0.5 mg/kg with recoveries of 92% and 97% respectively, and for cucumbers at 0.5 mg/kg, with recoveries of 100% and 101%.

Method PPQ-02 (Simpson, 1993) specifies blending the sample (50 g) with acetone (100 ml), filtration and transfer of a 50 ml aliquot to hexane/methylene chloride (100 ml, 1/1). The residual

aqueous layer is saturated with sodium chloride and extracted with methylene chloride (2 x 50 ml). The combined organic fractions are dried with sodium sulfate and concentrated to 1–2 ml. The concentrated extract is analysed by GLC with a 10 m x 0.53 mm HP-5 column and flame photometric detector. The detector displayed linear response from 0.26–52 µg/ml. Confirmation is by GC-MS. The method has been validated for dimethoate only, with strawberries and sweet potatoes. Duplicate samples fortified at 0.52 and 2.1 mg/kg were analysed. The recoveries are shown in Table 20. The method has been used on cabbage, asparagus, pasture grass, strawberries and sweet potatoes, and was used for the determination of residues on litchis in the supervised trials (Table 36).

A variation of method PPQ-02 was developed by Heather, *et al.* (1987). Chopped tomato (200 g) was macerated with acetone (2 x 200 ml) and filtered. The acetone was stripped under vacuum and the residual aqueous fraction extracted with hexane (2 x 100 ml). The aqueous solution was extracted with chloroform (1 x 200 ml, 5 x 100 ml) and the combined chloroform extracts were dried and stirred with decolourising charcoal. The solution was filtered and the solvent changed to acetone. The concentrated acetone extract was analysed by GLC on a 1 m x 2 mm column packed with OV-225.

Table 20. Recoveries of dimethoate by method PPQ-02.

Sample	Fortification, mg dimethoate/kg	Recovery, %		
		First analysis	Second analysis	Mean
Strawberries	0.52	111	111	111
	2.1	111	103	107
Sweet Potatoes	0.52	107	104	106
	2.1	103	102	102
Tomato (Heather variation)	0.02	70		
Tomato (Heather variation)	0.1	73		

A method for the extraction and determination of dimethoate and omethoate in or on strawberries has been published (Goodwin, *et al.*, 1985). A chopped sample (25 g) is blended with acetonitrile and filtered. Water is added to the filtrate and the acetonitrile stripped on a rotary evaporator. The aqueous solution is extracted with chloroform (3 x 25 ml) and the chloroform replaced by hexane. The final extract is analysed by GLC on a 2 m x 0.32 mm column of OV-225 on Chromosorb W with a specific thermionic detector. The mean recovery of dimethoate and omethoate was 93 ± 2% from 0.5, 1, 1.5 and 2 mg/kg fortifications.

Stability of pesticide residues in stored analytical samples

Cheminova submitted a detailed report of a study in the USA in 1993-4 on the storage stability of dimethoate and omethoate in potato tubers, orange fruit, sorghum grain, sorghum forage and cotton seed (Williams, 1994). The commodities were stored at –20°C until homogenized, when 50 g sub-samples of each homogenate, fortified separately with either 1.0 mg/kg dimethoate or 0.5 mg/kg omethoate were stored at -20°C. Duplicate samples were analysed at intervals, together with control samples and freshly fortified samples.

Analyses were by the ABC methods detailed above. All essential details and copies of supporting chromatograms were supplied. The results are shown in Table 21.

Table 21. Storage stability of dimethoate and omethoate in frozen samples fortified at 1.0 mg/kg and 0.5 mg/kg respectively.

Commodity	Period, days	Dimethoate			Omethoate		
		Apparent recovery, %	Freshly fortified control recovery, %	Corrected storage recovery, %	Apparent recovery, %	Corrected fortified control recovery, %	Corrected storage recovery, %
Potato	0	92	92	100	93	93	100
	39	77; 81	87	91	78; 76	83	93

Commodity	Period, days	Dimethoate			Omethoate		
		Apparent recovery, %	Freshly fortified control recovery, %	Corrected storage recovery, %	Apparent recovery, %	Corrected fortified control recovery, %	Corrected storage recovery, %
	70	91; 92	96	96	91; 92	95	97
	137	85; 86	95	90	84; 89	95	91
	188	88; 89	94	95	88; 89	93	96
	620	80; 76	88	89	87; 87	93	94
Orange fruit	0	84	84	100	81	81	100
	39	87; 87	93	94	88; 80	89	95
	70	95; 110	97	106	99; 97	94	104
	137	91; 86	99	90	102; 98	101	99
	188	95; 95	97	98	102; 103	102	101
	620	92; 88	89	101	107; 112	100	110
Sorghum Grain	0	91	91	100	91	91	100
	34	88; 86	85	103	84; 33	75	78
	67	74; 72	91	80	86; 90	97	91
	137	89; 90	94	96	84; 88	94	92
	185	92; 98	97	98	92; 93	97	96
	620	71; 68	106	70	77; 79	100	78
Sorghum Forage	0	76	76	100	85	85	100
	36	79; 73	85	90	74; 73	71	104
	69	98; 94	101	95	98; 97	104	94
	139	81; 78	86	93	80; 81	91	89
	187	82; 84	86	97	86; 86	86	100
	622	65; 72	94	73	84; 96	103	90
Cotton seed	82	93; 97	97	96	44; 50	53	87
	126	88; 91	95	95	52; 46	62	79
	189	87; 87	98	89	48; 53	67	76
	623	91; 92	103	92	78; 82	101	80

Cheminova referenced, but did not supply, storage stability data on lettuce and apples.

Definition of the residue

On the basis of the metabolism of dimethoate in plants and animals, the conclusions of the 1996 JMPR on the toxicology, the available analytical methods and the lack of significant data on omethoate *per se*, the Meeting concluded that the residue for compliance with MRLs should be defined as dimethoate. For the estimation of dietary intake the residue is based on the sum of dimethoate and omethoate, each considered separately.

USE PATTERN

The DTF provided numerous labels with translations. Extensive information on GAP was supplied by Australia and some additional information by the governments of the UK, Germany, The Netherlands and Thailand. The information is summarized in Tables 22 and 23.

Table 22. Registered uses of dimethoate.

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Abius	Australia	EC 400 g/l		0.00030		Foliar	7	
Alfalfa	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.24			Ground, aerial (min 20 l water/ha)	7	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Alfalfa	Hungary	Danadim 40 EC. 400 g/l	0.40			Foliar	14	
Alfalfa	Mexico	Perfekthion EC. 400 g/l	0.40	0.0013		Foliar	10	
Alfalfa	USA	Dimethoate 400 EC. 4 lbs/gal	0.56	0.012	1 per cutting	Foliar aerial, ground	10	
Amsoi	Netherlands	Perfekthion EC. 400 g/l	0.20		Repeat as needed	Foliar	21	Outdoor cultivation
Apples	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.075 kg/100 l water		>1	Foliar	7	
Apples	Australia	EC 400 g/l		0.00060		Foliar	7	
Apples	Belgium	Hermootrox EC. 400 g/l	0.04 kg/100 l water			Foliar	21	
Apples	Italy	Danadim EC. 400 g/l	0.048 kg/100 l water			Foliar, no aerial	20	
Apples	Mexico	Perfekthion EC. 400 g/l	0.50 (125 cc/100 l)	0.00050		Foliar	28	Assumed high volume = 1000 l/ha
Apples	Netherlands	400 g/l EC	0.30	0.0002	3	Foliar	21	Perfekthion label: 50 ml/100 l water, NOT for use in glasshouse
Apples	Sweden	Danadim 40 EC. 400 g/l	0.30	0.00075	1 (after blossom)	Foliar	28	Apply at bud formation, before blossoming, or one week after blossoming
Apples	UK	40 EC. 400 g/l	0.68	0.0025 low vol.; 0.00027 high vol.	4	Foliar	35	
Apples	USA	Dimethoate 400 EC. 4 lbs/gal		0.0006 (1 pt/100 gal water)	Not specified	Foliar aerial, ground	28	
Apricots	Australia (Qld)	Saboteur EC 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip		
Artichoke	Italy	Danadim EC. 400 g/l	0.06 kg/100 l water			Foliar, not aerial	20	
Asparagus	Belgium	Hermootrox EC. 400 g/l	0.20			Foliar	21	Wetter recommended
Asparagus	Denmark	Perfekthion 500 S EC. 500 g/l. Danadim 40 EC. 400 g/l	0.30; 0.32	0.00030; 0.00032		Foliar	14 (Perf)	
Asparagus	Italy	Danadim EC. 400 g/l	0.06 kg/100 l water			Foliar, not aerial	20	
Asparagus	Morocco	Rogor L 40 EC. 400 g/l	0.038 kg/ 100 l water			Foliar	20	
Asparagus	Netherlands	400 g/l EC	0.30	0.0006	4	At stem emergence	21	
Asparagus	USA	Dimethoate 400 EC. 4 lbs./gal.	0.56	0.012	5	Foliar aerial, ground, chemigation	180	
Avocado	Columbia	Perfekthion EC. 400 g/l	0.48	0.00048			14	Assumed high volume = 1000 l/ha
Avocado	Australia (Qld)	400 EC. 400 g/l	0.3	0.00030	Not specified	Foliar, high volume @ 1000 l/ha	7	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Avocado	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip		
Babacos	Australia	EC 400 g/l		0.00030		Foliar	7	
Bananas	Australia (Qld, NT, NSW)	EC. 400 g/l	0.30	0.00030	Not specified	Foliar, in at least 1000 l water/ha	7	
Bananas	Australia (NSW)	Rogor Diostop EC. 400 g/l		0.0060		Dip 20–60 sec.	Post-harvest	
Bananas	Australia (Qld, NSW)	Roxion 400 EC. 400 g/l		0.00060	1	Dip 10–60 sec.	Post-harvest	
Bananas	Australia (Qld)	EC. 400 g/l	150 ml/100 l water (600 ppm)		1	Post-harvest dip		
Bananas	New Zealand	EC. 500 g/l	?	?				120 ml/100 l water
Bananas	Reunion	Perfekthion EC. 400 g/l	150 ml/100 l water			Foliar	15	
Barley	Columbia	Perfekthion EC 400 g/l	0.30			Foliar	14; 7 (fodder)	
Barley	Netherlands	400 g/l EC	0.20	0.001	1	Foliar	14	
Beans	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.22; 0.50 high vol.	0.00050 high vol.	>1	Foliar, ground and aerial (min 20 l water/ha)	20	
Beans	Australia	EC. 400 g/l	0.30	0.00030 high vol.; 0.0064 low vol.	Repeat as needed	Foliar	7	
Beans	Belgium	Hermootrox EC. 400 g/l	0.20			Foliar	21	Field beans
Beans	Columbia	Perfekthion EC. 400 g/l	0.30			Foliar	14	
Beans, broad	Denmark	Perfekthion 500 S EC. 500 g/l	0.30	0.00030		Foliar	14	
Beans, horse	Denmark	Danadim 40 EC. 400 g/l	0.32	0.0021		Foliar		
Beans, long	Indonesia	Perfekthion 400 EC. 400 g/l	0.20	0.00020		Foliar		Assumed high volume = 1000 l/ha
Beans	Italy	Danadim EC. 400 g/l	0.06 kg/100 l water			Foliar, not aerial	20	
Beans, French, broad, runner	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	0	
Beans (pulses)	Netherlands	400 g/L EC	0.20	0.001	3	Foliar	21	With and without pods
Beans, broad, French, runner	UK	40 EC. 400 g/ha	0.34	0.0016	2	Foliar	14	
Beans, green, lima, snap, dry	USA	Dimethoate 400 EC. 4 lbs/gal	0.56	0.012	Not specified	Foliar aerial, ground, chemigation	0	
Beetroot	Australia (NSW)	Roxion 400 EC. 400 g/l	0.32	0.0064 (low vol.); 0.00030 high vol. @ 1000 l/ha	Repeat as needed	Foliar	7	
Beetroot	Denmark	Perfekthion 500 S EC. 500 g/l.	0.30; 0.32	0.00030; 0.00032		Foliar	14 (Perf)	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
		Danadim 40 EC. 400 g/l						
Beetroot	Netherlands	400 g/l EC	0.20	0.001	3	Foliar	21	Also applies to scorzonera root, witloof root, chicory root
Berries	Australia	400 g/l EC	0.32	0.00030 high vol.; 0.0064 low vol.	Repeat as needed	Foliar	7	
Berries	Denmark	Danadim 40 EC. 400 g/l	0.60	0.00030		Foliar		
Blackcurrant	UK	Dimethoate 40 EC. 400 g/l	0.34 low volume; 0.22 high volume	0.00062 low vol.; 0.00022 high vol.	3	Foliar	28	
Blackberries	Netherlands	400 g/l EC	0.24	0.00020	3	Foliar	21	Also raspberries
Brassica vegetables	Australia	Roxion 400 EC. 400 g/l	0.3	0.00030 high vol. @ 1000 l/ha	Not specified	Foliar	7	
Brassica vegetables	Netherlands	400 g/l EC	0.2	0.0005	3	Foliar	21	Specifies broccoli, cauliflower, head, Savoy, pointed and Chinese cabbage, kale, kohlrabi
Brassica vegetables	Thailand	400 g/l EC	0.4	0.00040	4	Foliar	14	
Brassica vegetables	UK	3.6% G (with 3.6% chlorpyrifos)	5.54 g ai/100 meters row; 1.84 kg/ha for 30 cm row spacing; at planting, transplanting; 2nd as a surface band		2	Soil incorporated; banded	28	Specifies broccoli, Brussels sprouts, cabbage, cauliflower, kale, collards, mustard, rape.
Brassica vegetables	UK	40 EC. 400 g/l	0.40	0.00040–0.00067	6	Foliar	7	
Broccoli	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	7	
Broccoli	USA	Dimethoate 400 EC. 4 lbs/gal	0.56	0.012	Not specified	Foliar ground, aerial, chemigation	7	
Brussels sprouts	Germany	400 g/l EC	0.24 0.36	0.0012 (200 l water/ha) 0.00040	2	Foliar	14	Higher rate if >50 cm
Brussels sprouts	USA (CA)	Dimethoate 400 EC. 4 lbs/gal	1.12	0.0012	6	Foliar ground, aerial	10	
Bush fruit	Denmark	Perfekthion 500 S EC. 500 g/l	0.6	0.00030		Foliar	14	
Cabbage	Columbia	Perfekthion EC. 400 g/l	0.20			Foliar	24	
Cabbage	Germany	400 g/l EC	0.24	0.00020–0.00040	2	Foliar	14	Specifies red, white, Savoy. See next entry.
Cabbage	Germany	400 g/l EC	0.4	0.002 (200 l water/ha)	1	Foliar	42	Specifies red, white, Savoy

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Cabbage	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	7	
Cabbage	Sweden	Danadim 40 EC. 400 g/l	0.0001 kg/linear m	0.0002		Directed to soil about root of plant		Use in early July
Cabbage	USA	Dimethoate 400 EC. 4 lbs/gal	0.56	0.012	Not specified	Foliar ground, aerial, chemigation	7	
Cacao	Reunion	Perfekthion EC. 400 g/l	150 ml/100 l water			Foliar	15	
Cacao	New Zealand	EC 500 g/l	?	?				120 ml/100 l
Cactus fruit	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l (400 ppm)		1	Post-harvest dip		
Canola	Australia	400 g/l EC	0.30	0.00030 @ 1000 l/ha	Repeat as needed	Foliar	14	
Canola	Australia	Roxion 400 EC. 400 g/l	165 ml/600 ml water/50 kg seed		1	Seed treatment	N/A	
Caraway seed	Netherlands	400 g/l EC	0.20	0.001	2	Foliar	21	
Carrot	Australia	EC 400 g/l	0.32	0.00030		Foliar	7	
Carrot	Germany	400 g/l EC	0.24	0.00040–0.0012	2	Foliar	14	
Carrot	Netherlands	400 g/l EC	0.20	0.001	3	Foliar	21	
Carrot	Sweden	Danadim 40 EC. 400 g/l	0.0001 kg/linear m	0.0002		Irrigation preparation, directed to plant roots		
Carrot	UK	40 EC. 400 g/l	0.34 low volume	0.0016	4	Foliar	14	
Casimiroas	Australia	EC 400 g/l		0.00030		Foliar	7	
Cauliflower	Columbia	Perfekthion EC. 400 g/l	0.20			Foliar	14	
Cauliflower	Germany	400 g/l EC	0.4	0.00067; 0.002 (Danadim label; 200 l water/ha)	1	Foliar	42	
Cauliflower	Mexico	Perfekthion EC. 400 g/l	0.4			Foliar	7	
Cauliflower	USA	Dimethoate 400 EC. 4 lbs/gal	0.56		Not specified	Foliar, ground, aerial, chemigation	7	
Celeriac	Belgium	Hermootrox EC. 400 g/l	0.20			Foliar	21	
Celeriac	Netherlands	400 g/l EC	0.40	0.002	2	Foliar	21	
Celery	Australia	Roxion 400 EC. 400 g/l	0.32	0.00030 (high vol. @ 1000 l/ha)	Repeat as needed	Foliar	7	
Celery	Italy	Danadim EC. 400 g/l	0.06 kg/100 l water			Foliar, no aerial	20	
Celery	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	7	
Celery	Netherlands	400 g/l EC	0.20	0.001	3	Foliar	21	
Celery	USA (FL)	Dimethoate 400 EC. 4 lbs/gal	0.56	0.012	Not specified	Foliar ground, aerial, chemigation	7	
Cereals	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.40			Foliar ground, aerial (min 20 l water/ha)	20	
Cereals	Australia	EC. 400 g/l	0.30 high volume; 0.036 low	0.00030 high vol.; 0.00072	Reapply as needed	Foliar	28	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
			volume	low vol. (ground boom); 0.0018 low vol. (aerial or misting machine)				
Cereals	Australia	400 EC. 400 g/l	0.30; 0.034 low volume	0.00030 high vol. @ 1000 l/ha; 0.0017 low vol. (mister)	Not specified	Foliar, boom, aerial, mister	28	
Cereals	Denmark	Danadim 40 EC. 400 g/l	0.80	0.0053		Foliar		
Cereals	Sweden	Danadim 40 EC. 400 g/l	0.32			Foliar	28	
Cereals	UK	40 EC. 400 g/l	0.34	0.0005; 0.00034	4	Foliar, ground or aerial	14 (ground) Mar. 31 (aerial)	Aerial: at least 20 l water/ha
Cherry	Australia	EC 400 g/l		0.00030		Foliar	7	
Cherry	Australia	400 g/l EC	50 ml/100L (200 ppm)		1	Post-harvest dip		
Cherry	Belgium	Hermootrox EC. 400 g/l	0.030 kg/100 l water			Foliar	14	
Cherry	Germany	400 g/l EC	0.6	0.00040	3	Foliar	21	
Cherry	Italy	Danadim EC. 400 g/l	0.048 kg/100 l water			Foliar, no aerial	20	
Cherry	Netherlands	400 g/l EC	0.3	0.0002	3	Foliar	14	Perfekthion label: 50 ml/100 l water. NOT for use in glasshouses.
Cherry	UK	40 EC. 400 g/l	0.68	0.0023 low vol.; 0.00027 high vol.	4	Foliar	21	
Cherry	USA (ID, OR)	Dimethoate 400 EC. 4 lbs/gal	1.12	0.0024	1	Foliar ground	21	
			0.28	0.0003	1			
Cherry	USA (ID, WA, OR)	Dimethoate 400 EC. 4 lbs/gal		0.0006	1	Foliar ground	≥7 days post-harvest	
Chickpeas	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	21	
Chicory – see Witloof								
Chilli peppers	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip		

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Chilli peppers	Indonesia	Perfekthion 400 EC. 400 g/l	0.20	0.00020		Foliar		Assumed high volume = 1000 l/ha
Chilli peppers	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	21	
Chokos	Australia	EC. 400 g/l	0.30	0.00030				
Citrus	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.75	0.00075	>1		20	
Citrus (except Meyer Lemons, Seville Oranges and Kumquats)	Australia	EC. 400 g/l	0.30	0.015 low vol. (misting machine or aerial); 0.00060 high vol.	Repeat as needed	Foliar	7	
Citrus	Columbia	Perfekthion EC. 400 g/l	1.2	0.0012			14	Assumed high volume = 1000 l/ha
Citrus	Italy	Danadim EC. 400 g/l	0.06 kg/100 l water			Foliar, not aerial	20	
Citrus	Morocco	Perfekthion EC. Rogor L 30 EC. 400 g/l	0.048-0.10 kg/100 l water			Foliar	21; 20	
Citrus	Reunion	Perfekthion EC. 400 g/l	100 ml/100 l water			Foliar	15	Do NOT apply to rough lemon or Seville oranges
Citrus	Thailand	400 g/l EC	0.85	0.0004			14	
Citrus	USA	Dimethoate 400 EC. 4 lbs/gal		0.00060	2 (for mature fruit)	Foliar ground		
			2.24	0.048	2 (for mature fruit)	Foliar aerial		
Citrus	USA	Dimethoate 400 EC. 4 lbs./gal		0.00090	2 (for mature fruit)	Foliar ground	45	
Citrus	USA (CA, AZ)	Dimethoate 400 EC. 4 lbs/gal		0.0060	Not specified	Foliar ground, in year trees first bear fruit	Not specifi ed	
Citrus	USA (CA, AZ)	Dimethoate 400 EC. 4 lbs/gal	2.24		Not specified	Soil drench in furrow about trees		Do not apply to trees that bear fruit within one year
Citrus	New Zealand	EC 500 g/l	?	?				80 ml/100 l
Clover	Australia	EC 400 g/l	0.30	0.00030		Foliar	1 (pregra ze)	
Clover	Australia	Saboteur EC. 400 g/l	600 ml in 2 L of water/100 kg seed		1	Seed treatment	Not applica ble	Do not use for animal feed.
Coffee	Argentina	Perfekthion EC. 400 g/l	1.0	0.0010		Foliar		Assumed high volume = 1000 l/ha
Coffee	Reunion	Perfekthion EC. 400 g/l	150 ml/100 l water			Foliar	15	
Coffee	New Zealand	EC 500 g/l	?	?				120 ml/100 l
Collards	USA	Dimethoate	0.28		Not	Foliar ground,	14	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
		400 EC. 4 lbs/gal			specified	aerial, chemigation		
Cotton	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.16			Ground, aerial (min 20 l water/ha)	14	
Cotton	Australia (NSW, WA, Qld)	400 EC. 400 g/l	0.30	0.004-0.0003 ground boom; 0.01 mister or aerial	Repeat as needed	Foliar	14	
Cotton	Mexico	Perfekthion EC. 400 g/l	0.60			Foliar	14	
Cotton	Morocco	Rogor L 40 EC. 400 g/l	0.038 kg/100 l water			Foliar	20	
Cotton	Reunion	Perfekthion EC. 400 g/l	0.40			Foliar	15	
Cotton	USA (CA, AZ)	Dimethoate 400 EC. 4 lbs/gal	0.56		2	Foliar ground, aerial, chemigation	14	
Cotton	USA	Dimethoate 400 EC. 4 lbs/gal	0.28		Multiple at 14 day intervals	Foliar	14	
Courgettes	Netherlands	Perfekthion EC. 400 g/l	0.20		Repeat as needed	Foliar	21	
Cowpea	Australia (NSW)	Roxion 400 EC. 400 g/l	0.32	0.0064 for ground boom; 0.016 for ground mister	2 (pre--bloom to full flowering)	Foliar	7	
Crucifers	Denmark	Perfekthion 500 S EC. 500 g/l. Danadim 40 EC. 400 g/l	0.30; 0.32	0.00030; 0.0021		Foliar	14 (Perf)	Such as cabbage, mustard, cauliflower (Perfekthion)
Cucumbers	Hungary	Danadim 40 EC. 400 g/l	0.48			Foliar	14	
Cucumber	Thailand	400 g/l EC	0.4	0.0008	`	Foliar	14	
Cucurbits	Australia	EC. 400 g/l	0.30	0.00030 high vol. @ 1000 l/ha	Repeat as needed	Foliar	1; 7 (NSW)	
Currants	Australia	EC 400 g/l		0.00030		Foliar	7	
Currants	Hungary	Danadim 40 EC. 400 g/l	0.32			Foliar	14	
Currants	Netherlands	400 g/l EC	0.24	0.0002 0.002 (1/3-1/11)	3	Foliar	21	Specifies black, red, white and gooseberries. Perfekthion label: 50 ml/100 l water. NOT for use in glasshouse.
Currants	Sweden	Danadim 40 EC. 400 g/l	0.2	0.0002		Foliar	28	Apply before blossoming or within one week after blossoming stops
Custard apples	Australia (Qld, NT)	Roxion 400 EC. Saboteur EC. 400 g/l	0.30	0.00030 high vol. @ 1000	Repeat as needed, usually	Foliar, high volume	7	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
				l/ha	late season			
Custard apples	Australia (Qld)	Saboteur EC. 400 g/l	100 ml /. 100 l (400 ppm)		1	Post-harvest dip.	7	Not for food/feed in NSW
Duboisa	Australia (Qld)	Saboteur EC. 400 g/l	0.30	0.003 high vol. @ 1000 l/ha	Repeat as needed, 7–10 day interval	Foliar	None specifi ed	
Egg plant	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l (400 ppm)		1	Post-harvest dip		
Endive	Netherlands	Perfekthion EC. 400 g/l	0.20			Foliar	21	Outdoor cultivation only.
Endive (escarole)	USA	Dimethoate 400 EC. 4 lbs/gal	0.28		Not specified	Foliar, ground, aerial, chemigation	14	
Feijoas	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l (400 ppm)		1	Post-harvest dip		
Fennel	Netherlands	400 g/l EC	0.20	0.001	3	Foliar	21	
Figs	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l (400 ppm)		1	Post-harvest dip		
Fruit	Switzerland	400 g/l EC	0.0004 kg/l (0.1%)			Foliar	21	
Fodder beet	Germany	400 g/l EC	0.16	0.00027	1	Foliar	35	
Fodder beet	Netherlands	400 g/l EC	0.40	0.002	3	Foliar		
Fodder beet	Switzerland	400 g/l EC.		0.0004 kg/l (0.1%)		Foliar	42	Last application before flowering
Forage crops	Australia	EC 400 g/l	0.30	0.00030				
Fruit trees	Morocco	Rogor L 40 EC. 400 g/l Perfekthion EC	0.048–0.06kg/100 l water			Foliar	20	Apricots, peaches
Fruits with seeds	Reunion	Perfekthion EC. 400 g/l	150 ml/100 l water			Foliar	15	Pome fruit ?
Garbanzo beans	USA	Dimethoate 400 EC. 4 lbs/gal	0.56		Not specified	Foliar, ground, aerial, chemigation	0	
Gherkins	Australia	EC. 400 g/l	0.30	0.00030		Foliar	1	
Gooseberries	Sweden	Danadim 40 EC. 400 g/l	0.20	0.0002		Foliar	28	Apply before blossoming or within one week after blossoming stops
Grain	Denmark	Perfekthion 500 S EC. 500 g/l	0.75	0.00075		Foliar	14	
Granadillas	Australia	EC. 400 g/l		0.00030		Foliar	7	
Grapefruit	Mexico	Perfekthion EC. 400 g/l	0.80 (200 cc/100 l water)	0.00080		Foliar	15	Assumed high volume = 1000 l/ha
Grapes	Australia (Queens-land)	Roxion 400 EC. Saboteur EC. 400 g /L	0.30	0.00030 high vol. @ 1000 l/ha	Not specified	Foliar, high volume	7	
Grapes	Hungary	Danadim 40 EC. 400 g/l	0.32			Foliar	14	
Grapes	Hungary	Rogor L40 EC. 400 g/l		0.0004		Foliar	14 (7?)	
Grapes	Mexico	Perfekthion EC. 400 g/l	0.60			Foliar	27	
Grapes	Morocco	Rogor L 40 EC. 400 g/l		0.00048		Foliar	21	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Grapes	Netherlands	400 g/l EC	0.30 (1/3–1/11) 0.24	0.0002	3	Foliar	28 (1/3-1/11) 21	
Grapes	USA (CA)	Dimethoate 400 EC. 4 lbs/gal	2.24	0.00067	Repeat as needed	Foliar	28	
Grass	Denmark	Danadim 40 EC. 400 g/l	0.80	0.0053				
Grass	Netherlands	Perfekthion EC. 400 g/l	0.20	0.0013		Foliar		Grass grown for seed.
Grass	USA (ID, OR, WA)	Dimethoate 400 EC. 4 lbs/gal			Not specified	Foliar	Not specifi ed.	Grass grown for seed only
Green-leafed vegetables	Denmark	Perfekthion 500 S EC. 500 g/l	0.30	0.00030		Foliar	21	Such as lettuce, spinach, Chinese cabbage, kale.
Guavas	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water. (400 ppm)		1	Post-harvest dip		
Hops	Hungary	Rogor 40L EC. 400 g/l	0.0002 kg per plant (0.5 L of a 0.1% solution)			Foliar	14	
Hops	UK	Dimethoate 40 EC. 400 g/l	0.34 high volume	0.00034	8	Foliar	14	Fuggles variety only
Kale	USA	Dimethoate 400 EC. 4 lbs/gal	0.28		Not specified	Foliar, ground, aerial, chemigation	14	
Kiwifruit	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip		
Kohlrabi	Denmark	Danadim 40 EC. 400 g/l	0.32	0.0021				
Leafy vegetables	Australia	400 g/l EC	0.32	0.00030 high vol. @ 1000 l/ha; 0.0064–0.016 low vol.	Repeat as needed	Foliar	7	Specifies cole crops, lettuce, silverbeet, beet, celery.
Leafy vegetables	Denmark	Danadim 40 EC. 400 g/l	0.32	0.00032		Foliar		
Leek	Netherlands	400 g/l EC	0.40 (0.20)	0.001	2 (3)	Foliar	21	
Legumes - pasture and fodder	Australia	EC 400 g/l	0.30	0.00030		Foliar	1 (pregra ze)	
Legumes – seed	Australia	EC 400 g/l	0.32	0.00030		Foliar	1 (pregra ze)	
Legume vegetables	Thailand	400 g/l EC	0.30	0.00040	8		14	
Lemons	Mexico	Perfekthion EC. 400 g/l	0.80 (200 cc/100 l water)	0.0080		Foliar	15	Assumed high volume = 1000 l/ha
Lentils	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.30				20	
Lentils	Australia	EC. 400 g/l	0.04			Foliar	7	
Lentils	USA	Dimethoate 400 EC. 4 lbs. gal	0.56		2	Foliar, ground, aerial, chemigation	14	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Lettuce	Australia	Roxion 400 EC. 400 g/l	0.32 low volume; 0.30 high volume	0.00030 high vol.; 0.0064 low vol.	Repeat as needed.	Foliar	7	
Lettuce	Columbia	Perfekthion EC. 400 g/l	0.20			Foliar	14	
Lettuce, Head	Germany	400 g/l EC	0.24	0.00020–0.00040	2	Foliar	21	
Lettuce	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	21	
Lettuce, Head	Netherlands	400 g/l EC	0.20	0.001	3	Foliar	21	Also crisphead lettuce
Lettuce	UK	40 EC. 400 g/l	0.34	0.0016 low vol.; 0.00034 high vol. @ 1000 l/ha	1	Foliar	28	
Lettuce, Head	USA	Dimethoate 400 EC. 4 lbs/gal	0.28		Not specified	Foliar, ground, aerial, chemigation	7	
Lettuce, Leaf	USA	Dimethoate 400 EC. 4 lbs/gal	0.28		Not specified	Foliar, ground, aerial, chemigation	14	
Leucaena	Australia	EC. 400 g/l	0.14			Foliar	1 (pre-graze)	
Linseed	Australia	EC. 400 g/l	0.30	0.00030		Foliar	14	
Litchi (lychees)	Australia	EC. 400 g/l	0.1 l/100 l	-		Post-harvest dip	0	
Litchi (lychees)	Australia (Qld, NSW)	EC. 400 g/l	75 ml/100 l water (300 ppm)		1	At-plant dip	N/A	Plants immersed in mixture for one min before planting. Some labels also specify persimmons and Chinese gooseberries
Loquats	Australia (Qld)	Saboteur EC. 400 g./L	100 ml/100 l water. (400 ppm)		1	Post-harvest treatment		
Lucerne	Australia	EC. 400 g/l	600 ml in 1.8 l of water/100 kg seed		1	Seed treatment	Not appli-cable	
Lucerne	Australia	Roxion 400. 400 g/l EC	0.30 high volume; 0.15 low volume	0.003 low vol. (ground boom); 0.008 low vol. (aerial or misting machine) ; 0.00030 high vol.	Repeat as needed	Foliar	1	
Lucerne	Netherlands	400 g/l EC	0.20	0.001	2	Foliar		
Lupins	Australia	400 g/l EC	0.32	0.016 low vol. (ground misting); 0.0064 low vol.		Foliar	14	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
				(ground boom)				
Lupins	USA	Dimethoate 400 EC. 4 lbs/gal	0.56		2	Foliar, ground, aerial, chemigation	0	
Maize	Australia	EC. 400 g/l	0.20			Foliar	28	
Maize	Columbia	Perfekthion EC. 400 g/l	0.24			Foliar	14	
Maize	Denmark	Perfekthion 500 S EC. 500 g/l. Danadim 40 EC. 400 g/l	0.30; 0.32	0.00030; 0.0021		Foliar	14 (Perfek-thion)	
Maize	Hungary	Rogor 40L EC. 400 g/l	0.80			Foliar	14	
Maize	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	14	
Maize	Netherlands	400 g/l EC	0.20	0.001	1	Foliar		
Maize	Reunion	Perfekthion EC. 400 g/l	0.32			Foliar	15	
Maize	USA	Dimethoate 400 EC. 4 lbs/gal	0.56		3	Foliar, ground, aerial, chemigation	14	
Mango	Australia	Roxion 400 EC. Saboteur EC. 400 g/l	0.30	0.00030	Not specified	Foliar	7	
Mango	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip	7	
Marrows	Australia	EC. 400 g/l	0.30	0.00030		Foliar	1	
Mate	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.30			Foliar, ground, aerial (min 20 l water/ha)	7	
Medics	Australia	EC. 400 g/l	0.30	0.00030		Foliar	1 (pre-graze)	
Melons	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	3	
Melons	USA	Dimethoate 400 EC. 4 lbs/gal	0.56		Not specified	Foliar, ground, aerial, chemigation	3	
Mulberries	Australia	EC. 400 g/l		0.00030		Foliar	7	
Mustard	Australia	EC. 400 g/l	0.30	0.00030		Foliar	14	
Mustard greens	USA	Dimethoate 400 EC. 4 lbs/gal	0.28		Not specified	Foliar, ground, aerial, chemigation	14	
Nectarine	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip		
Oats	Columbia	Perfekthion EC. 400 g/l	0.30			Foliar	14; 7 (fod-der)	
Oats	Netherlands	400 g/l EC	0.2	0.001	1	Foliar	14	
Oil seeds	Australia	EC. 400 g/l.	0.30 high vol.; 0.14 low vol.	0.00030 high vol.; 0.003 low vol. (ground boom): 0.007 low vol. (aerial or misting machine)	Not specified	Foliar	14	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Olives	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.075 kg/100 l water			Foliar ground, aerial (min 20 l water/ha)	20	
Olives	Italy	Danadim EC. 400 g/l	0.060 kg/100 l water			Foliar, no aerial	20	
Olives	Morocco	Rogor L 40 EC. 400 g/l. Perfekthion EC	0.056 kg/100 l water			Foliar	20	
Olives	Reunion	Perfekthion EC. 400 g/l	150 ml/100 l water			Foliar	15	
Onions	Australia	EC. 400 g/l	0.30	0.00030		Foliar	7	
Onions	Denmark	Perfekthion 500 S EC. 500 g/l	0.32	0.00030		Foliar	14	
Onions	Germany	400 g/l EC	0.24	0.00020–0.00040	2	Foliar	14	
Onions	Denmark	Danadim 40 EC. 400 g/l	0.32	0.00032		Foliar		
Onions	Netherlands	Perfekthion EC. 400 g/l	0.40				21	Spring; 1st year sets; 2nd year sets; picklers; silver-skin; shallots; leeks
Onions	Sweden	Danadim 40 EC. 400 g/l	0.0001 kg per linear m	0.0002		Irrigation preparation		
Onions	Sweden	Danadim 40 EC. 400 g/l	0.1% (400 ppm)			Dip		Dip sets for 15 minutes before planting
Oranges	Australia	EC	400 mg /L		1	Dip	0	Queensland only
Oranges	Mexico	Perfekthion EC. 400 g/l	0.80	0.00080		Foliar	15	Assumed high volume = 1000 l/ha
Pak Choi	Netherlands	Perfekthion EC. 400 g/l	0.20		Repeat as needed	Foliar	21	Outdoor cultivation only.
Passion fruit	Australia	Roxion 400 EC. Saboteur EC. 400 g/l	0.30	0.00030	Not specified	Foliar	7	
Oranges	Indonesia	Perfekthion 400 EC. 400 g/l	0.80	0.00080		Foliar		Assumed high volume = 1000 l/ha
Oranges	Mexico	Perfekthion 400 EC. 400 g/l	0.80 (200 cc/100 l water)			Foliar		Assumed high volume = 1000 l/ha
Parsnips	Australia	EC. 400 g/l	0.32	0.00030		Foliar	7	
Passion fruit	Australia	EC. 400 g/l		0.00030		Foliar	7	
Passion fruit	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip		
Pasture	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.40		>1		7	Apply early morning or late evening.

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Pasture	Australia	400 EC.	0.30	0.0060 low vol. (ground boom); 0.015 low vol. (aerial or misting machine) 0.00030 high vol.	Repeat as needed	Foliar	1 (pre-gra-zing)	
Pasture	Denmark	Perfekthion 500 S EC. 500 g/l	0.75	0.00075		Foliar	14	
Paw paw	Australia	Roxion 400 EC. Saboteur EC. 400 g/l	0.30	0.00030 high vol.	Not specified	Foliar	7	
Paw paw	Australia (Qld)	Saboteur EC. 400 g/l.	100 ml/100 l water (400 ppm)		1	Post-harvest dip		
Peanuts	Australia (Qld, NSW)	Roxion 400 EC. Saboteur EC. 400 g/l	0.14	0.0027 low vol.	Not specified	Foliar	7 or 14	
Peanuts	Australia	EC. 400 g/l	0.30	0.00030		Foliar	14	
Peanuts	Reunion	Perfekthion EC. 400 g/l	0.40			Foliar	15	
Peanuts	New Zealand	EC 500 g/l	0.40	?				
Peach	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.050 kg/100 l water			Foliar ground, aerial (min 20 l water/ha)	20	
Peach	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip		
Peach	Hungary	Rogor 40 L EC. 400 g/l	0.004 kg/10 L water			Foliar	7	
Peach	Italy	Danadim EC. 400 g/l	0.048 kg/100 l water			Foliar, no aerial	20	
Pear	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.075 kg/100 l water		>1	Foliar ground, aerial (min 20 l water/ha)	7	
Pear	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip		
Pears	Italy	Danadim EC. 400 g/l	0.048 kg/100 l water			Foliar, no aerial	20	
Pears	Mexico	Perfekthion EC. 400 g/l	0.50	0.00050		Foliar	28	
Pears	Netherlands	400 g/l EC	0.3	0.0002	3	Foliar	21	Perfekthion label: 50 ml/100 l water. Not for use in glasshouses
Pears	UK	Dimethoate 40 EC. 400 g/l	0.68 low volume; 0.34 high volume	0.0025 low vol.; 0.00034 high vol.	4	Foliar	35	
Pears	USA	Dimethoate 400 EC. 4 lbs/gal		0.00060	Not specified	Foliar, ground, aerial	28	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Peas	Australia	Saboteur EC. 400 g/l	0.32	0.00030 high vol.; 0.0064 low vol.	Repeat as needed	Foliar	7	
Peas	Australia	Roxion 400. Saboteur EC. 400 g/l	300 ml/900-1000 ml water/50 kg seed		1	Seed treatment	N/A	
Peas	Australia	Roxion 400. 400 g/l	0.32	0.00030	Not specified	Foliar	7	
Peas	Belgium	Hermootrox EC. 400 g/l	0.20			Foliar	21	
Peas	Denmark	Perfekthion 500 S EC. 500 g/l. Danadim 40 EC. 400 g/l	0.30; 0.32	0.00030; 0.0021		Foliar	14 (Perf)	
Peas	Hungary	Danadim 40 EC. 400 g/l	0.40			Foliar	14	
Peas	Italy	Danadim EC. 400 g/l	0.06 kg/100 l water			Foliar, not aerial	20	
Peas	Netherlands	400 g/l EC	0.20	0.001	3	Foliar	21	Dry peas and dry dwarf beans. Field beans for silage.
Peas	UK	40 EC. 400 g/l	0.34	0.00076-0.00034	6	Foliar	14	Aerial application: 25-60 l water/ha
Peas	USA	Dimethoate 400 EC. 4 lbs/gal	0.19		1	Foliar, ground, aerial, chemigation	0 (21 day grazing /hay restric-tion)	
Pecans	USA	Dimethoate 400 EC. 4 lbs/gal	0.37		Not specified	Foliar, ground, aerial	21	
Pepinos	Australia (Qld)	Saboteur EC. 400 g/l	100 ml /100 l water (400 ppm)		1	Post-harvest dip		
Peppers	Australia	Saboteur EC. 400 g/l	0.30	0.00030 high vol.; 0.0060 low vol.	Not specified	Foliar	7	
Peppers	Australia	Roxion 400 EC. 400 g/l	0.30	0.00030 high vol.; 0.0060 low vol.	Repeat as needed	Foliar	7	
Peppers	Australia	. 400 g/l	400 ppm			Dip		Queensland
Peppers	Hungary	Danadim 40 EC. 400 g/l	0.40			Foliar	14	
Peppers	USA	Dimethoate 400 EC. 4 lbs/gal	0.37		Not specified	Foliar, ground, aerial, chemigation	0	
Persimmons	Australia (Qld)	Saboteur EC. 400 g/l	100 ml /100 l water. (400 ppm)		1	Post-harvest dip		
Pigeon peas	Australia	EC. 400 g/l	0.32			Foliar	7 or 14	
Pineapple	Reunion	Perfekthion EC. 400 g/l	150 ml/100 l water			Foliar	15	
Pineapple	Australia	EC. 400 g/l		0.044		Foliar	14	
Pineapple	New Zealand	EC 500 g/l	?	?				120 ml/100 l

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Plum	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip		
Plum	Belgium	Hermootrox EC. 400 g/l	0.020 kg/100 l water			Foliar	21	
Plum	Germany	400 g/l EC	0.6	0.00040	3	Foliar	14	
Plum	Hungary	Rogor 40L EC. 400 g/l	0.004 kg/10 l water			Foliar	7	
Plum	Netherlands	400 g/l EC	0.3	0.0002 (0.002 for 1/3-1/11)	3	Foliar	21 (28 for 1/3–1/11)	Perfekthion label: 50 ml/100 l water. NOT for use in glasshouses
Plum	UK	Dimethoate 40 EC. 400 g/l	0.68 low volume; 0.34 high volume	0.0025 low vol.; 0.00034 high vol.	4	Foliar	21	
Pome fruit	Australia (NSW)	400 EC. 400 g/l	0.60	0.00060 high vol.	Not specified	Foliar	7	
Pome fruit	Australia	400 EC. 400g/l	0.30	0.00030 high vol.	Repeat at 3 week intervals as needed	Foliar	7	
Pome fruit	Denmark	Perfekthion 500 S EC. 500 g/l. Dandim 40 EC. 400 g/l	1.0	0.00050		Foliar	14 (Perf)	
Pome fruit	Germany	400 g/l EC	0.6	0.00040	3 (5 Danadim label; 0.1% per app)	Foliar	21	
Pome fruit	Hungary	Danadim 40 EC. 400 g/l	0.32			Foliar	14	
Pome fruit	Hungary	Rogor L40 EC. 400 g/l	0.004 kg/10 L water			Foliar	14	
Pomegranate	Australia (Qld)	Saboteur EC. 400 g/l	100 ml/100 l water (400 ppm)		1	Post-harvest dip		
Poppy seed	Netherlands	400 g/l EC	0.20	0.001	2	Foliar	21	
Potatoes	Australia	Roxion 400 EC. Saboteur EC. 400 g/l	0.30	0.00030 high vol.; 0.0060 low vol.	Repeat as needed	Foliar	7	
Potatoes	Belgium	Hermootrox EC. 400 g/l	0.20			Foliar	21	
Potatoes	Columbia	Perfekthion EC . 400 g/l	0.30			Foliar	14	
Potatoes	Denmark	Perfekthion 500 S EC. 500 g/l. Danadim 40 EC. 400 g/l	0.30; 0.32	0.00030; 0.0021		Foliar	14 (Perf)	
Potatoes	Germany	EC. 400 g/l	0.24	0.00040	1	Foliar	14	
Potatoes	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar		
Potatoes	Netherlands	400 g/l EC	0.20	0.001	4 (10 day interval)	Foliar	21	
Potatoes	UK	40 EC. 400 g/l	0.34	0.0016 low vol.; 0.00034 high vol.	2 (7 for seed potatoes only)	Foliar	June 30	Aerial application: 25-60 l water/ha
Potatoes	USA	Dimethoate 400 EC. 4 lbs/gal	0.56		Not specified	Foliar, ground, aerial, chemigation	0	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Quince	Australia	400 g/l EC	0.6	0.0006 @ 1000 l/ha	3	Foliar	7	
Rape	Australia	Roxion 400 EC. 400 g/l	165 ml/600 ml water/50 kg seed		1	Seed treatment	N/A	
Rape	Australia	Saboteur EC. 400 g/l	600 ml in 2 L of water/100 kg seed		1	Seed treatment	Not applica ble	See oilseed
Raspberries	Hungary	Danadim 40 EC. 400 g/l	0.32			Foliar	14	
Raspberries	UK	Dimethoate 40 EC. 400 g/l	0.68 low vol.; 0.22 high vol.	0.0013 low vol.; 0.00022 high vol.	4	Foliar	21	
Red beet	Australia	EC. 400 g/l	0.32	0.00030		Foliar	7	
Red beet/	Belgium	Hermootrox EC. 400 g/l	0.20			Foliar	21	Specified as “beet”
Red beet	Denmark	Perfekthion 500 S EC. 500 g/l. Danadim 40 EC. 400 g/l	0.75–0.80	0.0053		Foliar	14 (Perf.)	
Red beet/	Morocco	Rogor L 40 EC. 400 g/l Perfekthion EC	0.028 kg/100 l water 0.20 (Perfekthion)			Foliar	20	
Red beet	Reunion	Perfekthion EC. 400 g/l	0.32			Foliar	15	
Red beet/	UK	Dimethoate 40 EC. 400 g/l	0.40	0.00089 low vol.	2	Foliar	30	Aerial appli-cation: 25-60 l water/ha
Rhubarb	Netherlands	400 g/l EC	0.20	0.001	3	Foliar	21	
Rice	Reunion	Perfekthion EC. 400 g/l	0.32			Foliar	15	
Rice	New Zealand	EC 500 g/l	0.32	?				
Root vegetables	Australia	EC. 400 g/l	0.30	0.015-0.006 low vol.; 0.00030 high vol.	Repeat as needed	Foliar	7	
Rye	Germany	400 g/l EC	0.24	0.00040	1	Foliar, up to stage 55 (mid-head shooting)	21	
Rye	Netherlands	400 g/l EC	0.20	0.001	1	Foliar	14	
Safflower	Australia	EC. 400 g/l	0.30	0.00030		Foliar	14	
Safflower	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	14	
Safflower	USA (CA, AZ)	Dimethoate 400 EC. 4 lbs/gal	0.73		2	Foliar, ground, aerial, chemigation	14	
Salsify	Netherlands	Perfekthion EC. 400 g/l	0.20		Repeat if needed	Foliar	21	Pen cultivation
Santols	Australia	EC. 400 g/l		0.00030		Foliar	7	
Sapodillas	Australia	EC. 400 g/l		0.00030		Foliar	7	
Scarole	Netherlands	400 g/l EC	0.20	0.001	3	Foliar	21	
Silverbeet	Australia	Roxion 400 EC. 400 g/l	0.30 high volume; 0.32 low volume	0.0064 low vol.; 0.00030 high vol.	Repeat as needed	Foliar	7	
Sorghum	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.40			Foliar, ground, aerial (min 20 l water/ha)	20; 7 (fod-der)	
Sorghum	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	28	

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Sorghum	Reunion	Perfekthion EC. 400 g/l	0.32			Foliar	15	
Sorghum (milo)	USA	Dimethoate 400 EC. 4 lbs/gal	0.56		3	Foliar, ground, aerial, chemigation	28	
Soya beans	Argentina	Perfekthion S EC. 50 g/cm^3	0.60			Foliar, ground and aerial (min 20 l water/ha)	14	Use after flowering
Soya beans	Australia	Roxion 400 EC. 400 g/l	0.30	0.00030 high vol.; 0.0060 low vol.	Repeat as needed	Foliar	7	
Soya beans	Columbia	Perfekthion EC. 400 g/l	1.2	0.0012		Foliar	14	Assumed high volume = 1000 l/ha
Soya beans	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	21	
Soya beans	USA	Dimethoate 400 EC. 4 lbs/gal	0.56		Not specified	Foliar, ground, air, chemigation	21 (5 days for gra-zing)	
Spinach	Italy	Danadim EC. 400 g/l	0.06 kg/100 l water			Foliar, not aerial	20	
Spinach	Morocco	Rogor L 40 EC. 400 g/l	0.028 kg/100 l water			Foliar	20	
Spinach	Netherlands	400 g/L EC	0.20	0.001	3	Foliar	21	
Spinach	UK	Dimethoate 40 EC. 400 g/l	0.40	0.00089 low vol.	2	Foliar	June 30	Aerial application 25-60 L water /ha
Squash, Summer (courgettes)	Netherlands	400 g/l EC	0.20	0.0005	3	Foliar	2	
Stone fruit (except apricots and early peach)	Australia	400 EC. 400 g/l	0.30	0.00030 high vol.	Not specified	Foliar (typically 3)	7	
Stone fruit	Denmark	Perfekthion 500 S EC. 500 g/l. Danadim 40 EC. 400 g/l	1.0	0.00050		Foliar	14 (Perf)	
Stone fruit	Hungary	Danadim 40 EC. 400 g/l	0.32			Foliar	14	
Stone fruit	Reunion	Perfekthion EC. 400 g/l	150 ml/100 l water			Foliar	15	
Strawberries	Australia	Roxion 400 EC. Saboteur EC. 400 g/l	0.30	0.00030 high vol.	Repeat as needed (3 week intervals)	Foliar	1	
Strawberries	Denmark	Perfekthion 500 S EC. 500 g/l. Danadim 40 EC. 400 g/l	0.60	0.00030		Foliar	14 (Perf)	
Strawberries	Germany	400 g/l EC	0.4	0.00040	2	Foliar	Pre-flowe-ring; post-harvest	
Strawberries	Hungary	Danadim 40 EC. 400 g/l	0.32			Foliar	14	
Strawberries	Netherlands	400 g/l EC	0.24 (1/3-1/11) 0.20	0.0004	3		28 (1/3-1/11) 21	Perfekthion label: 50 ml/100 l water. NOT

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
								for use in glasshouses
Strawberries	UK	Dimethoate 40 EC. 400 g/l	0.34 low volume	0.00062	6	Foliar	21	
Sugar beet	Belgium	Hermootrox EC. 400 g/l	0.20			Foliar	21	Specified as “beet.”
Sugar beet	Germany	400 g/l EC	0.16	0.00027	1	Foliar	35	
Sugar beet	Hungary	Danadim 40 EC. 400 g/l	0.40			Foliar	14	
Sugar beet	Netherlands	400 g/l EC	0.40	0.002	3	Foliar		
Sugar beet	Reunion	Perfekthion EC. 400 g/l	0.32			Foliar	15	
Sugar beet	Sweden	Danadim 40 EC. 400 g/l	0.32			Foliar	28	
Sugar beet	Switzerland	400 g/l EC		0.0004 kg/l (0.1%)		Foliar	42	Last application before flowering
Sugar beet	UK	40 EC. 400 g/l	0.40	0.00089 low vol.; 0.00040 high vol.	2	Foliar	June 30	Aerial application 25-60 L water/ha
Sugar cane	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.16			Foliar, ground aerial (20 l water min/ha)		
Sugar cane	Indonesia	Perfekthion 400 EC. 400 g/l	0.80	0.00080		Foliar		Assumed high volume = 1000 l/ha
Sunflower	Australia	Roxion 400 EC. 400 g/l	0.30	0.00030 high vol.; 0.0060 low vol.	Repeat as needed	Foliar	14	
Sunflower	Australia	EC. 400 g/l	0.30	0.00030		Foliar	14	
Swede	Denmark	Perfekthion 500 S EC. 500 g/l	0.30	0.00030		Foliar	14	
Swede	UK	3.6% G, with 3.6% chlorpyrifos	5.54 g ai/100 m row; 1.84 kg ai/ha for 30 cm row spacing. 1st at planting or transplanting; 2nd as a surface band.		2	Soil incorporated; banded	2	
Sweet corn	Australia	EC. 400 g/l	0.20			Foliar	7	
Swiss chard	USA	Dimethoate 400 EC. 4 lbs/gal	0.28		Not specified	Foliar, ground, aerial, chemigation	14	
Tobacco	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.90		>1	Foliar, ground, aerial (min 20 l water/ha)	14	
Tobacco	Columbia	Perfekthion EC. 400 g/l	0.20			Foliar	14	
Tobacco	Morocco	Rogor L 40 EC. 400 g/l	0.038 kg/100 l water			Foliar	20	
Tobacco	Reuniion	Perfekthion EC. 400 g/l	0.48			Foliar	15	Also, 50 ml/20 l water for seedbeds and 100 ml/20 l water for transplants
Tobacco	New Zealand	500 g/l EC	0.50			Foliar		

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
Tomatoes	Australia	EC. 400 g/l	0.30; 0.34 (low volume)	0.00030 high vol.; 0.006 low vol. (misting machine)	2–3	Foliar	7	
Tomatoes	Australia	EC. 400 g/l	400 ppm			Dip	7*	Queensland
Tomatoes	Columbia	Perfekthion EC. 400 g/l	0.30			Foliar	14	
Tomatoes	Germany	400 g/l EC	0.24 0.36 0.48	0.0012 (200 l water/ha) 0.00040 0.00040	3	Foliar, under glass	3	<50 cm 50-125 cm >125 cm
Tomatoes	Italy	Danadim EC. 400 g/l	0.06 kg/100 l water			Foliar, not aerial	20	
Tomatoes	Mexico	Perfekthion EC. 400 g/l	0.60			Foliar	-	
Tomatoes	Morocco	Rogor L 40 EC. 400 g/l	0.038 kg/100 l water			Foliar	20–21	
Tomatoes	Thailand	400 g/l EC	0.25	0.00040	5	Foliar	14	
Tomatoes	UK	Dimethoate 40 EC. 400 g/l	0.34 high volume	0.00034 high vol.	8	7		
Tomatoes	USA	Dimethoate 400 EC. 4 lbs/gal	0.56		Not specified	Foliar, ground, aerial, chemigation	7	
Turnips	UK	3.6% G with 3.6% chlorpyrifos	5.54 g ai/100 meters of row; 1.84 kg ai/ha for 30 cm row spacing. 1st at planting or transplanting; 2nd as a surface band		2	Ground incorporated; banded	28	
Turnip, roots	USA	Dimethoate 400 EC. 4 lbs/gal	0.28		Not specified	Foliar, ground, aerial, chemigation	14	
Turnip, tops	USA	Dimethoate 400 EC. 4 lbs/gal	0.28		Not specified	Foliar, ground, aerial, chemigation	14	
Vegetables	Argentina	Perfekthion S EC. 50 g/100 cm^3	0.15; 0.50 high volume	0.00050 high vol.		Foliar	20; 7 (potato radish beet chicory yams kohl-rabi); 14 (onions garlic leeks)	Garden vegetables such as artichoke, broad bean, cabbage, potato, onion, tomato
Vegetables	Australia	Saboteur EC. 400 g/l	0.30	0.00030 high vol.; 0.0060 low vol.	Reapply as needed	Foliar	7	
Vegetables	Belgium	Hermotrox EC. 400 g/l	0.20			Foliar	21	Do not use on leafy vegetables. Do not use of

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*Post-treatment interval

Commodity	Country	formulation	Application				PHI, days	Note
			kg ai/ha	Spray concen-tration, kg ai/l	No.	Method		
								cucurbits ≤3 weeks before flowering.
Vegetables	Hungary	Rogor 40L EC. 400 g/l	0.004 kg/10 L water			Foliar	7	
Vegetables (glasshouse)	Morocco	Rogor L 40 EC. 400 g/l. Perfekthion EC	0.038 kg/100 l water.			Foliar	20	
Vegetables	New Zealand	500 g/l EC	?	?				120 ml/100 l
Vegetables	Reunion	Perfekthion EC. 400 g/l	150 ml/100 l water			Foliar	15	Carrots, cucumbers, beans, peas, onions, celery, tomatoes, cabbage, radish
Vegetables	Switzerland	400 g/l EC		0.0004 kg/l (0.1%)		Foliar	21	Mentions garlic, onion, cabbage
Walnut	Mexico	Perfekthion EC. 400 g/l	0.50	0.00050		Foliar	21	Assumed high volume = 1000 l/ha
Water melon	Indonesia	Perfekthion 400 EC. 400 g/l	0.20	0.00020		Foliar		Assumed high volume = 1000 l/ha
Watermelon	Mexico	Perfekthion EC. 400 g/l	0.40	0.00040		Foliar	3	Assumed high volume = 1000 l/ha
Wax jambus	Australia	EC. 400 g/l	0.30	0.00030		Foliar	7	
Wheat	Columbia	Perfekthion EC. 400 g/l	0.30			Foliar	14; 7 (fod-der)	
Wheat	Germany	400 g/l EC	0.24	0.00040	2	Foliar, up to stage 55 (mid-head shooting)	21	
Wheat	Mexico	Perfekthion EC. 400 g/l	0.40			Foliar	60	
Wheat	Netherlands	400 g/l EC	0.20	0.001	1	Foliar	14	Also, triticale
Wheat	Reunion	Perfekthion EC. 400 g/l	0.32			Foliar	15	
Wheat	UK	40 EC. 400 g/l	0.68 0.34	0.0031 0.00057-0.00034	4 4	Foliar, low volume Foliar, high volume	March 31 (aerial) 14 (gro-und)	Aerial application: 25-60 L water/ha
Wheat	USA	Dimethoate 400 EC. 4 lbs/gal	0.42		2	Foliar, ground, aerial	35 (grain) 14 (gra-zing imma-ture plant)	
Witloof (chicory)	Belgium	Hermootrox EC. 400 g/l	0.30			Foliar	21	
Witloof	Netherlands	400 g/l EC	0.30	0.0015	3	Foliar	21	
Witloof sprouts (chicory)	Netherlands	400 g/l EC	5.0	0.0005	1	Root tops	21	Clamp stage

Table 23. Registered uses of omethoate.

Commodity	Country	Formulation	Application				PHI, days	Note
			kg ai/ha	Spray concentration, kg ai/l	No.	Method		
Apples	Australia	EC 800 g/l	75 ml/100 l		Repeat as needed (14–21 day interval)	Foliar	7	Do not apply during flowering
Apples	Netherlands	EC 565 g/l	1.05 1.27	0.00071 0.00085	2 1	Foliar	21	
Bananas	Australia	EC 800 g/l	0.68		Repeat at needed	Foliar cover spray	4	
Canola	Australia	EC (SC) 290 g/l	2.4 l/2.5 l water/ 100 kg seed			Seed treatment		
Cereals	Australia	EC (SC) 290 g/l	0.035					
Citrus	Australia	EC 800 g/l	75 ml/100 l			Full cover spray	7	
Clover	Australia	EC (SC) 290 g/l	2.4 l/2.5 l water/ 100 kg seed					
Herbs	Australia	EC 50 g/l	60 ml/5 l water		14-21 day repeat	Foliar	7	Do not use in NSW
Legumes	Australia	EC (SC) 290 g/l	0.058					
Lucerne	Australia	EC (SC) 290 g/l	2.4 l/2.5 l water/100 kg seed			Seed treatment		
Lupins	Australia	EC 800 g/l	0.20			Full cover spray	14	
Mandarins	Australia	EC 800 g/l	65 ml/100 l		2	Full cover spray	7	
Oilseed	Australia	EC (SC) 290 g/l	0.035					
Onions	Australia	EC 800 g/l	0.56			Full cover spray	14	
Pasture	Australia	EC (SC) 290 g/l	0.058					
Peach	Netherlands	EC 565 g/l	1.05 1.27	0.00071 0.00085	2 1	Foliar	21	
Pears	Australia	EC 800 g/l	75 ml/100 l			Foliar	7	Do not apply during flowering
Pears	Netherlands	EC 565 g/l	1.05 1.27	0.00071 0.00085	2 1	Foliar	21	
Peas	Australia	EC (SC) 290 g/l	2.4 l/2.5 l water/100 kg seed			Seed treatment		
Plums	Netherlands	EC 565 g/l	1.05 1.27	0.00071 0.00085	2 1	Foliar	21	
Potatoes	Australia	EC 800 g/l	75 ml/100 l		Repeat as needed		7	
Vege-tables	Australia	50 g/l EC	60 ml/5 l water		Every 14-21 days	Foliar	7	

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of the residue trials are shown in Tables 24–55. The trials were reported in sufficient detail, with acceptable analytical information, unless otherwise noted.

The trials are reviewed in order of the Codex Alimentarius Classification of Foods and Feeds.

Citrus fruits

GAP was reported for Australia, Columbia, Italy, Mexico (lemons, oranges), Morocco, New Zealand, Reunion, Thailand and the USA.

Australia reported post-harvest trials on oranges (Noble, 1993). Oranges were dipped for 1 min in a 400 mg/l solution of dimethoate, air-dried, stored at 21°C and analysed for dimethoate 0 and 3 days after treatment. In a separate experiment, Valencia oranges were flood-sprayed with guazatine (1000 g/l, 10 sec), and 50–60 seconds later waxed with dimethoate at 400 mg/l. The oranges were dried in a drying tunnel at 32°C for 1.5 min. Samples were analysed 2 and 3 days after treatment. In a third experiment, oranges were flood-sprayed for 10 seconds with a mixture of guazatine at 1000 mg/l and dimethoate at 400 mg/l; some were then waxed. Waxed and unwaxed oranges were stored for 2 and 3 days before analysis. The analytical method was not specified. The results are shown in Table 24.

Table 24: Residues of dimethoate in or on oranges after post-harvest dip or wax treatments.

Treatment	Post-treatment interval, days	Dimethoate, mg/kg[1]			
		Peel	Pith	Pulp	Whole orange
400 mg/l dip	0	2.0	0.85	0.03	0.43
	3	2.2	0.35	0.03	0.43
Guazatine flood + Castle wax with dimethoate (400 mg/l)	2	1.4	0.24	(0.003)	0.20
	3	0.89	0.18	(0.002)	0.20
Guazatine flood + Peerless wax with dimethoate (400 mg/l)	2	0.57	0.15	(0.004)	0.22
	3	0.49	0.15	(0.003)	0.12
Guazatine (1000 mg/l) + dimethoate (400 mg/l) flood	2	0.29	0.09	(0.004)	0.09
	3	0.38	0.09	(0.004)	0.10
Guazatine (1000 mg/l) + dimethoate (400 mg/l) flood + Castle wax	2	0.92	0.16	(0.005)	0.10
	3	0.62	0.09	(0.006)	0.15
Guazatine (1000 mg/l) + dimethoate (400 mg/l) flood + milestone wax	2	0.78	0.28	(0.005)	0.17
	3	0.68	0.18	(0.01)	0.15

[1] Values in parenthesis are below the limit of determination (not specified)

GAP for Australia (Queensland only) specifies post-harvest treatment with a 400 mg/l dimethoate solution, 0-day PHI. It is a quarantine treatment only, for citrus destined for export to another state or country.

Pome fruits

GAP was reported for Argentina (apples, pears), Belgium (apples), Denmark (pome fruit), Germany (pome fruit), Hungary (pome fruit), Italy (apples, pears), Mexico (apples), The Netherlands (apples, pears), Sweden (apples), the UK (apples, pears), the USA (apples, pears), Australia (pome fruit), New South Wales), pears (Queensland, quince), Morocco (fruit trees) and Reunion (fruits with seeds).

The Netherlands reported two field trials on apples. Trees at Varik and Ophemert were treated with an EC formulation at 0.30 kg ai/ha, 1500 l water/ha. Fruits were collected 0, 7, 14 and 21 days after treatment and analysed by GLC with a flame photometric detector optimized for phosphorus. The stated limits of determination were 0.01 mg/kg for dimethoate and 0.1 mg/kg for omethoate. Germany provided summary data on one trial in which a 400 g/l EC formulation of dimethoate was applied to Boskop variety apple trees at a rate of 0.04 kg ai/ha in 1974. Three treatments were made at approximately 2-week intervals. Apple samples were collected 0, 14, 21 and 63 days after treatment. Residues were reported as the sum of dimethoate and omethoate. The DTF provided a tabular summary only of data on field trials in Germany and France (Pistel and Bleif, 1993). The results are shown in Table 25.

Table 25. Residues of dimethoate after application of EC formulation to apple trees.

Location, Year	Single application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate + Omethoate,[1] mg/kg	
Nordenstadt, Germany 1974	0.04 kg ai/hl	3	0	2.7	
			14	2	
			21	0.63	
			63	0.28	
Varik, Netherlands 1972	0.30 (1500 l water/ha)	1	0	0.16; 0.20; 0.21 (0.19)	
			7	0.10; 0.10; 0.09 (0.10)	
			14	0.06; 0.08; 0.08 (0.07)	
			21	0.03; 0.08; 0.10 (0.07)	
Ophemert, Netherlands 1972	0.30 (1500 l water/ha)	1	0	0.15; 0.20; 0.21 (0.19)	
			7	0.11; 0.10; 0.10 (0.10)	
			14	0.17; 0.19; 0.22 (0.19)	
			21	0.19; 0.15; 0.08 (0.14)	
				Dimethoate, mg/kg	Omethoate, mg/kg
Kappel, Germany 1982	0.42 (1500 l water/ha) 0.50 0.42 0.42 0.50	5	0	0.61	0.10
			7	0.38	0.10
			14	0.21	0.06
			21	0.16	0.05
			28	0.08	<0.05
Firmetsweiler, Germany 1982	0.42 (1500 l water/ha) 0.50 0.42 0.42 0.50	5	0	0.70	<0.05
			7	0.07	<0.05
			14	0.05	<0.05
			21	<0.05	<0.05
			28	<0.05	<0.05
Firmetsweiler, Germany 1982	0.42 (1500 l water/ha) 0.50 0.42 0.42 0.50	5	0	0.46	0.05
			7	0.14	<0.05
			14	0.06	<0.05
			21	<0.05	<0.05
			28	<0.05	<0.05
Rodersheim, Germany 1981	0.42–0-.50 (1500 l water/ha)	5	0	0.35	<0.05
			7	0.31	<0.05
			14	0.23	<0.05

Location, Year	Single application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate + Omethoate,[1] mg/kg	
			21	0.15	<0.05
			28	0.07	<0.05
Niederkirchen, Germany 1981	0.42–0.50 (1500 l water/ha)	5	0	<0.05	<0.05
			7	0.10	<0.05
			14	0.09	<0.05
			21	<0.05	<0.05
			28	<0.05	<0.05
Friedelsheim, Germany 1981	0.42–0.50 (1500 l water/ha)	5	0	0.13	<0.05
			7	0.05	<0.05
			14	0.06	<0.05
			21	0.08	<0.05
			28	<0.05	<0.05
Niederkirchen, Germany 1981	0.42–0.50 (1500 l water/ha)	5	0	0.43	<0.05
			7	0.18	0.05
			14	0.18	0.06
			21	0.26	0.06
			28	0.18	<0.05
				0.08	<0.05
Rubmaier, Germany 1981	0.42–0.50 (1500 l water/ha0	5	0	0.47	<0.05
			7	0.19	<0.05
			14	0.15	<0.05
			21	<0.05	<0.05
			28	0.05	<0.05
Eutin-Neudorf, Germany 1982	0.42–0.50 (1500 l water/ha)	5	0	0.32	<0.05
			7	0.07	<0.05
			14	<0.05	<0.05
			21	<0.05	<0.05
			28	<0.05	<0.05
Rodersheim, Germany 1982	0.6 (1500 l water/ha)	5	0	1.0	0.07
			14	0.36	0.05
			21	0.32	0.06
			28	0.34	0.07
			35	0.22	0.06
Niederkirchen, Germany 1980	0.67 (2000 l water/ha)	7	0	0.28	<0.05
			3	0.16	<0.05
			6	0.21	<0.05
			7	0.12	<0.05
			10	0.12	<0.05
			14	0.20	<0.05
			21	0.10	<0.05
			28	0.06	<0.05
Rodersheim, Germany 1980	0.67	7	0	0.43	<0.05
			3	0.10	0.07
			6	0.32	0.05
			7	0.28	<0.05
			10	0.84	0.16
			14	0.39	0.08
			21	0.06	0.07
			28	<0.05	<0.05

[1] No omethoate (<0.1 mg/kg) was found in the samples from The Netherlands

GAP for The Netherlands specifies three treatments, each at 0.30 kg ai/ha, with a 21-day PHI. GAP for Germany on pome fruit specifies 3 applications, each 0.6 kg ai/ha or 0.04 kg/hl and a 21-day PHI. The Table entries at a 21-day PHI reflect the GAP conditions.

The DTF provided summary data for supervised field trials on pears in Germany (Pistel and Bleif, 1993). No details were provided. The results are shown in Table 26.

Table 26. Residues of dimethoate and omethoate in or on pears from the foliar application of an EC formulation in Germany.

Location/Year/ Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Meckenheim, 1982/ Williams Christ	0.42 0.50 (1500 l water/ha)	5	0	0.85	0.17
			7	0.35	0.19
			14	<0.05	0.15
			21	<0.05	0.13
			28	<0.05	0.08
Meckenheim, 1982/ Williams Christ	0.60 (1500 l water/ha)	5	0	0.46	0.11
			14	0.08	0.10
			21	<0.05	0.08
			28	<0.05	0.07
			35	<0.05	<0.05
Deisendorf, 1982/ Williams Christ	0.60 (1500 ml water/ha)	5	0	0.46	0.07
			14	0.07	0.08
			21	0.01	0.04
			28	<0.01	<0.01
			35	<0.01	<0.01
Gau-Algesheim, 1982/ Alexander Lukas	0.28 (700 l water/ha)	5	0	0.42	0.23
			14	0.06	0.21
			21	<0.02	0.14
			28	<0.02	0.11
			35	<0.02	0.09
Kleinkarlbach, 1982/ Williams Christ	0.60 (1500 l water/ha)	5	0	0.64	0.05
			14	0.17	0.12
			21	0.03	0.05
			28	<0.01	0.01

The Netherlands reported summary supervised field trial data for the use of *omethoate* on apples. In two trials in 1971 apples were treated at 1.3 kg ai/ha, with 1500 l water/ha.. At PHIs of 0-21 days the omethoate residues were ≤0.1 mg/kg. GAP is 3 x 0.30 kg ai/ha, 21-day PHI.

Stone Fruit

GAP was reported for Australia, Belgium (cherry, plum), Denmark, Reunion, Argentina (peach), Germany (cherry, plum), Hungary, Italy (cherry), Morocco (fruit trees), The Netherlands (cherry, plum), the UK (cherry, plum) and the USA (cherry).

Cherries. Residue trials on sour cherries were reported from the USA (Karren, 1985). An EC concentrate (0.26 kg ai/l) was diluted with water (1.9 ml/l) and applied as a foliar spray at a rate of 15.1 l/tree (7.5 g ai/tree) at four locations in Utah in 1985, when ripening fruit were present. The PHI was 21 days. Samples were stored frozen until analysed, together with stored fortified controls, six months after collection by GLC with a nitrogen-phosphorus detector. The results are shown in Table 27.

Table 27. Residues in or on cherries collected ≥21 days after treatment of trees with dimethoate at 7.5 g ai/tree, Utah, USA.[1]

Location	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Total, mg/kg
1–Perry	21	0.25	0.34	0.59
	28	0.23	0.18	0.41
2–Kaysville	21	0.08	0.20	0.28[2]
	28	0.27	0.37	0.64
3–Payson	21	0.24	0.28	0.52
	28	0.05	0.41	0.46
4–Santaquin	21	0.76	0.28	1.04
	28	0.26	0.23	0.49

[1]Concurrent storage stability recovery for dimethoate: 88.4% ± 7.3 (n = 3; 0.04, 0.14, 0.23 mg/kg); for omethoate: 99.6% ± 7.4 (n = 3; 0.05, 0.16, 0.23 mg/kg)
[2]Reported as 1.28 mg/kg

US GAP specifies a foliar application to cherries at 1.12 kg ai/ha, PHI 21 days. The maximum number of cherry trees per hectare is about 1140. Thus, 7.5 g ai/tree corresponds to a maximum rate of 8.6 kg ai/ha, or 7.7 times the GAP rate. No trials were reported at the maximum GAP rate.

The DTF submitted summary data on supervised field trials with cherries in Germany (Pistel and Bleif, 1993). No details were provided. The results are shown in Table 28. GAP for the use of dimethoate on cherries in Germany is 3 x 0.6 kg ai/ha, 21-day PHI.

Table 28. Residues of dimethoate and omethoate in or on cherries from the foliar application of a dimethoate EC formulation in Germany.

Location/Year/ Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Meckenheim, 1983	0.72 (1800 l water/ha)	3	0	1.99	0.54
			14	0.14	0.47
			21	≤0.05	0.28
			28	0.05	0.14
			35	<0.05	0.20
Hollern, 1983 Schatten-Morellen	0.8 (2000 l water/ha)	3	0	3.93	0.36
			7	1.61	0.45
			14	0.72	0.48
			21	0.08	0.28
			28	0.04	0.22
Meckenheim, 1968 Hedelfinger Riesen	2 g/tree, 5–6 l water/tree	1	1	5.4	
			3	5.1	
			7	4.3	
			11	2.8	
			17	0.7	
Ingelheim, 1969 Schwarze Fruhe	2 g/tree, 5 l water/tree	3	0	0.77	0.02
			4	0.54	0.08

Location/Year/ Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
			7	0.35	0.10
			10	0.22	0.10
			14	0.07	0.10
Immenstaad, 1969 Schneiders Knorpel-Kirsche	0.8 (2000 l water/ha)	1	0	4.87	0.14
			4	1.00	0.27
			7	1.00	0.13
			10	0.58	0.19
			14	0.66	0.61
			21	0.19	0.27
Wackernheim, 1972 Hedelfinger	0.8 g/tree, 2 l water/tree	2	0	1.60	0.20
			2	1.30	0.30
			4	0.60	0.30
			10	0.30	0.50
			14	0.14	0.40
			21	0.02	0.20
Immenstaad, 1972 Schneiders Spate	0.80 (2500 l water/ha)	2	0	4.91	<0.01
			4	3.38	<0.01
			10	3.84	<0.01
			14	1.64	<0.01
			21	1.48	<0.01
Meckenheim, 1982 Schatten-Morelle	0.60 (1500 l water/ha)	3	0	1.32	0.20
			14	0.34	0.34
			21	0.06	0.27
			28	<0.05	0.22
			35	<0.05	0.17
Kirchheim, 1982 Schatten-Morelle	0.60 (1500 l water/ha)	4	0	2.04	0.17
			14	0.37	0.08
			21	0.06	0.03
Allmannsweiler, 1982 Schatten-Morelle	0.60 (1500 l water/ha)	3	0	3.88	0.87
			14	0.27	0.12
			21	0.03	0.05
			28	<0.01	0.01
			35	<0.01	0.02
Meckenheim, 1983	0.72 (1800 l water/ha)	3	0	1.99	0.54
			14	0.14	0.47
			21	<0.05	0.28
			28	<0.05	0.14
			35	<0.05	0.20
Schwabenheim, 1983	0.48 (1200 l water/ha)	3	0	1.74	0.41
			7	0.21	0.33
			14	0.02	0.21
			21	<0.02	0.11
			28	<0.02	0.11
Kleinkarlback, 1983	0.48 (1200 l water/ha)	3	0	2.29	0.99
			7	1.44	0.71
			14	0.42	0.54
			21	0.13	0.46
			28	0.075	0.45

Plums. The Netherlands provided information on 4 trials with plums in 1971 (Wit, 1972). The trials were at one location with two varieties of plums and two EC dimethoate formulations (200 g/l, 400 g/l). Dimethoate was applied once at a rate of 0.30 kg ai/ha, 150 water/ha. Samples were taken 0, 7 and 14 days after treatment and analysed by GLC with a flame photometric detector optimized for phosphorus. The limit of determination was shown to be 0.01 mg/kg for dimethoate and 0.1 mg/kg for omethoate. The results are shown in Table 29. GAP for plums in The Netherlands specifies 3 applications at 0.30 kg ai/ha, PHI 21days. The 14-day PHI is more than 30% below the GAP PHI and only one application was made. None of the trials met GAP conditions.

Table 29. Residues in or on plums from the application of dimethoate in The Netherlands, 1971.

Formulation/ variety	Application rate, kg ai/ha	Volume, l water/ha	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Total, mg/kg
Rogor EC 200 g/l Monsieur hatif	0.30	150	0	0.19 (0.06; 0.23; 0.29)	<0.1	<0.29
			7	0.01 (<0.01; <0.01; 0.01)	<0.01	<0.02
			14	0.11 (<0.01; <0.01; 0.30)	<0.01	<0.12
Rogor EC 200 g/l Warwickshire drooper	0.30	150	0	0.03 (0.01; 0.05; 0.03)	<0.01	<0.04
			7	0.02 (0.02; 0.02; <0.01)	<0.01	<0.03
			14	<0.01	<0.01	<0.02
Perfekthion EC. 400 g/l Monsieur hatif	0.30	150	0	0.13 (0.12; 0.06; 0.21)	<0.01	<0.14
			7	<0.01	<0.01	<0.02
			14	<0.01	<0.01	<0.02
Perfekthion EC. 400 g/l Warwickshire drooper	0.30	150	0	0.07 (0.04; 0.14; 0.04)	<0.01	<0.08
			7	<0.01	<0.01	<0.02
			14	0.02 (0.02; 0.02; 0.01)	<0.01	<0.03

The DTF reported supervised field trials with plums in Germany (Pistel and Bleif, 1993). No details were provided. The results are shown in Table 30. GAP for the use of dimethoate on plums in Germany is 3 x 0.6 kg ai/ha, 14-day PHI.

Table 30. Residues of dimethoate and omethoate in or on plums from the foliar application of a dimethoate EC formulation in Germany

Location/Year/ Variety	Application, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Meckensheim, 1981 Orthenauer	0.50 (1500 l water/ha)	4	0	0.10	<0.05
			3	0.07	<0.05
			7	0.05	<0.05
			14	0.05	<0.05
			21	<0.05	<0.05
Schriesheim, 1981 Haus-Zwetsche	0.50 (1500 l water/ha)	4	0	0.19	<0.05
			3	0.27	<0.05
			7	0.14	<0.05
			14	0.13	<0.05
			21	0.14	<0.05
			28	0.11	<0.05
Friedelsheim, 1981	0.50 (1500 l	4	0	0.14	<0.05

Location/Year/ Variety	Application, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Stanley	water/ha)				
			3	0.13	<0.05
			7	0.09	<0.05
			14	0.07	<0.05
			21	<0.05	<0.05
Rodersheim, 1981 Haus-Zwetsche	0.50 (1500 l water/ha)	4	0	0.17	<0.05
			3–28	≤0.05	≤0.05
Ruppertsberg, 1981 Auerbacher	0.50 (1500 l water/ha)	4	0	0.06	<0.05
			3–14	≤0.05	≤0.05
Gleidingen, 1982 Haus-Zwetsche	0.50 (1500 l water/ha)	4	0	0.16	
			3	0.12	
			7	0.11	
			14	0.10	
			21	0.08	
Roedersheim, 1982 Stanley	0.50 (1500 l water/ha)	4	0–21	≤0.05	≤0.05
Immenstaad, 1982 Bühler	0.50 (1500 l water/ha)	4	0	1.49	0.11
			3	1.13	0.14
			7	0.60	0.15
			14	0.15	0.12
			21	0.09	0.13
Horgenzell Vogelsang 1982 Italiener	0.50 (1500 l water/ha)	4	0	0.16	<0.05
			3	0.06	<0.05
			7-21	≤0.05	≤0.05
Immenstaad, 1982 Erfinger	0.50 (1500 l water/ha)	4	0	1.78	0.08
			3	1.56	0.10
			7	1.03	0.08
			14	0.75	0.08
			21	0.75	0.06
Achern-Sasbach, 1982	0.50 (1500 l water/ha)	4	0	1.00	0.19
			3	0.74	0.18
			7	0.28	0.12
			14	0.28	0.17
			21	0.17	0.17
Heidelsheim, 1982 Italiener	0.50 (1500 l water/ha)	4	0	0.19	<0.05
			3	0.09	<0.05
			7–21	≤0.05	≤0.05
Weisenheim am sand, 1982 President	0.40 (1200 l water/ha)	4	0	1.41	0.16
			3	1.09	0.22
			7	0.52	0.20
			14	0.24	0.22
			21	<0.05	0.10
Rodersheim, 1983 Orthenauer	0.60 (1500 l water/ha)	4	0	0.37	0.06

Location/Year/ Variety	Application, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
			14	0.09	0.05
			21	0.06	<0.05
			28-35	<0.05	<0.05
Immenstaad, 1981 Erginger	0.50 (1500 l water/ha)	4	0	0.72	0.05
			3	0.64	0.06
			7	0.86	0.09
			14	0.46	0.07
			21	0.41	0.08
Meckenheim, 1980 Auerbach	0.67 (2000 l water/ha)	5	0	0.14	<0.05
			3	0.07	<0.05
			5	0.06	<0.05
			7	0.06	<0.05
			10–28	<0.05	<0.05
Ruppertsberg, 1980 Orthenhausen	1.33 (2000 l water/ha)	5	0	0.21	<0.05
			3	0.11	0.06
			5	0.10	<0.05
			7	0.12	<0.05
			10	0.06	<0.05
			14	0.06	<0.05
			21–28	<0.05	<0.05
Ludendorf, 1981 Haus-Zwetsche	0.50 (1500 l water/ha)	4	0	0.17	<0.05
			3	0.18	<0.05
			7	0.32	<0.05
			14	0.36	<0.05
			21	0.21	<0.05
Riedersweiler, 1983 Haus-Zwetsche	0.80 (2000 l water/ha)	3	0	0.23	0.06
			7	0.13	0.05
			14	0.12	0.05
			21	0.05	0.03
			28	0.09	0.06
Meersburg, 1982 Haus-Zwetsche	0.80 (2000 l water/ha)	3	0	0.23	0.06
			7	0.13	0.05
			14	0.12	0.05
			21	0.05	0.03
			28	0.09	0.06
Ingelheim, 1982 Crydiemer	0.60 (1500 l water/ha)	3	0	0.15	0.13
			14	<0.02	0.15
			21	<0.02	0.12
			28	<0.02	0.09
			35	<0.02	0.08
Ingelheim, 1983 Crydiemer	0.50 (1250 l water/ha)	3	0	0.49	0.10
			14	0.06	0.12
			21	0.02	0.11
			28	<0.02	0.06
			35	<0.02	0.06
Karlsruhe, 1983 Zernowitzer	0.60 (1500 l water/ha)	3	0	0.26	0.04

Location/Year/ Variety	Application, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
			14	0.13	≤0.02
			21	0.02	<0.02
			28–35	<0.02	<0.02
Hove, 1983 Buehler	0.60 (1500 l water/ha)	3	0	0.58	0.07
			14	0.11	0.09
			21	0.11	0.14
			28	<0.02	0.05
			35	<0.02	0.04

The Netherlands provided summary supervised field trial data for the use of *omethoate* on plums in two trials in 1971. Plums were treated at 1.3 kg ai/ha, with 150 l water/ha. At PHIs of 0-21 days the omethoate residues were <0.1–0.1 mg/kg. Details were provided in Dutch. GAP is 3 x 0.3 kg ai/ha, 21-day PHI. The trials were not according to GAP.

Berries and other small fruit

Blueberries. GAP was reported for Australia (berries, grapes, strawberries), Denmark (berries, strawberries), Germany (strawberries), Hungary (currants, grapes, raspberries, strawberries), the UK (blackcurrants, raspberries, strawberries), Mexico (grapes), Morocco (grapes), The Netherlands (blackberries, currants, grapes, strawberries), Sweden (currants, gooseberries) and the USA (grapes). The USA currently has no GAP for blueberries.

Field trials in the USA were reported on the application of dimethoate to blueberry bushes in Maine (1993, 2 trials), Michigan (1994), New Jersey (1994), North Carolina (1994) and Washington (1994) (Samoil, 1996). The Maine trials were with lowbush blueberries and all other trials were with highbush plants. A 480 g ai/l EC formulation was applied with mistblower or airblast sprayers at a rate of 0.37 or 0.74 kg ai/ha and berries harvested 14 or 21 days after the single application. The samples were stored frozen for 333 –689 days before analysis by GLC with a flame photometric detector optimized for phosphorus. External standards were used, with a demonstrated linear calibration range of 1–5 ng for both omethoate and dimethoate. The method was validated at 0.05 mg/kg for dimethoate (83% recovery) and omethoate (57%). The recovery of omethoate was consistently low in concurrent fortified control samples (63 ± 10%, n = 14, at 0.05 mg/kg). The recovery was no better at 0.50 or 5.0 mg/kg. The recovery of dimethoate was 93 ± 16%, n = 14, at 0.05 mg/kg. The results are shown in Table 31.

Storage stability studies were conducted, although they encompassed only 82% of the storage period in the Maine trials. The recovery of omethoate at 0.10 mg/kg was 43 and 63% after 299 days and 38 and 49% after 568 days of frozen storage, and that of dimethoate at 0.10 mg/kg was 56 and 82% after 299 days and 50 and 62% after 568 days. The recoveries were not significantly different at 1.0 mg/kg. The reported residues may therefore be understated by about 50%.

Table 31. Residues from the foliar application of dimethoate EC formulation to blueberry bushes at 0.37 or 0.74 kg ai/ha (1993-1994, USA).

Location	Application rate, kg ai/ha	PHI, days	Vol., l/ha	Storage interval from collection to analysis, days	Dimethoate, mg/kg	Omethoate, mg/kg	Total Residue,[1,2] mg/kg
Maine #1	0.37	21	230	689	0.37 (0.37; 0.26; 0.49)	0.15 (0.12; 0.08; 0.26)	0.52
Maine #1	0.74	21	230	689	0.83 (0.90; 0.60; 1.0)	0.40 (0.36; 0.24; 0.60)	1.2

Location	Application rate, kg ai/ha	PHI, days	Vol., l/ha	Storage interval from collection to analysis, days	Dimethoate, mg/kg	Omethoate, mg/kg	Total Residue,[1,2] mg/kg
Maine #2	0.37	21	230	689	0.42 (0.37; 0.48)	0.10 (0.12; 0.09)	0.52
Maine #2	0.74	21	230	689	0.68 (1.01; 0.67; 0.36)	0.29 (0.40; 0.27; 0.21)	0.97
Michigan	0.37	14	470	333	0.32 (0.25; 0.40)	0.07 (0.06; 0.08)	0.39
New Jersey	0.37	14	2340	360	0.11 (0.14; 0.08)	0.06 (0.05; 0.07)	0.17
North Carolina	0.37	14	1020	405	0.16 (0.13; 0.23)	0.08 (0.06; 0.09)	0.24
Washington	0.37	21	350	336	<0.05 <0.05; <0.05)	<0.05 (<0.05; <0.05)	<0.10

[1]Values are not corrected for probable losses during frozen storage, nor for concurrent method recoveries
[2]No residues (<0.05 mg/kg) were found in control samples

The Government of Australia reported field trials on strawberries (Goodwin, 1984; Goodwin *et al.*, 1985). Three varieties of field strawberries were sprayed four times at weekly intervals with dimethoate solutions of 0.02, 0.03 and 0.05 kg ai/hl, with three replicates of each variety. The PHIs were 0 to 21 days. The dimethoate solutions were applied with knapsack sprayers to run-off, but actual treatment rates (kg ai/ha) were not reported. Analyses were by the multi-residue method PPQ-02 (Simpson, 1993). The recovery of dimethoate at 0.5 mg/kg was 111%. The results are shown in Table 32.

GAP in Australia for strawberries allows multiple applications at 0.30 kg ai/ha at three-week intervals, with a 1-day PHI. This is equivalent to 0.03 kg ai/hl (bold entries in Table 32), assuming a high-volume application of 1000 l per hectare.

Table 32. Combined residues of dimethoate and omethoate in or on strawberries following four applications of an EC formulation in Australia.

Rate, kg ai/hl	PHI, days	Variety	Residue range, mg/kg	Mean residue, mg/kg, n = 3
0.02	0	Naratoga	2.04–2.75	2.40
	1		1.39–2.05	1.78
	2		1.50–2.34	1.83
	3		1.05–1.68	1.28
	4		0.85–1.02	0.95
	7		0.73–0.92	0.82
	14		0.18–0.51	0.33
	21		0.12–0.16	0.14
	0	Tioga	2.91–3.58	3.33
	1		1.43–3.08	2.17
	2		1.00–1.83	1.37
	3		0.61–1.45	1.03
	4		0.42–1.46	0.81
	7		0.40–0.98	0.75
	14		0.07–0.14	0.11
	21		0.03–0.08	0.06
	0	Torrey	2.39–2.98	2.69
	1		1.23–2.83	1.98
	2		1.38–1.72	1.51
	3		0.94–1.04	0.99
	4		0.34–0.68	0.54
	7		0.22–0.49	0.36
	14		0.15–0.91	0.46
	21		0.24–0.49	0.34

Rate, kg ai/hl	PHI, days	Variety	Residue range, mg/kg	Mean residue, mg/kg, n = 3
0.030	0	Naratoga	2.50–5.30	3.80
	1		**2.01–2.38**	**2.25**
	2		2.09–2.30	2.17
	3		1.59–2.00	1.78
	4		0.98–1.69	1.31
	7		0.77–1.10	0.88
	14		0.16–0.50	0.30
	21		0.27-0.36	0.31
	0	Tioga	3.77–4.08	3.91
	1		**2.86–3.50**	**3.25**
	2		1.80–2.46	2.09
	3		1.21–1.63	1.42
	4		1.05–1.78	1.35
	7		0.70–0.96	0.82
	14		0.10–0.41	0.30
	21		0.20–0.63	0.29
	0	Torrey	2.63–3.60	3.23
	1		**1.31–2.64**	**2.18**
	2		0.98–1.74	1.45
	3		0.68–1.10	0.93
	4		0.30–0.72	0.54
	7		0.15–0.58	0.37
	14		0.11–0.18	0.15
	21		0.25-0.31	0.29
0.050	0	Naratoga	4.15–5.78	5.06
	1		4.05–5.49	4.67
	2		2.15–4.72	3.74
	3		1.85–2.74	2.39
	4		1.71–2.35	1.99
	7		0.61–1.32	1.00
	14		0.23–0.60	0.44
	21		0.30–0.36	0.33
	0	Tioga	6.09–7.40	6.59
	1		4.38–5.65	4.91
	2		2.65–5.16	3.75
	3		2.40–3.13	2.73
	4		0.81–1.91	1.45
	7		0.60–0.92	0.78
	14		0.45–0.67	0.57
	21		0.19–0.61	0.33
	0	Torrey	6.38–7.92	7.25
	1		5.55–6.72	5.95
	2		2.33–4.55	3.25
	3		1.71–2.13	1.95
	4		1.38–1.96	1.68
	7		1.02–1.26	1.18
	14		0.31–0.81	0.57
	21		0.27–0.57	0.47

The DTF reported summary data on supervised field trials with grapes in Germany and France (Pistel and Bleif, 1993). No details were provided. The results are shown in Table 33. GAP for the use of dimethoate on grapes in Germany and France was not reported. GAP in The Netherlands is 3 x 0.30, 21 or 28-day PHI.

Table 33. Residues of dimethoate and omethoate in or on grapes from the application of an EC formulation.

Location Year Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Schwabenheim, Germany, 1972 Silvaner	0.04 kg ai/hl	2	0	1.06	0.08
			7	0.59	0.12
			14	0.35	0.12
			21	0.24	0.12
			28	0.14	0.10
Schwabenheim, Germany, 1974 Silvaner	0.04 kg ai/hl	2	0	1.09	<0.02
			14	0.34	0.06
			21	0.31	0.09
			28	0.20	0.08
Schwabenheim, Germany, 1974 Müller-Thurgau	0.04 kg ai/hl	2	0	0.82	<0.02
			14	0.356	0.06
			21	0.39	0.10
			28	0.27	0.11
Vauvert, France, 1980 Carignan	0.34 (100 l water/ha)	1	27	0.89	0.19
Ste Hilaire, France, 1980 Groslot	0.33 (100 l water/ha)	1	45	0.34	0.18
Fronton, France, 1984 Negrette	0.23 (200 l water/ha)	1	0	2.07	<0.05
			7	0.83	0.07
			14	0.53	0.08
			28	0.27	0.11
			49	0.06	0.07
Rochecarbon, France, 1984 Chenin	0.23 (400 l water/ha)	1	0	1.13	<0.05
			7	0.25	0.05
			14	0.48	<0.05
			28	0.11	0.06
			86	<0.05	0.05
Gajan, France, 1984 Carignan	0.09 (400 l water/ha)	1	0	0.37	<0.05
			7	0.13	
			14	0.10	
			28, 51	<0.05	
Carignan, France, 1984 Carignan	0.09 (400 l water/ha)	1	0	1.73	<0.05
			7	0.17	<0.05
			14	0.09	<0.05
			28	<0.05	<0.05
			49	0.06	<0.05
Salles d'Armagnac, France, 1981 Colombard	0.23 (150 l water/ha)	1	57	0.11	0.11
Milhaud, France, 1981 grenache	0.23 (150 l water/ha)	1	26	0.11	0.11
Ailleville, France, 1982 Pinot Meunier	0.3 (180 l water/ ha)	1	53	0.13	0.07
St. Lambert du Lattay, France, 1982 Gros Lot	0.23 (100 l water/ha)	1	62	<0.5	<0.05
Montreal, France, 1982 Listan	0.23 (1000 l water/ha)	1	48	<0.05	<0.05
Montreal, France, 1982 Listan	0.23 (150 l water/ha)	4	24	0.21	0.14
Vauvert, France Carignan	0.23 (1000 l water/ha)	1	17	0.18	<0.05

Location Year Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Vauvert, France Carignan	0.23 (100 l water/ha)	2	17	1.18	0.11
Gallargues, France, 1982 Aramon	0.83 1.0 (500 l water/ha)	2	29	<0.05	<0.05
Gallician, France, 1982 Grenache	0.83 1.0 (500 l water/ha)	2	35	0.6	0.14
Fronton, France, 1982 Gamay	0.83 1.0 (500 l water/ha)	2	33	1.21	0.41
Tours, France, 1982 Cot Sur	0.5 (300 l water/ha) 0.62 (235 l water/ha)	2	40	0.78	0.43
Tours, France, 1982 Pineau de la Loire	0.5 (300 l water/ha) 0.62 (235 l water/ha)	2	54	0.66	0.31

The DTF reported supervised field trials with currants in Germany (Pistel and Bleif, 1993). No details were provided. The results are shown in Table 34. GAP for the use of dimethoate on currants in Germany was not reported. GAP for The Netherlands is 3 x 0.24 kg ai/ha, or 0.02 kg ai/hl, 21-day PHI.

Table 34. Residues of dimethoate and omethoate in or on currants from the application of a dimethoate EC formulation in Germany.

Location, Year, Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Winterborn, 1974 Silvergieters	0.60 (1500 l water/ha)	1	0	11.2	<0.02
			7	4.5	0.60
			15	0.40	0.40
			21	0.15	0.20
Deisendorf, 1974 Silvergieters	0.86 (2000 l water/ha)	3	0	8.0	0.06
			7	4.5	0.04
			14	0.32	<0.02
			21	0.12	<0.02
			28	0.45	<0.02
Schriesheim, Germany, 1983 Rondom	0.60 (1500 l water/ha)	2	0	5.2	0.22
			14	2.4	0.38
			28	1.4	0.56
			35	0.35	0.36
			42	0.27	0.31
Schriesheim, 1982 Rondom	0.60 (1500 l water/ha)	2	0	3.7	0.29
			7	2.0	0.29
			14	1.3	0.26
			21	0.67	0.29
			28	0.17	0.11
			35	0.11	0.08
Schwabenheim, 1973 Heros	0.04 kg ai/hl	1	0	0.58	<0.02
			14	0.15	0.08
			21	0.03	0.09
Schwabenheim, 1973 Heros	0.04 kg ai/hl	1	0	0.42	0.02
			7	0.20	0.12
			14	0.08	0.14
			21	0.05	0.11
Schwabenheim, 1973 Heros	0.04 kg ai/ha	2	0	0.58	0.02
			7	0.28	0.05
			14	0.15	0.08
			21	0.03	0.10

Location, Year, Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Deisendorf, 1973 Heros	0.809 (2000 l water/ha)	1	0	2.2	0.01
			4	2.1	0.02
			7	1.1	0.02
			10	0.40	0.02
Schwabenheim, 1982 Heros	0.40 (1000 l water/ha)	2	0	0.36	0.19
			7	0.11	0.26
			14	0.05	0.21
			21	0.02	0.19
			29	0.02	0.19
Schriesheim, 1982	0.60 (1500 l water/ha)	2	0	3.7	0.29
			7	2.0	0.29
			14	1.3	0.26
			21	0.67	0.29
			28	0.17	0.121
			35	0.11	0.08
Immenstaad, 1982 Jonkher Van Tets	0.60 (1500 l water/ha)	2	0	1.4	0.02
			7	0.27	0.01
			14	0.10	0.02
			21	<0.01	0.02
			28	<0.01	<0.01
Ebersweier, 1982 Macheraus Rote Riesentraube	0.60 (1500 l water/ha)	2	0	3.1	0.07
			7	1.2	0.03
			14	0.63	0.03
			21	0.47	<0.01
			28	0.35	<0.01
Schwabenheim, 1983 Red Lake	0.52 (1300 l water/ha)	2	0	1.9	0.30
			14	0.81	0.31
			21	0.68	0.26
			28	0.32	0.18
			35	0.18	0.17
			42	0.05	0.10
Schriesheim, 1983 Rondom	0.60 (1500 l water/ha)	2	0	5.2	0.22
			14	2.4	0.38
			28	1.4	0.46
			35	0.35	0.36
			42	0.27	0.31
Immenstaad, 1983 Jonkheer Van Tets	0.60 (1500 l water/ha)	2	21	0.12	0.05
			28	0.04	0.06
			35	<0.02	0.08
			42	<0.02	0.04
Hove, 1983 Red Lake	0.60 (1500 l water/ha)	2	0	15.	0.23
			14	4.9	0.30
			28	3.7	0.21
			35	2.3	0.24
			42	1.4	0.28

Assorted tropical and sub-tropical fruits–inedible peel.

Information on GAP was supplied for Columbia (avocado), Australia (avocado, banana, custard apple, feijoa, guava, kiwifruit, mango, passion fruit, persimmon, pineapple, pomegranate), New Zealand (banana, pineapple) and Reunion (banana, pineapple).

Australia (Queensland) reported field trials on avocados (Hargreaves *et al.*, 1982f), mangoes (Hargreaves *et al.*, 1984; Swaine *et al.*, 1984a,b) and litchis (Hamilton and Priestly, 1996). All trials were with post-harvest dips or sprays. The results for avocados and mangoes are shown in Table 35 and for litchis in Table 36.

Table 35. Dimethoate residues in or on avocados and mangoes from post-harvest treatment with dimethoate.

Fruit	Treatment	Withholding period, days	Dimethoate, mg/kg			Method of analysis
			Peel	Pulp	Whole fruit[1]	
Avocado	Dip 400 mg/l	0	1.3	0.02	0.20	Separate into peel, pulp, and seeds. Macerate, extract, sweep co-distil, GLC with FPD. Omethoate destroyed by co-distillation.
		3	0.6	0.02	0.10	
		6	0.7	0.02	0.11	
	Dip 800 mg/l	0	1.5	0.04	0.24	
		3	0.9	0.03	0.21	
		6	1.1	0.01	0.16	
Mango	High volume spray, 400 mg/l	0	2.2	0.024	0.27	
		3	0.52	0.04	0.11	
		7	0.14	0.05	0.05	
	Dip 500 mg/l	0	2.4	0.10	0.49	
		7	0.40	0.025	0.088	

[1] Calculated from weights of peel, pulp and seeds

Litchis (Wai Chee variety) were treated with either a dip solution of dimethoate (315 mg/l water, total volume 100 l, made from Perfekthion EC400) or a flood spray solution (290 mg/l, total volume 230 l). Each trial was with 10 kg fruit. After treatment the litchis were drained for 5 minutes, stored in plastic bags at 22°C and sampled for analysis at intervals of 0–5 days. The samples were separated into peel, stone and pulp and each component was weighed. Pulp and peel fractions were immediately analysed by method PPQ-02, validated by the determination of omethoate and dimethoate recoveries from fortified litchi peel and pulp; the recovery range 92–102%. The limits of determination for dimethoate and omethoate were shown to be 0.02 mg/kg in the pulp and 0.10 mg/kg in the peel. The results are shown in Table 36.

Table 36. Residues of dimethoate and omethoate in or on litchis from the post-harvest treatment (dip or flood spray) with a dimethoate EC formulation (Queensland, Australia, 1996).

Treatment	Days, post-treatment	Peel, mg/kg		Pulp, mg/kg		Whole fruit[1], mg/kg
		Omethoate	Dimethoate	Omethoate	Dimethoate	Dimethoate + omethoate
Dip 315 mg/l, 1 min	0	<0.1 <0.1	7.41 7.59	<0.02 <0.02	0.07 0.05	1.9 2.1
	1	0.13 0.22 0.18 0.21	5.87 5.14 4.60 5.17	<0.02 <0.02 <0.02 <0.02	0.57 0.59 0.66 0.66	1.8 1.6 1.5 1.7
	2	0.28 0.30	4.38 3.85	0.02 0.02	0.92 0.68	1.7 1.4
	5	0.47 0.45	1.90 2.58	0.02 0.02	0.98 0.99	1.2 1.4
Flood Spray, 290 mg/l, 10 sec	0	<0.1 <0.1	5.53 4.49	<0.02 <0.02	0.08 0.08	1.3 1.2
	1	0.11 <0.1 0.17 0.14	4.05 3.76 4.22 3.94	<0.02 <0.02 <0.02 <0.02	0.40 0.43 0.45 0.46	1.2 1.2 1.3 1.3
	2	0.14 0.12	3.11 2.97	0.02 <0.02	0.62 0.52	1.2 1.0
	5	0.40 0.40	1.53 1.59	<0.02 0.02	0.66 0.67	0.91 0.92

[1] Calculated from the peel and pulp weights and their residues

GAP for Australia specifies 0.1 l of a 400 g/l EC formulation (Perfekthion EC 400) per 100 l dip, or 400 ppm. The use is limited to Queensland and the post-treatment interval is 0 days for avocado and litchi and 7 days for mango.

Bulb vegetables

Information on GAP was received for The Netherlands (leeks, onions), Denmark (onions), Germany (onions) and Sweden (onions).

Germany provided summary reports of field trials on chives and leeks. No details were given and the analytical methods were not specified. Chives at 4 locations in Germany were treated with dimethoate (1975–1976), harvested 12–32 days after treatment and analysed for residues, presumably dimethoate. Leeks treated with a 0.1% dimethoate solution at two locations (1974) were harvested 0–48 days after treatment.. The DTF provided summary data on supervised field trials with onions in Germany (Pistel and Bleif, 1993). All the results are shown in Table 37. GAP in Germany for onions specifies 2 foliar treatments with an EC formulation, each 0.24 kg ai/ha, with a 14-day PHI. GAP in The Netherlands for leeks specifies 2 foliar applications with an EC formulation, each 0.40 kg ai/ha, or 3 treatments at 0.20 kg ai/ha, PHI 21 days.

Table 37. Residues of dimethoate in or on bulb vegetables from the application of an EC dimethoate formulation in Germany.

Crop	Location/Year/ Variety	Treatment rate, kg ai/ha or as specified	Growth stage/interval	PHI, days	Dimethoate, mg/kg	
Leek	Buttelborn, 1974	0.04 kg ai/hl	Two fingers strong	0	1.17	
				7	0.05	
				14, 21, 48	<0.02	
		0.04 kg ai/hl	35 cm high	0	0.12	
				7, 14, 21, 27	<0.05	
Chive	Mainz-Bretzenheim, 1976	0.32 2 l water/m^2	Sprouting plants	12	3.5 4.1	
	Frankfurt, 1976	0.32 2 l water/m^2		32	1.7	
	Frankfurt, 1976	0.32 2 l water/m^2		25	1.1	
	Gundelfingen, 1975	0.32 2 l water/m^2		?	0.23 0.27	
	Poppenreuth, 1975	0.32 or 0.8? 2 l water/m^2		13	0.17	
					Dimethoate, mg/kg	Omethoate, mg/kg
Onion	Hamburg-Kirchwerder, 1975 Allround	0.04 2 treatments	Not specified. 82-day interval	0	0.02	<0.01
				7	0.31	0.02
				14	0.14	<0.01
				21	0.04	<0.01
	Limburgerhof, 1975 Rocket	6.4 (drenching, 16,700 l water/ha) 0.24 (spraying, 600 l water/ha)	54-day interval	0	0.20	<0.05
				7-28	<0.05	<0.05

Crop	Location/Year/ Variety	Treatment rate, kg ai/ha or as specified	Growth stage/interval	PHI, days	Dimethoate, mg/kg	
					Dimethoate, mg/kg	Omethoate, mg/kg
	Schwabenheim, 1982 Zittauer Gelbe	0.2 g/m (drenching; 500 ml water/m) 0.2 g/m (drenching, 500 ml water/m) 0.24 (spraying, 600 l water/ha)	 11-day interval 66-day interval	0	0.02	<0.02
				7–28	≤0.02	≤0.02
	Schwabenheim, 1975 Zittauer Gelbe Riesen	0.24 600 l water/ha	1	0	0.12	<0.02
				7	0.10	<0.02
				14–21	≤0.02	≤0.02
	Schwabenheim, 1974 Zittauer Gelbe Riesen	0.2 g/m (drenching, 500 ml water/m)	2 (105-day interval)	0	0.04	<0.02
				7	0.08	<0.02
				14	0.04	≤0.02
				21	<0.02	<0.02
	Limburgerhof, 1982 Ontario	8 (drenching, 500 ml water/m) 0.24 (spraying, 600 l/ha)	2 (80-day interval)	0	0.20	<0.05
				7-28	≤0.05	≤0.05
	Gundlingen, 1982 Hyper	8 (drenching, 500 ml/m) 8 (drenching, 500 ml/m) 0.24 (spraying, 600 l/ha)	3 11-day interval 63-day interval	0	0.01	<0.01
				7–28	≤0.01	≤0.01
	Reichenau, 1982 Hyper	8 (drenching, 500 ml/m) 8 (drenching, 500 ml/m) 0.24 (spraying, 600 l/ha)	3 11-day interval 63-day interval	0	≤0.01	≤0.01

Brassica vegetables

Information on GAP was provided for Australia, Thailand, the UK, Mexico (broccoli, cabbage, cauliflower), The Netherlands (broccoli, Brussels sprouts, cabbage, cauliflower, kohlrabi), the USA (broccoli, Brussels sprouts–California, cabbage, cauliflower), Germany (Brussels sprouts, cabbage), Columbia (cabbage, cauliflower), Sweden (cabbage) and Denmark (crucifers, kohlrabi).

The Netherlands reported field trials on Brussels sprouts (Ministry of Health, Welfare and Sport, 1979), Germany provided data on Brussels sprouts, cauliflower and broccoli (Federal Biological Research Centre for Agriculture and Forestry), Cheminova provided data on Brussels sprouts (USA) and the DTF supplied data on cabbage (Germany, The Netherlands) and summary

information on trials on cauliflower, Brussels sprouts, white cabbage, Savoy cabbage and kohlrabi, all from Germany (Pistel and Bleif, 1993), but with no details. The DTF also reported supervised field trials in the UK on cauliflower, Brussels sprouts and cabbage (Partington, 1998). The results of all the trials are shown in Table 38.

Table 38. Residues of omethoate and dimethoate in or on brassica vegetables from the foliar application of a dimethoate EC formulations.

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
Cauliflower	Braunschweig, Germany 1983	0.24 600 l water/ha	2	0	0.79		
				7	0.08		
				14	<0.03		
				21	<0.03		
	Limburgerhof, Germany 1975 Candor	1.4 (drenching, 80 ml water/plant) 0.4 (spraying, 1000 l/ha)	2 (42 day interval)	0	0.70		Summary only
				7	0.09		
				14	0.04		
				21	<0.02		
	Limburgerhof, Germany 1974 Malinus	0.32 (drenching, 800 l water/ha) 0.32 (spraying, 800 l water/ha)	2 (49 day interval)	0	0.22		Summary only
				7	0.10		
				14	0.13		
				21	0.05		
	Schwabenheim, Germany 1973 Candor	80 mg/plant (drenching, 80 ml/plant) 0.4 kg/ha (spraying, 3100 l/ha) 0.4 kg/ha (spraying, 3100 l/ha)	3 (21 day interval) (22 day interval)	0	0.80	<0.02	Summary only
				7	0.04	0.03	
				14	<0.02	0.03	
				21	<0.02	0.05	
	Schwabenheim, Germany 1973 Candor	80 mg/plant (drenching, 80 ml water/plant) 0.4 kg/ha (spraying, 2100 l water/ha)	2 (21 day interval)	0	2.97	0.22	Summary only
				7	1.37	0.23	
				14	0.10	0.05	
				21	<0.02	0.02	
	Schwabenheim, Germany 1975 Lukra	32 mg/plant (drenching, 80 ml water/plant)	2 (47 day interval)	0	0.78		Summary only
				7	0.14		
				14	0.05		
				21	0.05		
	Limburgerhof, Germany 1974 Malinus	0.31 (800 l water/ha)	1	0	0.78		Summary only
				7	0.30		

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
				14	0.18		
				21	0.10		
	Schwabenheim, Germany 1969 Markstolz	32 mg/plant (drenching, 80 ml water/plant)	2	25	0.03	<0.02	Summary only
				30	0.02		
				35	0.02		
				42	0.02		
	Kiel, Germany 1973 Delfter Markt	80 ml/plant (drenching, 600 l/ha)	2	0	1.20	0.15	Summary only
				7	0.31	<0.01	
				14	0.17	<0.01	
				21	0.01	<0.01	
Cauliflower	Birchington, Kent, UK 1996	0.4 597-611 l water/ha	6 (7-8 day interval)	0 3 7 14 21	0.51 0.44 0.34 0.21 0.11	<0.01 <0.01 0.01 <0.01 0.01	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D 105%, O 101%. Max frozen storage 83 days.
	Kings Newton, Derbyshire, UK 1996	0.4 585-623	6 (7-8 day interval)	0 3 7 14 21	0.06 0.02 0.03 0.03 0.02	<0.01 <0.01 <0.01 <0.01 <0.01	DFG 236 (ethyl acetate; gel permeation). Max frozen storage 68 days.
	Gosberton Clough, Lincolnshire, UK 1996	0.4 587-620 l water/ha	6 (7 day interval)	0 3 7 14 21	0.37 0.42 0.11 0.02 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D 112, 105, 109%, O 85, 87, 100%. Max frozen storage 153 days.
	Gullane, East Lothian, UK 1996	0.4 583-603 l water/ha	6 (6-7day interval)	0 3 7 14 21	0.30 0.19 0.09 0.05 destruct	<0.01 <0.01 <0.01 <0.01 destruct	DFG 236 (ethyl acetate; gel permeation). Max frozen storage 130 days.
	Birchington, Kent, UK 1997	0.4 595-604 l water/ha	6 (7 day interval)	0 3 7 14 21	0.12 0.02 0.02 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg D 96, 84%, O 83, 70%. Max frozen storage 83 days.
	Elford, Stafford-shire, UK 1997	0.4 596-608 l water/ha	6 (7 day interval)	0 3 7 14 21	0.70 0.27 0.09 0.02 no sample	0.03 0.01 <0.01 <0.01 no sample	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D 99%, O 107%. Max frozen storage 144 days.

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
	Friskney, Lincolnshire, UK 1997	0.4 594-601 l water/ha	6 (7 day interval)	0 3 7 14 21	0.05 0.04 0.04 0.03 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	DFG 236 (ethyl acetate; gel permeation). Max frozen storage 82 days.
	Longniddry, East Lothian, UK 1997	0.4 593-601 l water/ha	6 (7 day interval)	0 3 7 14 21	0.04 0.02 0.02 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg fortification, D recovery 108%, O recovery 109%. Max frozen storage 100 days.
Broccoli	Braunschweig, Germany 1983	0.24 600 l water/ha	2	0	0.66		
				7	0.09		
				14	<0.05		
				21	<0.05		
Brussels sprouts	Limburgerhof, Germany 1974 Lancelot	0.32 (800 l water/ha)	2 (92 day interval)	0	0.21		Summary only
				7	0.12		
				14	0.06		
				21	0.02		
				28	<0.02		
	Swisttal, Germany 1982 Cor Valiant	0.24 (600 l water/ha)	3 (13 and 43 day inter-vals)	0	0.23	0.19	Summary only
				3	0.11	0.16	
				7	0.08	0.18	
				14	<0.05	0.16	
				21	<0.05	0.15	
	Limburgerhof, Germany 1982 Sprout Harald	0.24 (600–900 l water/ha)	3 (14 and 67 day inter-vals)	0	1.30	0.15	Summary only
				3	0.32	0.15	
				4	0.26	0.15	
				7	0.11	0.13	
				14	0.05	0.09	
				21	0.09	0.18	
	Landshut, Germany 1982 Prinz Ascold	0.24 (600 l water/ha) 0.36 (900 l water/ha)	2 (14 day interval) 1 (41 day interval)	0	0.20	0.37	Summary only
				3	0.14	0.28	
				7	<0.05	0.61	
				14	<0.05	0.30	
				21	<0.05	0.41	

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
	Oldenburg, Germany 1982	1.2 (0.0008 kg/l)	1	0	3.6		
				7	0.33		
				14	<0.1		
				21	<0.1		
	Hurth-Fischenich, Germany 1982	2.4 (0.0008 kg/l)	2	0	6.41		
				7	1.32		
				14	0.42		
				21	0.15		
	Berlin-Britz, Germany 1982	1.2 (0.0008 kg/l)	1	0	1.55		
				7	0.64		
				14	<0.1		
				21	<0.1		
	Hannover, Germany 1982	1.2 (0.0008 kg/la)	1	0	11.8		
			1	7	1.98		
				14	0.19		
				21	<0.1		
	Frankfurt, Germany 1982	1.2 (0.0008 kg/l)	1	0	0.27		
				7–21	<0.1		
	Mainz-Bretzenheim, Germany 1982	1.2 (0.0008 kg/l)	1	0	0.34		
				7–21	<0.1		
	Münster, Germany 1982	1.2 (0.0008 kg/l)	1	0	0.49		
				7	0.15		
				14–21	<0.1		
	Braunschweig, Germany 1982	1.2 (0.0008 kg/l)	1	0	2.09		
				7	0.41		
				14	0.15		
				21	<0.1		
	Tinte, Netherlands 1979	0.20 (1000 l water/ha)	3	7	0.07 (0.06-0.09)	0.01 (<0.01-0.02)	Method: extract with ethyl acetate; silica gel clean-up. GLC with FPD. Limits of determination: 0.005 dimethoate; 0.01 mg/kg omethoate. Dimethoate (0.11 mg/kg) 83%. Omethoate (0.13 mg/kg) 71%.
				14	0.02 (0.01-0.02)	<0.01	
				21	0.005 (<0.005-0.005)	<0.01	
	Breda, Netherlands 1979	0.20 (1000 l water/ha)	3	7	0.05 (0.02-0.06)	<0.01	
				14	0.06 (0.03-0.10)	<0.01	
				21	0.03 (0.01-0.04)	0.01 (<0.01-0.02)	
	Kerkwijk, Netherlands 1979	0.20 (1000 l water/.ha)	3	7	0.009 (0.005-0.01)	<0.01	
				14	0.008 (0.005-0.01)	0.02 (<0.01-0.04)	
				21	0.009 (<0.005-0.02)	<0.01	

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
	USA (Watsonville, California)	0.56 (940 l water/ha)	6	7	2.33	0.47	Method: Pesticide Analytical Manual, Vol. II. Results corrected for recoveries. Dimethoate 77–90% (0.1-4.0 mg/kg). Omethoate 80–98% (0.4–2.0 mg/kg)
				10	1.02	0.40	
				14	0.66	0.32	
		1.12 (940 l water/ha)	6	7	5.02	0.62	
				10	3.12	0.58	
				14	1.67	0.56	
Brussels sprouts	Bicker, Lincolnshire, UK 1996	0.4 591-624 l water/ha	6 (7-8 day interval)	0 3 7 14 21	0.45 0.21 0.11 0.03 0.02	0.02 0.02 0.02 <0.01 0.01	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D 108%, O 106%. Max frozen storage 86 days.
	Bicker, Lincolnshire, UK 1996	0.4 586-628 l water/ha	6 (7 day interval)	0 3 7 14 21	0.62 0.38 0.17 0.06 0.04	0.04 0.04 0.06 0.03 0.01	DFG 236 (ethyl acetate; gel permeation). Control samples showed significant dimethoate, e.g. 0.14 mg/kg at 0 days PHI. Max frozen storage 145 days.
	Gosberton clough, Lincolnshire, UK 1996	0.4 599-608 l water/ha	6 (7-8 day interval)	0 3 7 14 21	0.30 0.10 0.10 0.11 0.03	0.04 0.02 ≤0.01 <0.01 <0.01	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D 79%, O 94%. Max frozen storage 76 days.
	Longniddry, East Lothian, UK 1996	0.4 589-610 l water/ha	6 (6-7 day interval)	0 3 7 14 21	0.31 0.33 0.17 0.10 0.06	0.05 0.05 0.04 0.04 0.03	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D 104, 96%, O 94, 96%. Max frozen storage 103 days.
	Ickham, Kent, UK 1997	0.4 597-612 l water/ha	6 (7 day interval)	0 3 7 14 21	0.18 0.08 0.07 0.03 0.02	0.03 0.02 0.03 0.02 0.02	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D 111, 97%, O 114, 71%. Max frozen storage 69 days.

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
	Gosberton Clough, Lincolnshire, UK 1997	0.4 585-614 l water/ha	6 (7-8 day interval)	0 3 7 14 21	0.23 0.17 0.08 0.04 0.02	0.03 0.03 0.03 0.03 0.02	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D 99%, O 101%. Max frozen storage 68 days.
	Friskney, Lincolnshire, UK 1997	0.4 572-601 l water/ha	6 (6-8 day interval)	0 3 7 14 21	0.40 0.23 0.21 0.11 0.04	0.06 0.04 0.08 0.07 0.04	DFG 236 (ethyl acetate; gel permeation. Max frozen storage 29 days.
	Longniddry, East Lothian, UK 1997	0.4 600-601 l water/ha	6 (7 day interval)	0 3 7 14 21	1.1 0.88 0.46 0.10 0.03	0.13 0.13 0.17 0.11 0.07	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D 110, 89%, O 108, 82%. Max frozen storage 87 days.
Cabbage	Rheinland-Pfalz, Germany 1995	0.46 (333 l water/ha) 0.26 (423 l water/ha) 0.26 (417 l water/ha)	3 (1 x band; 2 x surface)	0	0.17	<0.01	Method: DFG 236. Calibration 0.02--0.75 µg/ml. Dimethoate recovery 77–105%, n = 8, at 0.01 and 1.0 mg/kg; omethoate: 70–81%, n = 8, 0.01 and 1.0 mg/kg. Variety: Wirosa, Growth stage 45 at last application.
				15	<0.01	<0.01	
				21	<0.01	<0.01	
	Rheinland-Pfalz, Germany 1995	0.46 (333 l water/ha) 0.25 (406 l water/ha) 0.60 (402 l water/ha)	3 (1 x band; 2X surface)	0	0.69	<0.01	Method DFG 236. Variety: Julius. Growth stage 43 at last application.
				14	<0.01	<0.01	
				21	<0.01	<0.01	
	Limburg, Netherlands 1995	0.42 (306 l water/ha) 0.25 (408 l water/ ha) 0.26 (420 l water/ha)	3 (1 x band; 2 x surface)	0	0.60	<0.01	Method DFG 236. Variety: Verosa. Growth stage 43 at last application
				13	<0.01	<0.01	
				19	<0.01	<0.01	
	Nord Brabant, Netherlands 1995	0.40 (296 l water/ha) 0.24 (389 l water/ha) 0.25 (409 l water/ha)	3 (1 x band; 2 x surface)	0	0.89	<0.01	Method 236. Variety: Winterkoning. Growth stage 43 at last application
				15	<0.01	<0.01	

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
				22	<0.01	<0.01	
White cabbage	Limburgerhof, Germany 1974 Dithmarscher Allerfrühester	0.32 (800 l water/ha)	2 (23 day interval)	0	1.93		Summary only
				7	0.16		
				14	0.07		
				21	<0.02		
White cabbage	Limburgerhof, Germany 1974	0.32 (800 l water/ha)	2 (23 day interval)	0	0.19		Summary only
				7	0.14		
				14	<0.02		
				21	<0.02		
White cabbage	Kiel, Germany. 1973 Weisskohl	32 mg/plant (80 ml water/plant)	2 (20 day interval)	0	1.75	0.39	Summary only
				7	0.02	0.01	
				14	0.02	0.02	
				21	<0.01	<0.01	
Savoy cabbage	Limburgerhof, Germany 1982	32 mg/plant (watering, 80 ml water/plant) 0.24 (600 l water/ha)	2 (15 day interval) (7 day interval) 2 (14 day interval)	0	1.32	0.54	Summary only.
				7	0.08	0.67	
				14	<0.05	0.53	
				21	<0.05	0.68	
				28	<0.05	<0.05	
Savoy cabbage.	Limburgerhof, Germany 1983 Grünkopf	32 mg/plant (80 ml water/plant) 0.24 (600 l water/ha)	2 (13 day interval) (4 day interval) (14 day interval)	0	2.14	0.19	Summary only
				7	0.43	0.38	
				14	<0.05	0.11	
				21	<0.05	0.09	
				28	<0.05	<0.05	
Savoy cabbage.	Limburgerhof, Germany 1983 Grünkopf	20 mg/m (watering, 30 ml water/m) 0.24 (600 l water/ha)	2 (7 day interval) (7 day interval) (14 day interval)	0	1.47	0.17	Summary only. .
				7	0.09	0.19	
				14	<0.05	0.13	
				21	<0.05	0.12	
				28	<0.05	0.14	

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
Savoy cabbage.	Limburgerhof, Germany 1969 Frühkofp	0.04 kg ai/hl		0	2.7		Summary only. .
				12	0.05		
Savoy cabbage.	Limburgerhof, Germany 1982	32 mg/plant (80 ml water/plant) 0.24 (600 l /ha)	2 (15 day interval) (7 day interval) 2 (15 day interval)	0	1.32	0.54	Summary only. .
				7	0.08	0.67	
				14	<0.05	0.53	
				21	<0.05	0.68	
				28	<0.05	<0.05	
Savoy cabbage.	Limburgerhof, Germany 1982 Früh-Wirsing	20 mg/m (watering, 30 ml/m) 0.24 (600 l water/ha)	2 (11 day interval) (11 day interval) 2 (14 day interval)	0	0.68	0.25	Summary only. .
				7	0.05	0.30	
				14	<0.05	0.66	
				21	<0.05	0.51	
				28	<0.05	0.34	
Savoy cabbage.	Reichenau, Germany 1982 Marner Frühkopf	20 mg/m (watering, 30 ml/m) 0.24 (600 l water/ha)	2 (11 day interval) (11 day interval) (13 day interval)	0	0.14	0.03	Summary only. .
				7	0.02	<0.01	
				14–28	<0.01	<0.01	
Savoy cabbage.	Mengen, Germany 1982 Marner Grünkopf	20 mg/m (watering, 30 ml water/m) 0.24 (600 l water/ha)	2 (11 day interval) (14 day interval) 2 (13 day interval _	0	0.28	0.05	Summary only. .
				7	0.02	0.03	
				14	<0.01	<0.01	
				21	<0.01	<0.01	
				28	<0.02	<0.01	

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
Savoy cabbage.	Mengen, Germany 1982 Marner Grünkopf	32 mg/plant (80 ml water/plant) 0.24	2 (11 day interval) (14 day interval) 2 (13 day interval)	0	0.37	0.05	Summary only. .
				7	0.02	0.02	
				14	0.01	0.01	
				21	<0.01	<0.01	
				28	<0.01	<0.01	
Savoy cabbage.	Reichenau, Germany 1982 Marner Frühkopf	32 mg/plant (80 ml water/plant) 0.24 (600 l water/ha)	2 (11 day interval) (10 day interval) 2 (13 day interval)	0	0.21	0.04	Summary only. .
				7	0.01	0.02	
				14	<0.01	<0.01	
				21	<0.01	0.01	
				28	<0.01	<0.01	
Savoy cabbage.	Schwabenheim, Germany 1982 Zieglers Vorbote	209 mg/m (watering, 20 ml water/m) 0.24 (600 l water/ha)	2 (9 day interval) (10 day interval) 2 (14 day interval)	0	0.96	0.40	Summary only. .
				7	<0.02	0.378	
				14	<0.02	0.31	
				21	<0.02	<0.02	
				28	<0.02	<0.02	
Savoy cabbage.	Schwabenheim, Germany 1983 Zieglers Vorbote	20 mg/m (watering, 30 ml water/m) 0.24 (500 l water/ha)	2 (10 day interval) (7 day interval) 2 (14 day interval)	0	1.34	0.16	Summary only. .
				7	<0.02	0.11	
				14	<0.02	0.17	
				21	0.15	0.03	
				28	0.07	0.11	
Savoy cabbage.	Schwabenheim, Germany 1983 Zieglers Vorbote	32 mg/plant (80 ml water/plant) 0.24 (50 0 l water/ha)	2 (10 day interval) (7 day interval) 2(14 day interval)	0	0.98	0.04	Summary only. .
				7	0.04	0.03	

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
				14	0.04	0.05	
				21	<0.02	0.03	
				28	<0.02	0.03	
Savoy cabbage.	Mengen, Germany 1983 Marner Frühkopf	2 g/m (3 l water/m) 0.24 (600 l water/ha)	2 (10 day interval) (7 day interval) 2 (14 day interval)	0	0.87	0.16	Summary only. .
				7	0.07	<0.02	
				14-28	<0.02	<0.02	
Savoy cabbage.	Mengen, Germany 1983 Marner Frühkopf	2 g/m (3 l water/m) 0.24 (600 l water/ha)	2 (11 day interval) (7 day interval) 2 (14 day interval)	0	0.96	0.07	Summary only. .
				7	0.22	0.05	
				14-28	<0.02	<0.02	
Savoy cabbage.	Kremper, Germany 1983 Marner Frühkopf	2 mg/m (3 L water/m) 0.24 (600 l water/ha)	2 (10 day interval) (14 day interval) 2 (14 day interval)	0	0.40	0.04	Summary only. .
				7	<0.02	0.03	
				14-28	<0.02	<0.02	
Savoy cabbage.	Kremper, Germany 1983 Marner Frühkopf	32 mg/plant 0.24 (600 l water/ha)	2 (10 day interval) (14 day interval) 2 (14 day interval)	0	0.68	0.07	Summary only. .
				7	0.08/	0.07	
				14–28	<0.02	<0.02	
Cabbage	Birlingham, Worcestershire, UK 1996	0.4 583-603 l water/ha	6 (7 day interval)	0 3 7 14 21	5.0 2.8 0.29 0.67 0.20	0.65 0.89 0.29 0.64 0.36	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D 100 %, O 113, 111%. Max frozen storage 107 days.

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
	Shepshed, Leicestershire, UK 1996	0.4 589-615 l water/ha	6 (7 day interval)	0 3 7 14 21	4.6 3.9 1.2 0.34 0.25	0.81 1.5 0.63 0.30 0.46	DFG 236 (ethyl acetate; gel permeation). Max frozen storage 127 days.
	Kings Newton, Derbyshire. UK 1996	0.4 584-638 l water/ha	6 (7 day interval)	0 3 7 14 21	5.3 2.7 1.0 0.82 0.99	0.29 0.29 0.15 0.22 0.35	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg D 111%, O 111%. Max frozen storage 80 days.
	Gullane, East Lothian, UK 1996	0.4 593-619 l water/ha	6 (7-8 day interval)	0 3 7 14 21	1.9 2.5 0.25 0.11 0.04	0.30 0.687 0.05 0.07 0.03	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg, D recovery 101%, O 111%. Max frozen storage 153 days.
	Manston, Ketn, UK 1997	0.4 594-610 l water/ha	6 (7 day interval)	0 3 7 14 21	2.9 0.52 0.07 0.05 0.06	0.58 0.30 <0.01 <0.01 0.02	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg D 111%, O 108%. Max frozen storage 81 days.
	Friskney, Lincolnshire, UK 1997	0.4 584-609 l water/ha	6 (7-8 day interval)	0 3 7 14 21	0.68 0.55 0.14 0.04 0.02	0.13 0.19 0.04 0.02 0.02	DFG 236 (ethyl acetate; gel permeation). Max frozen storage 107 days.
	Kings Newton, Derbyshire, UK 1997	0.4 593-601 l water/ha	6 (7-10 day interval)	0 3 7 14 21	2.8 1.5 0.82 0.71 0.23	0.11 0.25 0.28 0.25 0.17	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg D 77%, O 71%. Max frozen storage 80 days.
	Aberlady, East Lothian, UK 1997	0.4 597-604 l water/ha	6 (7 day interval)	0 3 7 14 21	0.85 0.70 0.04 0.01 0.01	0.27 0.38 0.02 <0.01 0.01	DFG 236 (ethyl acetate; gel permeation). Recoveries at 0.01 mg/kg D 92%, O 83%. Max frozen storage 94 days.
Kohlrabi	Limburgerhof, Germany 1976 Neuzucht Haubner	6.4 (watering, 16000 l water/ha) 0.24 (600 l water/ha)	2 (38 day interval)	0	9,5		Summary only.
				7	1.85		
				14	0.82; 0.40		
				21	0.72; 0.32		

Crop	Location, Year, Variety	Treatment rate, kg ai/ha	No. of applicns	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
	Schwabenheim, Germany 1969 Delikatess Weiss	32 mg/plant (80 ml water/plant)	2 (interval 10 days)	25	0.03		
				30-42	<0.02		

GAP in Germany specifies 1 application at 0.4 kg ai/ha, 42-day PHI for cauliflower, 2 x 0.24 kg ai/ha with a 14-day PHI or 1 x 0.4 kg ai/ha with a 42-day PHI for cabbage and 2 applications, 0.24 and 0.36 kg ai/ha, with a 14-day PHI for Brussels sprouts. No GAP was reported for broccoli in Germany, but GAP in The Netherlands specifies multiple applications at 0.2 kg ai/ha with a 21-day PHI. GAP for cabbage and Brussels sprouts in The Netherlands calls for repeat applications at 0.2 kg ai/ha with a 21-day PHI. GAP for Brussels sprouts in the USA (California only) allows up to six applications of 1.12 kg ai/ha, with a 10-day PHI. GAP for kohlrabi in Germany was not reported, but in Denmark the rate is 0.32 kg ai/ha, PHI not specified. GAP for foliar application to Brassica vegetables in the UK specifies 6 x 0.40 kg ai/ha, 7-day PHI.

Cucurbits

Australia reported trials on cucumbers, zucchini, rockmelons and watermelons. Rockmelons and cucumbers were treated with a post-harvest dip (Hargreaves and Heather, 1989). A 400 g/l EC formulation of dimethoate was diluted with water to a 400 mg/l solution. Twenty-four rockmelons were dipped, followed by 24 cucumbers. The dimethoate dip solution was analysed before and after the dippings and contained 409 mg/l and 404 mg/l respectively. Four samples each of rockmelon and cucumber were taken 0, 3 and 7 days after treatment and homogenized. The homogenates were stored at –12°C until analysis of duplicate samples by the method of Hargreaves and Heather (1989) described above.

Trials on the post-harvest dip treatment of zucchini (Hargreaves and Jackson, 1988) were similar except that chopped samples were stored frozen up to 3 weeks at –18°C and the homogenates were analysed by method M16.01.

Watermelons were dipped in a nominal 400 mg/l solution of dimethoate, shown by analysis to contain 375 mg/l before and 379 mg/l after dipping (Jackson and Cheyne, 1994). Duplicate samples of 4 melons were taken from storage at 13°C and 20°C at 0. 1, 2, 4 and 7 days after treatment. One quarter of each of the 4 melons was chopped and stored at -10°C until analysis by an unspecified method.

The results of all the trials are shown in Table 39.

Table 39. Residues of dimethoate in or on various cucurbits following a post-harvest dip in a 400 mg/l solution.

Commodity	Storage period, days	Dimethoate, mg/l
Rockmelon	0	1.2; 1.4 average 1.3
	3	1.3; 1.5 average 1.4
	7	1.3; 1.4 average 1.4
Cucumber	0	0.5, 0.5
	3	0.6; 0.6
	7	0.5; 0.6 average 0.6

Commodity	Storage period, days	Dimethoate, mg/l
Zucchini	0	1.8; 1.5 average 1.6
	3	1.7; 1.4 average 1.6
	7	1.6; 1.0 average 1.3
Watermelon	0 at 13°	0.19; 0.17 average 0.18
	1 at 13°	0.18; 0.17 average 0.18
	2 at 13°	0.14; 0.14
	4 at 13°	0.14; 0.12 average 0.13
	7 at 13°	0.15; 0.14 average 014
	0 at 20°	0.19; 0.17 average 0.18
	1 at 20°	0.18; 0.20 average 0.19
	2 at 20°	0.14; 0.20 average 0.16
	4 at 20°	0.14; 0.10 average 0.12
	7 at 20°	0.12; 0.16 average 0.14

GAP for cucurbits in Australia specifies a post-harvest dip or spray treatment with a 400 mg/l solution of an EC formulation and a 0-day withholding period. There are additional pre-harvest uses on various cucurbits in Australia.

Other fruiting vegetables

In trials in Australia (Bruce, 1988; Hamilton *et al.*, 1980; Hargreaves and Jackson, 1988; Hargreaves *et al.*, 1985; Heather *et al.*, 1987; Swaine *et al.*, 1984a) tomatoes were treated post-harvest by dipping or high volume (flood) spraying with a 400–500 mg/kg solution of dimethoate in water. The tomatoes were stored in ambient conditions and samples taken at intervals were homogenized and analysed for dimethoate residues by method M16.01. In the trials by Heather *et al.* omethoate was also determined by acetone extraction, exchange to chloroform, charcoal treatment and GLC with FPD. The results are shown in Table 40.

Table 40. Residues of dimethoate in or on tomatoes following post-harvest treatment with dimethoate in Australia.

Variety, Year	Treatment	Concentration of treatment solution, mg/l	Ambient storage period, days	Dimethoate, mg/kg
Green, 7 cm 1980	Dip (3 minutes)	425	0	0.59
			3	0.71
			7	0.26
1988	Dip	403	0	1.8, 1.5 average 1.6
			3	1.7, 1.4 average 1.6

Variety, Year	Treatment	Concentration of treatment solution, mg/l	Ambient storage period, days	Dimethoate, mg/kg
			7	1.6, 1.0 average 1.3
Floaradade (F), Redlander (R) 1988	Dip (1 minute)	428	0	F: 0.54, 0.64 average 0.59 R: 0.79, 0.73 average 0.76
			1	F: 0.41, 0.32 average 0.37 R: 0.39, 0.41 average 0.40
			3	F: 0.35, 0.39 average 0.37 R: 0.22, 0.32 average 0.27
			7	F: 0.19, 0.24 average 0.22 R: 0.24, 0.21 average 0.22
1983	Flood (high volume spray)	520	0	0.89, 0.78 (duplicate treatment) average 0.84 omethoate: <0.005
			3	0.69, 0.71 (duplicate treatment) average 0.70 omethoate: 0.03
			7	0.42, 0.25 (duplicate treatment) average 0.34 omethoate: 0.02
1986	Dip	420	0	0.54, 0.70 average 0.66
			3	0.43, 0.52 average 0.48
			7	0.27, 0.21 average 0.24
1984	Dip	425 (3 minutes)	0	0.58
			3	0.66
			7	0.26

Post-harvest GAP for tomatoes in Australia requires a dip in a 400 mg/l solution with a 7-day post-treatment holding period. There are additional pre-harvest foliar uses.

The DTF provided summary information only on supervised trials on tomatoes in Germany (Pistel and Bleif, 1993). No details of the trials or analyses were provided. The results are shown in Table 41.

Table 41. Residues of dimethoate and omethoate from the application of an EC formulation to tomatoes in Germany.

Location, Year Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Christinenthal 1975 Frembgens Rheinlands Ruhm	0.04 kg ai/hl	2 (35 day interval)	0	0.91	0.08

Location, Year Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
			1	0.51	0.04
			3	0.42	0.04
			8	0.22	0.07
Limburgerhof 1983 Surprise	0.48 (1200 l water/ha)	3 (13 day interval)	0	0.72	<0.05
			1	0.33	<0.05
			3	0.20	<0.05
			5	<0.05	<0.05
			7	0.11	<0.05
Limburgerhof 1975 Panase	0.4 (1000 l water/ha)	3 (21 day interval)	0	0.16	0.04
			4	0.05	0.05
			7	0.03	0.07
			14	<0.01	0.03
Schabenheim 1974 Tip Top	0.04 kg ai/hl	2 (10 day interval)	0	0.73	0.07
			1	0.23	0.06
			3	0.15	0.05
			7	0.06	0.07
Limburgerhof 1974	0.4 (1000 l water/ha)	3 (42 d, 20 day interval)	0	0.19	0.03
			3	0.12	0.06
			7	0.10	0.12
			14	0.05	0.16
			21	<0.02	0.02
Hamburg-Curslack 1975	0.04 kg ai/hl	2 (32 day interval)	0	0.12	0.02
			1	0.13	0.06
			2	0.31	0.03
			6	0.14	0.07
Schwabenheim 1975 Tip Top	0.4 (1000 l water/ha)	2 (31 day interval)	0	0.50	0.03
			1	0.25	0.03
			4	0.08	0.03
Schwabenheim 1975 Tip Top	0.4 (1000 l water/ha)	3 (22 day, 21 day interval)	0	0.36	0.07
			4	0.05	0.05
			7	0.03	0.06
			14	<0.02	0.05
Limburgerhof 1982 Muosa	0.72 (1800 l water/ha)	3 (14 day interval)	0	0.26	0.09
			1	0.53	0.14
			3	0.41	0.13
			5	0.24	0.12
			7	0.14	0.12
Opfingen 1982 Estrella	0.84 (2100 l water/ha)	3 (7 day, 8 day interval)	0	0.09	<0.01
			1	0.06	0.03
			3	0.01	0.01
			5	<0.01	0.02
			7	<0.01	<0.01
Bonn 1982 Luca	0.72 0.72 (1800 l water/ha)	3 (16 day interval) (13 day interval)	0	1.57	0.29

Location, Year Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
	0.84 (2100 l water/ha)				
			1	1.31	0.43
			3	0.80	0.32
			5	0.91	0.39
			7	0.59	0.36
Bonn 1983 Hellfrucht	0.36 (900 l water/ha) 0.48 0.48 (1200 l water/ha)	3 (14 day interval) (14 day interval)	0	0.06	<0.02
			1		0.03
			3	0.06	0.03
			5	0.04	0.03
			7	<0.02	<0.02
Frankfurt 1983 Angela	0.48 (1200 l water/ha)	3 (14 day interval)	0	0.08	0.21
			1	0.08	0.1`6
			3	0.06	0.09
			5	0.06	0.04
			7	0.07	0.04
Opfingen 1983 Luca	0.44 (1200 l water/ha)	3 (4 day, 14 day interval)	0	0.36	0.16
			1	0.19	0.16
			3	0.19	0.14
			5	0.12	0.14
			7	0.02	0.08

GAP for the use of dimethoate EC formulation on tomatoes specifies 3 applications, 0.24, 0.36 and 0.48 kg ai/ha, or 0.04 kg ai/hl, with a 3-day PHI. The use is for glasshouses.

Australia provided data on the post-harvest high-volume spray treatment of sweet peppers (capsicums) with 400 mg/l or 800 mg/l dimethoate in 1986 and 1994 (Hargraves, 1986; Hargreaves *et al.*, 1994). The 1986 samples were analysed by method M16.01. Three of them were also analysed for omethoate, using method PPQ-02 (Table 42). The method of analysis for the 1994 samples was not specified. GAP is 0.04 kg/100 l dip (400 mg/l) with no specified withholding period in Queensland only.

Table 42. Residues in or on sweet peppers from post-harvest spraying with dimethoate in Australia.

Year	Spray concentration, mg/l	Storage: days/temperature, °C	Dimethote, mg/kg	Omethoate, mg/kg
1986	390	0/?	0.97, 1.1 1.0 average	0.03
	390	3/?	0.68, 0.71 0.70 average	0.08
	390	7/?	0.29, 0.38 0.34 average	0.08
	800 nominal	0/?	2.0, 2.0	
		3/?	1.0, 1.5 1.2 average	
		7/?	0.95, 1.0 0.98 average	
		1/13	0.78, 1.05 0.91 average	

Year	Spray concentration, mg/l	Storage: days/temperature, °C	Dimethote, mg/kg	Omethoate, mg/kg
		2/13	0.63, 1.04 0.83 average	
		3/13	0.73, 0.85 0.79 average	
		7/13	0.63, 0.81 average 0.72	
		0/20	0.66, 0.72 0.69 average	
		1/20	0.75, 0.82 0.79 average	
		2/20	1.00, 0.82 0.91 average	
		3/20	0.62, 0.70 0.66 average	
		7/20	0.65, 0.54 0.60 average	

Leafy vegetables

Germany provided summary information on trials with dimethoate (400 g/l EC) on kale, spinach, chard and leaf lettuce in 1982-83. No analytical method was specified nor were any analytical recovery data provided. The DTF also provided summary information only without details on supervised trials on head lettuce and spinach in Germany (Pistel and Bleif, 1993). The results are shown in Table 43. No GAP was reported for leaf lettuce, kale, spinach or chard in Germany; GAP for head lettuce is 2 x 0.24 kg ai/ha, maximum 21-day PHI. GAP in The Netherlands for kale is 0.20 kg ai/ha, multiple applications, 21-day PHI; for spinach 0.20 kg ai/ha, 3 treatments maximum, 21-day PHI.

Table 43. Residues from the foliar application of dimethoate EC formulation to leafy vegetables in Germany.

Crop/Variety	Location/Year	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Chard (beet leaf)/Grüner Schnitt	Braunschweig, 1983	0.24 (600 l water/ha)	1	0	10.5	0.06
				7	0.43	0.08
				14-28	<0.03	<0.02
Kale/lerchen-zungen	Oldenburg, 1982	1.2 (1500 l water/ha)	1	0	14.0	
				7	1.96	
				14	0.27	0.36
				21	<0.05	
Kale/Niedriger Grüner Krauser	Hurth-Fischenich, 1982	1.2 (1500 l water/ha)	2 (7 day interval)	0	14.7	
				7	3	
				14	1.32	
				21	0.7	
Kale/Frosty	Braunschweig, 1982	1.2 (1500 l water/ha)	1	0	14.8	
				7	1.57	
				14	0.47	0.27
				21	0.1	
Kale/Benjo	Berlin-Britz, 1982	1.2 (1500 l water/ha)	1	0	13.7	
				7	1.23	
				14	0.1	0.3
				21	<0.05	

Crop/Variety	Location/Year	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Kale/Hammer	Griesheim, 1982	1.2 (1500 l water/ha)	1	0	9.46	
				7	0.44	
				14	0.05	0.13
				21	<0.05	
Kale/Westerlander Halbhoher Wundergrün	Mainz-Bretzenheim, 1982	1.2 (1500 l water/ha)	1	0	17.3	
				7	1.32	
				14	0.1	0.12
				21	<0.05	
Kale/Halbhoher Krauser	Münster, 1982	1.2 (1500 l water/ha)	1	0	11.6	
				7	5.31	
				14	0.24	0.51
				21	0.13	
Kale/Frosty	Hannover, 1982	1.2 (1500 l water/ha)	1	0	11.5	
				7	5.3	
				14	0.41	0.22
				21	0.18	
Leaf lettuce/Gelber Runder	Braunschweig, 1983	0.24 (600 l water/ha)	1	0	11.2	<0.2
				7	0.31	<0.2
				14	<0.03	<0.2
				21	<0.03	<0.2
Spinach/Atlanta	Braunschweig, 1983	0.24 (600 l water/ha)	1	0	20.7	<0.2
				7	0.72	<0.2
				14	<0.05	<0.2
				21	<0.03	<0.2
				27	<0.03	<0.2
Spinach/Medania	Limburgerhof, 1974	0.32 (800 l water/ha)	1	0	16.0	<0.01
				2	8.30	0.36
				4	3.80	0.32
				7	2.60	0.29
				14	1.10	0.45
Spinach/Universal	Schwabenheim, 1973	0.32 (800 l water/ha)	1	0	13.4	0.36
				2	3.12	1.09
				7	0.23	1.15
				14	0.03	0.35
Spinach/Matador	Schwabenheim, 1975	0.24 (600 l water/ha)	1	0	21.5	0.40
				4	5.40	1.46
				7	3.28	1.49
				14	0.90	1.35
				21	0.18	0.65
Head lettuce/Mona	Limburgerhof, 1974	0.32 (800 l water/ha)	3 (21 day, 1 day interval)	0	4.86	0.12
				7	2.40	0.33
				14	0.64	0.16
				21	0.09	0.10
				28	0.02	0.01
Head lettuce/Verpia	Limburgerhof, 1982	0.24 (600 l water/ha)	2 (14 day interval)	0	8.17	0.24
				7	0.12	<0.05
				14–28	<0.05	<0.05

Crop/Variety	Location/Year	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Head lettuce/Hilds Neckarriesen	Schwabenheim, 1982	0.24 (500 l water/ha)	2 (14 day interval)	0	4.97	0.29
				7	1.52	0.96
				14	<0.02	0.60
				21	<0.02	0.03
				28	<0.02	<0.02
Head lettuce/Victoria King	Ingelheim, 1983	0.24 (400 l water/ha)	2 (14 day interval)	0	4.54	0.04
				7	0.12	0.05
				14–28	<0.02	<0.02
Head lettuce/Frühlings-Grüss	Schwabenheim, 1966	0.6 (600 l water/ha)	1	21	<0.07	
		0.3 (600 l water/ha)	1	21	<0.07	
		0.6 (600 l water/ha)	1	14	<0.07	
		0.3 (600 l water/ha)	1	14	<0.22	
Head lettuce/	Schwabenheim, 1966	0.24 (600 l water/ha)	1	7	1.58; 0.61	
		0.12 (600 l water/ha)	1	7	0.89; 1.17	
		0.24 (600 l water/ha)	1	4	1.92; 2.53	
		0.12 (600 l water/ha)	1	4	0.94; 0.95	
Head lettuce/Hilmar	Schwabenheim, 1969	0.04 kg ai/hl	1	0	8.6	0.02
				4	1.98	0.23
				7	0.44	0.16
				10	0.12	0.08
				14	0.08	0.06
				21	0.07	0.06
Head lettuce/Hilmar	Schwabenheim, Germany/ 1969	0.04 kg ai/hl	6 (7 day, 3 day, 4 day, 3 day, 4 day interval)	0	3.76	0.09
				4	2.37	0.24
				7	0.71	0.19
				10	0.12	0.08
				14	0.10	0.07
				21	0.03	0.02
Head lettuce/Laibacher Eis	Schwabenheim, 1973	0.24 (600 l water/ha)	2 (15 day interval)	0	2.97	0.22
				4	0.94	0.23
				7	0.10	0.05
				14	<0.02	0.02
Head lettuce/Maikönig Treib	Schwabenheim, Germany/ 1973	0.52 (1300 l water/ha)	1	0	8.80	0.16
				4	4.84	0.60
				7	2.25	0.51
				14	0.53	0.31
				21	<0.02	0.05
Head lettuce/Primeur	Schwabenheim, Germany/ 1973	0.40 (1000 l water/ha)	2 (28 day interval)	0	8.80	0.16
				4	4.84	0.60
				7	2.25	0.51
				14	0.53	0.31
				21	<0.02	0.05

Crop/Variety	Location/Year	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Head lettuce/Attraktion	Shcwabenheim, 1969	0.24	6 (7 day, 4 day, 3 day, 4 day, 3 day interval)	0	5.32	<0.02
				4	0.54	0.08
				7	0.29	0.08
				10	0.13	0.07
				14	0.02	<0.02
				21	≤0.02	≤0.02
Head lettuce/Aurelia	Limburgerhof, 1969	0.04 kg ai/hl	1	0	4.70	
				3	1.40	
				4	0.40	
				7	0.30	
				14	0.02	
Head lettuce/Verpia	Limburgerhof, 1982	0.24 (600 l water/ha)	2 (14 day interval)	0	8.17	0.24
				7	0.12	<0.05
				14–28	≤0.05	≤0.05
Head lettuce/Capitan	Mengen, 1982	0.24 (600 l water/ha)	2 (11 day interval)	0	7.08	0.06
				7	2.96	0.27
				14	0.96	0.22
				21	0.24	0.06
				28	0.07	0.03
Head lettuce/Hilds Neckar-riesen	Schwabenheim, 1982	0.24 (500 l water/ha)	2 (14 day interval)	0	4.97	0.29
				7	1.52	0.96
				14	0.26	0.60
				21	≤0.02	0.03
				28	<0.02	<0.02
Head lettuce/Victoria Krieg	Schwabenheim, 1983	0.24 (400 l water/ha)	2 (14 day interval)	0	4.54	0.04
				7	0.12	0.05
				14–28	≤0.02	≤0.02
Head lettuce/Soraya[1]	Limburgerhof, 1983	0.24 (600 l water/ha)	2 (17 day interval)	0	~~7.71~~	~~0.33~~
				7	~~0.20~~	~~0.06~~
				14	~~0.06~~	~~2.53~~
				21	~~<0.05~~	~~1.80~~
				26	~~<0.05~~	~~1.61~~

[1]Total residue increased from day 7 to day 14 and the ratio of omethoate to dimethoate is anomalous.

Legume vegetables

The DTF reported numerous field trial on peas in 1994-1996 in Northern Europe, and Cheminova reported four trials in 1993 in the USA. DFG method 236 with gel permeation clean-up was used for the European trials and the ABC method with a charcoal/Celite clean-up in the USA. The results are shown in Table 44.

GAP for peas in Northern Europe ranges from a single application rate of 0.20 kg ai/ha in Belgium and The Netherlands to 0.32 kg ai/ha in Denmark and 0.34 kg ai/ha in the UK. The number

of applications is unspecified in Belgium and Denmark, 3 in The Netherlands and 6 in the UK. The PHI is 14 days in Denmark and the UK and 21 days in Belgium and The Netherlands. GAP for peas in the USA specifies one foliar application at 0.19 kg ai/ha, with a 0-day PHI for peas and pods.

Table 44. Residues of dimethoate and omethoate in or on peas from the foliar application of dimethoate EC formulations.

Location/Year/ Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Control recovery range, %	Reference/ comments
Middelfart, Denmark/ 1994/ Polar Vining	0.336	2 (14 d interval)	0	3.35 whole plant	0.108 whole plant	D/pod: 109, 128 O/pod: 97, 103 D/seed: 69, 75 O/seed: 66, 70 D/straw: 70, 91 O/straw: 69, 105 (0.01, 0.1 mg/kg)	Heyer and Schreitmuller, 1996, Doc. 533-5208.
			3	0.406 whole plant	0.145 whole plant		
			7	0.129 whole plant	0.108 whole plant		
			10	0.109 whole plant	0.069 whole plant		
			14	0.156 whole plant	0.071 whole plant		
			28 (commercial harvest)				
			14	<0.119 empty pod	0.049 empty pod		
			14	0.027 whole pod	0.015 whole pod		
			14	<0.01 seed	<0.01 seed		
			14	0.438 straw	0.134 straw		
Stratford upon Avon, UK/ 1994/ Scout Vining	0.348 0.344	2 (14 day interval)	0	8.52 whole plant	0.212 whole plant	D/whole plant: 80–110, n = 10 O/whole plant: 75-129, n= 12 D/empty pod: 58-99, n=3 O/empty pod: 68-81, n=3 D/whole pod: 79-97, n=3 O/whole pod: 61-80, n=3 D/seed:73-91, n=4 O/seed: 70–100, n=4 D/straw: 68-73, n=2 O/straw: 64-80, n=2 (0.01–0.1 mg/kg, except 0.01-3 mg/kg whole plant)	Heyer and Schreitmuller, 1996, Doc. 533-5209
			3	2.67 whole plant	0.242 whole plant		
			7	0.380 whole plant	0.092 whole plant		
			10	0.303 whole plant	0.139 whole plant		
			14	0.035 whole plant	0.025 whole plant		
			14	0.053 empty pod	0.012 empty pod		
			14	0.026 whole pod	0.022 whole pod		
			14	<0.01 seed	<0.01 seed		
			14	0.259 straw	0.155 straw		
Cropredy, UK/ 1994/ Solara Combining	0.340 0.344	2 (14 d interval)	0	3.703 whole plant	0.133 whole plant		
			3	1.172 whole plant	0.225 whole plant		
			7	0.218 whole plant	0.139 whole plant		
			10	0.022 whole plant	0.147 whole plant		
			14	0.065 empty pod	0.082 empty pod		
			14	0.018 whole pod	0.026 whole pod		
			14	<0.01 seed	<0.01 seed		
			14	0.670 straw	0.642 straw		
Goch, 1994/ Lambado vining	0.336	2 (14 d interval)	0	2.54 whole plant	0.069 whole plant	D/whole plant: 86, 114 O/whole plant: 59, 95 D/whole pod: 92, 120 O/whole pod: 73, 82 D/seed: 74, 101. O/seed: 71, 90 D/straw: 90, 108 O/straw: 97, 108 (0.01, 0.1 mg/kg	Heyer and Schreitmuller, 1996, Doc. 533-5210.
			3	0.64 whole plant	0.302 whole plant		
			7	0.12 whole plant	0.113 whole plant		
			10	0.08 whole plant	0.098 whole plant		
						(0.01, 0.1 mg/kg, except 0.01-9.9 mg/kg	

Location/Year/ Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Control recovery range, %	Reference/ comments
			14	<0.01 whole plant	<0.01 whole plant		
			14	<0.01 empty pod	<0.01 empty pod		
			14	≤0.01 whole pod	≤0.01 whole pod		
			14	<0.01 seed	<0.01 seed		
			14	<0.01 straw	<0.01 straw		
Brienen, 1995/ Mantracto Vining	0.374 0.363 0.370 0.371	4 (16, 6, 12 d interval)	0	7.10 whole plant	0.38 whole plant	D/whole plant: 67-94, n=8 O/whole plant: 55-86, n=8 D/whole pod: 75-84, n=4 O/whole pod: 58-74, n=4 D/straw: 76-95, n=3 O/straw: 49-74, n=3	Melkebeke, 1997, Doc. 533-5211; Melkebeke and. Geuijen, 1997, Doc. 533-5212; Lystbaek, 1997, Doc. 581-012; Bitz, 1997, Doc. 581-011.
			3	4.00 whole plant	0.36 whole plant		
			7	0.78 whole plant	0.36 whole plant		
			14	0.60 whole plant	0.11 whole plant		
			21	0.23 whole plant	0.05 whole plant		
			7	0.37 whole pod	0.61 whole pod		
			14	0.09 whole pod	0.03 whole pod		
			21	0.11 whole pod	0.05 whole pod		
			14	0.20 straw	0.12 straw		
			21	0.15 straw	0.03 straw		
Bedburg-Hau Louisendorf, 1995/ Avriso vining	0.331 0.376 0.366 0.364	4 (16, 6, 12 d interval)	0	5.15 whole plant	0.17 whole plant		
			3	2.13 whole plant	0.32 whole plant		
			7	0.89 whole plant	0.42 whole plant		
			14	0.05 whole plant	0.10 whole plant		
			21	0.02 whole plant	0.04 whole plant		
			7	0.21 whole pod	0.06 whole pod		
			14	0.04 whole pod	0.02 whole pod		
			21	<0.01 whole pod	<0.01 whole pod		
			14	0.03 straw	0.08 straw		
			21	0.02 straw	0.02 straw		
Vierlingsbeek, Netherlands/ 1995/ Polo vining	0.352 0.370 0.339 0.350	4 (18, 10, 20 d interval)	0	3.50 whole plant	0.15 whole plant		
			3	1.18 whole plant	0.31 whole plant		
			7	0.57 whole plant	0.27 whole plant		
			14	0.10 whole plant	0.13 whole plant		

Location/Year/ Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Control recovery range, %	Reference/ comments
			21	0.09 whole plant	0.12 whole plant		
			7	0.27 whole pod	0.06 whole pod		
			14	0.11 whole pod	0.03 whole pod		
			21	0.03 whole pod	0.04 whole pod		
			14	0.07 straw	0.19 straw		
			21	0.06 straw	0.07 straw		
Dennington, UK/ 1995/ Trek vining	0.345 0.361 0.347 0.352	4 (14, 13, 16 d interval)	0	4.16 whole plant	0.67 whole plant		
			3	1.04 whole plant	0.08 whole plant		
			7	0.30 whole plant	0.25 whole plant		
			14	0.06 whole plant	0.09 whole plant		
			21	0.03 whole plant	0.02 whole plant		
			7	0.13 whole pod	0.02 whole pod		
			14	0.04 whole pod	0.02 whole pod		
			21	<0.01 whole pod	0.01 whole pod		
			14	0.07 straw	0.12 straw		
			21	0.04 straw	0.02 straw		
Hojer, Denmark/ 1995/ Bodel combining	0.371 0.364 0.382 0.360	4 (14, 12, 11 d interval)	0	7.58 whole plant	0.39 whole plant	D/whole plant: 74-95, n=6, 0.01–8 mg/kg O/whole plant: 64-90, n=6, 0.01–0.5 mg/kg D/seed: 90 at 0.1 mg/kg O/seed: 81 at 0.01 mg/kg; 63 at 0.1 mg/kg	
			14	2.10 whole plant	0.29 whole plant		
			21	1.19 whole plant	0.14 whole plant		
			14	0.19 whole pod	0.20 whole pod		
			21	0.18 whole pod	0.12 whole pod		
			14	<0.01 seed	0.24 seed		
			21	<0.01 seed	<0.01 seed		
			14	1.37 straw	0.24 straw		
			21	2.03 straw	0.25 straw		
Wageningen, Netherlands/ 1996/ Delta combining	0.333 0.333 0.333 0.323	4 (10, 13, 14 d interval)	0	5.40 whole plant	0.35 whole plant		
			14	2.85 whole plant	0.18 whole plant		
			21	0.53 whole plant	0.036 whole plant		
			14	1.42 whole pod	0.18 whole pod		
			21	0.64 whole pod	0.052 whole pod		
			14	<0.01 seed	<0.01 seed		
			21	<0.01 seed	<0.01 seed		
			14	4.5 straw	0.24 straw		
			21	1.29 straw	0.052 straw		
Hillsboro, Oregon, US/ 1993/	0.19	1	0	0.39 0.50 0.44 average whole pod	0.02 0.02 whole pod	D/whole pod: 80-100, n=7 (0.01-3.0 mg/kg) O/whole pod: 83-120, n=7 (0.01-3.0mg/kg) D/vine: 70-100, n=9 (0.01-10 mg/kg). O/vine: 50-120, n = 9n=9 (0.01-10 mg/kg) D/hay: 70-100, n=9 (0.01-10 mg/kg). O/hay: 60-140,	Rice *et al.*, 1994, CHA-Doc. 170-DMT/ Two entries per cell are duplicate samples

Location/Year/ Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Control recovery range, %	Reference/ comments
			0	5.26 5.45 5.36 average vine	0.16 0.18 0.17 average vine		
			0	11.48 10.16 10.8 average hay	1.56 1.20 1.38 average hay		Hay contained 32.4% moisture
			3	0.22 0.19 0.10 average whole pod	0.07 0.06 0.06 average whole pod		
			3	2.97 3.78 3.38 average vine	0.39 0.45 0.42 average vine		
			3	5.867 7.67 6.76 average hay	1.01 1.76 1.38 average hay		
			7	0.09 0.08 0.08 average whole pod	0.10 0.09 0.10 average whole pod		
			7	2.06 1.18 1.62 average vine	0.47 0.36 0.42 average vine		
			7	5.92 2.03 3.98 average hay	1.06 0.86 0.96 average hay		
Moses Lake, Washington, US/ 1993	0.19	1	0	0.52 0.48 0.50 average whole pod	<0.01 ≤0.01 whole pod		
			0	4.34 4.83 4.58 average vine	0.05 0.03 0.04 average vine		
			0	10.49 9.22 9.86 average hay	0.49 0.26 0.38 average hay		Hay contained 23.9% moisture
			3	0.26 0.25 0.26 average whole pod	0.07 0.07 whole pod		
			3	1.83 2.53 2.18 average vine	0.25 0.21 0.23 average vine		
			3	5.25 6.956.10 average hay	0.39 0.37 0.38 average hay		
			7	0.19 0.20 0.20 average whole pod	0.10 0.09 0.10 average whole pod		
			7	3.58 3.38 3.48 average vine	0.43 0.21 0.32 average vine		
			7	5.15 4.47 4.81 average hay	0.52 0.280.40 average hay		

Location/Year/ Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Control recovery range, %	Reference/ comments
Lake Mills, Wisconsin, US/ 1993	0.19	1	0	0.39 0.34 0.36 average whole pod	0.02 0.02 whole pod		
			0	4.44 6.87 5.66 average vine	0.19 0.19 vine		
			0	1.68 1.64 1.66 average hay	0.75 0.76 0.76 average hay		Hay contained 58.0% moisture
			3	0.22 0.20 0.21 average whole pod	0.08 0.08 whole pod		
			3	1.43 0.87 1.15 average vine	1.13 0.54 1.0 average vine		
			3	0.95 1.25 1.10 average hay	0.59 0.80 0.70 average hay		
			7	0.10 0.09 0.10 average whole pod	0.06 0.07 0.06 average whole pod		
			7	0.27 0.18 0.22 average vine	0.40 0.36 0.38 average vine		
			7	0.40 0.33 0.36 average hay	0.78 0.72 0.75 average hay		
Verona, Wisconsin, US/ 1993	0.19	1	0	0.29 0.25 0.27 average whole pod	0.02 0.02 whole pod		
			0	5.84 6.52 6.18 average vine	0.29 0.35 0.32 average vine		
			0	8.08 10.40 9.24 average hay	1.51 1.82 1.66 average hay		Hay contained 35.2% moisture (11% expected).
			3	0.15 0.15 whole pod	0.07 0.07 whole pod		
			3	2.24 2.14 2.19 average vine	0.86 0.76 0.81 average vine		
			3	0.90 0.75 0.82 average hay	0.30 0.28 0.29 average hay		
			7	0.02 0.03 0.02 average whole pod	0.04 0.04 whole pod		
			7	0.10 0.09 0.10 average vine	0.06 0.12 0.09 average vine		

Location/Year/ Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Control recovery range, %	Reference/ comments
			7	0.09 0.17 0.13 average hay	0.07 0.13 0.10 average hay		

The DTF provided summary information only on supervised field trials on French beans in Germany (Pistel and Bleif, 1993). GAP for French beans in Germany was not reported, but GAP for beans (broad, French and runner) in the UK is 2 x 0.34 kg ai/ha, and in Denmark 0.30 kg ai/ha, both with a 14-day PHI. None of the trials complied with these conditions.

Table 45. Residues of dimethoate and omethoate from the foliar application of a dimethoate EC formulation to French beans in Germany.

Location/Year /Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Limburgerhof 1969 Orbit	0.04 kg ai/hl	1	0	0.60	<0.02
			4	0.50	<0.02
			7	0.50	<0.02
			17	0.10	<0.02
			24	<0.02	<0.02
Schwabenheim 1969 Saxa	0.04 kg ai/hl	6 (7 day, 4 day, 3 day, 3 day, 4 day interval)	0	0.20	0.02
			4	0.12	0.02
			7	0.14	0.04
			10	0.05	0.03
			14	<0.02	0.04
			21	<0.02	0.02
Schwabenheim 1974 Saxa	0.04 kg ai/hl	2 (20 day interval)	0	0.73	<0.02
			4	0.23	0.02
			7	0.14	0.05
			14	0.03	0.02
			21	<0.02	0.04

Pulses

Baron (1987) applied a 480 g/l EC formulation in 190 l/ha of water to mung bean foliage in Enid, Oklahoma, USA, in 1985. One plot was treated at a rate of 0.56 kg ai/ha and a second at 1.12 kg ai/ha. Samples were taken 14 and 37 days after the application. The pods were mature at the time of treatment. Results were provided only for the 0.56 kg ai/ha treatment and the 37-day PHI. A concurrent storage stability study showed very poor recoveries of both dimethoate (27–60% at 0.10 and 0.50 mg/kg) and omethoate (19–67% at 0.63 mg/kg fortification stored (frozen?) for 18 months. This closely approximated the storage period of the field trial samples. A standard method of analysis was used (Zweig). Analytical recoveries of omethoate were 71-85% at 0.15 mg/kg and of dimethoate 77–85% at 0.066 mg/kg. The residues from the 0.56 kg ai/ha treatment, 37-day PHI, were <0.02 mg/kg dimethoate and <0.07 mg/kg omethoate. The demonstrated lack of storage stability and the summary nature of the report make the study unacceptable. US GAP is 0.56 kg ai/ha, 0-day PHI.

Root and tuber vegetables

Information on GAP was made available for Australia (beetroot, potatoes, root vegetables, silverbeet), Belgium (potatoes, red beet, sugar beet), Columbia (potatoes), Denmark (beetroot, red beet, swede), The Netherlands (beetroot, fodder beet, sugar beet), Germany (fodder beet, potatoes, sugar beet), Hungary (sugar beet), Switzerland (fodder beet, sugar beet), Mexico (potatoes), Morocco (red beet),

Reunion (red beet, sugar beet), the UK (potatoes, red beet, sugar beet, swede, turnip), USA (potatoes, turnip) and Sweden (sugar beet).

The DTF reported field trials on potatoes in Germany, Denmark, the UK and The Netherlands (Flatt, 1996, 1997; Bitz, 1997; Melkebeke and Geuijen, 1997). The results are shown in Table 46. All samples were analysed by DFG method 236 for omethoate and dimethoate. The validated limit of quantification for both omethoate and dimethoate was 0.01 mg/kg. Control recoveries in 1994 at 0.02 and 0.1 mg/kg were 103–125% for dimethoate and 97–115% for omethoate. Recoveries in 1995 were 98–115% for dimethoate and 70–87% for omethoate (n = 5, 0.005–0.2 mg/kg).

The DTF also supplied summary reports of potato trials in Germany in the 1970s and early 1980s (Pistel and Bleif, 1993). These are included in Table 46, although no details of the field conditions, sampling, sample handling and storage, or method of analysis were given.

GAP in Germany, Denmark, The Netherlands and the UK is similar with application rates of 0.20–0.34 kg ai/ha and a 14–21-day PHI. The number of applications is unspecified in Denmark, 1 in Germany, 2 in the UK and 4 in The Netherlands.

Table 46. Residues in or on potatoes grown in Northern Europe after the foliar application of dimethoate.

Location/ Year	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
North Rhine-Westphalia, Germany 1994	0.34 (220 l water/ha)	2 (14 day interval)	7	0.01	<0.01	Second application at beginning of flowering. Samples stored frozen for 275 days before analysis.
			14	≤0.01	≤0.01	
Fyn, Denmark 1994	0.34 (220 l water/ha)	2 (30 day interval)	7	0.03	<0.01	Stored frozen for 128 days before analysis.
			14	≤0.01	≤0.01	
Nierswalde (Goch), Germany 1995	0.33 (216 l water/ha) 0.35 (227 l water/ha)	2 (14 day interval)	14, 21, 28	≤0.01	≤0.01	Stored frozen for 7 months before analysis
Renkum, The Netherlands 1995	0.34 (217 l water/ha) 0.33 (213 l water/ha)	2 (14 day interval)	14, 21, 28	≤0.01	≤0.01	Stored frozen for 7 months before analysis
Martlesham, UK 1995	0.33 (211 l water/ha) 0.32 (210 l water/ha)	2 (14 day interval)	14, 21, 28	≤0.01	≤0.01	Stored frozen for 7 months before analysis.
Schwabenheim, Germany 1982	0.32-0.48 (500 l water/ha)	2 (14 day interval)	0–35	≤0.02	≤0.02	Summary results.
Schwabenheim, Germany 1973	0.48 (800 l water/ha) 0.40 (1000 l water/ha) 0.32 (1000 l water/ha)	3 (37 day, 75 day interval)	0–28	≤0.02	≤0.02	Summary results
Honingen, Germany 1973	0.32 (600 l water/ha) 0.40 (600 l water/ha) 0.48 (600 l water/ha)	3 (29 day, 37 day interval)	0	0.06	0.02	Summary results
			7	0.70	<0.01	
			14	0.02	≤0.01	
			21	0.02	<0.01	
			28	0.01	<0.01	
Schwabenheim, Germany 1973	0.48 (800 l water/ha) 0.40 (1000 l water/ha) 0.32 (1000 l water/ha)	3 (7 day, 75 day interval)	0–28	≤0.02	≤0.02	Summary results
Schwabenheim, Germany 1982	0.48 0.40 0.32 (500 l water/ha)	3 (14 day interval)	0–35	≤0.02	≤0.02	Summary results
Ersingen, Germany	0.48	3 (14 day, 13	0-35	<0.01–0.01	<0.01–0.01	Summary results

Location/ Year	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
1982	0.40 0.32 (400 l water/ha)	day interval)				
Dirmstein, Germany 1982	0.48 0.40 0.32 (400 l water/ha)	3 (14 day interval)	0	<0.01	<0.01	
			7	0.01	0.01	
			14	<0.01	0.02	
			21	0.02	<0.01	
			28–36	<0.01	<0.01	

Cheminova reported data on turnips (Samoil, 1998). Turnips were treated three times with a 480 g ai/l EC formulation of dimethoate, each application being 0.28 kg ai/ha. The trials were in 1994 in Arkansas, California, Florida, Georgia, Ohio (2 trials) and Texas, USA. The volume per ha varied with the location: Arkansas 300 l /ha, California 550 l/ha, Florida 280 l/ha, Georgia 470 l/ha, Ohio 500 l/ha, 650 l/ha, Texas 280 l/ha. The samples were analysed by the ABC method. Recoveries from tops and roots fortified at 0.1, 0.5 and 5.0 mg/kg were reported to be 69–124% and 75–109% respectively for dimethoate and 78–123% and 81–108% but no details for omethoate were provided. The results are shown in Table 47.

Samples were stored frozen up to 10 months before extraction and analysis. Storage stability tests for ≥382 days with tops and roots fortified at 0.1 and 5 mg/kg with dimethoate and omethoate showed the residues to be stable.

The US GAP for turnips is 0.28 kg ai/ha with a 14-day PHI. The trials were conducted at the maximum rate and minimum PHI.

Table 47. Residues of dimethoate and omethoate in or on turnip tops and roots after foliar application of dimethoate EC (3 x 0.28 kg ai/ha).

Location/year	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Fayetteville, Arkansas 1994	0.28	3 (7 day interval)	14	<0.1 top <0.1 root	<0.1 top <0.1 root
Salinas, California 1994	0.28	3 (7 day interval)	14	<0.1 top <0.1 root	<0.1 top <0.1 root
Gainesville, Florida 1994	0.28	3 (7 day interval)	14	0.532; 0.562 top <0.1 root	0.207; 0.210 top <0.1 root
Tifton, Georgia 1994	0.28	3 (7 day interval)	14	0.114; 0.179 top <0.1 root	(0.068; 0.092) top <0.1 root
Willard, Ohio 1994	0.28	3 (8-10 day interval)	14	<0.1 top <0.1 root	<0.1 top <0.1 root
Willard, Ohio 1994	0.28	3 (7 day interval)	14	<0.1 top <0.1 root	<0.1 top <0.1 root
Weslaco, Texas 1994	0.28	3 (8–9 day interval)	14	<0.1 top <0.1 root	<0.1 top <0.1 root

The DTF reported sugar beet trials in Northern Europe (Flatt, 1995; Melkebeke and Geuijen, 1995; Bitz, 1997). An EC formulation was applied to sugar beet foliage twice at 14- or 15-day intervals at 0.42 kg ai/ha at three locations. Samples of whole plants, leaves and roots were analysed

by DFG method 236, with charcoal clean-up. The results are shown in Table 48. Concurrent tests at 0.01-0.2 mg/kg showed recoveries of 98–109% for dimethoate in roots and 74–118% in leaves, and 60–88% for omethoate in roots and 72-76% in leaves. In the 1994 trials recoveries from roots (0.02 and 0.10 mg/kg, n = 6) were 93-115%, mean 103%, for dimethoate, and 71–95%, mean 81%, for omethoate. Recoveries from whole plants (0.10 and 2.52 mg/kg, n = 6) were 89-111%, mean 99% for dimethoate and 63-92%, mean 75%, for omethoate.

The DTF also reported sugar beet trials in Germany in the 1970s and early 1980s (Pistel and Bleif, 1993). These are included in Table 48, although no details of the field conditions, sampling, sample handling and storage, or method of analysis were given.

The GAP for sugar beet in Germany specifies 1 application of 0.16 kg ai/ha with a 35-day PHI, in The Netherlands a maximum of 3 foliar applications of 0.40 kg ai/ha with no stated PHI, in the UK 1 or 2 foliar applications at 0.40 kg ai/ha with the last application before 30 June, and in Belgium 0.20 kg ai/ha with no maximum number of applications and a 21-day PHI.

Table 48. Residues of dimethoate and omethoate in sugar beet after foliar treatment with a dimethoate EC formulation (2 x 0.42 kg ai/ha).

Location Year	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
Goch, Germany 1995	0.419 (448 l/ha) 0.424 (455 l/ha)	2 (14 day interval)	0	7.0 whole plant	0.25 whole plant	
			3	0.79 whole plant	0.23 whole plant	
			14	<0.01 root <0.02 leaf	<0.01 root 0.11 leaf	
			28 and 35	≤0.01 root ≤0.01 leaf	≤0.01 root ≤0.01 leaf	
Renkum, Netherlands 1995	0.433 (464 l/ha) 0.439 (470 l/ha)	2 (15 day interval)	0	10. whole plant	0.29 whole plant	
			3	1.7 whole plant	0.20 whole plant	
			13	≤0.01 root 0.06 est. leaf	≤0.01 root 0.17 leaf	
			27	<0.01 root <0.01 leaf	<0.01 root 0.02 leaf	
			34	<0.01 root <0.01 leaf	<0.01 root <0.01 leaf	
Coney Weston, UK 1995	0.413 (443 l/ha) 0.418 (448 l/ha)	2 (14 day interval)	0	8.8 whole plant	0.21 whole plant	
			3	1.6 whole plant	0.23 whole plant	
			14	≤0.01 root 0.10 est. leaf	≤0.01 root 0.05 leaf	
			28	<0.01 root <0.01 leaf	<0.01 root <0.01 leaf	
			35	<0.01 root 0.03 leaf	<0.01 root <0.01 leaf	
East Midlands, UK 1994 Saxon	0.084 (220 l water/ha) 0.40 (450 l water/ha)	2 (20 day interval)	0	8.65 whole plant	0.05 whole plant	12-14 expanded true leaves growth stage.
			3	0.68 whole plant	0.09 whole plant	
			14	<0.01 whole plant	0.04 whole plant	
			28	≤0.01 root	≤0.01 root	
			89	<0.01 root	<0.01 root	Normal harvest
North Rhine-Westphalia, Germany 1994 Evita	0.084 (220 l water/ha) 0.40 (450 l water/ha)	2 (14 day interval)	0	4.67 whole plant	0.19 whole plant	0–2 weeks after full crop cover (stage 46)
			3	1.59 whole plant	0.31 whole plant	
			14	0.11 whole plant	0.20 whole plant	
			28	≤0.01 root	≤0.01 root	
			35	<0.01 root	<0.01 root	
			93	<0.01	<0.01	Normal harvest

Location Year	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
Fyn, Denmark 1994 Matador	0.084 0.40	2 (interval 11 days)	0	5.57 whole plant	0.06 whole plant	0-2 weeks after full crop cover (stage 45)
			3	2.75 whole plant	0.22 whole plant	
			14	0.04 whole plant	0.06 whole plant	
			28	<0.01 root	<0.01 root	
			35	<0.01 root, leaf	<0.01 root, leaf	
			93	<0.01 root	<0.01 root	Normal harvest
Christinenthal, Germany 1972 Polybeta	0.32	2 (interval 19 days)	0–107	<0.01	<0.01	Summary information only.
Limburgerhof, Germany 1982 Kawemono	0.32 (400 l water/ha)	4 (interval 35, 2, 8 days)	0	5.33 leaf <0.05 root	<0.05 leaf <0.05 root	First application after 8 true leaf stage. Summary information only
			15-35	Leaf <0.05 Root <0.05	Leaf <0.05 Root <0.05	
Schwabenheim, Germany 1982 Kawemono	0.32 (400 l water/ha)	4 (interval 20 d, 14 d, 9 d)	0	Leaf 7.16 plant<0.02	Leaf 1.14 plant<0.02	8 true leaf stage. Summary information only
			14	Leaf <0.02 plant<0.02	Leaf 0.46 Plant <0.02	
			21	Leaf <0.02 plant <0.02	Leaf 0.22 Plant <0.02	
			28	plant<0.02 Leaf <0.02	Leaf 0.09 Plant <0.02	
			35	plant<0.02 Root <0.02	Leaf 0.05 Plant <0.02	
Schwabenheim, Germany 1972	0.32 (800 l water/ha)	2 (interval 21 days)	0	Root <0.02 Top 2.80	Root <0.02 Top 0.23	Normal harvest 46 days after last treatment. Summary information only.
			14	Root <0.02 Top <0.02	Root <0.02 Top 0.03	
			28	Root <0.02 Top <0.02	Root <0.02 Top 0.03	
			42	Root <0.02 Top <0.02	Root <0.02 Top <0.02	
			56	Root <0.02 Top <0.02	Root <0.02 Top <0.02	
Offstein, 1982 Monopur	0.32 (400 l water/ha)	4 (interval 13, 15, 20 days)	0	Plant 3.60	Plant 0.09	Summary information only. 10 true leaf stage at first treatment.
			7	Plant 0.18	Plant 0.04	
			14	Plant 0.01	Plant 0.01	
			21	Plant <0.01	Plant <0.01	
			28	Plant <0.01	Plant <0.01	
			36	Beet <0.01 Foliage <0.01	Beet <0.01 Foliage <0.01	

The DTF supplied summary reports of field trials on carrots in Germany in the 1970s and early 1980s (Pistel and Bleif, 1993). The results are shown in Table 49, although no details were given. Germany supplied summary information on trials on radishes and long radishes (Table 50).

GAP for carrots in Germany requires two applications at 0.24 kg ai/ha or 0.04 kg ai/hl, with a 14-day PHI. No GAP was reported for radishes. CLICK HERE for continue

Table 49. Residues from the application of a dimethoate EC formulation to carrots, in Germany.

Location Year Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Hurth-Fischenich, 1979 Lange rote Stumpfe	0.6 (600 l water/ha)	2 (13 day interval)	14	0.097	0.053
			21	0.014	0.006
			28	0.006	0.004
Schmiden, 1979 Tip-Top	0.6	2 (14 day interval)	14	0.127	
			21	<0.001	
			28	<0.001	
Lubeck, 1979 Lange rote Stumpfe ohne Herz	0.6 (600 l water/ha)	2 (14 day interval)	14	0.02	0.02
			21	0.007	<0.002
			28	0.002	<0.002
Mainz, 1979 Lange rote Stumpfe ohne Herz	0.68 (650 l water/ha)	2 (28 day interval)	14	0.001	<0.002
			21	<0.001	<0.002
			28	<0.001	<0.002
Merdingen, 1979 Kieler rote	0.6 (600 l water/ha)	2 14 day interval)	14	0.001	<0.002
			21	<0.001	<0.002
			28	<0.001	<0.002
Koln-Auweiler, 1979 Touchon	0.6 (600 l water/ha)	2 (14 day interval)	14	0.013	0.002
			21	0.014	0.013
			28	0.006	0.012
Oldenburg, 1979 Nantaise	0.6 (600 l water/ha)	2 (14 day interval)	14	0.006	0.004
			21	0.007	0.002
			28	0.002	<0.002
Buttelborn, 1979 Fanal	0.6 (600 l water/ha)	2 (14 day interval)	14	0.019	0.004
			21	0.021	0.002
			28	0.027	<0.002
Hallbergmoos, 1979 Winterperfektion	0.6 (600 l water/ha)	2 (14 day interval)	14	0.008	0.003
			21	<0.001	<0.002
			28	<0.001	<0.002
Limburgerhof, 1982 Mokum	8 (watering) (20000 l water /ha)	1	21	0.59	<0.05
			29	0.38	<0.05
			35	0.20	<0.05
			42	0.12	<0.05
			49	0.06	<0.05
Schwabenheim, 1982 Rotin	8 (watering) (20000 l water/ha)	1	21	<0.02	0.06
			28–56	<0.02	<0.02
Mengen, 1982 Hilds Fanal	8 (watering, 20000 l water/ha) 0.24 (spray) 0.24 (spray, 600 l water/ha)	3 31 day 14 day interval	0–35	≤0.01	≤0.01
Reichenau, 1982 Nantaise	8 (watering, 20000 l water/ha) 0.24 (spraying) 0.24 (spraying, 600 l water/ha)	 31 day interval 14 day interval	0–35	≤0.01	≤0.01
Kiel, 1973 Lange Stumpfe ohne Herz	8 (watering, 20000L water/ha)	2 (21 day interval)	28	0.06	<0.01
			42	0.05	<0.01

Table 50. Residues from the application of a dimethoate EC formulation to long radishes and radishes in Germany.

Location Year Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Long Radish					
Mainz-Bretzenheim, 1988 Minovase Summereross Nr. 3	0.2 ml of 0.04% solution per m watering (0.08 g ai/m)	1	0	2.8	<0.05
			7	3.1	<0.05
			14	0.5	<0.05
			21	<0.1	<0.05
			27	<0.1	<0.05
Frankfurt, 1988 Rex	0.2 ml of 0.04% solution per m watering	1	0	13	0.3
			7	3.1	0.2
			14	0.8	0.2
			21	0.1	<0.05
			28	<0.1	<0.05
München, 1988 Rex	0.2 ml of 0.04% solution per m watering	1	0	11	
			7	2.7	0.2
			14	1.4	<0.05
			21	0.5	<0.05
			28	0.4	<0.05
Berlin-Britz, 1988 Rex	0.2 ml of 0.04% solution per m watering	1	0	18	0.2
			7	1.3	<0.05
			14	0.4	<0.05
			21	<0.05	<0.05
			28	<0.05	<0.05
Braunschweig, 1988 April Cross	0.2 ml of 0.04% solution per m watering	1	0	3.2	<0.05
			7	2.9	<0.05
			14	1.9	<0.05
			21	0.2	<0.05
			28	<0.1	<0.05
Bankholzen, 1988 Neckarruhm	5.0 (12500 l water/ha)	1	0	59.	0.3
			7	2.1	0.1
			14	1.1	<0.05
			21	0.4	<0.05
			28	0.2	<0.05
Braunschweig, 1988 Rex	0.2 ml of 0.04% solution per m watering	1	0	3.1	0.3
			7	1.9	<0.05
			14	2	<0.05
			21	0.3	<0.05
			28	0.2	<0.05
Saarlouis-Lisdorf, 1988 April Cross	0.2 ml of 0.04% solution per m watering	1	0	26.	0.6
			7	1.4	<0.05
			14	0.8	<0.05
			21	0.3	<0.05
			28	<0.05	<0.05
Radish					
Schifferstadt, 1966 Weisser Neckarruhm	2 (drenching. 5000 l water/ha)	2 (30 day interval)	0	2.14	<0.02
			7	0.79	0.09
			13	0.54	0.10
			20	<0.1	<0.02
Schwabenheim, 1966	0.16 g/m	1	21	0.19	

Location Year Variety	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
	0.4 l water/m				
		2 (28 day interval)	21	0.12	
Braunschweig, 1988 April Cross	0.2 g/m 0.5 l water/m	1	0	3.2	<0.10
			7	2.9	<0.1
			14	1.9	<0.1
			21	0.2	<0.1
			28	<0.1	<0.1
Braunschweig, 1988 Rex	0.2 g/m 0.5 l water/m	1	0 (root + foliage)	3.1	0.30
			7 (root)	1.9	<0.1
			14	2.0	<0.1
			21	0.3	<0.1
			28	0.2	0.1
München, 1988 Rex	0.2 g/ 0.5 l water/m	1	0	11	0.20
			7	2.7	<0.1
			14	1.4	<0.1
			21	0.5	<0.1
			28	0.4	<0.1
Saarlouis-Lisdorf, 1988 April Cross	0.2 g/m 0.5 l water/m	1	0 (root + foliage)	26	0.6
			7 (root)	1.4	<0.1
			14	0.8	<0.1
			21	0.3	<0.1
			28	<0.1	<0.1
Mainz-Bretzenheim, 1988 Minorase Summercross No. 3	0.2 g/m 0.5 l water/m	1	0	2,8	<0.1
			7	3.1	<0.1
			14	0.5	<0.1
			21	<0.1	<0.1
			28	<0.1	<0.1
Moos, 1988 Necharruhm	5 (drenching, 12500 l water/ha)	1	0 (root + foliage)	59	0.3
			7 (root + foliage)	2.1	0.1
			14 (root)	1.1	<0.1
			21	0.4	<0.1
			28	0.2	<0.1
Frankfurt, 1988 Rex	0.2 g/m 0.5 l water/m	1	0 (root + foliage)	13	0.30
			7 (root + foliage)	3.1	0.20
			14 (root + foliage)	0.8	0.20
			21 (root + foliage)	0.1	<0.05
			28 (root + foliage)	<0.1	<0.05
Berlin-Britz, 1988 Rex	0.2 g/m 0.5 l water/m	1	0 (root + foliage?)	18	0.20
			7	1.3	<0.1
			14	0.4	<0.1
			21	<0.1	<0.1
			28	<0.1	<0.1
Schwabenheim, 1971 Saxa	0.04 g ai/hl	1	14	0.22; 0.13	
			21	0.16; 0.11	
Schwabenheim, 1971 Eiszapfen	0.04 g ai/hl	2 (7 day interval)	14	0.04; 0.06	
			21	0.03; <0.02	

Stalk and stem vegetables

Cheminova reported field trials on asparagus in Washington, Indiana, North Carolina and New York, where a 480 g ai EC formulation was applied 4-6 times at 0.56 and 1.12 kg ai/ha (Samoil, 1994). The applications were made post-harvest to the plants. Samples were analysed by standard methods (Steller and Pasarela, 1972; Zweig) with the results shown in Table 51. The samples were stored frozen. Storage studies were said to be adequate to cover the storage period for all samples except those in New York, but only the New York period was reported (627 days).

GAP is 5 x 0.56 kg ai/ha, 180-day PHI.

Table 51. Residues of dimethoate and omethoate in or on asparagus from the foliar application of dimethoate EC formulation in the USA.

Location Year	Application rate, kg ai/ha	No. of applications	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Comments
Vincennes, Indiana 1984	0.56	6	208	<0.02	<0.02	Method (Steller): Blend with methylene chloride, clean-up on silica gel with Darco G-60, GLC with FPD. Dimethoate recovery: 82-98% at 0.05 mg/kg; 95-111% at 0.10 mg/kg. Omethoate recovery: 89-107% at 0.05 mg/kg; 89-126% at 0.10 mg/kg. Storage stability: 110-125% recovery of dimethoate, 94-109% of omethoate, 171 days.
	1.12	6	208	<0.02	<0.02	
Raleigh, North Carolina 1987	0.38	4	207	<0.03	<0.12	Method (Zweig): blend with methylene chloride, change to acetone, GLC with FPD. Dimethoate recovery 77-102%, 0.5-1 mg/kg. Omethoate recovery 75-102%, 0.84–1.7 mg/kg.
	0.76	4	214	<0.03	<0.12	
Geneva, New York 1985	0.56	5	260-270	<0.02	<0.02	Method: Stetten. Dimethoate recovery 85-109%. Omethoate 72-82%, 0.1-0.4 mg/kg. Storage stability: dimethoate recovery 106-108%, omethoate 72-91% after 417 days, 0.2 mg/kg. Samples stored 627 days.
	1.12	5	260 – 270	<0.02	<0.02	
Yakima, Washington 1984	0.56	5	196	<0.02	<0.02	Method and storage stability, as Indiana
	1.12	5	196	<0.02	<0.02	

The Netherlands provided summary information in English on indoor trials with Witloof chicory in 1972 and 1983 and a complete report in Dutch. Analysis involved extraction with ethyl acetate, concentration of the extract and GLC with thermionic detection (1972) or flame photometric detection (1984). The results are given in Table 52. GAP for Witloof sprouts is 1 x 5.0 kg ai/ha, 21-day PHI.

Table 52. Residues from the application of a 400 g/l EC dimethoate formulation to Witloof chicory sprouts in The Netherlands.

Location Year Variety Note	Application rate, kg ai/ha	No. of treatments	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Recovery at
Groerbeek, 1972 West Friden low temperature forcing	5.0 (10000 l water/ha)	2 (5 day interval)	36	0.12 range 0.11–0.15	0.12 range 0.11-0.14	D: 90% at 0.1 O: 80% at 0.1 (n = 10)
Groerbeek, 1972 West Friden high temperature forcing	5.0 (10000 l water/ha)	2 (19 day interval)	50	0.14 (range 0.13-0.15)	0.15 range 0.13–0.18	
Brakel, 1972	5.0 (10000 l water/ha)	2 (36 day interval)	36	0.16 range 0.14-0.18	0.21 range 0.19-0.24	
Brakel, 1973	5.0 (10000 l water/ha)	2 (34 day interval)	35	0.14 range 0.10-0.22	0.16 range 0.12-0.20	
Alkmaar, 1983 Liber L.O. water culture	?	1	20	0.40 range 0.19-0.62	0.32 range 0.25-0.44	D: 107% at 0.25 (n = 2) 104% at 0.5 (n = 2) O: 103% at 0.4 (n = 4) 96% at 0.8 (n = 4)

Cereal grains

GAP was reported for Argentina (cereals, sorghum), Australia (cereals), Denmark (cereals, maize), Sweden (cereals), the UK (cereals, wheat), Columbia (maize, wheat), Hungary (maize), The Netherlands (maize, rye), Reunion (maize, rice, sorghum), the USA (maize, sorghum, wheat), New Zealand (rice), Germany (rye, wheat) and Mexico (maize, sorghum, wheat).

Chemninova reported field trials on sorghum in the USA (Rice *et al.*, 1994). Six trials were conducted in 1993 in Kansas, Nebraska and Texas, where a 480 g/l EC formulation of dimethoate was applied three times at 7 day intervals at 0.56 kg ai/ha. Ground equipment was used to apply a water dilution of 140-190 l/ha. Grain, forage and hay were collected at 28-days.

Samples were stored frozen and analysed within 3.5 months by the ABC method. The results are shown in Table 53. GAP is 3 x 0.56 kg ai/ha, 28-day PHI.

Table 53. Residues in or on sorghum from the foliar application of a dimethoate EC formulation at 3 x 0.56 kg ai/ha, 28 day PHI, in USA.

Location Year	Dimethoate, mg/kg	Omethoate, mg/kg	Concurrent fortification recovery		
			Fortification range, mg/kg/ No. of analyses	Dimethoate range, mean	Omethoate range, mean
GRAIN					
Peru, Kansas 1993	≤0.01	≤0.01	0.01 – 3 8	90–100 97	89–110 98
Sedan, Kansas 1993	≤0.01	≤0.01			
York, Nebraska 1993	Sample lost	Sample lost			

Location Year	Dimethoate, mg/kg	Omethoate, mg/kg	Concurrent fortification recovery		
			Fortification range, mg/kg/ No. of analyses	Dimethoate range, mean	Omethoate range, mean
Osceola, Nebraska 1993	≤0.01	≤0.01			
Uvalde, Texas 1993	≤0.01	≤0.01			
Idalou, Texas 1993	≤0.01	≤0.01			
FORAGE					
Peru, Kansas 1993	0.01; <0.01 mean 0.01	≤0.01	0.01 – 0.20 8	85–92 87	78–110 91
Sedan, Kansas 1993	0.01; 0.02 mean 0.02	≤0.01			
York, Nebraska 1993	≤0.01	≤0.01			
Osceola, Nebraska 1993	≤0.01	≤0.01			
Uvalde, Texas 1993	≤0.01	≤0.01			
Idalou, Texas 1993	≤0.01	≤0.01			
HAY					
Peru, Kansas 1993	≤0.01	≤0.01	0.01, 0.05, 0.20	90, 102, 90 94	110, 100, 86 99
Sedan, Kansas 1993	≤0.01	≤0.01			
York, Nebraska 1993	≤0.01	≤0.01			
Osceola, Nebraska 1993	<0.01; 0.01 mean 0.01	≤0.01			
Uvalde, Texas 1993	≤0.01	≤0.01			
Idalou, Texas 1993	≤0.01	≤0.01			

The DTF reported supervised field trials for the application of dimethoate to barley in Northern Europe in 1995–1996 (Blitz, 1997; Melkebeke, 1997; Melkebeke and Geuijen, 1997). Eight trials were conducted in Denmark, Germany, The Netherlands and the UK, where winter and spring barley were treated 4 times with dimethoate at rates of 0.66–0.74 kg ai/ha for the first two applications and 0.32–0.37 kg ai/ha for the third and fourth applications. The last application was made at the soft dough growth stage. Samples of whole plants, ears, residual plants, grain and straw taken on the day of the final application and at subsequent intervals were analysed by a method on the basis of DFG method 236 for which validation data were listed in the Analytical Methods Section. The results are shown in Table 54.

The DTF also supplied a summary report of a barley field trial in Germany in 1982 (Pistel and Bleif, 1993) but no details were given. The data were excluded from the Table because the sample descriptions were imprecise (e.g. “corn”).

Table 54. Residues of dimethoate and omethoate in or on barley from four foliar application of a dimethoate EC formulation in Northern Europe. About 250 l water/ha.

Location Year Variety	Application, kg ai/ha	Interval, days	Sample	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Louisendorf, 1995 Winter barley, Catania	0.74 0.74 0.37 0.34	 6 4 13	Plant (without root)	0	5.31	0.07
			Grain	14	1.43	0.06
			Straw	14	2.81	0.07
			Plant	14	2.68	0.07
			Grain	21	0.64	0.02
			Straw	21	0.93	0.02
Doorwerth, Netherlands 1995 Spring barley, Reggea	0.72 0.72 0.36 0.35	 7 24 38	Plant	0	5.37	0.03
			Grain	14	0.10	<0.01
			Straw	14	0.13	<0.01
			Plant	14	0.13	<0.01
			Grain	21	0.03	<0.01
			Straw	21	0.03	<0.01
Martlesham, UK 1995 Winter barley, Halanon	0.73 0.72 0.35 0.33	 4 3 51	Plant	0	7.08	0.05
			Grain	14	0.49	<0.01
			Straw	14	1.59	0.03
			Plant	14	0.90	0.02
			Grain	21	0.46	<0.01
			Straw	21	1.64	0.04
Fyb, Denmark 1996 Winter barley, pastoral	0.68 0.68 0.34 0.34	 9 12 28	Plant	0	5.07	0.04
			Grain	14	0.73	0.10
			Straw	14	0.44	0.11
			Plant	14	0.58	0.10
			Grain	21	0.02	0.06
			Straw	21	0.92	0.09
			Grain	28	0.12	0.02
			Straw	28	0.25	0.03
			Plant	28	0.22	0.03
Posterhold, Netherlands 1996 Spring barley, magda	0.68 0.68 0.34 0.34	 13 9 19	Plant	0	8.27	0.14
			Grain	14	0.03	0.01
			Plant	14	0.09	0.01
			Grain	21	<0.01	<0.01
			Straw	21	0.02	<0.01
			Grain	28	<0.01	<0.01
			Straw	28	0.02	<0.01
			Plant	28	0.03	<0.01

Location Year Variety	Application, kg ai/ha	Interval, days	Sample	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg
Tudderen, 1996 Winter barley, Babylon	0.68 0.68 0.34 0.34	 13 9 19	Plant	0	7.35	0.18
			Grain	14	0.41	0.03
			Straw	14	0.55	0.03
			Plant	14	0.75	0.05
			Grain	21	0.40	0.01
			Straw	21	0.16	0.03
			Plant	21	0.65	0.02
			Grain	28	0.29	0.01
			Straw	28	0.37	0.01
			Plant	28	0.11	0.03
Steventon, UK 1996 Winter barley, Halcyon	0.69 0.71 0.34 0.32	 8 14 31	Plant	0	5.94	0.04
			Grain	14	0.07	0.02
			Straw	14	0.88	0.07
			Plant	14	0.40	0.04
			Grain	21	0.0;9	0.02
			Straw	21	0.64	0.03
			Plant	21	0.55	0.03
			Grain	28	0.07	0.02
			Straw	28	0.76	0.03
			Plant	28	0.42	0.02
Bentley, UK 1996 Winter barley, Manitou	0.66 0.67 0.35 0.33	 7 13 28	Plant	0	4.24	0.04
			Grain	14	0.06	0.01
			Straw	14	0.20	0.03
			Plant	14	0.11	0.03
			Grain	21	0.02	<0.01
			Straw	21	0.19	0.01
			Plant	21	0.19	0.02
			Grain	28	0.02	<0.01
			Straw	28	0.18	<0.01
			Plant	28	0.14	0.02

GAP for barley in The Netherlands is a single application at 0.20 kg ai/ha with a 14-day PHI, in the UK 4 foliar applications of 0.34 kg ai/ha with a 14-day PHI, in Denmark 0.80 kg ai/ha with no specified PHI, and in Sweden 0.32 kg ai/ha with a 28-day PHI. GAP for Germany was not reported.

The DTF reported two supervised field trials on the application of dimethoate to maize in Denmark (Heyer, 1995; Bitz, 1997). Dimethoate was applied once at 0.32 kg ai/ha and samples of whole plants (above ground), cobs and grain taken at intervals were stored frozen until analysed by DFG method 236, a period of about 5 months. Concurrent fortified control samples were also analysed. The results are shown in Table 55.

GAP for maize in Denmark specifies foliar treatment at 0.30-0.32 kg ai/ha with a 14-day PHI. The PHIs of the grain samples in the trials are much longer at 28 and 35 days.

Table 55. Residues of dimethoate and omethoate in or on maize commodities from the foliar application of a dimethoate EC formulation at 0.32 kg ai/ha in Denmark in 1994.

Location/ Variety	Sample	PHI, days	Dimethoate, mg/kg	Omethoate, mg/kg	Concurrent analytical recoveries, %		
					Range, mg/kg No. (n)	Dimethoate	Omethoate
Rojleskovvej, Middefart, Denmark Earliking E1 (sugar maize)	Whole plant (aerial)	0	13.2	<0.01	0.01–5 (D) 9 0.01 – 0.20 (O) 8	82–118 99	59–82 67
		7	0.52	0.093			
		16	0.023	<0.01			
		21	0.024	<0.01			
		28, 35	<0.01	<0.01			
	Cob	28	<0.01	<0.01	0.01, 0.20 2	91, 92	90, 76
		35	<0.01	<0.01			
	Grain	28	<0.01	<0.01	0.01, 0.20 2	100, 94	90, 72
		35	<0.01	<0.01			
Hyllehojvej, Middelfart, Denmark Earliking E1 (sugar maize)	Whole plant (aerial)	0	12.3	<0.01	As first trial		
		7	0.22	0.032			
		16	0.18	0.060			
		21	0.12	0.062			
		28, 35	<0.01	<0.01			
	Cob	28	<0.01	<0.01	As first trial		
		35	<0.01	<0.01			
	Grain	28	<0.01	<0.01	As first trial		
		35	<0.01	<0.01	As first trial		

The DTF reported field trials on wheat in Northern Europe (Melkebeke and Geuijen, 1997; Flatt, 1996; Bitz, 1997). Four applications of an EC formulation were made to plots in four countries in 1995, the first two applications at 0.68 kg ai/ha and the second two at 0.34 kg ai/ha. The final applications were carried out at the soft to hard dough stage, about 14 days before commercial harvest, except in Germany in 1994 where the final treatment was at the medium milk stage. Samples of whole plants (except roots), grain, ears and residual parts and straw taken at intervals after the last application were stored frozen until analysed by DFG method 236. Analytical recoveries were determined concurrently. The results are shown in Table 56.

The DTF also supplied summary reports of trials in Germany in the 1970s and 1982 (Pistel and Bleif, 1993) but no details were given. The results are shown in Table 56.

GAP for wheat in Germany is 2 x 0.24 kg ai/ha, 21-day PHI; in The Netherlands, 1 x 0.20 kg ai/ha, 14-day PHI; in the UK, 4 x 0.68 kg ai/ha at low volume or 4 x 0.34 kg ai/ha high volume, 14-day PHI; in Denmark 0.80 kg ai/ha, no PHI.

Table 56. Residues of dimethoate and omethoate in or on wheat fractions from the foliar application of a dimethoate EC formulation (2 x 0.68 kg ai/ha + 2 x 0.34 kg ai/ha) in Northern Europe.

Location Year Variety	Application rate, kg ai/ha	Interval, days	Sample	PHI, days	Dimethoate[1], mg/kg	Omethoate[1], mg/kg
Wilson, UK 1994 Winter wheat, Riband	0.68 0.68 0.34 0.34 (250 l water/ha)	15 8 35	Whole plant	0	4.66	0.02
				3	1.15	0.12
				7	0.92	0.09
				Harvest (24-28)	0.24	0.03
			Ear/residual	14	0.37/	0.03/
			Grain	21	0.03	<0.01
				Harvest (24-28)	0.02	<0.01
			Straw	21	0.71	0.04

Location Year Variety	Application rate, kg ai/ha	Interval, days	Sample	PHI, days	Dimethoate[1], mg/kg	Omethoate[1], mg/kg
				Harvest (24-28)	0.65	0.05
Aston-on-Trent, UK 1994 Spring wheat, Candenza	0.68 0.69 0.34 0.34 (250 l water/ha)	15 6 39	Whole plant	0	7.39	0.02
				3	2.23	0.03
				7	2.38	0.05
				Harvest (24-28)	1.55	0.06
			Ear/residual	14	1.61	0.04
			Grain	21	0.23	<0.01
				Harvest (24-28)	0.19	<0.01
			Straw	21	1.90	0.05
				Harvest (24-28)	1.96	0.05
Middelfart, Denmark 1994 Winter wheat, Marabu	0.68 0.68 0.34 0.34 (250 l water/ha)	16 6 48	Whole plant	0	3.60	0.34
				3	2.03	0.06
				7	1.66	0.06
				14	1.13	0.05
				Harvest (24-28)	0.22	0.01
			Ears/residual	14	1.31/	0.05/
			Grain	21	0.04	<0.01
				Harvest (24-28)	0.02	<0.01
			Straw	21	1.41	0.04
				Harvest (24-28)	0.48	0.02
Goch, Germany 1994 Winter wheat, Haven	0.68 0.68 0.34 0.34 (250 l water/ha)	13 16 46	Whole plant	0	5.81	0.01
				3	3.02	0.11
				7	1.75	0.13
				14	0.74	0.08
				Harvest (24-28)	0.19	0.01
			Ear/residual	14	0.91/	0.11/
			Grain	21	0.06	<0.01
				Harvest (24-28)	0.07	<0.01
			Straw	21	0.24	0.02
				Harvest (24-28)	0.28	0.01
Hojer, Denmark 1995 Winter wheat, Hussar	0.74 0.74 0.37 0.36	7 15 58	Whole plant	0	7.03	0.04
				3	6.65	0.08
				7	5.32	0.09
				14	5.20	0.12
				21	3.32	0.11
			Ear/residual	7	5.52/5.99	0.09/0.10
			Grain	14	0.10	<0.01
				21	0.10	<0.01
			Straw	14	8.95	0.17
				21	6.78	0.16
Brienen, Germany 1995 Winter wheat, Grif	0.75 0.74 0.38 0.35	6 20 54	Whole plant	0	7.35	0.02
				3	1.46	0.03
				7	1.44	0.04
				14	1.50	0.05
				21	1.03	0.05
			Ear/residual	7	1.96/1.30	0.05/0.03
			Grain	14	0.12	<0.01
				21	0.12	<0.01
			Straw	14	2.37	0.08
				21	2.11	0.06

Location Year Variety	Application rate, kg ai/ha	Interval, days	Sample	PHI, days	Dimethoate[1], mg/kg	Omethoate[1], mg/kg
Marknesse, Netherlands 1995 Spring wheat, Minaret	0.72 0.72 0.36 0.36	7 31 42	Whole plant	0	5.60	0.09
				3	3.17	0.20
				7	2.16	0.14
				14	1.62	0.13
				21	1.41	0.12
			Ear/residual	7	2.10/2.27	0.24/0.04
			Grain	14	0.11	0.01
				21	0.11	0.02
			Straw	14	2.23	0.13
				21	2.69	0.15
Badingham, UK 1995 Winter wheat, Riband	0.72 0.72 0.34 0.36	7 15 63	Whole plant	0	4.73	0.02
				3	2.77	0.05
				7	3.20	0.08
				14	3.03	0.09
				21	2.03	0.10
			Ear/residual	7	2.94/4.24	0.08/0.06
			Grain	14	0.09	<0.01
				21	0.09	<0.01
			Straw	14	4.42	0.12
				21	3.32	0.11
Kleindarlbach, Germany 1974 Kolibri	0.26 (600 l water/ha)	2 (interval 14 day)	Grain	15	0.01	0.04
			Straw	15	0.19	0.03
			grain	24	<0.01	0.02
			Straw	24	0.12	0.02
Jerxheim, Germany 1970 Jubilar	0.18 (450 l water/ha)	1	Grain (?)	48	<0.02	
Obersuelzen, Germany 1982 Vuka	0.24 (400 l water/ha)	2 9 (interval 17 day)	Plant	0	3.27	0.08
			Plant	13	0.12	0.09
			Plant	20	0.06	0.04
			Plant 28	28	0.02	0.02
			Grain	56	<0.01	<0.01
			Straw	56	<0.01	<0.01
?, Germany 1982 Okapi	0.24 (400 l water/ha)	2 (interval 16 day)	r.a.c. (?)	0	2.28	0.07
				14	0.09	0.09
				21	0.01	0.02
				28	0.02	<0.01
				35	<0.01	<0.01
				51	<0.01	0.01
Schwabenheim, Germany 1971 Kolibri	0.24	2 (interval 15 day)	Grain	65	<0.02	
			Straw	65 (?)	<0.02	
Schwabenheim, Germany 1971 Kolibri	0.24 (600 l water/ha)	2 (interval 15 day)	Grain	50	<0.02	
			Straw	50	<0.05	

Location Year Variety	Application rate, kg ai/ha	Interval, days	Sample	PHI, days	Dimethoate[1], mg/kg	Omethoate[1], mg/kg
Schwabenheim, Germany 1971 Kolibri	0.24	3 (interval 14 day, 7 day)	Grain	14–35	≤0.02	
			Straw	14	<0.02	
			Straw	21	0.24	
			Straw	35	0.21	
Kleinkarlback, Germany 1974 Kolibri	0.26 (600 l water/ha)	2 (interval 14 day)	r.a.c. (?)	15	0.01	0.04
				24	<0.01	0.02
Talling, Germany 1974 Kolibri	0.24	2 (interval 7 day)	r.a.c. (?)	14	<0.02	<0.02
				21	<0.02	<0.02
Obersulzen, Germany 1982 Vuka	0.24 (400 l water/ha)	2 (interval 7 day)	Plant	0	3.27	0.08
			Plant	13	0.12	0.09
			Plant	20	0.06	0.04
			Plant	28	0.02	0.02
			Grain	56	<0.01	<0.01
			Straw	56	<0.01	<0.01
Ruchheim, Germany 1982 Vuka	0.24 (400 l water/ha)	2 (interval 13 day)	Plant	0	1.96	0.12
			Plant	13	0.05	0.05
			Plant	20	<0.05	<0.05
			Plant	27	<0.05	<0.05
			Grain	35-42	≤0.05	≤0.05
			Straw	35-42	≤0.05	≤0.05

[1]Concurrent recoveries 1994
Grain (0.1-0.5 mg/kg, n=8) dimethoate 81-95%, mean 88%; omethoate 67-79%, mean 72%
Ear (0.02-0.50, n=4) dimethoate 82-96%, mean 90%; omethoate 64-70%, mean 67%
Whole plant (0.10-2.5, n=17) dimethoate 74-96%, 88%; omethoate 60-87%, mean 70%
Straw (0.20-1.02, n=6), dimethoate 93-108%, mean 102%; omethoate 63-91%, mean 76%
Concurrent recoveries 1995
Grain (0.01–0.2, n = 4) dimethoate 80–110%, mean 96%; omethoate 78-97%, mean 84%
Ear (0.01, 2.5, n = 2) dimethoate 112, 101%; omethoate 64, 87%
Whole plant (0.01–6, n = 9) dimethoate 72–125%, mean 96%; omethoate 66–95%, mean 82%
Straw (0.01, n = 2) dimethoate 83, 82%; omethoate 59–88%, mean 70%.

Feeding studies

No information.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information. CLICK HERE for continue

In processing

Cheminova reported processing studies on oranges, tomatoes, potatoes, cotton seed, maize and wheat, all with dimethoate EC formulations containing 480 g ai/l applied at about five times the GAP rate.

In the study on oranges (Rice, *et al.*, 1994) dimethoate (480 ai/l EC) was applied to orange trees with ground equipment in southern Florida in 1993 at 4.5 g ai/. About 1880 l of spray mix was applied per hectare so that the rate was about 8.5 kg ai/ha. Two applications were made with a 14-day retreatment interval. The PHI was 14 days. Oranges and processed commodities were analysed by the ABC method, with celite/charcoal used for clean-up. The residue on the unwashed oranges was 1.82 mg/kg dimethoate and 0.17 mg/kg omethoate. The water content of the oranges was 82.3%.

The oranges (400 kg) were processed by a standard commercial procedure within 18 days of harvest. The fruits were washed and then extracted with an FMC in-line juice extractor equipped with continuous water-spray nozzles. The juice stream passed continuously from the extractor through a modified FMC Model 35 finisher with a 0.05 cm screen to remove the frits. The oil/water emulsion was next passed over a shaker screen feeder to remove additional insoluble fibres (peel frits). The oil/water emulsion was allowed to stand for 5 or more hours and the lower water phase was drained and the concentrated oil emulsion centrifuged (laboratory scale) to yield cold-pressed oil. Peel from the extractor was collected in 200 l drums. A fraction was chopped in a Fitzpatrick comminuting machine, yielding wet pulp which was mixed with a lime slurry at the rate of 0.3% lime and passed through a press. The press cake was dried in a triple-pass direct-fired drier at 143°C.

The results are given in Table 57. Samples were stored frozen and analysed within 30 days.

Table 57. Residues of omethoate and dimethoate in the processed commodities of oranges treated with dimethoate (2 x 8.5 kg ai/ha, 14 day PHI, about 4x GAP rate).

Sample	Dimethoate, mg/kg, mean and (duplicates)	Control analysis		Omethoate, mg/kg, mean and (duplicates)	Control analyses		Processing factors
		Range, mg/kg No.	Recovery range and mean, %		Range, mg/kg No.	Recovery, %	
Oranges (unwashed)	1.44 (1.07; 1.82)	0.01–0.50 8	95–110 101	0.14 (0.12; 0.17)	0.01–0.50 8	82 –120 100	-
Oranges (washed)	1.50 (1.98; 1.03)			0.16 (0.20; 0.12)			1.0, 1.1
Juice	0.20 (0.20; 0.21)	0.01–0.50 7	102–110 107	0.03 (0.03; 0.03)	0.01–0.50 7	90–107 99	0.14; 0.21
Dried pulp	3.05 (3.18; 2.92)	0.01–0.50 7	69–84 79	0.24 (0.24; 0.24)	0.01–0.50 7	63–80 72	2.1; 1.7
Molasses	8.43 (8.14; 8.73)	0.01–0.50 7	70–100 87	0.88 (0.71; 1.06)	0.01–0.50 7	66–101 90	5.8; 6.3
Oil	0.28 (0.18; 0.29)	7 0.01–0.50	80 – 100 93	<0.01 (<0.01; <0.01)	0.01 – 0.50 7	65–120 79	0.19; <0.07

In a tomato processing study (Rice and Willliams, 1995) dimethoate was applied as a foliar spray 4 times to tomatoes at 2.8 kg ai/ha in the San Joaquin Valley, central California, USA. The retreatment interval and the PHI were 7 days. The applications were made with about 185 l of spray. Analyses were by the ABC method within 31 days of processing.

Control and treated tomatoes (340-350 kg) were treated by a simulated commercial process. They were washed in a four step sequence of flume and spray, then crushed and heated to 91°C (hot break). The hot crush mixture was filtered, yielding tomato juice and wet pomace. Part of the pomace was dried on trays in a dehydrator (30 hours at 68°C). A portion of the juice was canned (50 minutes at 115°C), and another condensed to purée in a vacuum evaporator. The percentage of National

Tomato Soluble Solids (NTSS) was determined and some of the purée was canned. Some was condensed to paste in a vacuum kettle, and a third portion (1.5 kg) was combined with other ingredients (1.7 kg) to prepare ketchup.

The results are given in Table 58. The tomatoes were processed within 24 hours of harvest and samples were analysed within 31 days of processing. The residues in all control samples were <0.01 mg/kg.

Table 58. Residues of dimethoate and omethoate in tomatoes and tomato processed commodities from the foliar application of dimethoate (2.8 kg ai/ha, 7 day PHI, 5 x GAP rate).

Sample	Dimethoate, mg/kg, mean and (duplicates)	Control analysis		Omethoate, mg/kg, mean and (duplicates)	Control analysis		
		Range, mg/kg No.	Recovery range and mean, %		Range, mg/kg No.	Recovery, %	Processing factors
Tomato	0.18	0.01–0.50 7	80–96 89	0.06	0.01–0.50 7	100–116 110	-
Juice	0.02	0.01 and 0.50 2	100; 97	<0.01	0.01 and 0.50 2	110; 104	0.11; 0.17
Wet pomace (64% water)	0.11	0.01 and 0.50 4	83–93 89	0.02	0.01 and 0.50 4	85–110 100	0.61; 0.33
Dry pomace (2.4% water)	0.10	0.01 – 0.50 7	70–104 87	0.01	0.01 – 0.50 7	70 –114 97	0.56; 0.17
Purée	0.30	0.01 and 0.50 2	80; 97	0.06	0.01 and 0.05 2	80; 114	1.7; 1
Paste	0.53	0.01 – 0.50 7	90–110 98	0.08	0.01–0.50 7	60–107 88	2.9; 1.4
Ketchup	0.33	0.01 and 0.50 2	90; 101	0.06	0.01 and 0.50 2	60; 106	1.8; 1

In a potato processing study by Rice *et al.* (1994) dimethoate was applied to potato plants in the Yakima Valley of Washington, USA, in 1993 at 2.8 kg ai/ha three times at 7-day intervals with ground equipment. About 190 l of water mixture was applied per hectare. The pre-harvest interval was 0 days. Samples from control and treated plots were analysed for dimethoate and omethoate by the ABC method. The potatoes were processed within 39 days of harvest, and the processed commodities extracted for analysis within 26 days of processing and then analysed within 6 days. All samples were stored frozen until analysis.

A 20-kg sample of potatoes was processed into chips by a process that simulated commercial practice, although they were not a variety that chippers would use. The potatoes were washed, culled, peeled with an abrasive peeler, and inspected to remove rotten potatoes and green tissue. A restaurant-style cutter was used to slice the potatoes into chips of about 1.6 mm thickness, which were placed in a tub of warm water to remove surface starch. The chips were deep-fried in fat at 177°C for 60–90 seconds, drained on a draining tray and salted. The commercial process uses a continuous deep fat fryer at 185°C for 60 seconds.

An additional sample was processed into granules (flakes) and wet peel. The variety, Russet Burbank Venhuizen, is a high-solids potato not suitable for the fresh market but very suitable for processing into granules. A 20-kg sample was tub-washed, sorted and steamed for 45 sec at 85 psi, then scrubbed with an abrasive peeler to remove the loosened peel. The collected peel was pressed and blended with cut trim waste to yield wet peel. About 18 kg of peeled potatoes were cut into 1.3 cm slabs with a restaurant-style slicer and spray-washed with cold water for 30 sec to remove free starch. The slices were cooked in a 120 l steam-jacketed kettle at 74°C for 20 minutes and cooled, and

a 15 kg aliquot steam-cooked at 100°C for 45 minutes. The potatoes were mashed in a Hobart grinder and mixed with food additives. The commercial process would add granules at this stage to absorb moisture and to separate individual potato cells, but this would dilute the processed sample with foreign granules. The granules were therefore prepared by taking a 1 kg sub-sample of the mashed potatoes and drying to 10% moisture on a fluid bed dryer at 93°C, yielding about 400 g. The dried sample was mixed with 1 kg of mashed potatoes and the fluid bed drying process was repeated. The addition and drying procedure was conducted a total of 5 times to produce 1.5 kg of dehydrated potato flakes. The flakes were screened with 30 and 60 mesh screens and the product retained by the 60 mesh was taken as the potato granule fraction.

Tubers, chips, granules and wet and dry peel were analysed by the ABC method. The method was validated for dimethoate and omethoate in tubers, dry peel and chips at 0.01, 0.05 and 0.50 mg/kg, and in granules and wet peel at 0.01–1.0 mg/kg. Concurrent recoveries were determined for tubers only. The results are shown in Table 59.

Table 59. Residues of omethoate and dimethoate in potatoes and their processed commodities from treatment with a dimethoate EC formulation at 3 x 2.8 kg ai/ha, 0-day PHI.

Sample	Dimethoate, mg/kg, mean and (duplicates)	Control analysis		Omethoate,' mg/kg, mean and (duplicates)	Control analysis		Concentra-tion factor (dimethoate)
		Range, mg/kg No.	Recovery range and mean, %		Range, mg/kg No.	Recovery, %	
Tubers (79% water)	0.09[1]	0.01; 0.1 concurrent	100; 100	<0.01	0.01; 0.10 concurrent	80; 119	-
Granules (5% water)	0.01	0.01-1.0 9	90-106 98	<0.01	0.01-1.0 9	101-130 112	0.12 (D)
Chips (4% water)	<0.01	0.01-0.50 7	91-120 100	<0.01	0.01-0.50 7	77-130 96	0.12 (D)
Wet peel (83% water)	0.02	0.01-1.0 9	85-97 89	<0.01	0.01-1.0 9	80-120 010	0.23 (D)
Dry peel (6% water)	0.06	0.01-0.50 7	80-93 83	<0.01	0.01-0.50 7	76-100 87	0.67 (D)

[1] Washing reduced the residue to 0.07 mg/kg

In a cotton seed processing study (Rice *et al.*, 1994) dimethoate was applied twice to cotton in Uvalde, Texas, USA in 1993 at a rate of 2.8 kg ai/ha (140 l/ha) with a 13-day retreatment interval. Cotton seed was harvested 14 days after the second application and processed 44 days after harvest. The processed commodities were extracted for analysis within 42 days of processing, and the seed within 80 days of harvest. All samples were stored frozen.

Processing was by procedures that simulated commercial practice. The cotton seed was saw ginned to remove the lint and the delinted seed mechanically cracked and screened to separate hulls from kernels. The kernels plus some residual hulls were heated, flaked and extracted with hexane. The spent flakes were treated with forced warm air to remove residual hexane. The crude oil was miscella-refined. About 52 kg cotton was ginned and delinted to produce 17.5 kg delinted seed which yielded 11.4 kg kernels and 5.52 kg hulls. Solvent extraction of 11 kg kernels gave 2.3 kg crude oil and 8.3 kg meal.

Samples were analysed by the ABC method. The method was validated for dimethoate and omethoate in meal, hulls and oil at 0.01–0.50 mg/kg and for dimethoate only in soapstock at 0.02 and 0.05 mg/kg. Recoveries of omethoate from soapstock were not acceptable. Concurrent recoveries were determined for cotton seed only. Results were reported for delinted but not for crude cotton seed; they should also . Data should have been provided for the crude seed. The results are shown in Table 60.

Table 60. Residues of dimethoate and omethoate in cotton seed and its processed commodities from the foliar application of a dimethoate EC formulation at 2 x 2.8 kg ai/ha with a PHI of 14 days.

Sample	Dimethoate, mg/kg, mean and (duplicates)	Control analysis		Omethoate,' mg/kg, mean and (duplicates)	Control analysis		Concen-tration factor (dimethoate)
		Range, mg/kg No.	Recovery range and mean, %		Range, mg/kg No.	Recovery, %	
Delinted cotton seed	0.03	0.01 concurrent	90	<0.01	0.01 concurrent	80	-
Meal	0.04	0.01 – 0.50 7	78–90 83	<0.01	0.01 – 0.50 7	66–90 82	1.4
Hulls	0.08	0.01 – 0.50 7	83–90 87	<0.01	0.01 – 0.50 7	81 – 100 90	2.7
Crude oil	0.02	0.01 – 0.50 7	90–120 105	<0.01	0.01 – 0.50 7	99–140 116	0.67
Refined oil	<0.01	-	-	<0.01	-	-	0.34
Soapstock	<0.02	0.02 – 0.05 4	70-82 76	Not determined	0.03 – 0.05 4	28–40 31	0.67

In a maize processing study (Rice *et al.*, 1994). Dimethoate was applied three times to field corn in Danville, Iowa, USA in 1993, at 2.8 kg ai/ha (190 l/ha). The retreatment interval was 7 days and the PHI was 14 days.

The maize was both dry milled and wet milled by batch processes that resemble the commercial continuous processes. Whole corn grain samples were dried, aspirated and screened. For dry milling, the whole grain was conditioned to 20–22% moisture and impact-milled in a Ripple mill, then dried (70°C for 30 min) and passed over a 0.32 cm screen. The retained material was a mixture of large grits, germ and hull (bran) and was separated into the three components by aspiration and additional milling. Material that passed through the screen was processed into medium and small grits, coarse meal, meal and flour by sifting through a series of sieves. The germ was conditioned to 12% moisture, heated to 105°C, flaked and pressed in an expeller t liberate part of the crude oil. The residual presscake with oil was extracted 3 times with hexane at 60°C. The miscella was separated into crude oil and hexane at 90°C in a laboratory vacuum evaporator or rotary evaporator and the oil was heated to 176°C to remove hexane. The remaining presscake was air-dried and ground to form meal. The crude oil from the expeller was combined with the crude oil from the hexane extraction and refined according to AOCS method Ca9a52, yielding refined oil and soapstock.

A second batch of dried, aspirated and screened maize was processed by wet milling. The grain was steeped in water containing 0.2% sulfur dioxide at 54°C for 22–48 hours. The product was ground in a Bauer mill and floated in salt water to remove the germ. The germ was dried (90°C) to a final moisture content of 7–10%. The cornstock was ground twice in a mill containing 0.48 and 0.32 cm screens. Material retained by the 0.32 cm screen was collected and dried as bran. The cornstock passing through the 0.32 cm screen was further milled and screened. Material passing through a 43 micron screen was considered to be a starch and gluten mixture. The mixture was refrigerated to allow the starch and gluten to settle from the water. The starch and gluten were then separated by batch centrifugation. The germ fraction was adjusted to 12% moisture, heated to 105°C, flaked and pressed in an expeller. This produced crude oil and presscake. The presscake was treated as in dry milling.

The maize was stored frozen and processed within three months of harvest. The maize and processed commodities were analysed by the ABC method within 12 days of processing. The method was validated by the concurrent analysis of fortified control samples of grain, grits, meal, flour, starch and crude oil (produced by wet and dry milling). The results are shown in Table 61. Grain dust (aspirated grain fractions) was not analysed: it accounted for about 1% of the grain weight.

Table 61. Residues of dimethoate and omethoate in maize and its processed commodities from the foliar application of a dimethoate EC formulation at 2 x 2.8 kg ai/ha, 14 day PHI.

Sample	Dimethoate, mg/kg, mean and (duplicates)	Control analysis		Omethoate, mg/kg, mean and (duplicates)	Control analysis		Concentration factor (dimethoate)
		Range, mg/kg No.	Recovery range and mean, %		Range, mg/kg No.	Recovery, %	
Corn grain	0.06	0.01 – 0.50 7	80–92 87	<0.01	0.01 – 0.50 7	77–100 86	
Grits	0.02	0.01 – 0.50 7	87–94 90	<0.01	0.01 – 0.50 7	83 – 110 92	0.34
Meal	0.02	0.01 – 0.50 7	76–100 88	<0.01	0.01 – 0.50 7	74 – 100 88	0.34
Flour	0.02	0.01 – 0.50 7	91–100 96	<0.01	0.01 – 0.50 7	82 – 120 101	0.34
Starch	<0.01	0.01 – 0.50 7	80–90 86	<0.01	0.01 – 0.50 7	80–100 86	0.17
Crude oil (wet milled)	<0.01	0.01 – 0.50 7	78–90 87	<0.01	0.01 – 0.50 7	66–100 78	0.17
Refined oil (wet milled)	<0.01	Not determined		<0.01	Not determined		0.17
Crude oil (dry milled)	0.02	0.01, 0.02 2	120 90	0.03	0.01, 0.02 2	90 70	0.34 >3 (omethoate)
Refined oil (dry milled)	<0.01	Not determined		<0.01	Not determined		0.17

In a wheat processing study (Rice *et al.*, 1994) dimethoate was applied once at 2.1 kg ai/ha with ground equipment in 177 l water/ha. The PHI was 37 days and 50-kg samples were stored frozen until processed 48 days after harvest.

The batch processing was designed to mimic the continuous commercial process. Whole wheat samples were cleaned by aspiration and screening. The aspirated grain dust was separated by sieving but not analysed. The cleaned grain was adjusted to 16% moisture, milled and sieved. This produced bran (730 micron screen retention), middlings (390 and 240 micron screen retentions), low grade flour (132 micron screen retention) and patent flour (below 132 microns). The middlings were reduced to flour with a roller mill (4 passes, with sieving each time). The final material retained by the 390 and 240 micron screens was considered to be shorts and the fractions retained and passed by 132 micron filter were designated as before. The low grade flour and patent flour from the reducing steps were combined with the corresponding flours from the break steps. Conditioned wheat weighing 2.4 kg was processed into bran (3.5 kg), shorts (7.8 kg), low grade flour (6.1 kg), patent flour (3.1 kg) and middlings (1.8 kg).

The processed commodities were stored frozen for 21–64 days before analysis by the ABC method. Concurrent fortified control samples were also analysed. The results are shown in Table 62. Processing factors could not be calculated because none of the samples contained quantifiable residues.

Table 62. Residues of Dimethoate and Omethoate in or on Wheat Processed Commodities from the Foliar Application of a Dimethoate EC formulation at 2.1 kg ai/ha (5X), 37 day PHI (GAP = 0.42 kg ai/ha, 35 day PHI).

Sample	Dimethoate, mg/kg, mean and (duplicates)	Control analysis		Omethoate, mg/kg, mean and (duplicates)	Control analysis	
		Range, mg/kg No.	Recovery range and mean, %		Range, mg/kg No.	Recovery, %
Grain	<0.01	0.01-0.5 7	90-96 92	<0.01	0.01, 0.05	103-120 110

Sample	Dimethoate, mg/kg, mean and (duplicates)	Control analysis		Omethoate, mg/kg, mean and (duplicates)	Control analysis	
		Range, mg/kg No.	Recovery range and mean, %		Range, mg/kg No.	Recovery, %
Bran	<0.01	0.01, 0.05	90,86 concurrent	<0.01	0.01-0.5 7	100, 88 concurrent
Middlings	<0.01	0.01-0.5 7	80-99 93	<0.01	0.01-0.5 7	91-100 97
Shorts	<0.01	0.01-0.5 7	90-102 95	<0.01		92-120 106
Low grade flour	<0.01			<0.01	0.02-0.5 7	
Patent flour	<0.01	0.02-0.5 7	78-140 92 (sd 23)	<0.01	0.02-0.5 7	77-124 93 (sd 17)

Residues in the edible portion of food commodities

No information except as indicated in the supervised trials and processing studies.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Australia provided monitoring data on residues in commodities in trade. An outbreak of papaya fruit fly in the Cairns district of Queensland in 1995 led to the enactment of a plant quarantine zone, with fruit exported from the zone being treated with dimethoate or fenthion post-harvest dips or sprays at 400 mg/l. Commodities from north Queensland delivered to the Brisbane markets were monitored for residues of dimethoate, fenthion and malathion. Analytical method PPQ-02 was used to determine dimethoate + omethoate, with a reporting limit of 0.01 mg/kg. The ranges of residues found is shown in Table 63. (Hamilton *et al.*, 1998).

Table 63. Monitoring data for dimethoate + omethoate in or on fruit and vegetables exported from the Queensland quarantine zone, 11/95–06/96, following disinfestation treatment with a dimethoate post-harvest spray or dip (400 mg/l).

Commodity	Total no. of samples	Number of samples with dimethoate ranges, mg/kg								
		≤0.01	>0.01 – ≤0.02	>0.02 – ≤0.05	>0.05– ≤0.1	>0.1 – ≤0.2	>0.2 – ≤0.5	>0.5 – ≤1.0	>1.0- ≤2.0	>2.0- ≤5.0
Avocado	96	61	1	9	7	16	2			
Banana	211	2	1	1		1	512	114	38	3
Carambola	15					1	2	1	7	4
Egg plant	7						4	1	2	
Lime	32					2	15	13	2	
Litchi	106	9			1	3	8	61	2	
Mango	121	59	5	7	14	10	21	4	1	
Passion fruit	60						17	22	18	3
Paw paw	247	9	3	83	96	44	9	1	2	
Pomelo	7	1		1	1	1	3			
Pumpkin	6			1	2	2	1			
Rambutan	16					1	2	4	8	1
Sapote	7				1	1	4	1		
Star apple	5					1	2	1	1	
Zucchini	8						1	1	6	

Dimethoate was included in the onion monitoring programme of the Australian National Residue Survey. Dimethoate and omethoate were absent (<0.01 mg/kg dimethoate, <0.05 mg/kg omethoate) from 47 samples taken in 1995 (Hamilton *et al.*, 1998).

Australia reported information on residues in food as consumed (Hamilton *et al.*, 1998). The 1994 Australian Market Basket Survey estimated the total dietary intake of certain pesticides for six different sub-populations. Simulated diets for these groups were developed from the National Dietary Surveys and each of the foods in the diet was prepared for consumption and analysed for dimethoate and other selected pesticides. Dimethoate was found in 9 commodities: apple juice (0.0013 mg/kg average, 0.02 mg/kg max), green beans (0.0004 mg/kg average, 0.01 mg/kg max), blueberries (0.0211 mg/kg average, 0.07 mg/kg max), white cabbage (0.0029 mg/kg average, 0.05 mg/kg max), sweet peppers (0.0029 mg/kg average, 0.03 mg/kg max), seeded grapes (0.0046 mg/kg average, 0.11 mg/kg max), lettuce (0.0031 mg/kg average, 0.03 mg/kg max), peaches (0.0611 mg/kg average, 0.22 mg/kg max) and pears (0.0042 mg/kg average, 0.10 mg/kg max). The estimated intake as a percentage of the ADI of 0.02 mg/kg bw/day ranged from 0.1% for adult males and boys and girls aged 12 years to 0.5% for toddlers aged 2 years. Details were not provided.

The Netherlands provided summary information on surveys for residues of dimethoate in food in commerce for the period 1994–1996. No details were provided. The information is given in Table 64.

Table 64. Residues of dimethoate in food in commerce in The Netherlands, 1994–1996.

Commodity	No. of samples analysed	Samples with residues <LOD (0.05 mg/kg)	Samples with Residues 0.05-1 mg/kg	Samples with residues >1 mg/kg	Mean residue, mg/kg
Grapefruit	301	299	2	0	<0.05
Tangerines	560	536	24	0	<0.05
Oranges	902	822	80	0	<0.05
Lemons	243	231	12	0	<0.05
Apples	1495	1464	31	0	<0.05
Cherries	252	234	18	0	<0.05
Peaches	252	248	4	0	<0.05
Nectarines	221	216	5	0	<0.05
Plums	437	437	0	0	<0.05
Grapes	667	619	46	2	<0.05
Strawberries	2378	2371	7	0	<0.05
Blackberries	244	243	0	1	<0.05
Currants (red, black, white)	450	443	7	0	<0.05
Avocados	125	123	2	0	<0.05
Kiwi	223	221	2	0	<0.05
Litchis	35	32	3	0	<0.05
Mangoes	191	188	2	1	<0.05
Passion fruit	40	40	0	0	<0.05
Other fruits and products	385	373	12	0	<0.05
Radishes	1010	1008	2	0	<0.05
Garlic	35	35	0	0	<0.05
Onions (small)	97	95	2	0	<0.05
Tomatoes	1108	1108	0	0	<0.05
Peppers	1525	1519	6	0	<0.05
Cucumbers	951	947	4	0	<0.05
Gherkins/pickle	43	42	1	0	<0.05
Courgettes	296	203	3	0	<0.05
Melons	390	382	8	0	<0.05
Watermelons	19	18	7	0	<0.05
Broccoli	154	153	1	0	<0.05
Cauliflower	348	347	1	0	<0.05
Chinese cabbage	297	287	10	0	<0.05
Other leaf cabbage	99	98	1	0	<0.05
Kohlrabi	31	31	0	0	<0.05
Lambs lettuce	268	267	1	0	<0.05
Lettuce	3306	3284	20	2	<0.05
Iceberg lettuce	471	445	26	0	<0.05

Commodity	No. of samples analysed	Samples with residues <LOD (0.05 mg/kg)	Samples with Residues 0.05-1 mg/kg	Samples with residues >1 mg/kg	Mean residue, mg/kg
Endive	1137	1128	9	0	<0.05
Spinach	440	437	1	2	0.09
Watercress	10	9	1	0	<0.05
Witloof (chicory)	457	428	29	0	0.14
Parsley	368	365	3	0	<0.05
Other herbs	148	143	5	0	<0.05
Beans (fresh, with pod)	617	581	36	0	<0.05
Beans (fresh, without pod)	39	35	4	0	<0.05
Peas (fresh, with pod)	46	45	1	0	<0.05
Peas (fresh, without pod)	123	114	8	1	<0.05
Other legumes (fresh)	8	7	1	0	<0.05
Celery	233	230	3	0	<0.05
Fennel	52	52	0	0	<0.05
Leek	441	440	1	0	<0.05
Other stem vegetables	341	338	3	0	<0.05
Mushrooms	384	383	1	0	<0.05
Beans	2	1	1	0	<0.05
Other pulses (dried)	42	41	1	0	<0.05
Other arable products	699	692	7	0	<0.05
Maize	37	37	0	0	<0.05

The Netherlands also supplied similar information on residues of omethoate in food in commerce for the same period (Table 65).

Table 65. Residues of omethoate in food in commerce in The Netherlands, 1994–1996.

Commodity/MRL	No. of samples analysed	Samples with residues <LOD (0.05 mg/kg)	Samples with Residues 0.05-1 mg/kg	Samples with residues >1 mg/kg	Mean residue, mg/kg
Apples/0.2	1495	1491	3	1	<0.02
Cherries/0.4	252	251	1	0	<0.02
Grapes/0.1	667	660	5	2	<0.02
Strawberries/0.1	2378	2378	0	0	<0.02
Currants (red, black, white)/0.1	450	450	0	0	<0.02
Other fruits and products/0.2	385	384	1	0	<0.02
Tomatoes/0.2	1108	1108	0	0	<0.02
Peppers/0.2	1525	1519	6	0	<0.05
Cauliflower/0.2	348	347	1	0	<0.02
Chinese cabbage/0.2	297	296	1	0	<0.02
Kohlrabi/0.2	31	30	1	0	<0.02
Lettuce/0.2	3306	3305	1	0	<0.02
Iceberg lettuce/0.2	471	470	1	0	<0.02
Endive/0.2	1137	1136	1	0	<0.02
Spinach/0.4	440	439	0	1	<0.02
Witloof (chicory)/0.4	457	450	6	1	<0.02
Beans (fresh, with pod)/0.2	617	615	2	0	<0.02
Beans (fresh, without pod)/0.2	39	38	0)?)	0	<0.02
Peas (fresh, without pod)/0.2	123	121	1	1	<0.02

NATIONAL MAXIMUM RESIDUE LIMITS

National maximum residue limits were not reported by the DTF or Cheminova. National MRLs reported by the governments of Australia, Germany and The Netherlands are shown below.

Country	Commodity	MRL, mg/kg	Residue definition
DIMETHOATE (027)			
Australia	Cereal grains	0.05	Dimethoate + Omethoate, expressed as dimethoate (0.05 is the approximate LOD)
	Edible offal (mammalian)	0.05	
	Eggs	0.05	
	Fruiting vegetables, cucurbits	2	
	Fruits (except strawberry, litchi, peaches)	2	
	Litchi	5	
	Lupin (dry)	0.5	
	Lupin, forage	1	
	Meat (mammalian)	0.05	
	Milks	0.05	
	Oilseed (except peanut)	0.1	
	Peaches	T5	
	Peanut	0.05	
	Peppers sweet (capsicums)	1	
	Poultry, edible offal of	0.05	
	Poultry meat	0.05	
	Strawberry	5	
	Tomato	1	
	Vegetables (except lupin, dry; peppers, sweet; tomato)	2	
Germany	Vegetable	1	Dimethoate
	Fruit	1	
	Cereals	0.2	
	Tea	0.2	
	Other foods of plant origin	0.05	
The Netherlands	Fruit	1	Dimethoate (parent compound)
	Vegetables	1	
	Tea	0.2	
	Other food commodities	0.05	(0.05 is the LOD)
OMETHOATE (055)			
Australia	Cereal grains	0.05	Omethoate (0.05 is the approximate LOD)
	Edible offal (mammalian)	0.05	
	Eggs	0.05	
	Fruits	2	
	Legume animal feeds (fresh weight)	20	
	Lupin (dry)	0.1	
	Lupin forage	0.5	
	Meat (mammalian)	0.05	
	Milks	0.05	
	Miscellaneous fodder and forage crops (fresh weight)	20	
	Oilseed	0.05	
	Peppers, sweet (capsicums)	1	
	Poultry, edible offal of	0.05	
	Poultry meat	0.05	
	Straw, fodder (dry, and hay of cereal grains and other grass-like plants	20	
	Tomato	1	
	Vegetables (except lupin; peppers, sweet; tomato)	2	
Germany	Hops	10	
	Artichokes	0.4	
	Witloof	0.4	
	Spices	0.4	
	Cherries	0.4	
	Oilseeds	0.4	
	Spinach	0.4	
	Remaining vegetables	0.2	

Country	Commodity	MRL, mg/kg	Residue definition
	Remaining fruits	0.2	
	Small fruits and berries, except grapes	0.1	
	Leek	0.1	
	Tea	0.1	
	Root and tuber vegetable	0.1	
	Bulb vegetable	0.1	
	Other foods of plant origin	0.05	
The Netherlands	Cherries	0.4	Omethoate (parent compound)
	Table and wine grapes	0.1	
	Strawberries (other than wild)	0.1	
	Other small fruit and berries (other than wild)	0.1	
	Other fruit	0.2	
	Root and tuber vegetables	0.1	
	Onions	0.1	
	Spinach	0.4	
	Witloof	0.4	
	Leeks	0.1	
	Globe artichokes	0.4	
	Other vegetables	0.2	
	Tea	0.1	
	Other food commodities	0.02	(0.02 is the limit of determination)
FORMOTHION (042)			
Germany	Citrus fruit	0.2	Formothion
	Vegetable	0.1	
	Remaining fruit	0.1	
	Tea, tealike products	0.05	
	Other foods of plant origin	0.01	
The Netherlands[1]	Citrus fruit	0.2	Formothion
	Other fruit	0.1	
	Vegetables	0.1	
	Cereals	0.05	(0.05 is the limit of determination)
	Other food commodities	0 (0.05)	

[1]Not authorized for use in this country

APPRAISAL

Dimethoate, *O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate, is a contact and systemic insecticide typically applied as an emulsifiable concentrate (EC) diluted in water at 0.3 – 0.7 kg ai/ha. The toxicology was reviewed in 1996 and an ADI of 0.002 mg/kg bw was allocated to the sum of dimethoate and omethoate, expressed as dimethoate. Omethoate, *O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorothioate, is a metabolite of dimethoate and a systemic pesticide. Since 1986, the JMPR has estimated separate maximum residue levels for dimethoate and omethoate. Formothion, *S*-[formyl(methyl)carbamoylmethyl] *O,O*-dimethyl phosphorodithioate, is metabolized by plants to dimethoate and omethoate. No Codex MRLs or draft MRLs exist for formothion. Its toxicology was last reviewed in 1969 but no ADI was allocated.

The three compounds are now re-evaluated within the CCPR Periodic Review Programme, but as no information on formothion was submitted the evaluation refers only to dimethoate and omethoate.

Animal metabolism

Metabolism studies were reported for rats, goats and chickens. In the rat studies, three metabolites were identified in urine: *O,O*-dimethyl hydrogen phosphorothioate (7%), *O,O*-dimethyl hydrogen phosphorodithoate (25%) and dimethoate carboxylic acid (36%).

Leghorn chickens were given oral doses (0.9 mg/kg bw/day) of [*methoxy*-^{14}C]dimethoate for 7 days. The radioactive residue levels in the liver, muscle, fat, egg yolk (last day) and egg white (last day) were 0.64, 0.09, 0.038, 0.34 and 0.15 mg/kg respectively. The liver residue (0.82 mg/kg as dimethoate) was shown to consist mainly of phosphorylated natural products (33% of the TRR), omethoate (10% of the TRR) and dimethoate carboxylic acid (16% of the TRR). Phosphorylated natural products were significant proportions of the residue in muscle (36-46% of the TRR), egg white (50%), and egg yolk (35%). Dimethoate was not found in any of the samples. Omethoate was absent from muscle and fat, but found in egg whites at 3% of the TRR (0.004 mg/kg) and liver after protease treatment.

Dimethoate labelled on the methoxy carbons was administered orally to goats once daily for 3 consecutive days at 1.6 mg/kg bw/day. The concentrations of ^{14}C as dimethoate were liver 1.2 mg/kg, kidney 0.15 mg/kg, muscle 0.07 mg/kg, fat 0.05 mg/kg, and milk (48–60 h) 0.23 mg/kg. Much of the residue was characterized as phosphorylated natural products, 35% of the TRR in the liver, 32% in the kidneys, 53% in the muscle, and 53% in the milk. Dimethoate was not found in any sample and omethoate was found only in the liver (0.12 mg, 10% of the TRR) after protease treatment of the extraction residue. Urine was shown to contain dimethoate carboxylic acid, dimethyl hydrogen phosphorothioate and dimethyl hydrogen phosphate. The metabolism in both poultry and ruminants is consistent with the formation of the sulfoxides of omethoate and dimethoate carboxylic acid. The sulfoxides would react with nucleophiles, leading to phosphorylated natural products.

The Meeting concluded that the metabolism of dimethoate and omethoate in animals is adequately understood.

Plant metabolism

The metabolism of [^{32}P]dimethoate in sugar beet, maize, cotton, peas, potatoes and beans has been reported. The reports were summaries which did not provide the customary detail. Generally, the main components of the radiolabelled residue were dimethoate, omethoate, dimethoate carboxylic acid, dimethyl hydrogen phosphate and *O,O*-dimethyl hydrogen phosphorodithioate, indicating oxidation to omethoate, omethoate carboxylic acid and dimethoate carboxylic acid, and cleavage of the P-S linkage either before or after oxidation. A difference from animal metabolism is that the sulfoxide is apparently not formed.

Dimethoate is water-soluble and considerable translocation of foliar dimethoate might be expected. The metabolism studies with maize, cotton, potatoes and peas indicated the extent of penetration of residues into the leaves, but no detailed study on residue translocation was reported.

The Meeting concluded that the plant metabolism studies were incomplete, both because a detailed study was not provided and because translocation was not adequately addressed.

Environmental fate

Studies were reported on confined rotational crops, degradation, dissipation and mobility in soil, adsorption and desorption, photodegradation on soil, and aquatic dissipation.

In the confined rotational crop study, soil was treated with [^{14}C]dimethoate at a rate of 0.56 kg ai/ha. Lettuce, turnips and wheat were planted after 30 and 120 days and grown to maturity. The radioactive residues were highest in the 30-day plantings, ranging from 0.008 mg/kg as dimethoate in

turnip roots to 0.045 mg/kg in wheat straw. A substantial proportion of each crop sample (30-60% of the TRR) was characterized as polar compounds or polar hydroxy compounds. The crops planted after 120 days showed very low radioactive residues, ranging from 0.001 mg/kg in turnip roots to 0.02 mg/kg in wheat straw.

The Meeting concluded that inadvertent residues in rotational crops would not be significant, that the low residue levels consisted mainly of polar metabolites and that dimethoate and omethoate concentrations under field conditions would be below 0.01 mg/kg, a typical lower limit of quantification.

When the degradation of [^{14}C]dimethoate in soil under aerobic and anaerobic conditions was studied its half-life in sandy loam soil under aerobic conditions was 2.4 days, with two products identified: dimethyl hydrogen phosphorothioate and *O*-demethyl-dimethoate. Radioactive carbon dioxide accounted for 75% of the applied radioactivity after 180 days, indicating mineralization as the ultimate fate. The half-life of dimethoate under anaerobic conditions (after two days of aerobic conditioning) was 4 days. The same products were identified.

Soil dissipation studies in the UK and the USA showed that dimethoate does not migrate readily below the top 15 cm and that the half-life is 2–4 days. In other studies half-lives of dimethoate in soil were 9.8 days in bean plots, 6.0 days in grape plots and 7.8 days in bare soil. A lysimeter test in Germany showed that radiolabelled dimethoate had little tendency to migrate downward through the soil, with 17% of the recovered radioactivity in the top 12 cm.

The Meeting concluded that dimethoate was degraded at a moderate rate in soil with a half-life of about 4 days, and that it migrates only slowly under normal agricultural conditions.

Leaching studies were reported with four types of soil. Dimethoate is readily leached, with the rate of leaching decreasing with increasing loam content of the soil, but leaching is offset by the short half-life in soil.

The half-lives of dimethoate in two water/sediment systems were 13 and 17 days. The only identified product was demethyl-dimethoate.

In a study of the photodegradation of dimethoate on soil the half-life in sunlight was 10 days, but the half-life in the dark was 8 days. The Meeting concluded that photodegradation was not significant.

Methods of residue analysis

Adequate methods exist for data collection, monitoring, and the enforcement of MRLs. The methods are similar and involve maceration of the substrate with solvent, typically acetone/water, and extraction of the (concentrated) macerate with chloroform or methylene chloride. Extracts are sometimes cleaned up on a column of celite or Florisil or by GPC. Some Australian methods use sweep co-distillation with ethyl acetate after the chloroform extraction, but this step destroys omethoate. The final extracts are analysed on a gas chromatograph equipped with a capillary column and a flame photometric detector (FPD). The typical lower limits of quantification are 0.01 mg/kg for both dimethoate and omethoate.

Extensive recovery data were presented for the most common methods.

Stability of stored analytical samples

The stabilities of dimethoate and omethoate on fortified analytical samples of tubers, oranges, sorghum grain, sorghum forage and cotton seed during frozen storage were determined. The Meeting concluded that dimethoate was stable on all these commodities for at least 1.7 years and that

omethoate was also stable on all of them with the possible exception of cotton seed, from which a 20% loss may have occurred during the first 5 months with no subsequent decrease.

Definition of the residue

On the basis of the metabolism of dimethoate in plants and animals, the conclusions of the 1996 JMPR on the toxicology, the available analytical methods and the lack of significant data on omethoate *per se*, the Meeting concluded that the residue for compliance with MRLs should be defined as dimethoate. The MRLs for omethoate should be considered for withdrawal because no data were reported to support omethoate MRLs. For the estimation of dietary intake the residue is based on the sum of dimethoate and omethoate, each considered separately.

Residues resulting from supervised trials

Supervised trials were reported on oranges (post-harvest), apples, pears, cherries, plums, blueberries, strawberries, grapes, currants, avocados (post-harvest), litchis (post-harvest), chives, leeks, Brussels sprouts, cabbages, cauliflowers, broccoli, kohlrabi, cucumbers (post-harvest), zucchini (post-harvest), rockmelons (post-harvest), watermelons (post-harvest), tomatoes, sweet peppers, kale, spinach, chard, lettuce, peas, French beans, mung beans, potatoes, turnips, sugar beet, carrots, long radishes, asparagus, sorghum, barley, maize, wheat and witloof chicory.

Oranges. Post-harvest trials were reported from Australia. Only one residue was reported at the specified 0-day post-treatment holding period. The data were insufficient to estimate a maximum residue level or STMR. The Meeting recommended withdrawal of the existing CXLs for dimethoate and omethoate in citrus fruits.

Pome fruit (apples and pears). Supervised field trials on apples in The Netherlands and Germany were reported. Two trials in The Netherlands and 10 in Germany complied with GAP for apples and pears (3 x 0.02 kg ai/hl (0.30 kg ai/ha), 21-day PHI, and 3 x 0.04 kg ai/hl (0.6 kg ai/ha), 21-day PHI respectively). Two trials were reported with the use of omethoate on apples in The Netherlands, with residues as high as 0.1 mg/kg, but this is insufficient for the estimation of residues from the use of omethoate *per se*. Four supervised field trials in Germany with foliar application of dimethoate to pears complied with GAP. The residues of dimethoate in apples and pears in rank order were 0.01, 0.03, <0.05 (5), 0.06, 0.07, 0.08, 0.10, 0.14, 0.15, 0.16, 0.26 and 0.30 mg/kg. The residues of omethoate from the use of dimethoate were 0.04, <0.05 (6), 0.05 (2), 0.06 (2), 0.07, 0.08 and 0.13 mg/kg. The Meeting estimated a maximum residue level for dimethoate of 0.5 mg/kg and an STMR of 0.065 mg/kg, and an STMR for omethoate of 0.05 mg/kg.

Cherries. In four supervised trials in the USA the application rate was about 7.7 times the GAP rate. Ten trials in Germany complied with GAP (3 x 0.04 kg ai/hl (0.6 kg ai/ha), 21-day PHI). The residues of dimethoate were <0.02, <0.05, <0.05, 0.03, 0.06, 0.06, 0.08, 0.13, 0.19 and 1.5 mg/kg, and those of omethoate were <0.01, 0.03, 0.05, 0.11, 0.27, 0.27, 0.28, 0.28, 0.28 and 0.46 mg/kg. The Meeting estimated a maximum residue level for dimethoate of 2 mg/kg, and STMRs for dimethoate of 0.06 mg/kg and for omethoate of 0.27 mg /kg.

Plums. Four replicate trials in The Netherlands could not be used to estimate a maximum residue level because the PHI of 14 days was less than the GAP 21-day PHI and one of the trials showed a significant residue at 14 days. Twenty-three trials according to GAP (3 x 0.04 kg ai/hl (0.6 kg ai/ha), 14-day PHI) were reported from Germany, with residues of dimethoate of <0.02, <0.05 (6), 0.05, 0.06, 0.07, 0.09, 0.10, 0.11, 0.12 (2), 0.13 (2), 0.15, 0.24, 0.28, 0.36, 0.46 and 0.75 mg/kg and of omethoate of <0.02, <0.05 (10), 0.05 (3), 0.07, 0.08, 0.12 (2), 0.14, 0.17 and 0.22 mg/kg. The Meeting estimated a maximum residue level for dimethoate of 1 mg/kg , an STMR for dimethoate of 0.10 mg/kg and an STMR for omethoate of 0.05 mg/kg.

Blueberries. Supervised field trials were reported from the USA. There is no current GAP.

Strawberries. Three varieties were treated at various rates in replicate plots in Australia, but the combined residue of dimethoate and omethoate was measured and only 3 residues were from GAP conditions (0.30 kg ai/ha, 1-day PHI). There were insufficient data to estimate a maximum residue limit or STMR and the Meeting recommended withdrawal of the CXL for strawberry.

Grapes. Supervised field trials were reported from France and Germany, but without corresponding GAP. GAP for The Netherlands is 3 x 0.02 kg ai/hl (0.24-0.30 kg ai/ha), 21- or 28-day PHI. GAP for Hungary is 0.04 kg ai/hl (0.32 kg ai/ha) with a 14-day PHI. Seven trials in France were close to these conditions. The residues were 0.11, 0.18, 0.21, 0.48, 0.53, 0.89 and 1.2 mg/kg of dimethoate and <0.05, <0.05, 0.08, 0.11, 0.11, 0.14, 0.19 mg/kg of omethoate. The Meeting estimated a maximum residue level for dimethoate of 2 mg/kg, and STMRs for dimethoate of 0.48 mg/kg and for omethoate of 0.11 mg/kg.

Currants. Supervised field trials were carried out in Germany but no GAP was reported. GAP for The Netherlands is 3 x 0.24 kg ai/ha, 21-day PHI, but none of the German trials complied with it. The Meeting recommended withdrawal of the existing CXL for currant, black.

Sub-tropical fruits with inedible peel. Two supervised trials each on avocados, mangoes and litchis, post-harvest dips or high-volume sprays, were reported from Australia. The residues belonged to different populations and could not be combined for evaluation. There were therefore insufficient data to estimate maximum residue levels or STMRs.

Leeks. One supervised trial in Germany complied with GAP for The Netherlands, assuming an application of 1000 l of spray solution per ha. One trial was inadequate to estimate a maximum residue level or STMR.

Onions. Seven supervised field trials according to GAP (2 x 0.24 kg ai/ha, 14-day PHI) were reported from Germany. The residues were <0.01, 0.01, <0.02, <0.02, 0.04, <0.05 and <0.05 mg/kg of dimethoate and <0.01, <0.01, <0.02, <0.02, <0.02, <0.05 and <0.05 mg/kg of omethoate. The Meeting estimated a maximum residue level of 0.05* mg/kg for dimethoate and STMRs of 0.02 mg/kg for both dimethoate and omethoate.

Cauliflowers. Nine field trials on cauliflowers in Germany were not according to GAP. Eight trials in the UK complied with UK GAP for brassica vegetables (6 x 0.40 kg ai/ha, 7-day PHI). The residues were 0.02, 0.02, 0.03, 0.04, 0.09, 0.09, 0.11 and 0.34 mg/kg of dimethoate and <0.01 (8) and 0.01 mg/kg of omethoate. The Meeting estimated a maximum residue level of 0.5 mg/kg for dimethoate and STMRs of 0.065 mg/kg for dimethoate and 0.01 mg/kg for omethoate.

Broccoli. Only one supervised trial was reported, which did not comply with GAP. A maximum residue level or STMR could not be estimated.

Brussels sprouts. Four supervised field trials in Germany (GAP 0.24 and 0.36 kg ai/ha, 14-day PHI), three in The Netherlands (GAP 0.2 kg ai/ha repeated, 21-day PHI), one in the USA (GAP 6 x 1.12 kg ai/ha, 10-day PHI) and eight in the UK (GAP 6 x 0.40 kg ai/ha, 7-day PHI) complied with national GAP. The residue in the US trial (3.12 mg/kg) was an outlier and was not included. In one of the UK trials there was an unacceptable concentration of residue in the control. In the remaining trials the residues of dimethoate were 0.005, 0.009, 0.03, <0.05, <0.05, 0.05, 0.06, 0.07, 0.08, 0.10, 0.11, 0.17, 0.21 and 0.46 mg/kg, and those of omethoate were <0.01, <0.01, <0.01, 0.01, 0.02, 0.03, 0.03, 0.04, 0.07, 0.08, 0.09, 0.16, 0.30 mg/kg (omethoate was not determined in one of the German trials). The Meeting estimated a maximum residue level of 1 mg/kg for dimethoate and STMRs of 0.065 mg/kg for dimethoate and 0.03 mg/kg for omethoate.

Cabbage. Twelve supervised field trials on cabbages in Germany (8 Savoy and 4 head) complied with GAP (0.4 kg ai/ha, 42-day PHI or 2 x 0.24 kg ai/ha, 14-day PHI), as did eight on head cabbages in the

UK (6 x 0.40 kg ai/ha, 7-day PHI) and two in The Netherlands (0.2 kg ai/ha repeated, 21-day PHI). The residues in head cabbages were in two population groups, those in Germany and The Netherlands ranging from <0.01 to 0.07 mg/kg dimethoate and <0.01 to 0.02 mg/kg omethoate and those in the UK ranging from 0.04 to 1.2 mg/kg dimethoate and <0.01 to 0.64 mg/kg omethoate. In the UK trials only one residue (of omethoate) was below the LOD. In the German and Dutch trials, 4 of 6 dimethoate residues and 4 of 5 omethoate residues were below the LOD. The residues of dimethoate in the population with highest residue levels (UK) were 0.04, 0.07, 0.14, 0.25, 0.67, 0.82, 0.99 and 1.2 mg/kg, and those of omethoate in the same population were <0.01, 0.02, 0.04, 0.05, 0.28, 0.35, 0.63 and 0.64 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg for dimethoate and STMRs of 0.46 mg/kg for dimethoate and 0.165 mg/kg for omethoate on head cabbages except Savoy cabbage.

The residues of dimethoate on Savoy cabbages in Germany were <0.01 (2), <0.02 (4) and <0.05 (2) and of omethoate <0.01 (2), <0.02 (2), 0.13, 0.17, 0.31 and 0.66 mg/kg. The Meeting estimated maximum residue levels of 0.05* mg/kg for dimethoate and STMRs of 0.02 mg/kg for dimethoate and of 0.075 mg/kg for omethoate on Savoy cabbage.

Kohlrabi. Two supervised trials in Germany complied with UK GAP but were insufficient to estimate a maximum residue level or STMR.

Cucumbers, zucchini, cantaloupes. A single trial on each in Australia with post-harvest treatment was reported. One trial is insufficient for the estimation of a maximum residue level or STMR.

Watermelons. Two post-harvest trials in Australia at maximum GAP (400 mg/l dip, 0-day post-treatment interval) were inadequate for the estimation of a maximum residue level or STMR.

Tomatoes. Six post-harvest trials in Australia were according to GAP (400 mg dimethoate/l solution dip, 7-day post-treatment interval), but only dimethoate was determined. Fourteen trials in Germany complied with GAP (3 foliar applications, 0.24, 0.36, 0.48 kg ai/ha or 0.04 kg ai/hl, 3-day PHI). The 20 dimethoate residues in rank order were 0.01, 0.05 (2) 0.06 (2), 0.08, 0.12, 0.15, 0.19, 0.20, 0.22, 0.24, 0.26 (2), 0.31, 0.34, 0.41, 0.42, 0.80 and 1.3 mg/kg. The 14 omethoate residues were 0.01, 0.03 (3), 0.04, <0.05, 0.05 (3), 0.06, 0.09, 0.13, 0.14 and 0.32 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg for dimethoate and STMRs of 0.21 mg/kg for dimethoate and 0.05 mg/kg for omethoate.

Sweet peppers. Three trials in Australia with post-harvest dip treatment of sweet peppers were according to the Queensland GAP of 0.04 kg dimethoate per 100 l of dipping solution with no specified holding period. The Meeting concluded that three trials were inadequate for the estimation of maximum residue levels or STMRs and recommended withdrawal of the existing CXL for peppers.

Kale. Eight supervised field trials were carried out in Germany, but no relevant GAP was reported. The Meeting could not evaluate the data and recommended withdrawal of the existing CXL.

Chard, leaf lettuce. One trial in Germany on each crop was reported but without relevant GAP. The data were inadequate.

Head lettuce. Twelve supervised trials reported from Germany complied with GAP (2 x 0.24 kg ai/ha, 21-day PHI). One trial was not evaluated because the total residues increased substantially from 7 to 14 days and the dimethoate/omethoate ratio at 14 and 21 days was quite different from that in the other trials. The residues of dimethoate were <0.02 (7), <0.05 (2), 0.09 and 0.24 mg/kg, and those of omethoate were <0.02 (3), 0.02, 0.03, 0.03, <0.05, <0.05, 0.05, 0.06 and 0.10 mg/kg. The Meeting estimated a maximum residue level of 0.5 mg/kg for dimethoate and STMRs of 0.02 mg/kg for dimethoate and 0.03 mg/kg for omethoate.

Spinach. Two of four supervised trials in Germany complied with the GAP of The Netherlands (0.20 kg ai/ha, 21-day PHI). The Meeting considered the data inadequate and recommended the withdrawal of the existing CXL.

Peas. Supervised trials according to GAP were reported from Denmark (2 trials; GAP 0.32 kg ai/ha, 14-day PHI); the UK (3 trials; GAP 6 x 0.34 kg ai/ha, 14-day PHI); Germany (3 trials according to UK GAP); The Netherlands (2 trials; GAP 3 x 0.20 kg ai/ha, 21-day PHI) and the USA (4 trials; GAP 0.19 kg ai/ha, 0-day PHI). The dimethoate residues were <0.01, 0.018, 0.026, 0.027, 0.03, 0.04, 0.04, 0.09, 0.19, 0.27, 0.36, 0.44, 0.50 and 0.64 mg/kg, and the omethoate residues <0.01, <0.01, 0.015, 0.02 (5), 0.022, 0.026, 0.03, 0.04, 0.052 and 0.20 mg/kg. The Meeting estimated a maximum residue level of 1 mg/kg for dimethoate and STMRs of 0.065 mg/kg for dimethoate and 0.02 mg/kg for omethoate.

Beans. Three trials on French beans in Germany were not according to GAP. A single trial on mung beans in the USA complied with GAP (0.56 kg ai/ha, 0-day PHI). The data on beans were inadequate.

Potatoes. Nine trials in Germany (GAP 0.24 kg ai/ha, 14-day PHI) and one each in the UK (GAP 2 x 0.34 kg ai/ha), The Netherlands (GAP 4 x 0.20 kg ai/ha, 21-day PHI) and Denmark (GAP 0.30–0.32 kg ai/ha, 14-day PHI) were according to national GAP. The residues of dimethoate were <0.01 (6), 0.01, <0.02 (4) and 0.02 mg/kg and those of omethoate were <0.01 (6), 0.01, <0.02 (4) and 0.02 mg/kg. The Meeting estimated a maximum residue level of 0.05 mg/kg for dimethoate and STMRs of 0.01 mg/kg each for dimethoate and omethoate.

Turnips, turnip greens. Seven trials in the USA complied with GAP (0.28 kg ai/ha, 14-day PHI). The residues of dimethoate and omethoate in the roots were <0.1 mg/kg in all the samples. The Meeting estimated a maximum residue level for dimethoate of 0.1 mg/kg and STMRs of 0.1 mg/kg each for dimethoate and omethoate in garden turnips.

The residues of dimethoate on the turnip tops (greens) were <0.1 (5), 0.25 and 0.55 mg/kg and those of omethoate were <0.1 (6) and 0.20 mg/kg. The Meeting estimated a maximum residue level of 1 mg/kg for dimethoate and STMRs of 0.1 mg/kg each for dimethoate and omethoate in turnips greens.

Sugar beet roots and tops. Two trials in the UK complied with UK GAP (2 x 0.40 kg ai/ha, before June 30) and one each in Denmark and The Netherlands with Dutch GAP (3 x 0.40 kg ai/ha, no PHI). Most of the six trials in Germany (GAP 0.16 kg ai/ha, 35-day PHI) were at about twice the GAP rate, but could be included in the evaluation because the residues were at the limit of quantification at the appropriate PHI. The residues of dimethoate in the roots were <0.01 (7), <0.02 (2) and <0.05 mg/kg, and those of omethoate were <0.01 (7), <0.02 and <0.05 mg/kg. The Meeting estimated a maximum residue level for dimethoate of 0.05 mg/kg and STMRs for dimethoate and omethoate of 0.01 mg/kg each in sugar beet (roots).

The residues of dimethoate on the tops were <0.01 (2), <0.02, <0.05, 0.06 and 0.10 mg/kg and those of omethoate <0.01 (2), <0.02, <0.05, 0.05 (2), and 0.17 mg/kg. The Meeting estimated a maximum residue level for dimethoate of 0.1 mg/kg and STMRs for dimethoate and omethoate of 0.05 mg/kg each for sugar beet leaves or tops.

Carrots. Only two of 14 trials in Germany complied with GAP (2 x 0.24 kg ai/ha, 14-day PHI). The Meeting recommended withdrawal of the existing CXL.

Radishes. Twenty trials were carried out in Germany, but no GAP was reported for Germany or any other country. The Meeting could not estimate a maximum residue level or STMR.

Asparagus. In four supervised field trials in the USA which were according to GAP (5 x 0.56 kg ai/ha, 180-day PHI) the residues of dimethoate were <0.02 (3) and <0.03 mg/kg, and those of omethoate

were <0.02 (3) and <0.12 mg/kg. In three additional trials at twice the GAP rate the residues of dimethoate and omethoate were all below the LOD (<0.02 mg/kg). The Meeting estimated a maximum residue level for dimethoate of 0.05* mg/kg and STMRs for dimethoate and omethoate of 0.02 mg/kg each.

Barley grain and straw. Supervised field trials according to GAP were reported from Denmark (GAP 0.80 kg ai/ha; 1 trial), The Netherlands (GAP 0.20 kg ai/ha, 14-day PHI; 2 trials), Germany (2 trials according to Dutch GAP) and the UK (GAP 4 x 0.34 kg ai/ha, 14-day PHI; 3 trials). The residues of dimethoate in the grain were 0.03, 0.06, 0.07, 0.10, 0.41, 0.49, 0.73 and 1.43 mg/kg and those of omethoate <0.01 (2), 0.01 (2), 0.02, 0.03, 0.06 and 0.10 mg/kg. The Meeting estimated a maximum residue level for dimethoate of 2 mg/kg and STMRs of 0.255 mg/kg for dimethoate and 0.015 mg/kg for omethoate in barley grain.

The residues of dimethoate on the straw were 0.09, 0.13, 0.20, 0.44, 0.55, 0.88, 1.59 and 2.81 mg/kg and those of omethoate <0.01, 0.01, 0.03 (3), 0.07 (2) and 0.11 mg/kg. The Meeting estimated STMRs for straw of 0.495 mg/kg for dimethoate and of 0.03 mg/kg for omethoate.

Maize. Two supervised field trials were reported from Denmark, but the PHIs were at least twice the GAP interval. The Meeting could not estimate a maximum residue level or STMR.

Sorghum (grain, forage and hay). Six trials in the USA complied with GAP (3 x 0.56 kg ai/ha, 28-day PHI). All the residues of dimethoate and omethoate in the 5 samples of grain analysed were <0.01 mg/kg. The Meeting estimated a maximum residue level for dimethoate of 0.01* mg/kg and STMRs of 0.01 mg/kg each for dimethoate and omethoate in sorghum grain.

The residues of dimethoate on the forage were <0.01 (4), 0.01 and 0.02 mg/kg and those of omethoate all <0.01 mg/kg. The residues of dimethoate on the hay were <0.01 (5) and 0.01 mg/kg and of omethoate all <0.01 mg/kg. The Meeting estimated STMRs for forage and hay of 0.01 mg/kg each for dimethoate and omethoate.

Wheat grain and straw. One trial each in The Netherlands, Denmark, the UK and Germany complied with UK GAP (4 x 0.68 kg ai/ha low volume, 4 x 0.34 kg ai/ha high volume, 14-day PHI) and three trials in Germany complied with German GAP (2 x 0.24 kg ai/ha, 21-day PHI). The residues of dimethoate in the grain were <0.01, <0.02 , <0.05, 0.09, 0.10, 0.11 and 0.12 mg/kg, and those of omethoate were <0.01 (3), 0.01, 0.02 and <0.05 mg/kg. The Meeting estimated a maximum residue level for dimethoate of 0.2 mg/kg and STMRs of 0.09 mg/kg for dimethoate and 0.01 mg/kg for omethoate in wheat grain.

The residues of dimethoate in or on the straw were <0.02, <0.05, 0.12, 2.23, 2.37, 4.42 and 8.95 mg/kg, and of omethoate <0.02, 0.02, <0.05, 0.08, 0.12, 0.13 and 0.17 mg/kg. The Meeting estimated a maximum residue level of 10 mg/kg for dimethoate and STMRs of 2.23 mg/kg for dimethoate and 0.08 mg/kg for omethoate in wheat straw and fodder, dry.

Chives. Five supervised field trials were carried out in Germany, but no GAP was reported for any country. No maximum residue level or STMR could be estimated.

Witloof chicory. Five trials in The Netherlands did not comply with GAP (5.0 kg ai/ha, 21-day PHI) because the PHIs all exceeded 35 days. The Meeting recommended withdrawal of the existing CXL for witloof chicory (sprouts).

Feeding studies

No feeding studies were reported but the studies of metabolism in hens and goats indicated that dimethoate and omethoate are extensively metabolized. Dimethoate was undetectable in all the

samples and omethoate was found only in hen and goat livers and egg whites after protease treatment of the residue from the solvent extractions.

Possible ruminant feed items include apple pomace, barley grain and straw, wheat grain and straw, potato culls, processed potato waste, sorghum grain, forage and hay, sugar beet tops, molasses and pulp, and turnip roots and tops. Poultry feed may include barley grain and sorghum grain. There was no information available on residues in apple pomace, potato waste and culls or sugar beet molasses and pulp and potential residues in these commodities could not be estimated.

The maximum residues found in supervised field trials with feed items, e.g. wheat straw at 2 mg/kg dimethoate and 0.2 mg/kg omethoate and barley grain at 2 mg/kg dimethoate and 0.1 mg/kg omethoate, indicate that a dairy cow would receive about 7 ppm dimethoate and 0.2 ppm omethoate in the diet and poultry about 1.7 ppm dimethoate and 0.2 ppm omethoate. The metabolism studies were at levels equivalent to 10 ppm dimethoate in the diet for poultry and 30 ppm for goats, or about 5 and 15 times the highest estimated dietary burdens. In the metabolism studies, omethoate was found in liver (0.12 mg/kg in goats, 0.082 mg/kg in hens) and egg whites (0.004 mg/kg). From the calculated dietary burdens, the maximum omethoate residues are estimated to be 0.008 mg/kg in ruminant liver, 0.016 mg/kg in poultry liver, and 0.0008 mg/kg in egg whites.

The Meeting estimated maximum residue levels for ruminant and poultry commodities at the limit of determination, 0.05* mg/kg, for dimethoate. The residues are likely to be much less than 0.05 mg/kg, but the Meeting considered 0.05 mg/kg to be the practical limit of quantification that can be routinely achieved in the laboratory. The Meeting also estimated STMRs of 0 mg/kg each for dimethoate and omethoate in the same commodities.

Processing studies

Processing studies were reported on oranges, tomatoes, potatoes, cotton seed, maize and wheat. The raw wheat and cotton seed contained no quantifiable residues and processing factors could not be determined for these crops. The processing factors and estimated STMRs for the other processed commodities were as follows.

Processed Commodity	Processing factor		Raw agricultural commodity STMR, mg/kg		Processed commodity STMR, mg/kg	
	Dimethoate	Omethoate	Dimethoate	Omethoate	Dimethoate	Omethoate
Orange juice	0.14	0.21	Not available	Not available		
Orange oil	0.19	0.07	Not available	Not available		
Tomato juice	0.11	0.17	0.21	0.05	0.03	0.009
Tomato purée	1.7	1	0.21	0.05	0.4	0.05
Tomato paste	2.9	1.4	0.21	0.05	0.6	0.07
Tomato ketchup	1.8	1	0.21	0.05	0.4	0.05
Potato granules (flakes)	0.12	-	0.01	0.01	0.002	0.002
Potato chips	0.12	-	0.01	0.01	0.002	0.002
Refined cotton seed oil	0.34	-	Not available	Not available		
Maize meal	0.34	-	Not available	Not available		
Maize grits	0.34	-	Not available	Not available		
Maize flour	0.34	-	Not available	Not available		
Maize starch	0.17	-	Not available	Not available		
Refined maize oil	0.17	-	Not available	Not available		

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels for dimethoate listed below (first table).

No data were submitted to support the existing MRLs for omethoate and the Meeting accordingly recommended their withdrawal (second table).

The Meeting concluded that the combined intakes of dimethoate and omethoate, adjusted as explained below (Dietary Risk Assessment), might exceed the ADI for dimethoate. The maximum residue levels estimated for dimethoate are therefore recommended for use as MRLMs, not MRLs.

Definition of the residue for compliance with MRLs: dimethoate.

Definition of the residue for the estimation dietary intake: sum of dimethoate and omethoate, each considered separately.

Dimethoate

Commodity		Recommended MRLM, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
FP 0226	Apple	W[1]	1	
VS 0621	Asparagus	0.05*	-	0.02
FI 0327	Banana	W	1 Po	
GC 0640	Barley	2	-	0.255
AS 0640	Barley straw and fodder, dry	-	-	0.495
VR 0574	Beetroot	W	0.2	
VB 0402	Brussels sprouts	1	2	0.065
VB 0041	Cabbages, Head[2]	2	2	0.46
VB 0403	Cabbage, Savoy	0.05*	-	0.02
VR 0577	Carrot	W	1	
MO 0812	Cattle, Edible offal of	0.05*	-	0
VB 0404	Cauliflower	0.5	-	0.065
VS 0624	Celery	W	1	
FS 0013	Cherries	2	2	0.06
FC 0001	Citrus fruits	W	2	
FB 0278	Currant, Black	W	2	
PE 0112	Eggs	0.05*	-	0
FB 0269	Grapes	2	1	0.48
DH 1100	Hops, dry	W	3	
VL 0480	Kale	W	0.5	
VL 0482	Lettuce, Head	0.5	2	0.02
MF 0100	Mammalian fats (except milk fats)	0.05*	-	0
MM 0096	Meat of cattle, goats, horses, pigs and sheep	0.05*	-	0
ML 0107	Milk of cattle, goats and sheep	0.05*	-	0
OR 0305	Olive oil, refined	W	0.05*	
FT 0305	Olives	W	1	
DM 0305	Olives, processed	W	0.05*	
VA 0385	Onion, Bulb	0.05*	0.2	0.02
FS 0247	Peach	W	2	
FP 0230	Pear	W[1]	1	
VP 0063	Peas (pods and succulent = immature seeds)	1	0.5	0.065
VO 0051	Peppers	W	1 Po	
FS 0014	Plums (including Prunes)	1	0.5	0.1
FP 0009	Pome fruits	0.5	-	0.065
VR 0589	Potato	0.05	0.05	0.01

Commodity		Recommended MRLM, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
	Potato granules			0.002
	Potato chips			0.002
PO 0111	Poultry, Edible offal of	0.05*	-	0
PF 0111	Poultry fats	0.05*	-	0
PM 0110	Poultry meat	0.05*	-	0
MO 0822	Sheep, Edible offal of	0.05*	-	0
GC 0651	Sorghum	0.01*	-	0.01
AF 0651	Sorghum forage (green)	-	-	0.01
AS 0651	Sorghum straw and fodder, dry	-	-	0.01
VL 0502	Spinach	W	1	
FB 0275	Strawberry	W	1	
VR 0596	Sugar beet	0.05	0.05	0.01
AV 0596	Sugar beet leaves or tops	0.1	1 T	0.05
VO 0448	Tomato	2	1 Po	0.21
JF 0448	Tomato juice			0.03
	Tomato purée			0.4
	Tomato paste			0.6
	Tomato ketchup			0.4
VR 0506	Turnip, Garden	0.1	0.5	0.1
VL 0506	Turnip greens	1	-	0.1
GC 0654	Wheat	0.2	-	0.09
AS 0654	Wheat straw and fodder, dry	10	-	2.23
VS 0469	Witloof chicory (sprouts)	W	0.5	

[1]Replaced by recommendation for Pome fruits
[2]Except Savoy cabbage

Omethoate

Commodity		Recommended MRLM (mg/kg)		STMR (mg/kg)
CCN	Name	New	Previous	
FP 0226	Apple	W	2	
FS 0240	Apricot	W	2	
VS 0620	Artichoke, Globe	W	0.5	
VS 0621	Asparagus	-	-	0.02
FI 0327	Banana	W	0.2*	
GC 0640	Barley	-	-	0.015
AS 0640	Barley straw and fodder, dry	-	-	0.03
VP 0061	Beans, except broad bean and soya bean	W	0.2	
VB 0400	Broccoli	W	0.2	
VB 0402	Brussels sprouts	W	0.2	0.03
VB 0403	Cabbage, Savoy	-	-	0.075
VB 0041	Cabbages, Head	W	0.5 T	0.165
VR 0577	Carrot	W	0.05	
VB 0404	Cauliflower	W	0.2	0.01
VS 0624	Celery	W	0.1	
GC 0080	Cereal grains	W	0.05	
FS 0013	Cherries	W	2	0.27
FC 0001	Citrus fruits	W	2	
VC 0424	Cucumber	W	0.2	
FB 0278	Currant, Black	W	2	
FB 0269	Grapes	W	2	0.11
DH 1100	Hops, dry	W	3	
VL 0480	Kale	W	0.2	
VL 0482	Lettuce, Head	W	0.2	0.03
VL 0483	Lettuce, Leaf	W	0.2	
VA 0385	Onion, Bulb	W	0.5	0.02

Commodity		Recommended MRLM (mg/kg)		STMR (mg/kg)
FS 0247	Peach	W	2	
FP 0230	Pear	W	2	
VP 0063	Peas (pods and succulent = immature seeds)	W	0.1	0.02
VO 0051	Peppers	W	1	
FS 0014	Plums (including Prunes)	W	1	0.05
FP 0009	Pome fruits	-	-	0.05
VR 0589	Potato	W	0.05	0.01
	Potato chips			0.002
	Potato granules			0.002
GC 0651	Sorghum	-	-	0.01
AF 0651	Sorghum forage (green)	-	-	0.01
AS 0651	Sorghum straw and fodder, dry	-	-	0.01
VL 0502	Spinach	W	0.1	
FB 0275	Strawberry	W	1	
VR 0596	Sugar beet	W	0.05	0.01
AV 0596	Sugar beet leaves or tops	W	1T	0.05
VO 0448	Tomato	W	0.5	0.05
JF 0448	Tomato juice	-	-	0.009
	Tomato purée			0.05
	Tomato paste			0.07
	Tomato ketchup			0.05
VR 0506	Turnip, Garden	W	0.2	0.1
VL 0506	Turnip greens	-	-	0.1
GC 0654	Wheat	-	-	0.01
AS 0654	Wheat straw and fodder, dry	-	-	0.08
VS 0469	Witloof chicory (sprouts)	W	0.5	

FURTHER WORK OR INFORMATION

Desirable

A plant metabolism study that provides detailed results and includes data on translocation is highly desirable. A root crop is suggested.

DIETARY RISK ASSESSMENT

The Meeting considered approaches to the dietary risk assessment of mixed residues of dimethoate and omethoate, resulting from the use of dimethoate. Noting that the ADI for omethoate had been withdrawn by the JMPR (Evaluations 1996, Part II – Toxicological), the Meeting considered that it would be inappropriate to rely on the previous omethoate ADI in the dietary risk assessment. However, the Meeting noted that the toxicity of omethoate was generally about ten times that of dimethoate across a range of toxic endpoints dependent upon cholinesterase inhibition, reflecting the fact that it is an active metabolite of dimethoate. The Meeting considered that it would be appropriately conservative to multiply the omethoate component of the residue by a tenfold factor, for comparison of the combined residues with the current dimethoate ADI.

STMRs for dimethoate derived from residues of dimethoate in or on commodities have been combined with STMRs for omethoate derived from residues of omethoate arising from the use of dimethoate multiplied by a factor of 10. Dietary intakes estimated from the combined adjusted STMRs were compared with the dimethoate ADI (0.002 mg/kg bw).

The International Estimated Daily Intakes for the GEMS/Food European diet was 140% of the ADI. International Estimated Daily Intakes for the other four GEMS/Food regional diets were in the range of 10 to 80% of the ADI. The Meeting concluded that the combined dietary intakes of dimethoate and omethoate residues, expressed as described above, may exceed the ADI for dimethoate for the European diet. The recommended MRLs are therefore designated as MRLMs.

The Meeting identified wheat, tomatoes and potatoes as the main contributors to the dietary exposure.

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DINOCAP (087)

EXPLANATION

Dinocap is a contact fungicide used to control powdery mildew on many crops and is also used as a non-systemic acaricide. It has been evaluated several times by the JMPR. In 1992 the JMPR recommended withdrawal of the temporary MRLs and in 1993 the CAC agreed to delete dinocap from the Codex list. In the present evaluation dinocap is therefore considered as a new compound.

The manufacturer has provided residue data on grapes, apples, cucurbits, strawberries, peppers, peaches, apricots and tomatoes for review by the present Meeting.

IDENTITY

ISO common name: dinocap

Chemical name

IUPAC: 2,6-dinitro-4-octylphenyl crotonates and 2,4-dinitro-6-octylphenyl crotonates in which "octyl" is a mixture of 1-methylheptyl, 1-ethylhexyl and 1-propylpentyl groups.

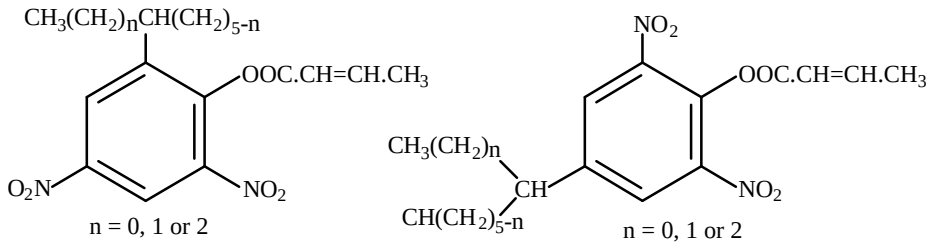
CA: 2-butenoic acid, 2-isooctyl-4,6-dinitrophenyl ester and 2-butenoic acid, 4-isooctyl-2,6-dinitrophenyl ester.

CAS No.: [39300-45-3] (for isomer mixture)

CIPAC No.: 98

Synonyms: RH-23,004, DNOPC

Structural formula:



2,4-dinitro-6-octyl (2,4-DNOPC)

2,6-dinitro-4-octyl (2,6-DNOPC)

Molecular formula: $C_{18}H_{24}N_2O_6$

Molecular weight: 364.18

Physical and chemical properties

Technical material

Technical dinocap consists of a mixture of the 2,4-dinitro-6-octyl isomers and 2,6-dinitro-4-octyl isomers (2,4-DNOPC and 2,6-DNOPC) in a ratio of about 2,6:1.

Vapour Pressure:

Temperature (°C)	Vapour pressure (Pa)
20	5.64×10^{-7}
25	3.33×10^{-6}
30	8.29×10^{-6}

Purity: 92% (minimum)

Melting point: >-25ºC (freezing point -6.5ºC)

Octanol/water partition coefficient at 20.5ºC (Betteley, 1997a):
log P_{ow}: 6.55 and 6.45 for the 2,4-dinitro and 2,6-dinitro isomers respectively.
log P_{ow}: 3.85 and 3.93 for the corresponding phenols.

Solubility: dinocap is soluble in most organic solvents in water at 20ºC (Betteley, 1994):
1.5×10^{-4} g/l for 2,4-dinitro isomer
1.15×10^{-4} g/l for 2,6-dinitro isomer

Hydrolysis (Winwick, 1998a):

pH	Test substance	Half-life, days	
		20ºC	30ºC
4	2,4-DNOPC	447	91.4
	2,6-DNOPC	114	55
7	2,4-DNOPC	30.4	30.5
	2,6-DNOPC	16.2	14.8
9	2,4-DNOPC	9.25	2.34
	2,6-DNOPC	3.65	1.01

Relative density: 1.13

Photolysis (Winwick, 1998b): The 2,4- and 2,6-isomer mixtures had half-lives in aqueous buffer solutions at PH 4 of 0.63 and 0.73 days respectively

Formulations

Dinocap is available as an emulsion concentrate containing 350 g ai/l and a wettable powder containing 185 g ai/kg. Other formulations have been developed in which dinocap is mixed with other fungicides.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Rats and mice. In a rat feeding study in 1970 one adult male and one adult female were dosed daily for seven days with 11.7 mg [^{14}C]2,4-DNOPC (the main component of commercial dinocap). The rats were killed 6 hours after the final dose. Dinocap residues were rapidly eliminated in the faeces and urine of both the male and female, the excreted radioactivity being 72.9% and 71.9% of the dose in the male and female respectively. Residues did not appear to accumulate in any tissues except in the digestive tract, which contained 7.6% and 11.3% of the administered dose in the male and female respectively (Honeycutt and Garstka, 1976a).

Table 1. Distribution of radioactivity in rats (Honeycutt and Garstka, 1976a).

Sample	^{14}C, % of administered dose	
	Male	Female
Urine	14.9	19.9
Faeces	58.0	52.0
All tissues except digestive tract	2.9	3.8
Unwashed digestive tissue	7.6	11.3
Exhaled CO_2	0.02	0.02
Cage washing	11.1	5.7
Total	94.5	92.7

The urine and faeces were analysed to identify the main metabolites, using GLC, mass spectrometry and nuclear magnetic resonance. The two main extractable metabolites of 2,4-DNOPC in rat urine were identified as 2,4-dinitro-6-(1-methyl-7carboxyheptyl)phenol (27% of the total ^{14}C in the urine) and 2,4-dinitro-6-(1-methyl-5-hydroxyheptyl)phenol (37%). Two minor metabolites in the faeces were identified as 2,4-dinitro-6-(2-octyl)phenol (2,4-DNOP, 5% of the total ^{14}C in the faeces) and 2,4-dinitro-6-(1-methyl-5-hydroxyheptyl)phenol (4%) (Honeycutt and Garstka, 1976b).

Another study of pharmacokinetics and metabolism was conducted with male mice and rats dosed with [^{14}C]2,4-DNOPC, the mice at 0.5, 3, and 25 mg/kg and the rats at 3, 50, and 100 mg/kg. Urine and faeces were collected for 24 hours after dosing and analysed by HPLC with UV spectrometric detection (Udinsky *et al.*, 1986). The metabolic profiles in mice and rats were different. In mice, three metabolite peaks dominated the chromatograms and at least five other compounds were present in significant amounts, whereas rat urine showed only two major metabolite peaks. Incubation of urine from each species with three types of glucuronidase and arylsulfatase had little effect on the HPLC profile, suggesting that conjugation did not contribute significantly to producing the main metabolites in the urine.

Most of the metabolites in mouse urine were substituted at the phenolic group, whereas the main metabolites in the rat urine were free phenols. In the mouse urine, the radioactivity decreased from 61% to 24% of the dose as the dose increased from 0.5 to 25 mg/kg. By contrast, no significant dose-related trends were evident in the excretion of total radioactivity or individual metabolites in rat urine.

In another study to elucidate the metabolism of dinocap in rats and mice after oral exposure, Potter (1996) treated six male rats and 15 male mice with single gavage doses, of 2,4-DNOPC labelled with ^{13}C and ^{14}C, the rats at 100 mg/kg and mice at 25 mg/kg. The 2-4-dinitro mixture was selected because it is the main component of the technical material and is representative of dinocap metabolism. Urine was collected for 24-hour periods ending at 24, 48, 72 and 96 hours after dosing. The metabolites were identified by HPLC and mass spectrometry and the radioactivity was quantified by LSC.

Only the urinary metabolites were examined since they appear to be a more complex mixture than those in the faeces. DNOPC was rapidly metabolized and excreted into the urine of both rats and mice. Approximately 30.9% of the administered DNOPC was excreted in rat urine and 58.3% in mouse urine. In both more than 90% of the urinary ^{14}C was excreted within 24 hours after administration, so only the 0-24 h urine was analysed.

Twelve urinary metabolites from rats and thirteen from mice were identified and quantified, accounting for 99% of the ^{14}C in rats and approximately 89% of that in mice. The structures of the identified metabolites are shown in Figures 1 and 2.

Figure 1. Urinary metabolites of DNOPC in mice.

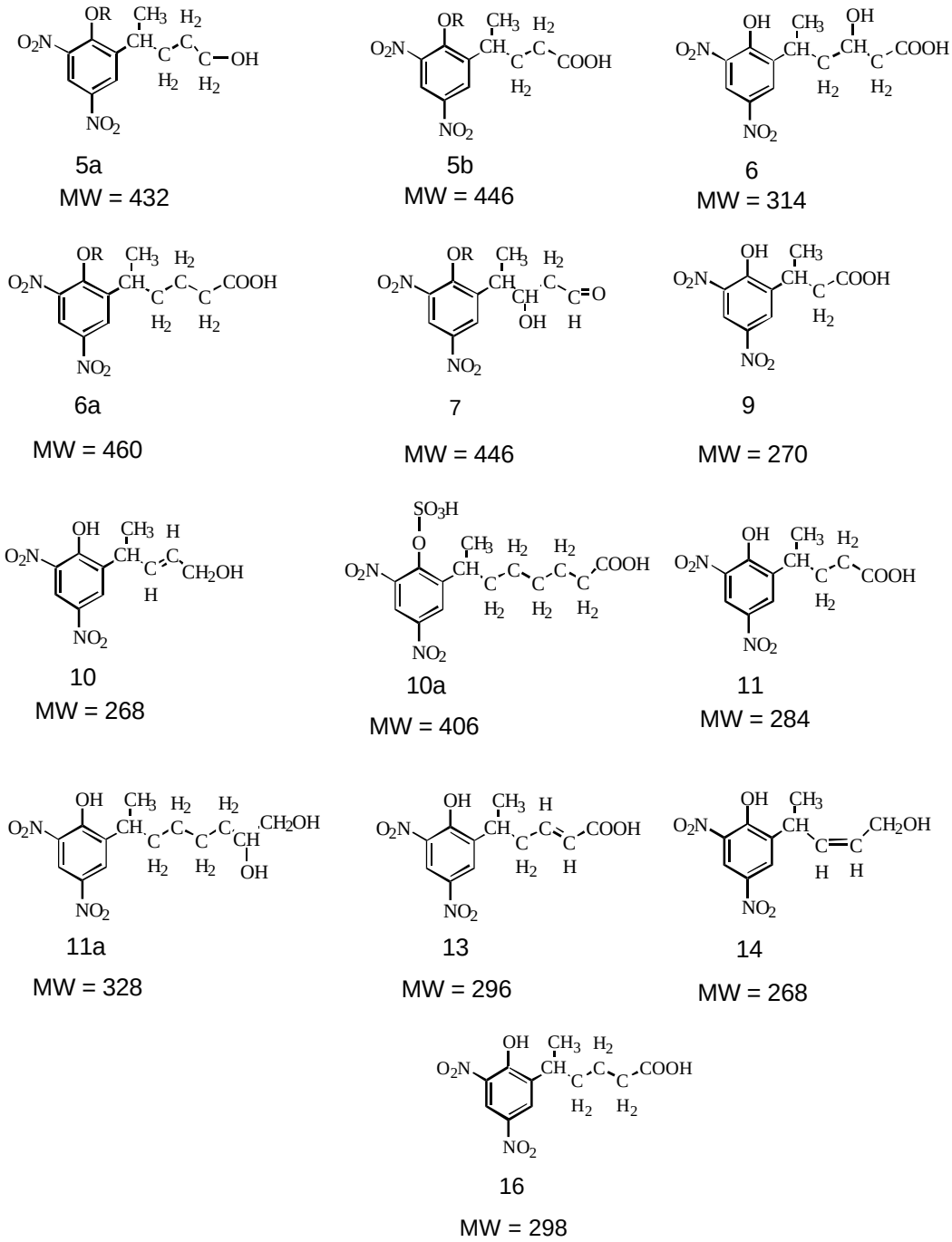
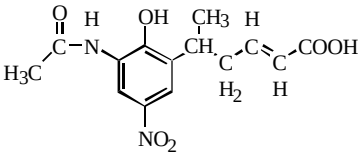


Figure 2. Urinary metabolites of DNOPC in rats.



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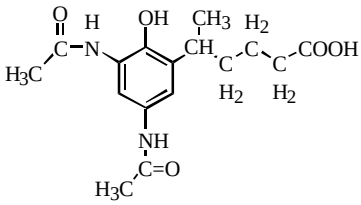

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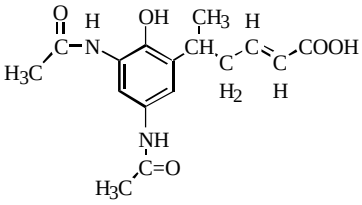

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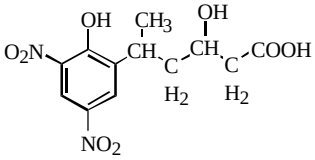

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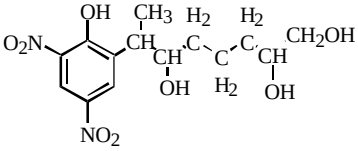

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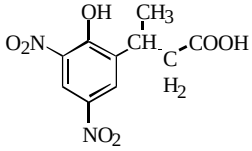

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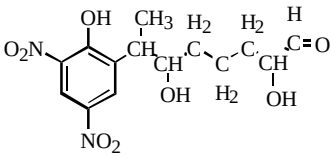

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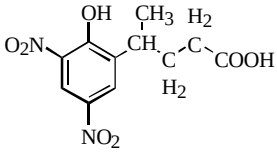

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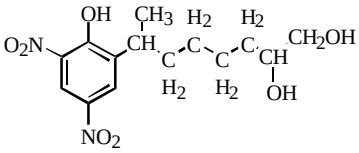

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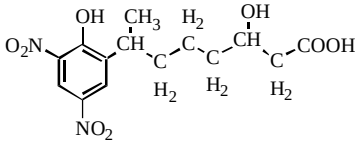

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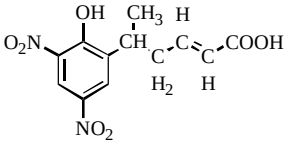

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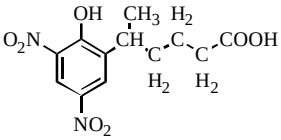

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The metabolites appear to be produced by following processes.

1. Fatty acid β-oxidation: 5 metabolites in rats (67.3% of the ^{14}C); 5 metabolites in mice (45%).
2. Fatty acid β-oxidation: 1 metabolite in rats (18% of the ^{14}C); 3 metabolites in mice (28%).
3. In rats only, fatty acid β-oxidation followed by reduction of the nitro groups and *N*-acetylation: 3 metabolites (4.5%).
4. In mice only, fatty acid α- and β-oxidation followed by conjugation: 4 metabolites (6.5%), one a sulfate conjugate.
5. Multiple mono-oxygenation: 3 metabolites in rats (4.37%); 1 metabolite in mice (1.13%).

The proposed schemes for DNOPC metabolism in rats and mice are shown in Figures 3 and 4 respectively.

Table 2. DNOPC metabolites identified in rat and mouse urine.

Metabolite	% of total rat urinary metabolites	% of total mouse urinary metabolites
5-(3-acetamido-2-hydroxy-5-nitrophenyl)hex-2-enoic acid	2.12	
5-(3,5-diacetamido-2-hydroxyphenyl)hexanoic acid	2.39	
4-(2-hydroxy-3,5-dinitrophenyl)pentanol, phenolic conjugate		1.73
4-(2-hydroxy-3,5-dinitrophenyl)pentanoic acid, phenolic conjugate		1.73
5-(2-hydroxy-3,5-dinitrophenyl)-3-hydroxyhexanoic acid	4.21	8.09
5-(2-hydroxy-3,5-dinitrophenyl)hexanoic acid, phenolic conjugate		1.56%
7-(2-hydroxy-3,5-dinitrophenyl)octane-1,2,6-triol	1.26	
4-(2-hydroxy-3,5-dinitrophenyl)-3-hydroxypentanal		1.49
3-(2-hydroxy-3,5-dinitrophenyl)butanoic acid	1.83	6.0
7-(2-hydroxy-3,5-dinitrophenyl)-2,6-dihydroxyoctanal	1.56	
4-(2-hydroxy-3,5-dinitrophenyl)pent-2-enol		1.24
7-(2-hydroxy-3,5-dinitrophenyl)octanoic acid, phenolic sulfate		1.23
4-(2-hydroxy-3,5-dinitrophenyl)pentanoic acid	17.97	23.9
7-(2-hydroxy-3,5-dinitrophenyl)octane-1,2-diol	1.55	1.13
7-(2-hydroxy-3,5-dinitrophenyl)-3-hydroxyoctanoic acid	0.42	
5-(2-hydroxy-3,5-dinitrophenyl)hex-2-enoic acid	2.66	8.95
4-(2-hydroxy-3,5-dinitrophenyl)pent-2-enol		2.78
5-(2-hydroxy-3,5-dinitrophenyl)hexanoic acid	58.2	21.92
Total	94.17	81,75

Figure 3. Proposed metabolic pathways of dinocap in rats.

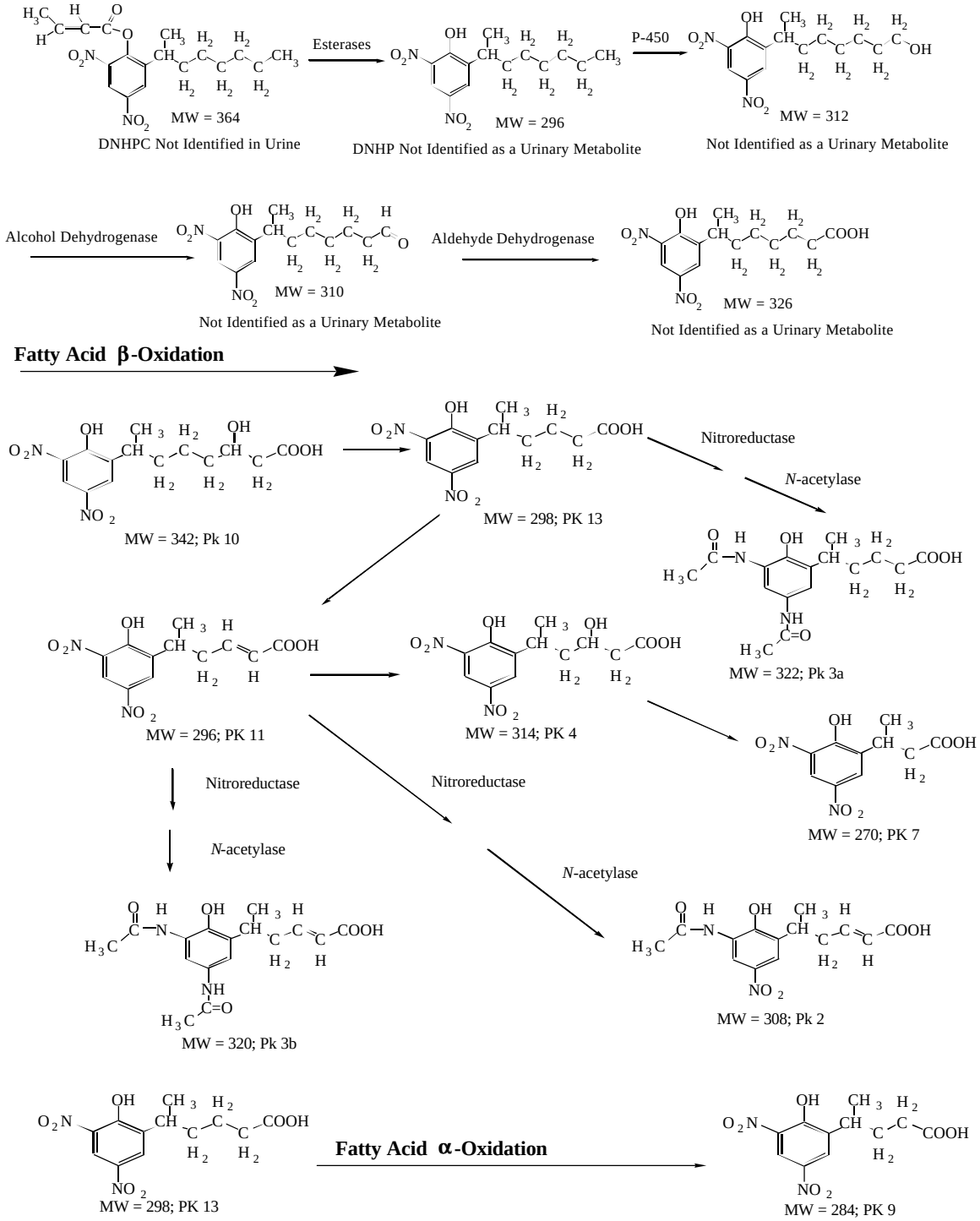
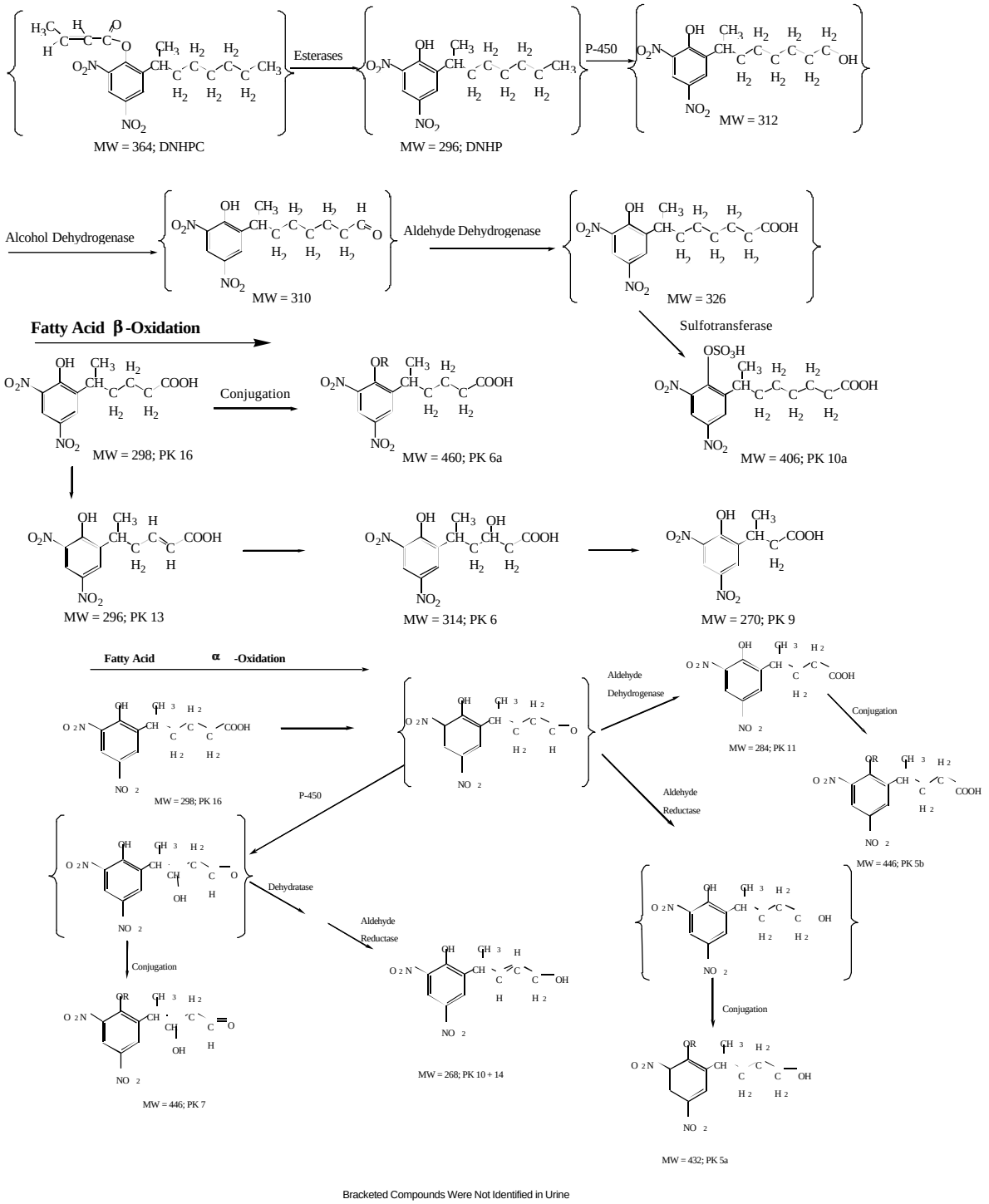


Figure 4. Proposed metabolic pathways of dinocap in mice.



Cows. Three cows were dosed by gelatine capsule containing sugar cane with dinocap technical uniformly labelled with ^{14}C in the phenyl ring. The five-week study was divided into three periods, one week with all cows dosed with control capsules, the next two weeks with the three cows dosed at a level equivalent to 0.1 ppm in the diet and the final two weeks during which the cows were dosed at 0, 0.03 and 1.0 ppm (Graham and Bornak, 1972). The dose regimen is shown in Table 3.

Table 3. Cows, dose regimen.

Week	Dose equivalent, ppm in the diet			
	Control	Cow 1	Cow 2	Cow 3
1	0	0	0	0
2	0	0.1	0.1	0.1
3	0	0.1	0.1	0.1
4	0	0	0.3	1.0
5	0	0	0.3	1.0

Samples of urine and faeces were taken for 24-hour periods during the second week of each test period. Milk samples were collected daily. Cows 2 and 3 were slaughtered at the end of the study and cow 1 at the end of week 3. Aliquots of milk and urine were radio-assayed and the ^{14}C in the organs and tissues was measured by combustion and LSC. No activity was detectable in any muscle, kidney, liver, fat or milk samples (LOD 0.04 mg/kg, except fat 0.08 mg/kg).

The main route of elimination was in the faeces with small amounts in the urine. Table 4 shows the dinocap residues in the faeces and urine at 23 and 37 days.

Table 4. Dinocap residues in urine and faeces of dosed cows.

Day	Cow	^{14}C, mg/kg as dinocap and % of TRR				Urine + faeces, % of TRR
		Urine		Faeces		
		mg/kg	% of TRR	mg/kg	% of TRR	
23	1	0.008	1.5	0.072	130	131.5
	2	ND		0.073	100	100
	3	0.015	7.9	0.041	62	69.9
37	2	0.02	4.4	0.2	105	109.4
	3	0.06	3.1	0.47	69	72.1

Samples were refrigerated rather than frozen before analysis and the specific activity of the test mixture was low (0.75 mCi/g).

Bioaccumulation in fish. The uptake and bioconcentration of [^{14}C]2,4-DNOPC by bluegill sunfish were studied in a flow-through system for 28 days of exposure at levels of 0.2 µg/l and 1 µg/l, followed by 14 days depuration. Concentrations of 2,4-DNOPC in the water were measured by LSC. Fish were taken for analysis at 0, 1, 3, 7, 14, 21 and 28 days during the exposure phase and 1, 3, 7, 10 and 14 days during the depuration phase. Total radioactive residues were determined in edible and inedible tissues and in whole fish, and the uptakes and bioconcentration factors determined. Radioactive residues increased within 1 to 3 days to steady levels which were maintained throughout the exposure period at both concentrations (Corden, 1998).

The ^{14}C residues and the calculated bioconcentration factors (BCFs) at the low and high concentrations are shown in Tables 5 and 6.

Table 5. Residues and bioconcentrations factors in fish exposed to 0.2 µg dinocap/l (Corden, 1998).

Day	Water, µg/l	Edible, µg/g	Edible, BCF	Inedible, µg/g	Inedible, BCF	Whole fish, µg/g	Whole fish, BCF
Exposure phase							
1	0.19	0.016	84	0.25	1320	0.15	790
3	0.22	0.027	120	0.27	1200	0.18	820
7	0.21	0.014	67	0.39	1900	0.2	950
14	0.2	0.027	140	0.33	1700	0.19	950
21	0.19	0.034	180	0.24	1300	0.13	680
28	0.2	0.033	170	0.43	2200	0.22	1100
Depuration phase							
1	nd	0.014		0.14		0.079	
3	nd	0.009		0.033		0.02	
7	nd	0.006		0.02		0.014	
10	nd	0.006		0.018		0.012	
14	nd	0.004		0.015		0.009	

nd: <0.004 µg/l

Table 6. Residues and bioconcentrations factors in fish exposed to 1.0 µg dinocap/l (Corden, 1998).

Day	Water, µg/l	Edible, µg/g	Edible, BCF	Inedible, µg/g	Inedible, BCF	Whole fish, µg/g	Whole fish, BCF
Exposure phase							
1	1.07	0.18	170	0.98	920	0.54	510
3	1.04	0.22	210	1.01	970	0.65	630
7	0.96	0.08	83	1.31	1400	0.69	720
14	0.97	0.17	180	1.19	1200	0.74	760
21	0.99	0.12	120	1.2	1200	0.65	660
28	0.98	0.24	250	1.63	1700	0.94	960
Depuration phase							
1	nd	0.1		0.87		0.48	
3	nd	0.049		0.16		0.1	
7	nd	0.043		0.11		0.073	
10	nd	0.03		0.092		0.059	
14	nd	0.028		0.07		0.048	

nd: <0.004 µg/l

The elimination half-lives calculated for edible and inedible tissues and whole fish were as follows.

	Elimination half-life, days		
	Edible tissue	Inedible tissue	Whole fish
Low dose	0.7	0.7	0.6
High dose	0.6	0.9	0.9

Plant metabolism

Metabolism studies with [^{14}C]2,4-DNOPC were conducted on apples, cucumbers and squash.

Apples. An apple tree was treated with a single foliar application of an EC formulation containing 45.6% ai at a rate equivalent to 1.96 kg ai/ha, four times the normal maximum application (0.49 kg ai/ha). Two untreated trees were used as control (Dohmeier, 1993).

Apples and leaves were harvested from treated and control trees on the day of application, both before and after treatment, and after 7, 14, and 21 days. The samples were stored frozen for one year before analysis. Half of each fruit sample was analysed as whole fruit, and the other half peeled and the peel and pulp analysed separately. The total radioactivity in the samples was determined by radiocombustion with the results shown in Table 7.

Table 7. Radioactivity in apples treated with dinocap.

PHI	^{14}C, mg/kg as dinocap				
	Whole fruit	Pulp	Peel	Pulp + peel	Leaves
0	1.37	0.25	16.7	2.9	195
7	2.38	0.13	12.8	2.3	113
14	1.67	0.15	12.97	2.2	76.3
21	1.57	0.12	10.1	1.57	70.6

More than 92% of the radioactivity at each PHI was associated with the peel. The samples were extracted with methanol which extracted more than 90% of the radioactivity from the day 0 samples and 40-60 % from the aged samples. When the residues extracted by methanol were partitioned with hexane and ethyl acetate most of the radioactivity (80-90%) passed into the hexane. An additional 30-45% of the total radioactivity in the aged fruit samples could be released with 0.1 M NaOH in methanol. After adjusting the pH of the extract 80-95% of this radioactivity could be partitioned into ethyl acetate. The total radioactivity recovered in the neutral and alkaline methanolic extracts was more than 80% in all cases. The results are shown in Table 8.

Table 8. Distribution of radioactivity in extracts of apple peel and whole apples.

Fraction/ extract	% of total radioactivity							
	0 days		7 days		14 days		21 days	
	Peel	whole fruit	Peel	Whole fruit	Peel	Whole fruit	Peel	Whole fruit
Hexane/MeOH	88.1	91.8	41.6	46.2	26.3	25.7	20.2	25.2
EtOAc/MeOH	8.2		14.1	10.2	12.1	11.8	11.3	10.3
Aqueous/MeOH	0.4	0.4	3.8	5.3	6.3	5.4	8.3	9.6
EtOAc/MeOH NaOH	_	_	31.7	19.0	41.1	40.1	45.1	32.5
Aqueous/MeOH/ NaOH .	_	_	1.3	2.0	2.1	2.3	2.3	8.1
Post-extraction solid	3.3	2.8	7.5	9.1	12.1	14.3	12.8	13.2

Peel samples were analysed six months after the whole fruit, showing that the nature of the residues did not change dramatically during storage.

The parent 2,4-DNOPC and the metabolite 2,4-DNOP were identified in the hexane and ethyl acetate fractions of the fruit extracts by TLC and reverse phase HPLC. The parent decreased from 73% of the total radioactivity at day 0 to 23% at day 7, 11% at 14 and 8% at 21 days.

Table 9. Residues of 2,4-DNOPC and 2,4-DNOP in fruit.

PHI, days	^{14}C, mg/kg as 2,4-DNOPC	
	2,4-DNOPC	2,4-DNOP
0	2.12	0.06
7	0.52	0.08
14	0.25	0.05
21	0.12	0.03

The half-life of 2,4-DNOPC was 5.2 days, showing that it was rapidly degraded on the fruit surface. The phenol metabolite was present at low concentrations, 2-4% of the total radioactivity at all sampling intervals, and appeared to be quickly metabolized to many polar compounds, none of them individually accounting for more than 7% of the total radioactivity. They could not be identified.

An additional study was conducted to provide information on the identity of the unidentified metabolites of 2,4-DNOPC in apples (Dohmeier, 1994). The test substance was 2,4-DNOPC, uniformly labelled with ^{13}C and ^{14}C in the phenyl ring, applied to a single apple tree as an EC formulation at a rate of 1.96 kg ai/ha.

Apple peel samples were extracted three times with MeOH in a blender and the extract was partitioned with hexane. The post-extraction solids were treated with methanolic NaOH solution to release additional radioactivity. After acidification, the methanolic base extract was partitioned with ethyl acetate.

The hexane fraction was cleaned up by silica gel chromatography and the residues eluted with increasing concentrations of methanol in methylene chloride. Fractions containing radioactivity but not 2,4-DNOPC or 2,4-DNOP were methylated and fractionated by TLC and HPLC and the purified components analysed by GC-MS. The resulting mass spectra allowed tentative structures to be proposed.

The methanolic base extracts were evaporated, and the solutes redissolved in ethyl ether and chromatographed on silica gel. The residues were eluted with increasing concentrations of ethyl acetate in ethyl ether followed by increasing concentrations of methanol in ethyl acetate. Individual fractions were analysed by normal and reverse-phase TLC.

As photolysis was identified as a possible degradation pathway for 2,4-DNOPC on the apple surface, a mixture of ^{14}C- and ^{13}C-labelled 2,4-DNOPC was irradiated with a Hanau “Sun test” lamp for 26 hours. The photolysis products were methylated and cleaned up on Florisil columns and by TLC and HPLC. The isolated products were analysed by GC-MS, and their spectra compared with the spectra of the metabolites isolated from apple peel.

Photolysis appears to be a significant pathway for the degradation of 2,4-DNOPC in plants: two metabolites identified in apple peel were also identified as photoproducts.

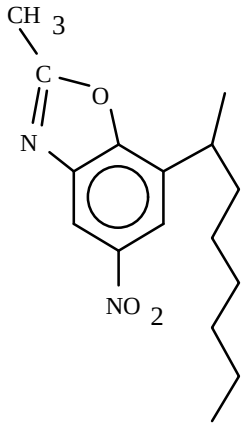
The structures of five metabolites identified by GC-MS are shown in Figure 5.

The proposed pathway for their formation involves reduction of a nitro group to the amine and hydrolysis of the crotonyl ester to the phenol. Metabolites are then formed by reaction of the amine with formic or acetic acid to form amides, or by intramolecular transfer of the crotonyl group to form the crotonamide. Ring closure of the amides then forms benzoxazoles. The fraction containing most radioactivity was the ethyl acetate extract of the alkaline methanol extract. Individual metabolites could not be isolated. The influence of pH on the partitioning of the radioactivity in this fraction indicated that one or both nitro groups had been reduced to the corresponding amine. The amines could readily form conjugates with acids to form amides. Hydrolysis of the fraction with NaOH produced more polar radioactive residues, consistent with hydrolysis of amides to amines.

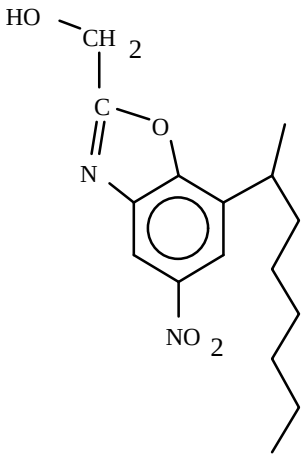
Table 10. Metabolites isolated from hexane fraction from MeOH extract of apple peel.

Metabolite	Conc., mg/kg as dinocap	% of total radioactivity
A	0.006	0.3
B	0.001	0.1
C	0.002	0.1
D	0.007	0.4
E	0.001	0.1

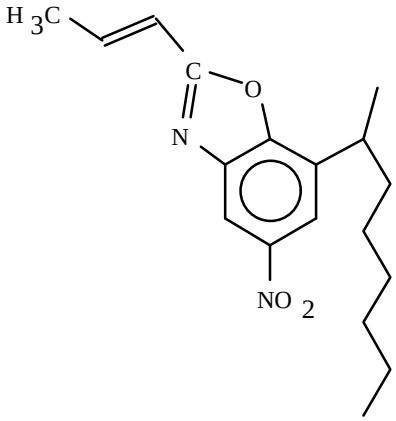
Figure 5. Metabolites identified in apples (Dohmeier, 1994).



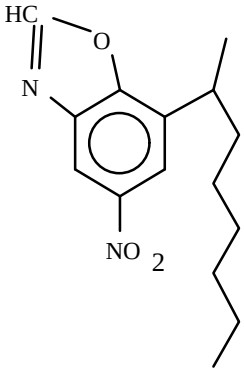
2-methyl-5-nitro-7-(2-octyl) benzoxazole



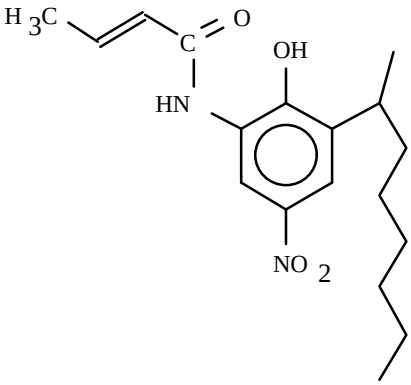
2-(hydroxymethyl)-5-nitro-7-(2-octyl) benzoxazole



2-(1-propenyl)-5-nitro-7-(2-octyl) benzoxazole



5-nitro-7-(2-octyl) benzoxazole



2-hydroxy-5-nitro-3-(2-octyl)-phenyl crotonamide

Cucumbers. The distribution and rate of decrease of residues after a single treatment with [^{14}C]2,4-DNOPC at 0.56 kg ai/ha were studied. Samples of leaves, stems and soil were taken 0, 8, 21, 34, 48, and 63 days after treatment, and of fruits at 21, 48 and 63 days. The samples were assayed by combustion and LSC (Honeycutt, 1976a).

Table 11. Residues in cucumbers treated with [^{14}C]2,4-DNOPC.

PHI	Residues, mg/kg as DNOPC						
	Leaves	Stems	Flowers	Immature fruit	Mature Fruit		
					Peel	Pulp	Whole
0	38.2	3.6	-	-			
8	28.9	3.9	5.4	-			
21	4.1	0.7	1.0	1.0			
34	2.5	0.6	0.5	-			
48	1.1	0.4		0.2	0.15	0.11	0.16
63	1.4	0.5					0.09

The ^{14}C residues dissipated rapidly from the cucumber leaves and stems, with half-lives of 11.8 and 18.8 days respectively. The residues in the soil in which the cucumbers were grown dissipated at a much lower rate (0.45 mg/kg at day 0 and 0.31 mg/kg at final harvest in the top 2.5 cm).

Cucumber leaves from day 8 were analysed by TLC for metabolites. Twenty eight metabolites were detected but only the parent compound and DNOP were identified.

Table 12. Relative levels of dinocap and metabolites in cucumber leaves after 8 days.

Metabolite	% of extractable residue	% of total residue
Two unidentified	0.9	0.4
2,4-DNOPC	0.7	0.3
2,4-DNOP	5.7	2.4
Unidentified	19.4	8.2
Unidentified	3.9	1.6
Unidentified	3.1	1.3
12 polar metabolites	66.1	27.8
Unextractable	-	58.0

Cucumbers harvested at 48 and 63 days were extracted with acetone and the post-extraction solid analysed by combustion and radio-assay. The acetone extract was redissolved in acetone/water and partitioned twice with methylene chloride. The organic phases were combined and concentrated to dryness, and the residue redissolved in petroleum ether/methylene chloride. The concentrated extract was analysed by TLC and radioactive bands quantified by LSC (Honeycutt, 1976a). The results are shown in Table 13.

Table 13. Relative levels of dinocap and metabolites in cucumbers after 48 and 63 days (Honeycutt, 1976a)

Compound or fraction	% of total ^{14}C	
	48 days	63 days
2,4-DNOPC	0.7	3.5
2,4-DNOP	0.6	4.5

Compound or fraction	% of total ^{14}C	
	48 days	63 days
Unidentified	0.9	1.3
Unidentified	0.6	0
Unidentified	0.4	1.5
Unidentified	0.6	2.3
Unidentified	0.9	3.3
Unidentified	1.1	3.8
Polar metabolites	1.4	5
Aqueous fraction	40	35
Unextractable	52	40

Squash. Formulated [^{14}C]2,4-DNOPC was applied three times at a rate of 0.56 kg ai/ha to two rows of squash (Early Straight Neck variety). The squash plants were in bloom at the time of the first treatment. Whole plants were sampled 0, 7, 17, 25, 32, 40, 53, 66 and 80 days after the first application (0, 8, 15, 23, 36, 49 and 63 days after the final application). Fruit samples were taken from 15 days after the final application. Soil cores taken at three different places in the plot at each sampling were sectioned in 0-2.5, 2.5-7.6, and 7.6-15.2 cm depths and the three sections at each depth pooled.

Samples were assayed for radioactivity by combustion and LSC (Honeycutt and Garstka, 1976d). The results are shown in Table 14.

Table 14. Residues in squash treated three times post-emergence with [^{14}C]2,4-DNOPC.

Days after 1st treatment	^{14}C, mg/kg as dinocap					
	Leaves	Root and stems	Immature whole fruit	Mature fruit		
				Peel	Pulp	Whole
0	4.2					0.14
7 (after 2nd treatment)	44.0	8.2				0.36
17 (after 3rd treatment)	34.8	3.1				0.11
25	17.5	3.3				0.35
32	12.2	1.9		0.58	0.15	0.25
40	11.9	1.8		0.19	0.08	0.21
53	4.2	1.5	0.02	0.70	0.19	0.09
66	2.7	0.7	0.04	0.15	0.06	0.18
80	1.7	0.7	0.06			

The half-life of the radioactivity in the leaves was 8 days. The leaves sampled at this time were extracted twice with benzene and the fruit twice with acetone. The fruit extract was partitioned 3 times with petroleum ether/methylene chloride, and the organic phases combined and dried with sodium sulfate. The organic and aqueous phases from the fruit extraction were radio-assayed. The organic extracts from the leaves and fruit were concentrated and analysed by TLC. Radioactive bands on the TLC plates were visualized by autoradiography. The radioactivity was eluted from each band with acetone or methanol and the eluates radio-assayed.

Table 15. Extractable radioactivity in fractions from extracts of squash leaves and fruit 8 days after last of 3 applications of [^{14}C]2,4-DNOPC.

Fraction	Sample	% of TRR
Benzene extract	leaves	14
Unextractable	leaves	86
Acetone extract	fruit	42
Unextractable	fruit	58
Organic phase[1]		45
Aqueous phase[1]		44

[1] From partition of acetone extract

2,4-DNOP was the main metabolite in the leaves and was also found in the fruit. About 6 unidentified metabolites were found in the fruit and 10 in the leaves, none of which individually accounted for more than 10% of the TRR.

The distribution of radioactivity in the fruit and leaves 8 days after the last treatment is shown in Table 16.

Table 16. Radioactive residues in extracts of squash fruit and leaves, 8 days after last application of [^{14}C]2,4-DNOPC.

Sample	Compound	% ^{14}C	% of ^{14}C
Fruit	2,4-DNOP	3	1.3
	2,4-DNOPC	14	5.9
	Unidentified	1	0.4
	Unidentified	1	0.4
	Unidentified	2	0.8
	Two unidentified	13	5.5
	Organosoluble polar metabolites	13	5.5
	Water-soluble polar metabolites	50	21
	Unextractable	-	57.6
Leaves	2,4-DNOP	34	4.8
	2,4-DNOPC	23	3.2
	Unidentified	4	0.6
	Unidentified	2	0.3
	Unidentified	2	0.3
	Unidentified	2	0.3
	Two unidentified	7	1.0
	Two unidentified	3	0.4
	Unidentified	4	0.6
	Organosoluble polar metabolites	12	1.7
	Unextractable	-	86.0

The ^{14}C residues in the top section of the soil (0-2.5 cm) decreased from 0.43 mg/kg after the last treatment to 0.40 mg/kg 63 days later. The ^{14}C residues in the other sections were low.

A comparative TLC study of metabolites of [^{14}C]2,4-DNOPC from rat urine and faeces, cucumbers and squash was conducted to determine whether any metabolites not found in either rat urine or faeces were among the metabolites in squash or cucumbers (Honeycutt, and Garstka, 1976c). The metabolites from cucumbers and squash were very similar in their TLC behaviour. The metabolites from

rat faeces were closer in their TLC behaviour to those from cucumber and squash than to those from rat urine. The urine metabolites were the most polar of any from the four sources tested. ^{14}C photoproducts of DNOPC from squash leaf surfaces were similar in polarity to cucumber, squash and faeces metabolites.

Environmental fate in soil

A study in 1971 determined the rate of dissipation of dinocap in silt loam soil, the effect of a higher than normal application rate on overall microbial activity and the activity of dinocap *in vitro* against selected soil micro-organisms. The study was not according to FAO Guidelines, but showed that after 170 days 34.7% of the initial radioactivity was trapped as $^{14}C0_2$ and 53.3% was accounted for in the soil. The rate of degradation of dinocap gradually decreased with time, which was attributed to the depletion of substrate and the depressed rate of microbial activity (Fisher, 1971).

To measure the decline of ^{14}C-dinocap from greenhouse-aged soil and to characterize the bound ^{14}C residues, sandy loam and silt loam soils were fortified at 5 and 10 mg/kg in open containers in the greenhouse (24-32ºC) and sampled at frequent intervals for 270 days. A portion of the silt loam soil was transferred at 30 days from aerobic to anaerobic conditions for an additional 60 days to compare aerobic and anaerobic degradation. Soil samples were analysed by TLC, and bound ^{14}C residues characterized as associated with the fulvic or humic acid components of the soil organic matter (Honeycutt *et al.*, 1976). The characteristics of the soils are shown in Table 17 and the residues in Table 18.

Table 17. Physical properties of soils.

	Sandy loam	Silt loam
Organic matter, %	2.59	3.83
pH	5.5	5.5
Sand, %	71.0	13.0
Silt, %	22	65
Clay, %	7	22
CEC meq/100g	7	10.1
Moisture capacity, %	12.5	15.6

Table 18. Residues in soils fortified at 5 and 10 mg/kg (Honeycutt *et al.*, 1976).

Day	^{14}C, mg/kg as dinocap		
	Silt loam, 5 mg/kg	Sandy loam, 5 mg/kg	Sandy loam, 10 mg/kg
0	4.4	4.6	8.8
15	5.1	3.9	7.7
30	4.1	4.3	8.0
60	3.7	4.2	7.1
90	2.8	2.8	4.0
120	2.5	2.5	4.8
187	1.9	2.6	4.7
270	2.5	2.5	5.0

The half-lives for the disappearance of the radioactivity from the silt loam and sandy loam treated with 5 mg/kg were 134 and 199 days respectively. A number of unidentified polar and non-polar degradation products were detected by TLC.

In another study the degradation of ring-labelled [^{14}C]dinocap was investigated in standard German soils 2.2 (Neuhofen Neu) and 2.3 (Hatzenbuhl) and in one German agricultural soil (Eschweiller) under laboratory conditions at a concentration of 9 mg ai/kg soil. In soil 2.2, the influence of an organic fertiliser in the form of alfalfa meal was examined. The soils were incubated at 15 and 25ºC in the dark for 100 days (Mittelstädt and Fuhr, 1982). Table 19 shows the characteristics of the soils.

Table 19. Soil characteristics.

	Soil 2.2, Neuhofen Neu	Soil 2.3, Hatzenbuhl	Eschweiller agricultural soil
pH	6.8	4.7	5.9
Organic matter, %	2.1	1.7	1.4
Total N, %	0.24	0.12	0.12
Clay, %	8.3	6.9	12.0
Silt	6.3	13.6	28.4
Fine sand	73.8	38.6	58.3
Coarse sand	11.6	40.9	1.4
Ca (meq/100g)	12.8	2.1	11.8
Total sorption capacity, meq/100 g	15.3	6.3	11.2
Exchangeable cations, meq/100 g	14.1	3.6	12.8

Moist CO_2-free air was passed over the soils, and the CO_2 produced was absorbed in 1N NaOH. Samples of the soils were exhaustively extracted after 30 and 100 days incubation and the extracts were examined by HPLC and TLC. Total radioactivity in the soil was determined by combustion and LSC. Recovery of the total radioactivity was in the range 83-102.2% of the applied material. The results are shown in Table 20.

Table 20. Degradation of ^{14}C-Dinocap in German Soils, $^{14}CO_2$ evolution and total radioactivity.

Days, sample	^{14}C, % of applied					
	Soil 2.2, 25ºC	Soil 2.2 + alfalfa, 25ºC	Soil 2.2 15ºC	Soil 2.3, 25ºC	Soil 2.3, 15ºC	Agricultural soil, 25ºC
1, CO_2 trap	0.02	0.02	0.02	0.01	0.01	0.1
11, CO_2 trap	0.43	0.96	0.08	0.1	0.03	3.9
30, CO_2 trap	1.75	2.4	0.32	0.59	0.08	15.6
100, CO_2 trap	4.99	5.14	1.41	3.34	0.57	32.3
100, soil	93.9	90.5	81.6	98.9	100.8	55.3
Total ^{14}C recovery	98.9	95.6	83	102.2	101.3	87.6

Mineralization in the agricultural soil was much greater, with 15.6 and 32.3% of the applied radioactivity evolved as CO_2 after 30 and 100 days respectively. The quantity of organoextractable radioactivity decreased during the study. In standard soil 2.3 70% of the applied radioactivity was organosoluble after 100 days incubation at 25ºC with up to 22% bound in the soil. The only major degradation product identified was 2,4-DNOP. Several others were detected but individually these accounted for no more than 2% of the applied radioactivity, and after 100 days less than 1%.

Lewis (1995) determined the rate and route of [^{14}C]dinocap degradation in sandy loam, silty loamy sand, loamy sand and clay loam soils. The soil characteristics are shown in the Table 21.

Table 21. Characteristics of the test soils.

	Sandy loam	Silty loamy sand	Loamy sand	Clay loam
Organic carbon, %	2.3	1.9	1.2	3.0
Organic matter, %	4.0	3.3	2.1	5.2
CEC,[1] meq/100g soil	15.6	16.0	10.2	28.2
Sand, %	54	49	70	30
Silt, %	36	40	16	37
Clay, %	10	11	14	33
PH (1:2.5 in 1M KCl)	5.5	6.7	4.8	7.1
Water holding capacity (% w/w) -0.33 bar	27.00	18.8	13.0	35.8
-0.001 bar	68.4	57.7	49.6	87.5
Microbial biomass (µg C/g soil):				
Pre-study	447.6	186.24	59.9	1023.59
Post-study, 20ºC	328.6	257.45	42.47	1085.56
Post-study, 10ºC	322.74	NA	NA	NA

NA: not applicable
[1] Cation-exchange capacity

To study routes of degradation in the sandy loam soil over a 123-day period, soil samples (50 g dry weight equivalent) in a common chamber in the dark were maintained at 20ºC (the sandy loam also separately at 10ºC). Moistened CO_2-free air was drawn through the chamber and the effluent air passed through a series of traps. After a pre-incubation period of three days, [^{14}C]2,4-DNOPC was applied to each unit at a rate of 2.6 kg ai/ha, approximately five times the highest use rate of 0.52 kg ai/ha. Duplicate incubation units were removed for analysis at 0, 1, 3, 8, 14, 30, 60, 91 and 123 days after application.

The rate of degradation was measured in the four soils at 20ºC and in the sandy loam soil also at 10ºC. After a pre-incubation period of 3 days in the dark at 20ºC, [^{14}C]2,4-DNOPC was applied to each soil at a rate of 1 kg ai/ha. Duplicate samples were removed on days 0, 1, 3, 8, 14, 30, and either 60 or 100 days depending upon the soil.

The soil samples were extracted with neutral, acidic and basic methanol and the extracts assayed for radioactivity by LSC. Samples from the route study taken on day 60 were fractionated into fulvic acid, humic acid and humin, and assayed by LSC to determine the bound residues. Controls were used to determine the microbial biomass. The degradation rates in the four soils are given in Table 22.

Table 22. Degradation rates of 2,4-DNOPC in soil.

Soil	Temp., ºC	Application rate, kg ai/ha	DT-50, days	DT-90, days
Sandy loam	20	2.6	14.9	49.4
Sandy loam	10	1.0	31.2	103.7
Silty loamy sand	20	1.0	8.2	27.4
Loamy sand	20	1.0	24	79.8
Clay loam	20	1.0	4.1	13.5

The results of HPLC analysis of the sandy loam soil treated with 2,4-DNOPC at a rate of 2.6 kg ai/ha and 20ºC are shown in Table 23.

Table 23. HPLC analysis of sandy loam soil (Lewis, 1995).

Days	% of applied radioactivity			
	DNOPC	DNOP	Unknown	Unresolved background
0	92.34	1.69	0.87	1.40
1	87.0	5.88	ND	1.01
3	79.77	8.08	ND	1.96
8	60.92	11.63	0.24	2.0
14	45.11	13.47	ND	0.7
30	16.47	5.59	2.53	0.13
60	6.11	1.47	0.84	0.06

ND: not detected

The main degradation product was DNOP. Degradation was more rapid in the two soils of pH 6.7 and 7.1 than in those of pH 4.8 and 5.5, indicating that chemical hydrolysis to DNOP is a main route of degradation in soil. 2,4-DNOPC was degraded rapidly in all the soils, at a lower rate at 10ºC than at 20ºC.

The fate of labelled 2,4-DNOPC and 2,6-DNOPC was investigated separately in a sandy loam soil (pH 5.8 and 1.8% organic carbon) under aerobic conditions at an application rate of 0.52 kg ai/ha. The soil was allowed to acclimatise in darkness for 7 days before adding the test substances, then incubated in darkness at 20 ± 2ºC for 120 days. The microbial biomass was determined at the beginning (285 µgC/g) and end (255 µgC/g) of the incubation period (Whittle, 1998).

Duplicate samples taken immediately after application of the test substance and after 1, 3, 7, 14, 30, 59, 90 and 120 days incubation were analysed by LSC, HPLC and TLC. 2,4-DNOP and 2,6-DNOPC were quantified by reverse-phase HPLC. The results are shown in Table 24.

Table 24. Degradation of 2,4- and 2,6-DNOPC in sandy loam soil (Whittle, 1998).

Time after application, days	% of applied radioactivity	
	2,4-DNOPC	2,6-DNOPC
0	97.6	98.4
1	93.3	90.6
3	78.6	67.4
7	59.2	31.8
14	39.4	14.1
30	29.9	4.2
59	17.7	1.8
90	15	1.6
120	7.8	1.9

Calculated DT-50 and DT-90 values for 2,4-DNOPC were 10.0 and 112.9 days respectively. 2,6-DNOPC was degraded more rapidly with DT-50 and DT-90 values of 4.5 days and 16.4 days.

The principal route of degradation was hydrolysis to 2,4-DNOP or 2,6-DNOP with subsequent incorporation into bound residues. In both cases the polar material and minor components remained unidentified. At 120 days, significant mineralization of both isomers to $^{14}CO_2$ was observed (22.4% and 36.7% of the AR for 2,4-DNOPC and 2,6-DNOPC respectively).

Adsorption and desorption

The adsorption and desorption of dinocap were investigated in four agricultural soils, sandy loam, loam, loamy sand and clay loam in aerobic conditions (Hawkins *et al*., 1992b). The characteristics of the soils are shown in Table 25.

Table 25. Soil characteristics.

	Sandy loam	Loam	Loamy sand	Clay loam
Sand, %	58	46	84	36
Silt, %	26	43	12	33
Clay, %	15	11	3	31
Organic Carbon, %	1.57	3.66	0.87	2.15
pH	7.4	6.8	7.2	7.7
CEC (meq/100g)	13.2	24.2	5.7	22

Sieved samples of the soils (1g dry weight) were mixed with 20 ml of 0.01 M $CaCl_2$. Solutions of ring-labelled [^{14}C]2,4-DNOPC were added to triplicate soil samples to give final dinocap concentrations of 0.1, 0.05, 0.025 and 0.01 mg/l. Test samples were shaken for 2 hours in the dark at 25ºC. After centrifugation the supernatant was decanted, the volume recorded and duplicate aliquots were analysed for radioactivity by LSC.

Desorption was determined with the same samples. Fresh 0.01 M $CaCl_2$ (20 ml) was added and the soil samples shaken for a further two hours in the dark at 25ºC. Soil and solutions were separated by centrifugation and analysed as before. A second desorption step followed. The radioactivity remaining in the soils was determined by combustion and LSC and the dinocap in the soils and solutions by HPLC. The results are shown in Tables26-28.

Table 26. Recovery of radioactivity in the aqueous solutions, soil extracts and extracted soils after 2 hours equilibration.

	% of applied radioactivity			
	Sandy loam	Loam	Loamy sand	Clay loam
Aqueous solution	13.0	10.5	18.0	8.2
Soil extracts	84.8	88.9	80.9	94.7
Unextractable	2.0	3.8	1.2	4.1
Total recovered	99.8	103.2	100.1	107

Table 27. Recovery of radioactivity in the aqueous solutions, soil extracts and extracted soils after adsorption and two desorption equilibrations.

	% of applied radioactivity			
	Sandy loam	Loam	Loamy sand	Clay loam
Adsorption solution	15.5	7.7	18.2	10.0
Desorption solution 1	5.9	2.8	7.8	4.5
Desorption solution 2	5.3	2.4	5.1	4.2
Soil extract	66.8	82.5	62.1	72.2
Unextractable	2.6	4.0	1.1	8.7
Total	96.1	99.4	94.3	99.6

Table 28. Proportions of 2,4-DNOPC and other radioactive components in aqueous solutions and soil extracts after adsorption and two desorption equilibrations.

Radioactive components	% of radioactivity in solution			
	Sandy loam	Loam	Loamy sand	Clay loam
Soil extract				
2,4-DNOPC	82.8	82.8	89.9	70.8
Others	17.2	17.2	10.1	29.2
Aqueous solution				
2,4-DNOPC	39.6	26.4	53.2	20.9
Others	60.4	73.6	46.8	79.1

Freundlich adsorption and desorption coefficients were calculated from the results.

Table 29. Adsorption coefficients of 2,4-DNOPC in soils.

Soil	OC %	K_a	K_{oc}
Sandy loam	1.57	114	7260
Loam	3.66	206	5630
Loamy sand	0.87	133	15300
Clay sand	2.15	176	8190

OC: organic carbon
K_a: Freundlich adsorption coefficient
K_{oc}: adsorption coefficient per unit organic carbon

Dinocap was strongly adsorbed by the soils studied and can be classified as having low mobility in soil. Adsorption was greater than would have been expected in the low organic carbon soil indicating that other factors are also important in the adsorption to soil. Dinocap was more strongly adsorbed than its degradation products.

Leaching

A laboratory study was carried out on five soils classified as clay, clay loam, silt loam, sandy loam and silty clay loam (Graham, 1971). [^{14}C]dinocap was mixed with the soils at a rate of approximately 156 mg/kg (to simulate the application of 0.227 kg ai/ha), and applied to the top of duplicate soil columns (25.5 cm). The columns were saturated with water and the equivalent of 2.5 cm rain per week was allowed to percolate through them over a period of nine weeks. Leachates and column segments were analysed. In all five soils, the radioactivity in the top segment was 70% or more of the total radioactivity

recovered, which ranged from 74% of that applied in silt loam to 96% in clay loam. In only silt loam and clay loam was radioactivity detectable in the leach water. It can be concluded that dinocap and/or its degradation products are not leached extensively in a range of different soils.

In another laboratory leaching study sandy loam soil fortified with ^{14}C-dinocap at a rate of 5 mg/kg was aged in a greenhouse for a period of 30 days before addition to the 30 cm test column (Fisher, 1975). Leachates were collected daily for 44 days and radio-assayed. After 44 days the column was disassembled into 5 cm segments for the top 15 cm and 7.5 cm for the bottom 15 cm, and all the segments were radio-assayed.

No appreciable ^{14}C was detected in the leachates collected throughout the period, and combustion assays of the soil indicated that all the radioactivity was in the first and second segments, showing that soil-aged dinocap residues are not leached in a sandy loam soil.

A similar study was carried out with a silt loam soil (OM 2%, pH 6.1) aged in a greenhouse for 102 days. Additional columns were prepared using untreated soil as a control and soil freshly fortified with [*phenyl*-^{14}C]2,4-D as a reference (Streelman, 1980). Duplicate 30 cm glass columns were filled with silt loam soil, and 7.6 cm layers of untreated soil and soil fortified with labelled dinocap or 2,4-D at 5 mg/kg were added to the tops of the columns. On each working day for the next 46 days, 55 ml of water (equivalent to 1.3 cm of rainfall) was added dropwise to each column. No dinocap or 2,4-D was found in the leachate for the first two weeks and thereafter the radioactivity was only slightly above the limit of determination (1 µg/l). The total radioactivity found in the eluate was on average 0.28% of the applied dinocap and 0.05 % of the 2,4-D.

Radio-assay of the soil immediately after fortification with dinocap gave a value of 5.14 mg/kg. After ageing for 102 days the level was 2.8 mg/kg. Radioactivity was also recovered from the pot in which the soil was aged (13% of the applied ^{14}C). The remaining radioactivity was assumed to have been lost as volatile degradation products. In the dinocap-treated soils a mean of 83.4% of the radioactivity applied to the columns was recovered from the soils, and more than 90% of the recovered radioactivity was found in the top 5 cm of the soil columns. The distribution of radioactivity is shown in Table 30.

Table 30. Distribution of radioactivity in aged soil columns (Streelman, 1980).

Soil depth, cm	Column 1		Column 2	
	mg/kg as dinocap	% of recovered ^{14}C	mg/kg as dinocap	% of recovered ^{14}C
0-5	0.766	99	0.69	91.6
5 -10 cm	0.007	1	0.027	3.6
10-15	ND		0.24	3.2
15-22.5	ND		0.006	0.8
22.5-30	ND		0.006	0.8

The greater movement of the radioactivity in the second column was considered to be due the activity of an earthworm later observed in this column. It can be concluded that aged dinocap residues will not be leached from a silt loam soil even under exaggerated laboratory conditions.

Environmental fate in water/sediment systems

The solubility of dinocap in water at 20ºC was determined in two studies by a column elution method. In the first only 2,4-DNOPC was determined (Betteley, 1994). In the second the solubilities of [^{14}C]2,4-DNOPC and [^{14}C]2,6-DNOPC and the corresponding phenols were determined at flow rates of 300 and 600 ml/hr, in water buffered at pH 5 (Betteley, 1997b). The results are shown in Table 31.

Table 31. Solubilities of dinocap and dinocap phenols in water (Betteley, 1997b).

Isomer mixture	Water solubility at 20ºC, g/l	
	Flow rate 300 ml/hr	Flow rate 600 ml/hr
2,4-DNOPC	1.46×10^{-4}	3.3×10^{-4}
2,6-DNOPC	1.15×10^{-4}	1.19×10^{-4}
2,4-DNOP	2.87×10^{-5}	3.0×10^{-5}
2,6-DNOP	8.17×10^{-4}	5.31×10^{-4}

The octanol/water partition coefficients of 2,4-DNOPC, 2,6-DNOPC and the phenols were determined by an HPLC method (Betteley , 1997a) with the following results.

	log P_{ow} (20.5ºC)
2,4-DNOPC	6.55 ± 0.33
2,6-DNOPC	6.45 ± 0.33
2,4-DNOP	3.85 ± 0.33
2,6-DNOP	3.93 ± 0.33

The hydrolysis of dinocap was determined in buffered solutions at pH 5, 7 and 9 by Streelman (1981). Who concluded that the hydrolysis was base-catalysed, occurring rapidly at pH 9 and quite slowly at pH 5.

The hydrolysis of 2,4- and 2,6-DNOPC and DNOP in aqueous buffer solutions pH 4, 7 and 9 was determined by Winwick (1998a). [^{14}C]DNOPC and [^{14}C]DNOP were added separately to buffer solutions at a concentration of 50 µg/l (about half the reported water solubility of DNOPC) and incubated at 20ºC and 30ºC. The rate of hydrolysis was monitored by HPLC with the following results.

Test substance	pH	Half-life, days	
		20ºC	30ºC
2,4-DNOPC	4	447	91.4
	7	30.4	30.5
	9	9.25	2.34
2,6-DNOPC	4	114	55
	7	16.2	14.8
	9	3.65	1.01

The only major degradation product of DNOPC in all the solutions was the phenol, DNOP. There was no significant degradation of DNOP at any pH at 20ºC or 30ºC.

The photolysis of labelled dinocap was investigated in a 0.1 mg/l aqueous pH 5 buffer solution at 25ºC. Test samples were irradiated continuously with a Xenon arc for 367 hours, equivalent to 82.84 days of summer sunlight at 30º N. Duplicate samples of both irradiated and control solutions were taken at approximately 1, 2, 4, 6 and 24 hours and 5 and 15 days. The radioactivity was measured by LSC, and TLC and HPLC were used to identify and quantify degradation products (Hawkins *et al.*, 1992a).

The photolytic degradation of 2,4-DNOPC was found to be biphasic with initial and terminal half-lives equivalent to 4.9 and 57.2 hours of summer sunlight at 30º N respectively. The main degradation product was $^{14}CO_2$, accounting for approximately 55% of the applied radioactivity after 367 hours of irradiation. 2,4-DNOP was an important product during the first 120 hours, accounting for 19.4% of the applied radioactivity, but declined to a level of 1.6% at 367 hours. The dark control samples showed no significant degradation until 120 hours of irradiation, and contained 76.4% of the applied radioactivity at 367 hours.

Another study was conducted to investigate the aqueous photolysis of 2,4- and 2,6-DNOPC and DNOP uniformly labelled in the phenyl ring ^{14}C- DNOPC and DNOP were added separately to sterile, aqueous pH 4 buffer solutions at a concentration of 50 µg/l. The test samples were irradiated continuously with a xenon arc for periods up to 10 hours, equivalent to 2.1 days of summer sunlight at 40º N, and maintained at 25 ± 1ºC . Control samples were incubated in the dark. Solutions containing DNOP were irradiated for periods of up to 96.1 hours equivalent to 19.3 days of summer sunlight at 40º N (Winwick, T. 1998b). Volatile radioactivity was trapped and solutions were analysed by HPLC.

The half-lives of the test substances were as follows.

Test Substance	Half-life, days
2,4-DNOPC	0.63
2,6-DNOPC	0.73
2,4-DNOP	8.71
2,6-DNOP	20.82

Two photodegradation products of DNOPC were identified as DNOP and CO_2. The cumulative amounts of $^{14}CO_2$ accounted for 5.2 and 5.1% of the applied radioactivity from 2,4-DNOPC and 2,6-DNOPC respectively. DNOP could not be quantified because it had a similar retention time to other photodegradation products. The only identified photodegradation product of DNOP was CO_2. Other products were not resolved by HPLC.

The aerobic aquatic degradation of dinocap was studied in two water/sediment systems containing sandy loam from two sites in the UK (BCH: Brown Carrick Hill and HB: Hinchigbrooke). The systems were incubated in the dark with 0.01 mg/l of [^{14}C]2,4-DNOPC at 20 ± 1ºC for periods up to 100 days with a humidified air flow maintained above the water but both sediments remaining anaerobic (Elsom *et al.*, 1993). The characteristics of the two systems are shown in Table 32.

Table 32. Water/sediment characteristics.

	BCH sandy loam system		HB sandy loam system	
	soil	water	soil	water
Sand, %	70.4		52.4	
Silt, %	24.0		38.4	
Clay, %	5.6		9.2	
OM, %	2.3		18.2	
CEC meq/100g	12.3		53.6	
Microbial biomass µgC/g	43 (a) 36 (b)		220 (a) 274 (b)	
pH	6.2	7.7	7.4	7.3
O_2, %				

	BCH sandy loam system		HB sandy loam system	
	soil	water	soil	water
under surface 5 cm above surface		98 95		66 58
Water source		ditch carrying hill catchment flow		pond

(a) at application (b) at the end of the study

Duplicate samples were taken at intervals and assayed for radioactivity by LSC. The aqueous phases were extracted with diethyl ether and the sediments successively with acetonitrile, methanol and dioxane before drying and treatment with NaOH to separate fulvic and humic acid fractions. The extracts were analysed by TLC. Volatile degradation products were collected. The results are shown in Table 33.

Table 33. Distribution of radioactivity in two sandy loam systems (Elsom *et al.*,1993).

Days incubation	% of applied radioactivity							
	BCH system				HB system			
	Water	Sediment	Traps	Total	Water	Sediment	Traps	Total
0	101.2 101.5	<LOD <LOD	-	101.2 101.5	99.9 100.3	0.3 0.6		100.2 100.9
1	87.6 91.3	9.6 5.1	<LOD	97.2 96.4	93.1 82.7	5.5 16.2	<LOD	98.6 98.9
2	94.1 92.5	5.1 1.5	<LOD	99.2 94.0	88.0 87.7	10.2 6.8	<LOD	98.2 94.5
7	72.4 55.8	19.8 26.5	<LOD 0.6	92.2 82.9	54.1 47.8	29.0 29.7	<LOD	83.1 77.5
14	48.4 56.9	30.4 26.0	1.3 0.4	80.1 83.3	32.5 30.4	56.6 55.1	0.4 1.4	89.5 86.9
21	41.0 57.7	30.4 30.0	1.6 1.3	73.0 89.0	44.4 52.0	43.9 43.4	2.0 0.9	90.3 96.3
30	43.0 46.9	41.2 45.1	1.1 0.6	85.3 92.6	18.2 13.9	63.2 81.3	2.2 2.7	83.6 97.9
61	14.2 13.2	47.4 65.0	8.2 8.7	69.8 86.9	7.1 15.9	82.9 57.0	4.4 5.2	94.4 78.1
100	11.8 9.2	40.7 47.5	13.3 13.5	65.8 70.2	6.5 6.4	78.4 68.0	5.0 8.6	89.9 83.0

No significant quantities of volatile radioactivity were recovered during the first 30 days of the study and no dinocap was detected at 60 or 100 days after treatment in either system. TLC analysis of the water samples indicated that dinocap was hydrolysed to DNOP and this was followed by binding of other water-soluble degradation products to the sediments. Approximate half-lives were calculated to be 7.3 and 4.1 days in the BCH and HB systems respectively.

Residues in rotational crops

Beans, oats and turnips were grown in soil plots which had been used the previous year for residue decline studies with [^{14}C]2,4-DNOPC on cucumbers (0.56 kg ai/ha) and squash (3 application at 0.56 kg ai/ha). Approximately 200 days after the application of [^{14}C]2,4-DNOPC to the cucumber and squash plots, they were rototilled and oats and turnips were sown. Beans were planted 250 days after the application of the DNOPC. All the rotational crops were allowed to grow to maturity. Samples were taken at various times during the growing season and at final harvest (Honeycutt and Garstka, 1976e).

Radioactive residues in all the samples were [0.02 mg/kg and in the final harvest samples [0.01 mg/kg.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Dinocap is a mixture of six dinitro-octylphenyl crotonates, three of 2,4-DNOPC and three of 2,6 isomers of 2,6-DNOPC. In each group the octyl substituents are mixtures of 1-methylheptyl, 1-ethylhexyl and 1-proylpentyl.

Crops. Methods have been developed for apples, grapes, cucumbers, peppers, peaches and melons, and processed commodities derived from them. All are similar: the crotonate isomers are converted to the corresponding phenols which are methylated. The analytical standards are 2,4-DNOPMe and 2,6-DNOPMe.

Samples are extracted with methanol by Soxhlet or maceration and hydrolysed with 1 N NaOH to convert the dinocap isomers to phenols. The methanolic solution is partitioned with hexane, the hexane fraction is discarded, and the methanol phase acidified with HCl and partitioned again with hexane. After solvent evaporation the residue is taken up in diethyl ether, methylated with diazomethane, and cleaned up by silica gel column chromatography. Quantification is by programmed temperature GLC with an ECD or NPD. The six peaks are measured separately and then combined to give a total peak height or area. The method was first described for apples (Brackett, 1991).

A confirmatory method for apples was validated using both EC and NP detectors. Modification included homogenization rather than Soxhlet extraction and scaled-down methylation with diazald rather than diazomethane. Samples were fortified with 0.05, 0.1, and 1.0 mg/kg of 2,4- and 2,6- dinocap. The LOD was 0.05 mg/kg. Recoveries by the ECD were 69 to 98% and by the NPD 60 to 101% (Howie, 1997).

In another validation study with various crops (Lees, 1997) a limit of determination of 0.05 mg/kg was achieved for grapes, wine and grape juice, apple purée and juice, strawberry preserve and jam, cucumbers and peppers. Recoveries from samples fortified at 0.05, 0.1 and 1 mg/kg with 2,4-DNOPC and 2,6-DNOPC were >70% in all the commodities at all fortification levels.

Another study was conducted in 1997 to evaluate the method for melons, peaches, tomatoes, canned tomatoes, tomato purée, ketchup and juice, peach preserve and juice, and apple pomace. Quantification was by GLC on a DB 608 capillary column with an ECD. The LOD in all the commodities was 0.05 mg/kg. Recoveries from samples fortified at 0.05, 0.1 and 1 mg/kg ranged from 71 to 109% (Lees, 1998i).

Water. Dinocap residues are extracted with methylene chloride. The crotonates are hydrolysed with 1 N NaOH, and the hydrolysate is neutralized with HCl, partitioned with ethyl acetate/hexane (1:1) and cleaned up on a silica gel column. Quantification is by HPLC on a C-18 column with UV detection at 265 nm. The reported LOD was 1 µg/l. The mean recovery from various types of water was 80.6 ± 6.0% at fortification levels of 1 to 10 µg/l (Burton, 1995a).

Soil. Dinocap residues are extracted from soil samples for one hour with acetone/methanol/4 N HCl (100:10:5). After adding NaCl and more HCl the extract is partitioned with hexane. The dinocap isomers

are converted to the phenols by hydrolysis in 4 N NaOH, the solution is neutralized and partitioned with hexane/ethyl acetate and cleaned up on a silica gel column. The phenol residues are determined by HPLC as above. The reported LOD was 0.1 mg/kg and the mean recovery at fortification levels of 0.1 and 1 mg/kg was 78% (Burton, 1995b).

Stability of residues in stored analytical samples

Grape and apple samples fortified with a mixture of 2,4-DNOPC and 2,6-DNOPC standard at 1 mg/kg . were stored at approximately -20ºC for 24 months in the dark, together with untreated controls. Analysis was by the method of Brackett (1991) with minor modifications. At intervals three stored control samples, two stored fortified samples and two freshly fortified control samples were analysed (Gillis, 1995). The results are shown in Table 34.

Table 34. Stability of dinocap in grapes and apples stored at –20 ± 5ºC (Gillis, 1995).

Days, storage	0	30	99	218	370	551	769
GRAPES							
Analytical recovery %	95.5	90	90	98	96.5	88.5	103
Residue remaining %	88.5	87.5	89.5	96.5	108	77	81.5
APPLES							
Analytical recovery %	93.5	90	93.5	97	71.5	81.5	102
Residue remaining %	87	85.5	72	68	58	68.5	60

There was only a very slight decrease of the residues in grapes after 24 months storage at -20ºC, but a more marked decrease in apples.

The stability of dinocap at levels of 1 mg/kg in cucumbers, tomatoes, peaches, apples and strawberries stored for 9 months in the dark at approximately -20ºC was determined. It was reported that the study would be continued for 24 months of storage (Lees, 1998j). The analytical method for apples was modified slightly by increasing the extraction solvent volumes to improve the extraction efficiency. The results, uncorrected for procedural recoveries are given in Table 35.

Table 35. Stability of dinocap in apples, cucumbers, peaches, tomatoes and strawberries.

Days storage	0-1	30-37	106-113	181-190	271-273
APPLES					
Analytical recovery %	82	91	87	91	93
Residue remaining %	81	89	81	107	105
CUCUMBERS					
Analytical recovery %	101	81	94	94	89
Residue remaining %	95	94	102	105	101
PEACHES					
Analytical recovery %	99	87	95	90	92
Residue remaining %	96	92	96	98	105
TOMATOES					
Analytical recovery %	102	85	93	72	86
Residue remaining %	94	96	107	82	97
STRAWBERRIES					

Days storage	0-1	30-37	106-113	181-190	271-273
Analytical recovery %	99	81	76	91	92
Residue remaining %	96	83	81	108	104

Definition of the residue

The results of metabolism studies showed that the dinocap isomers are readily hydrolysed to the corresponding phenols. The analytical methods used in residue trials quantify the residues of dinocap and their phenol metabolites as the methylated phenols and express the results as dinocap. The Meeting concluded that the residues should be defined as the sum of the dinocap isomers and dinocap phenols, expressed as dinocap, both for compliance with MRLs and for the estimation of dietary intake.

USE PATTERN

Dinocap is a contact fungicide used to control powdery mildew (*Unicicula neactor, Podosphaera or Sphaerotheca spp., Leveillula taurica and Erysphe cichoracearum*) on many crops, and is also used as a non-systemic acaricide. The printed labels indicate multiple applications but do not specify a maximum. It was reported to the Meeting that proposed changes in the PHIs are pending for stone fruits in Italy, Portugal and Spain, and for strawberries in Portugal and Spain. The registered uses are shown in Table 36 are those whose labels were submitted to the Meeting.

Table 36. Registered uses of dinocap.

Crop	Country	Form.	Application				PHI, days
			Field or greenhouse	kg ai/ha	kg ai/hl	No.	
Apples	Austria	WP	F	<0.27	0.022		21
	Austria	EC	F	<0.26	0.018		21
	Belgium	WP	F	<0.2-0.33	0.009-0.011		21
	Bulgaria	EC	F	0.18-0.26	0.018		21
	Czech Rep.	EC	F	0.26	0.018		35
	France	WP	F	0.18-0.27	0.018		28
	France	EC	F	0.17-0.26	0.0175		
	Greece	WP	F	0.33-0.42	0.016-0.021		20
	Greece	EC	F	0.35	0.018		20
	Hungary	EC	F	0.11-0.32	0.011-0.021		30
	Hungary	WP	F	0.11-0.32	0.011-0.022		30
	Israel	EC	F		0.007-0.014		21
	Italy	WP	F	0.35-0.42	0.018-0.021	3-6	20
	Italy	EC	F	0.35-0.42	0.018-0.021		20
	Morocco	WP	F		0.015-0.021		21
	Morocco	EC	F	0.16	0.018		21
	Poland	WP	F	0.41	0.04-0.08		21
	Portugal	EC	F	0.18	0.018		21
	Portugal	WP	F	0.18-0.22	0.018-0.021		21
	Rumania	EC	F	0.18-0.26	0.018		21
	Slovenia	EC	F	0.25-0.34	0.017-0.023		28
	Slovenia	WP	F	0.27-0.33	0.018-0.022		28
	Spain	WP	F	0.21-0.32	0.021		21
	Spain	EC	F	0.21-0.32	0.021		21
	UK	EC	F	0.39-0.49		<10	14

Crop	Country	Form.	Application				PHI, days
			Field or greenhouse	kg ai/ha	kg ai/hl	No.	
Apricot	France	WP	F	0.18-0.27	0.018		7
	France	EC	F	0.17-0.26	0.017		7
	Greece	WP	F	0.22-0.27	0.015-0.018		20
	Greece	EC	F	0.26-0.31	0.018-0.021		20
	Italy	WP	F	0.21-0.31	0.015-0.021		20
	Italy	EC	F	0.21-0.26	0.014-0.018		20
	Morocco	EC	F	0.26	0.018		21
	Morocco	WP	F	0.33	0.015-0.022		21
	Portugal	WP	F	0.15-0.18	0.015-0.018		21
	Spain	WP	F	0.21-<0.32	0.021		21
	Spain	EC	F	<0.32	0.021		21
Cucumbers	Belgium	WP	G	<0.2-0.33	0.013-0.022		
	Czech Rep	EC	F/G	0.21	0.014		7
	France	WP	F/G	0.18	0.018		3
	France	EC	F/G	0.17	0.018		3
	Greece	EC	F/G	<0.12-0.17	0.012-0.018		7
	Greece	WP	F/G	<0.1-0.18	0.01-0.018		7
	Hungary	EC	F/G	0.06-0.14	0.011-0.018		3 G 7 F
	Hungary	WP	F/G	0.05-0.14	0.009-0.018		3 G 7 F
	Israel	EC	F/G	0.26			7
	Italy	WP	F/G	0.1-0.18	0.01-0.018		7
	Italy	EC	F/G	0.12-0.18	0.012-0.018		7
	Morocco	EC	F/G	0.18	0.018		21
	Morocco	WP	F/G	0.073	0.014		21
	Poland	WP	F	0.11	0.018-0.02		4
	Portugal	WP	F/G	<0.09-0.15	0.009-0.015		7
	Portugal	EC	F/G	0.07-0.32	0.011-0.014		7
	Rumania	EC	F	0.11-0.14	0.018		7
	Slovakia	EC		0.21	0.014		7
	Slovenia	WP		0.15-0.18	0.015-0.018		42
	Spain	EC	F/G	0.21-0.63	0.011		7
	Spain	WP	F/G	0.11			7
Grapes	Austria	WP	F	<0.29	0.018		21
	Austria	EC	F	<0.28	0.018		21
	Czech Rep	EC	F	0.26	0.018		35
	France	WP	F	0.21	0.018		21
	France	EC	F	0.21	0.011-0.021		21
	Greece	WP	F	<0.1-0.18	0.01-0.018		20
	Greece	EC	F	<0.14-0.17	0.014-0.017		20
	Hungary	EC	F	0.18-0.28	0.018-0.028		30
	Hungary	WP	F	0.18	0.018		30
	Israel	EC	F	0.07-0.14	0.007-0.014		35
	Italy	WP	F	0.16-0.32	0.016-0.021		20
	Italy	EC	F	0.15-0.21	0.015-0.021		20
	Morocco	WP	F	0.11	0.015-0.021		
	Portugal	EC	F	0.18	0.0175		21
	Portugal	WP	F	<0.18-0.21	0.018-0.021		21
	Rumania	EC	F	0.18	0.018		21
	Slovakia	EC	F	0.26	0.018		35
	Slovenia	EC	F	0.15-0.19	0.015-0.019		42
	Spain	WP	F	0.21			21

Crop	Country	Form.	Application				PHI, days
			Field or greenhouse	kg ai/ha	kg ai/hl	No.	
	Spain	EC	F	0.21			21
Melons	Belgium	WP	G	<0.2-0.33	0.013-0.022		
	France	WP	F/G	0.18	0.018		3
	France	EC	F/G	0.16-0.17	0.017		3
	Greece	WP	F/G	<0.1-0.18	0.01-0.018		7
	Greece	EC	F/G	<0.12-0.17	0.012-0.018		7
	Italy	EC	F/G	0.18	0.011-0.018		7
	Italy	WP	F/G	0.18	0.011-0.018		7
	Morocco	EC	F	0.16	0.016		10
	Portugal	EC	F/G	0.07-0.32	0.007-0.011		7
	Portugal	WP	F/G	0.09-0.44	0.009-0.015		7
	Spain	EC	F/G	0.21-0.63	0.011		7
Nectarines	Greece	WP	F	<0.22-0.27	0.015-0.018		20
	Greece	EC	F	<0.26-0.31	0.018-0.021		20
	Italy	WP	F	0.21-0.31	0.015-0.021		20
	Italy	EC	F	0.21-0.26	0.014-0.018		20
	Spain	WP	F	0.32	0.021		21
	Spain	EC	F	<0.32	0.021		21
Peaches	France	WP	F	0.18	0.018		7
	France	EC	F	0.17-0.26	0.018		7
	Greece	WP	F	<0.22-0.27	0.015-0.018		20
	Greece	EC	F	<0.26-0.31	0.018-0.021		20
	Italy	WP	F	0.21-0.31	0.015-0.021		20
	Italy	EC	F	0.21-0.32	0.014-0.018		20
	Morocco	EC	F	0.26	0.018		
	Morocco	WP	F	0.33	0.015-0.021		
	Portugal	WP	F	0.15-0.18	0.015-0.018		21
	Portugal	EC	F	0.11-0.14	0.011-0.014		21
	Slovenia	EC		0.23-0.29	0.015-0.019		42
	Slovenia	WP		0.17-0.27	0.011-0.018		42
	Spain	WP	F	<0.32	0.021-0.026		21
	Spain	EC	F	<0.32	0.021-0.026		21
Peppers	Greece	EC	F/G	<0.12-0.17	0.012-0.018		7 G 20 F
	Morocco	WP	F/G	0.073	0.014-0.021		
	Morocco	EC	F/G	0.18	0.018		
	Portugal	WP	F/G	0.09-0.45	0.009-0.015		21
	Portugal	EC	F/G	0.07-0.32	0.007-0.011		21
	Spain	WP	F/G	0.11			7
	Spain	EC	F/G	0.21-0.32	0.011		7
Summer squash	Belgium	WP	G	<0.2-033	0.013-0.022		
	France	WP	F/G	0.18	0.018		3
	France	EC	F/G	0.17	0.017		3
	Israel	EC	F/G	0.26	0.014		7
	Italy	WP	F/G	0.1-0.18	0.01-0.018		7
	Italy	EC	F/G	0.12-0.18	0.012-0.018		7
	Morocco	EC	F	0.16	0.016		10
	Portugal	WP	F/G	0.09-0.15	0.009-0.015		7
	Spain	EC	F/G	0.21-0.63	0.011		7
Strawberries	Belgium	WP	F/G	0.2-0.33	0.013-0.022		21
	France	EC	F	0.16	0.016		3
	Morocco	EC	F	0.16	0.016		10
	Poland	WP	F	0.68	0.03		21

Crop	Country	Form.	Application				PHI, days
			Field or greenhouse	kg ai/ha	kg ai/hl	No.	
	Portugal	EC	F/G	0.09-0.11	0.009-0.011		21
	Spain	EC	F	0.32	0.021		7
	UK	EC	F	0.39	0.019	5	7
Tomatoes	Greece	EC	F/G	0.12-0.18	0.012-0.018		7 G 20 F
	Morocco	EC	F/G	0.18	0.018		14
	Morocco	WP	F/G	0.073	0.014-0.021		14
	Poland	WP	F	0.11	0.018-0.02		4
	Portugal	WP	F/G	0.09-0.44	0.009-0.015		21
	Portugal	EC	F/G	0.07-0.32	0.007-0.011		21
	Spain	EC	F/G	0.21-0.32	0.011		7
	Spain	WP	F/G	0.11			7

RESIDUES RESULTING FROM SUPERVISED TRIALS

Trials were carried out in Europe on a number of crops. The samples were analysed by the GLC method of Brackett (1991), with a reported LOD of 0.05 mg/kg. The results were not corrected for analytical recoveries unless noted. Analytical recoveries were generally >80%, so using corrected or uncorrected results should not significantly influence the interpretation.

Residues were generally quantified as the sum of the heights or areas of all six isomer peaks, but owing to interfering peaks present in some samples the sum of four or five peaks was used. Where the sum of the three 2,4- or 2,6-DNOPC peaks is below 0.05 mg/kg the residue of that group of isomers is recorded as <0.05 mg/kg irrespective of the total residue measured by summing the six peaks.

Apples. Trials were conducted on several varieties of apples in France, Greece, Italy and the UK from 1990 to 1997.

Two field trials were carried out on Golden Delicious and Red Chief apples at two locations in France in 1996. Dinocap was used at a rate of 0.021 kg ai/hl, with application intervals of 10 days and spray volume of 700-800 and 1500-2700 l/ha. Samples were stored frozen for 202-294 days before analysis (Lees, 1998c). The samples taken 14 days after the last application were processed into apple juice and apple purée. No dinocap residues were found in the processed commodities.

Summary information from four field trials in Italy, two in 1991 and two in 1993, was submitted. In the 1993 trials dinocap was applied 4 times to plots of 16 trees in spray volumes of 1500 l/ha at intervals of 21-28 days. The reported LOD was 0.04 mg/kg and recoveries were 70-102%.

In two other trials in Italy in 1996, dinocap EC was applied at the GAP rate, but with a higher number of applications. Each plot of 6 trees was sprayed at 2000 l/ha at intervals of 13-15 days. The sampling-to-analysis interval (SAI) ranged from 210 to 266 days. Recoveries were 77-88%.

In trials in Greece and Italy in 1997 (Sutcliffe, 1998a) the EC (350 g/l) or WP (18%) was sprayed 6 times on plots of 6 trees at intervals of 10-14 days and with spray volume of 1500 l/ha in Greece and 1150-1450 l/ha in Italy.

Several trials were conducted at various locations in the UK from 1990 to 1997. In four trials in 1990 the EC formulation was applied with an airblast or knapsack sprayer at a rate of 0.49 kg ai/ha, 3 to 7 applications at 12- to 24-day intervals. Samples were stored at -20ºC for 400 to 500 days before analysis. Residues decreased from 0.25-0.59 mg/kg on day 0 to [0.05 mg/kg at 14 days.

In six trials according to GAP in 1991, two on small plots and four on plots of 0.5-2 ha, 3 to 8 applications of the EC formulation were made at intervals of 6 to 21 days. Samples were stored at -20ºC for 60 days before analysis. In the two small-plot trials a normal xylene-based and a xylene-free formulation were compared. The xylene-based formulation was applied at the GAP rate of 0.49 kg ai/ha, the xylene-free formulation at 0.49 and 0.98 kg ai/ha. There was essentially no difference between the residue levels.

In two field trials in 1992 on plots of 4 trees the EC formulation was applied 11 or 12 times with a motorised knapsack sprayer at the GAP rate with spray volumes of 2000 l/ha, spraying to run-off, at intervals of 12-14 days. The final applications were made at 7-day intervals to fruit at a growth stage of 8-9 cm. Residues were quantified as the sum of the first four isomer peaks. Recoveries were 73-88%. The SAI was 10 days.

In 1997 the EC and WP formulations were each sprayed 10 times at 10-14 day intervals with a motorised knapsack sprayer. In trials T1 and T2 the spray volume was 1500 l/ha and in T3 and T4 500 l/ha. Samples were stored frozen before analysis for 58 to 194 days (Lees, 1998h). At day 0 the 2,4-DNOPC residues were higher than the 2,6-; at the GAP PHI of 14 days both groups were <0.05 mg/kg. Samples from two locations at 14 days PHI were processed to purée, juice and pomace.

The results of all the trials are shown in Table 37.

Table 37. Residues of dinocap in apples. Underlined residues are from treatments according to GAP.

Country, Location, Year	Application				PHI, days	Dinocap, mg/kg[1]			Ref.
	Form.	No	kg ai/ha	kg ai/hl		2,4 -	2,6 -	Total	
France 1996	EC	6	0.16-0.19	0.021	0	<0.05	<0.05	0.06	Lees, 1998c
					14	<0.05	<0.05	<0.05	
					21	n.d	n.d	<u><0.05</u>	
France 1996	EC	6	0.31-0.58	0.021	0	0.20	0.09	0.29	Lees, 1998c
					14	0.06	<0.05	0.09	
					21	<0.05	<0.05	<u><0.05</u>	
Greece, 1997	EC	6	0.31	0.021	0	0.35	0.17	0.52	Sutcliffe, 1998a
					14	<0.05	<0.05	<0.05	
					21	<0.05	<0.05	<u><0.05</u>	
Greece 1997	WP	6	0.32	0.021	0	0.32	0.12	0.45	
					14	<0.05	<0.05	0.07	
					21	<0.05	<0.05	<u><0.05</u>	
Italy 1991	EC	2	0.38	0.021	0	0.17	0.09	0.26	Pessina, 1993a
					18	<0.05	<0.05	<u><0.05</u>	
Italy 1991	EC	2	0.25	0.021	0	0.1	0.07	0.13	
					18	<0.05	<0.05	<u><0.05</u>	
Italy 1993	EC	4	<0.32	0.021	0			0.06	Pessina, 1993f
					20			<u><0.04</u>	
Italy 1993	EC	4	0.15-0.26	0.021	0			0.05	
					20			<u><0.04</u>	
Italy 1997	EC	6	0.31-0.42	0.021	0	0.21	0.10	0.31	Lees, 1998c

Country, Location, Year	Application				PHI, days	Dinocap, mg/kg[1]			Ref.
	Form.	No	kg ai/ha	kg ai/hl		2,4 -	2,6 -	Total	
					14	0.07	<0.05	0.11	
					21	0.07	<0.05	0.09	
Italy 1997	EC	6	0.31-0.42	0.021	0	0.26	0.11	0.37	
					14	0.05	<0.05	0.08	
					21	<0.05	<0.05	<0.05	
Italy 1997	EC	6	0.24-0.31	0.021	0	0.1	<0.05	0.15	Sutcliffe, 1998a
					14	n.d	n.d	<0.05	
					21	n.d	n.d	<0.05	
Italy 1997	WP	6	0.24-0.31	0.021	0	0.07	<0.05	0.1	
					14	<0.05	<0.05	<0.05	
					21	n.d.	n.d	n.d	
UK Cambs 1990	EC	4	0.49	0.088	0			0.43	Murray, 1992a
					5			0.24	
					7			0.2	
					10			0.21	
					17			<0.05	
UK Cambs. 1990	EC	7	<0.49	0.025	0			0.25	
					3			0.11	
					5			0.05	
					9			<0.05	
					14			<0.05[2]	
UK Essex 1990	EC	4	0.49	0.088	0			0.59	Murray, 1992a
					5			0.05	
					10			0.05	
					14			<0.05	
UK Essex 1990	EC	3	0.49	0.039	0			0.49	
					5			0.09	
					10			0.08	
					14			0.05	
UK Oxford 1991	EC	8	0.49	0.025	0			0.44	Murray, 1992c
					7			0.11	
					14			0.08	
			0.49	0.025	0			0.58	
					7			0.17	
					14			<0.05	
			<0.98	0.049	14			<0.05	
UK 1991	EC	6	0.49	0.088	0			0.31	Murray, 1992c
					14			<0.05	
UK 1991	EC	3	0.49	0.088	0			0.17	
					15			<0.05	
UK 1991	EC	8	<0.49	0.025	0			0.35	Murray, 1992c
					7			<0.05	with xylene
					14			<0.05	
			<0.49	0.025	0			0.37	Murray, 1992c
					7			0.06	without xylene.
					14			<0.05	
			<0.98	0.049	14			<0.05	
UK 1991	EC	5	0.25	0.29	4			0.14	

Country, Location, Year	Application				PHI, days	Dinocap, mg/kg[1]			Ref.
	Form.	No	kg ai/ha	kg ai/hl		2,4 -	2,6 -	Total	
					12			0.06	
UK 1991	EC	4	0.18	0.063	0			0.67	Murray, 1992c
					15			0.08	
UK 1992	EC	11	<0.49	0.025	0			0.13[3]	Murray, 1993
					14			<0.05[3]	
UK 1992	EC	12	<0.49	0.025	0			0.34[3]	
					14			0.11[3]	
UK Nottingham	EC	10	0.36-0.38	0.025	0	0.19	0.08	0.27	Lees, 1998h
1997 T 1					7	<0.05	<0.05	0.07	
					14	<0.05	<0.05	0.06	
	WP	10	0.36-0.38	0.025	0	0.15	0.06	0.21	
					7	0.08	<0.05	0.11	
					14	<0.05	<0.05	<0.05	
UK Kent	EC	10	0.37-0.38	0.025	0	0.18	0.09	0.27	Lees, 1998h
1997 T 2					7	<0.05	<0.05	<0.05	
					14	<0.05	<0.05	0.08	
	WP	10	0.36-0.38	0.025	0	0.22	0.1	0.32	
					7	0.06	<0.05	0.1	
					14	<0.05	<0.05	0.05	
UK Gloucester-shire	EC	10	0.46-0.5	0.098	0	0.2	0.1	0.3	Lees, 1998h
1997 T 3					7	<0.05	<0.05	0.05	
					14	<0.05	n.d	<0.05	
	WP	10	0.49-0.5	0.098	0	0.18	0.07	0.25	
					7	<0.05	<0.05	0.05	
					14	<0.05	<0.05	<0.05	
UK Kent	EC	10	0.49-0.51	0.098	14			0.08	Lees, 1998h
1997 T 4	WP	10	0.47-0.5	0.098	14			0.07	

[1] Calculated from the sum of 6 peaks unless otherwise stated
[2] Average of 4 replicates
[3] Sum of 4 peaks

Grapes. Several field trials were conducted on grapes in France, Germany, Greece, Italy and Portugal representing northern and southern European regions.

Three field trials were carried out in France and six in Portugal in 1991. Only summary data were submitted. Samples were first analysed by a method that quantified only the parent compound and then re-analysed (Conraux, 1993d) by the method of Brackett (1991).

In a field trial in France in 1992 residues were determined in Merlot grapes, must and wine after 6 applications at 0.21 kg ai/ha (Conraux, 1993m). The reported LOD was 0.04 mg/kg and the recovery 78.5 ± 12.4 %. Grape samples were stored at -18ºC for 90 days before analysis. Residues in the must and wine were below the LOD.

In two field trials in Southern France in 1996 the EC formulation was applied 6 times almost to run-off to Ugni Blanc and Syrah grapes by knapsack sprayer at intervals of 10-14 days. The interval

before the last application was 7 days. The first applications were made 12 weeks before mid-normal commercial harvest. Samples harvested 0, 14 and 21 days after the last application were stored frozen for 240-270 days before analysis (Lees, 1998b).

In 1997 in Northern France and Germany different wine grape varieties were treated eight times with the EC or WP formulations at 10-14 day intervals at 0.021 kg/hl, the first treatment at a growth stage 6-7 leaves unfolded and the last at the beginning of ripening. The SAI ranged from 57 to 127 days (Fielden 1998a). Recoveries ranged from 70 to 107%. It was reported that processing studies with grapes from these trials were in progress.

Residues of dinocap were determined in grapes, grape juice, and young and mature wine at two locations in Germany in 1996. The EC formulation was applied eight times by motorised knapsack sprayer at intervals of 10 to 16 days. Residues of 2,4-dinocap were higher than those of 2,6-dinocap at all time (Lees, 1998a)

In two trials in 1997 in Greece plots of grapes (1 row of 14.4m /plot) were sprayed six times with the EC or WP formulations in volumes of 1500 l/ha at intervals of 10 days (14 days before the last treatment). Harvested samples were stored frozen for 36-57 days before analysis (Sutcliffe, 1998b).

Five field trials were carried out at different locations in Italy in 1993 and grapes were vinified in two of them. The reported LOD was 0.05 mg/kg and recoveries >90%. Details were not reported (Pessina, 1993e).

In two trials at two locations in Italy in 1992 on two grape varieties and their processed products there were 6 applications to plots of 90 plants starting at the pre-flowering stage at intervals of 17-22 days. Samples were stored at -20ºC for approximately 3 months. The reported LOD was 0.04 mg/kg (Pessina, 1993g).

In 1993 four trials were conducted in Italy with dinocap WP and EC. Six sprays were applied from flowering to pre-ripeness at intervals of 10 to 22 days. Dinocap was applied at high volume (1000-1500 l/ha) with a knapsack sprayer to two wine varieties in plots of 46-52 plants. Samples harvested at maturity were analysed with a reported LOD of 0.04 mg/kg and recoveries of 103-114%. The SAI was 140-150 days (Pessina, 1994e).

In two trials in Italy in 1996 the EC formulation was applied almost to run-off 6 times to Chardonnay and Riesling vines by a knapsack sprayer at intervals of 10-14 days (7 days before the last application). The first applications were 12 weeks before mid-normal commercial harvest (pea-size berries). Samples taken 0, 14 and 21 days after the last application were stored frozen for 240-270 days before analysis (Lees, 1998b).

In other trials in Italy in 1997 on different varieties of wine grapes the EC and WP formulations were applied to plots of 8-14 plants six times at intervals of 10-14 days. Samples were stored at -18ºC for 60-178 days before analysis (Sutcliffe, 1998b).

In two trials in Portugal in 1992 the EC formulation was applied at 0.18 kg ai/ha to triplicate plots of 10 plants. Samples were stored at -18ºC before analysis for 83 days. The reported LOD was 0.04 mg/kg and the mean recovery 79.3 ± 12% (Conraux, 1993g).

A residue decline trial was carried out in Portugal in 1992, with 1 or 2 applications at 0.18 kg ai/ha, the first at the beginning of the colour change of the grapes. Samples were stored at -18ºC for 84

days before analysis. The reported LOD was 0.04 mg/kg and the mean recovery 76.8%. Residues decreased from 1.65 mg/kg at 0 day to <0.04 mg/kg after 28 days (Conraux, 1993h). The results were corrected for recovery.

Five trials were conducted in Spain in 1991. The EC formulation (350 g/l), dinocap (325 g/l) + myclobutanil (75 g/l), and dinocap (160 g/l) + fenbuconazole (75g/l) formulations were applied to table grapes. Samples were stored at -18ºC for 40 days before analysis. The analytical method quantified only the total diphenyl crotonates. The reported LOD was 0.02 mg/kg and the recovery 90%.

The results are shown in Table 38.

Table 38. Residues of dinocap in grapes. Underlined residues are from treatments according GAP.

Country, Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
France 1991	EC	8	0.096	0.019	45			<0.02	Conraux, 1993d
	EC	7	0.096	0.48	46			<0.02	Conraux, 1993d
	EC	10	0.21	0.11	21			<0.04	
France South 1992	EC	6	0.21		14			0.1 (0.07-0.13)	Conraux, 1993m
France South 1992	EC	6	0.21		14			0.1	Conraux, 1994b
France South 1996	EC	6	0.17-0.21	0.021	0	0.14	0.08	0.22	Lees, 1998b
					14	<0.05	<0.05	<0.05	
					21	<0.05	<0.05	<0.05	
France South 1996	EC	6	0.15-0.16	0.021	0	0.05	<0.05	0.08	Lees, 1998b
					14	n.d.	<0.05	<0.05	
					21	<0.05	n.d.	<0.05	
France North 1997	EC	8	0.06-0.22	0.021	0	0.64	0.3	0.94	Fielden, 1998a
T 1					7	0.21	0.12	0.33	
					14	0.20	0.12	0.32	
					21	0.09	0.05	0.14	
					28	0.14	0.08	0.22	
France North 1997	EC	8	0.08-0.34	0.021	0	1.31	0.75	2.06	Fielden, 1998a
T 2					7	0.58	0.34	0.92	
					14	0.43	0.25	0.68	
					21	0.26	0.16	0.42	
					28	0.20	0.13	0.33	
France North 1997	EC	8	0.06-0.22	0.021	0	0.82	0.4	1.22	Fielden, 1998a
T 3					7	0.37	0.22	0.59	
					14	0.23	0.12	0.35	
					21	0.22	0.13	0.35	
					28	0.14	0.08	0.22	
France North 1997	EC	8	0.09-0.34	0.021	0	1.02	0.48	1.50	Fielden, 1998a
T 4					7	0.51	0.29	0.80	
					14	0.31	0.16	0.47	
					21	0.37	0.22	0.59	

Country, Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
					28	0.27	0.17	0.44	
France North 1997	WP	8	0.07-0.22	0.021	0	0.62	0.31	0.94	Fielden, 1998a
T 1					7	0.31	0.17	0.48	
					14	0.15	0.08	0.23	
					21	0.14	0.08	0.22	
					28	0.18	0.09	0.27	
France North 1997	WP	8	0.08-0.34	0.021	0	1.38	0.64	2.02	Fielden, 1998a
T 2					7	0.78	0.4	1.18	
					14	0.49	0.29	0.78	
					21	0.32	0.18	0.50	
					28	0.28	0.16	0.44	
France North 1997	WP	8	0.06-0.21	0.021	0	0.74	0.37	1.11	Fielden, 1998a
T 3					7	0.46	0.26	0.72	
					14	0.25	0.14	0.39	
					21	0.17	0.11	0.28	
					28	0.18	0.10	0.28	
France North 1997	WP	8	0.08-0.34	0.021	0	0.70	0.27	0.97	Fielden, 1998a
T 4					7	0.46	0.19	0.65	
					14	0.38	0.20	0.58	
					21	0.14	0.08	0.22	
					28	0.28	0.15	0.43	
Germany 1996	EC	8	0.08-0.42	0.021	0	1.30	0.67	1.97	Lees, 1998a
T 1					7	0.96	0.56	1.52	
					14	0.40	0.25	0.65	
					21	0.41	0.25	0.66	
					28	0.26	0.16	0.42	
Germany 1996	EC	8	0.20-0.35	0.063	0	1.16	0.60	1.76	Lees, 1998a
T 2					7	0.63	0.40	1.03	
					14	0.46	0.28	0.74	
					21	0.40	0.27	0.67	
					28	0.28	0.18	0.46	
Germany 1996	EC	8	0.09-0.33	0.021	0	0.82	0.48	1.30	Lees, 1998a
T 3					7	0.5	0.32	0.82	
					14	0.33	0.22	0.55	
					21	0.20	0.13	0.33	
					28	0.27	0.19	0.46	
Germany 1997	EC	8	0.08-0.34	0.021	0	0.45	0.23	0.68	Fielden, 1998a
T 1					7	0.45	0.25	0.70	
					14	0.20	0.12	0.32	
					21	n.d..	n.d.	n.d.	
					28	0.11	0.07	0.18	
Germany 1997	EC	8	0.08-0.34	0.021	0	1.07	0.67	1.74	Fielden, 1998a
T 2					7	0.29	0.21	0.50	
					14	0.26	0.15	0.41	

Country, Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
					21	0.13	0.09	0.22	
					28	0.09	0.05	0.14	
Germany 1997	WP	8	0.09-0.34	0.021	0	0.86	0.43	1.29	Fielden, 1998a
T 1					7	0.51	0.28	0.79	
					14	0.23	0.13	0.36	
					21	0.16	0.1	0.26	
					28	0.12	0.07	0.19	
Germany 1997	WP	8	0.08-0.34	0.021	0	1.03	0.69	1.72	Fielden, 1998a
T 2					7	0.40	0.22	0.62	
					14	0.32	0.17	0.49	
					21	0.24	0.12	0.36	
					28	0.15	0.07	0.22	
Greece 1997	EC	6	0.31	0.021	0	0.74	0.44	1.18	Sutcliffe, 1998b
					14	0.07	0.06	0.13	
					21	0.10	0.10	0.20	
Greece 1997	WP	6	0.32	0.021	0	0.80	0.41	1.21	Sutcliffe, 1998b
					14	0.14	0.10	0.24	
					21	0.06	0.05	0.11	
Italy 1991	EC	7	0.175	0.06	0			0.20	Pessina, 1993e
					32			<0.05	
Italy 1991	EC	5	0.16	0.018	0	0.36	0.74	1.10	Pessina, 1993e
					20	0.13	0.17	0.30	
Italy 1991	EC	3	0.18	0.06	54	<0.05	<0.05	<0.05	Pessina, 1993e
Italy 1991	EC	5	018	0.018	0	0.09	0.21	0.30	Pessina, 1993e
					20	<0.05	<0.05	<0.05	
					40	<0.05	<0.05	<0.05	
					60	<0.05	<0.05	<0.05	
Italy 1991	WP	7		0.11	32			<0.05	Pessina, 1993e
Italy 1992	EC	6	0.27-0.31	0.018	0			0.26	Pessina, 1993g
					20			<0.04	
Italy 1992	EC	6	0.17-0.21	0.018	0			0.27	Pessina, 1993g
					20			<0.04	
Italy 1993	WP	6	0.17-0.26	0.022	0			0.30	Pessina, 1994e
					20			<0.04	
Italy 1993	EC	6	0.24-0.32	0.021	0			0.65	Pessina, 1994e
					20			<0.04	
Italy 1993	WP	6	0.25-0.33	0.022	0			0.54	Pessina, 1994e
					20			<0.04	
Italy 1993	EC	6	0.16-0.24	0.021	0			0.34	Pessina, 1994e
					20			<0.04	
Italy 1996	EC	6	0.21-0.32	0.021	0	0.31	0.16	0.47	Lees, 1998b
					14	0.05	<0.05	0.09	
					21	0.05	<0.05	0.08	
Italy 1996	EC	6	0.21-0.32	0.021	0	0.38	0.23	0.61	Lees, 1998b
					14	0.06	<0.05	0.09	
					21	0.06	<0.05	0.09	
Italy 1997	EC	6	0.21-0.32	0.021	0	0.17	0.10	0.27	Sutcliffe, 1998b
T 1					14	n.d.	n.d.	<0.05	
					21	n.d.	n.d.	<0.05	
Italy 1997	WP	6	0.22-0.32	0.021	0	0.31	0.13	0.44	Sutcliffe, 1998b

Country, Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
T 1					14	n.d.	n.d.	<0.05	
					21	n.d.	n.d.	<0.05	
Italy 1997	EC	6	0.22-0.32	0.021	0	0.39	0.2	0.59	Sutcliffe, 1998b
T 2					14	0.1	0.05	0.15	
					21	0.06	0.05	0.11	
Italy 1997	WP	6	0.2-0.32	0.021	0	0.54	0.21	0.75	Sutcliffe, 1998b
T 2					14	<0.05	<0.05	<0.05	
					21	n.d.	n.d.	n.d.	
Italy 1997	EC	6	0.21-0.32	0.021	0	0.3	0.19	0.49	Sutcliffe, 1998b
T 3					14	0.18	0.11	0.29	
					21	n.d.	n.d.	<0.05	
Italy 1997	WP	6	0.21-0.32	0.021	0	0.19	0.09	0.28	Sutcliffe, 1998b
T 3					14	<0.05	<0.05	<0.05	
					21	<0.05	<0.05	<0.05	
Portugal 1991	EC	1	0.18	0.073	0			<0.04 [1]	Conraux, 1993d
					7			0.15	
					14			<0.04	
Portugal 1991	EC	2	0.18	0.073	0			2.1 [2]	Conraux, 1993d
					7			0.28	
					14			0.05	
					22			<0.02	
Portugal 1991	EC	1	0.18	0.073	0			0.62	Conraux, 1993d
					7			0.07	
					14			0.06	
					22			<0.04	
Portugal 1991	EC	8	0.18	0.073	14			<0.04 [1]	Conraux, 1993d
Portugal 1991	EC	7	0.18	0.073	15			<0.04 [1]	Conraux, 1993d
Portugal 1992	EC	1	0.18	0.073	0			0.79	Conraux, 1993g
					7			0.06	
					14			0.06	
					21			0.06	
					28			<0.04	
		2	0.18	0.073	0			0.22	
					7			0.06	
					14			<0.04	
					21			<0.04	
					28			<0.04	
Portugal 1992	EC	1	0.18	0.073	0			0.93	Conraux, 1993h
					7			0.33	
					14			0.2	
					21			0.2	
					28			<0.04	
		2	0.18	0.073	0			1.65	
					7			0.36	
					14			0.08	
					21			0.3	
					28			<0.04	
Spain 1991	EC	7	0.065-0.21	0.028	36			<0.02	Jousseaume, 1993a
Spain 1991	EC	7	0.065-0.73	0.028	35			<0.02	
Spain 1991	EC	6	0.1-0.66		36			<0.02	

Country, Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
Spain 1991	EC	6	0.1-0.66		35			<0.02	
Spain 1991	EC	1	0.26	0.021	0			<0.02	
					14			<0.02	
					22			<0.02	
					28			<0.02	

[1] Re-analysed
[2] Not re-analysed

Strawberries. Several trials were conducted in France, Italy, Spain and the UK.

Summary data were submitted from two field trials in France in 1991, where the EC formulation was applied to two 5 m plots of strawberries (two varieties) with spray volumes of 400-500 l/ha at intervals of 7 days, starting at flowering. Samples were stored frozen for 13 months before analysis. The reported LOD was 0.04 mg/kg and the mean recovery 74.9% (Conraux, 1993b).

A trial was carried out in France in 1992 where dinocap was applied 6 times to a plot of 80 plants, with spray volumes of 500 l/ha and application intervals of 7 days. Samples were stored at -18ºC for 57 days before analysis. The reported LOD was 0.05 mg/kg and the mean recovery 69.7% (Conraux, 1993n)

In field trials in Southern France in 1996 at different locations and on different varieties the EC formulation was applied with the first application at flowering and the last application when most fruit were ripe. Strawberry plots (52 to 72 m^2) were sprayed with 400 to 900 l/ha at intervals of 10-14 days. Samples harvested 0, 3 and 7 days after the last treatment were stored at -20ºC up to 398 days before analysis (Lees, 1998d).

In indoor trials in Italy in 1997 the EC and WP formulations were applied 4 times at rates of 0.16 to 0.33 kg ai/ha. Samples were harvested 0, 3 and 7 days after the last treatment. Residues decreased from 1.57 mg/kg at day 0 to 0.08 mg/kg at day 7. Since detailed reports of the trials were not submitted the results were not evaluated.

Two field trials were conducted in Spain (Gerona) in 1992, where a 4 m^2 strawberry plot was treated with one and two applications of the EC formulation at 0.26 kg ai/ha, starting at the mature growth stage with a 7-day application interval and spray volumes of 800 l/ha. Samples were stored at -18ºC for 112 days before analysis (Conraux, 1993i).

Two small-plot trials and two growers trials with 5-7 applications were carried out in the UK in 1990, the first (T.1) with application intervals of 12-38 days and a spray volume of 250 l/ha, the second with application intervals of 11 to 25 days, and the third and fourth with intervals of 4 to 18 days. The spray volume in the last three trials was 2000 l/ha. Samples were stored for about 16 months at -18ºC before analysis with an LOD of 0.05 mg/kg and mean recovery of 80% (Murray, 1992b).

Four small field trials on 30 m^2 plots in the UK in 1993 were with EC and WP treatments at rates of 0.49 kg ai/ha and 0.98 kg ai/ha, at intervals of 10-14 days and spray volumes of 500 l/ha. Samples were stored at -18ºC for 3-4 months before analysis by GLC with an ECD (Murray, 1994).

In another two field trials at two locations in the UK in 1996 the EC formulation was applied to strawberry plots (each 4 rows of 150 m) starting at flowering at intervals of 10 days with spray volumes of 1200-1600 l/ha. Samples were taken 0 and 3 days after the last treatment and stored at -18ºC for a maximum of 362 days before analysis. Samples from day 3 were processed to jam and preserves (Lees, 1998f).

The results are shown in Table 39.

Table 39. Residues of dinocap in strawberries. Underlined residues are from trials according to GAP.

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg			Reference, Comments
		Form.	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
France 1991	F	EC	7	0.18	0.044	0			0.18	Conraux, 1993b
						3			<0.04	re-analysed samples
						7			<0.04	
France 1991	F	EC	6	0.18	0.035	0			0.18	
						3			0.06	
						7			<0.04	
France 1992	F	EC	6	0.18	0.035	0			0.36	Conraux, 1993n
						3			0.16	
						7			0.06	
France 1996	F	EC	6	0.09-0.12	0.021	0	0.19	0.1	0.28	Lees, 1998d
T 1						3	<0.05	<0.05	0.05	
South						7	<0.05	<0.05	<0.05	
France 1996	F	EC	6	0.09-0.12	0.021	0	0.18	0.09	0.27	Lees, 1998d
T 2						3	<0.05	<0.05	0.05	
South						7	<0.05	<0.05	<0.05	
France 1996	F	EC	6	0.08-0.2	0.021	0	0.14	0.06	0.21	Lees, 1998d
T 3						3	0.05	<0.05	0.06	
						7	<0.05	<0.05	<0.05	
France 1996	F	EC	6	0.16-0.2	0.021	0	0.3	0.29	0.59	Lees, 1998d
T 4						3	0.22	0.1	0.33	
						7	0.08	<0.05	0.11	
Italy 1997	G	EC	4	0.31-0.32	0.021	0	0.9	0.39	1.29	No report submitted
						3	0.99	0.39	1.38	
						7	0.72	0.35	1.06	
Italy 1997	G	EC	4	0.16-0.23	0.021	0	0.28	0.11	0.4	
						3	0.12	0.06	0.19	
						7	0.07	<0.05	0.1	
Italy 1997	G	WP	4	0.24-0.33	0.021	0	1.13	0.44	1.57	
						3	0.94	0.42	1.36	No report submitted
						7	0.6	0.26	0.86	
Italy 1997	F	WP	4	0.16-0.23	0.021	0	0.34	0.14	0.47	No report submitted
						3	0.12	0.06	0.18	
						7	0.05	<0.05	0.08	
Spain 1992	F	EC	1	0.26	0.033	0			0.42	Conraux, 1993i

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg			Reference, Comments
		Form.	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
						7			<0.04	
						13			<0.04	
			2	0.26	0.033	0			0.32	
						7			<0.04	
						13			<0.04	
UK 1990 T 1	F	EC	5	0.21	0.084	5			<0.05	Murray, 1992b
						8			<0.05	Grower trial
						12			<0.05	
						15			<0.05	
UK 1990 T 2	F	EC	7	<0.49	0.024	3			0.58	Murray, 1992b
						6			0.31	Grower trial
						13			0.11	
						16			0.05	
UK 1990 T 3	F	EC	6	<0.49	0.024	0			1.66	Murray, 1992b
						5			0.24	
						8			0.08*	*average of 4 analyses
						15			0.05	
						18			<0.05	
UK 1990 T 4	F	EC	6	<0.49	0.024	0			1.05	Murray, 1992b
						4			0.25	
						7			0.09	
						14			<0.05	
						17			<0.05	
UK 1993 T 1	F	EC	5	0.49	0.1	0			0.79	Murray, 1994
						3			0.32	
						7			0.14	
						14			<0.05	
	F	EC	5	0.98	0.2	0			2.31	
						7			0.37	
UK 1993	F	WP	5	0.49	0.1	0			0.76	Murray, 1994
T 1						7			0.33	
		WP	5	0.98	0.2	0			2.56	
						7			0.44	
UK 1993	F	EC	5	0.49	0.1	0			0.26	Murray, 1994
T 2						3			0.19	
						7			0.06	
						14			<0.05	
UK 1993	F	WP	5	0.49	0.1	0			0.1	
T 2						7			<0.05	
UK 1993	F	EC	5	0.49	0.1	0			0.85	Murray, 1994
T 3						3			0.58	
						7			0.21	
						14			0.06	
UK 1993	F	WP	5	0.49	0.1	0			0.67	
T 3						7			0.06	
UK 1993										
T 4	F	EC	5	0.49	0.1	0			1.53	Murray, 1994

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg			Reference, Comments
		Form.	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
						3			0.9	
						7			0.32	
						14			0.13	
UK 1993	F	EC	5	0.49	0.1	0			0.67	
T 4						7			0.06	
UK 1996	F	EC	6	0.32-0.41	0.027	0	0.34	0.17	0.5	Lees, 1998f
						3	0.15	0.08	0.23	
UK 1996	F	EC	6	0.37-0.44	0.027	0	0.5	0.24	0.74	
						3	0.2	0.11	0.31	

Apricots. A single field trial was conducted in Italy in 1995, where a plot of 6 trees was sprayed 4 times with the EC formulation at a rate of 0.021 kg ai/hl at 14-day intervals with spray volumes of 1000-1500 l/ha. Samples were stored for approximately 11 months before analysis. The results are shown in Table 40 (Pessina, 1995).

Peaches. In a field trial in Greece in 1997 the EC formulation was applied four times on plots of 6 trees at intervals of 10-14 days. Samples were stored at -20ºC for 126-153 days before analysis (Sutcliffe, 1998d).

Trials were conducted at two locations in Italy in 1991 on plots of 28 trees. Only a summary of these trials was reported (Pessina, 1993d).

Trials in Italy in 1992 on 10-tree plots of two varieties of peaches were with 3 applications of the EC formulation by knapsack sprayer with 15-day application intervals and spray volumes of 1500 l/ha. The first application was to fruit of 6 cm diameter and the last at pre-ripening. Samples were stored at -20ºC for 6 months before analysis (Pessina 1993j).

In another field trial in Italy in 1993 4 applications of the EC or WP formulation were made to plots of 9 plants, variety Maria Bianca, with spray volumes of 1000-1200 l/ha and application intervals of 7 days. The first application was made to nut-sized fruit and the last to fully grown peaches. Samples were taken 0, 7 and 14 days after the last treatment and were stored at -20ºC for 6 months before analysis. The fruit without stones were analysed but the results were expressed on a whole-fruit basis (Pessina, 1994d).

In trials on three peach varieties at three different locations in Italy in 1997 dinocap was applied to plots of 8 trees four times during the growing season by backpack lance sprayer at a rate of 0.021 kg ai/hl (1200-1500 l/ha) at intervals of 10-14 days. Samples were stored at -20ºC for 66 to 163 days before analysis. Residues were expressed on the whole fruit including stone. Samples from day 14 were processed to juice and preserve. The reported LOD was 0.05 mg/kg and recoveries were 81-95% (Sutcliffe, 1998d).

Trials in Spain in 1992 were with 1 or 2 applications of the EC formulation at a rate of 0.026 kg ai/hl to plots of 3 trees with spray volumes of 1000 l/ha. Samples were stored at -18ºC for 114 days before analysis. The reported LOD was 0.04 mg/kg and the mean recovery 83.5 ± 13.7%.

The results are shown in Table 40.

Table 40. Residues of dinocap in stone fruits. Underlined residues are from trials according to GAP.

CROP Country Year	Application				PHI, days	Dinocap, mg/kg			Reference Comments
	Form	No	kg ai/ha	kg ai/hl		2.4-	2.6-	Total	
APRICOTS									
Italy 1995	EC	4	0.31	0.021	0			0.21	Pessina, 1995a
					3			<0.04	
					7			0.05	
					14			<0.04	
					21			<u><0.04</u>	
PEACHES									
Greece 1997	EC	4	0.27-0.31	0.021	0	0.45	0.2	0.66	Sutcliffe, 1998d
					3	0.26	0.15	0.41	
					7	0.19	0.11	0.3	
					14	0.05	<0.05	0.09	
					21	<0.05	<0.05	<u><0.05</u>	
Italy 1991	EC	4	<0.35	0.018	7	<0.04	<0.04	<u><0.04</u>	Pessina, 1993d
					14	<0.04	<0.04	<0.04	
					27	<0.04	<0.04	<0.04	
					38	<0.04	<0.04	<0.04	
Italy 1991	EC	4	<0.26	0.018	0	0.12	0.06	0.18	Pessina, 1993d
					7	<0.04	<0.04	<0.04	
					20	<0.04	<0.04	<u><0.04</u>	
					30	<0.04	<0.04	<0.04	
Italy 1992	EC	3	<0.26	0.018	0			0.12	Pessina, 1993j
					15			<0.04	
Italy 1992	EC	3	<0.26	0.018	0			0.08	Pessina, 1993j
					15			<0.04	
Italy 1993	WP	4	0.2	0.018	0			0.21	Pessina, 1994d
					7			<u><0.04</u>	
					14			<0.04	
Italy 1993	EC	4	0.22	0.018	0			0.18	Pessina, 1994d
					7			<u><0.04</u>	
					14			<0.04	
Italy 1997	EC	4	0.25-0.32	0.021	0	0.18	0.09	0.27	Sutcliffe, 1998d
					3	0.09	0.05	0.14	
					7	0.05	<0.05	<u>0.09</u>	
					14	n.d.	n.d.	n.d.	
					21	n.d.	n.d.	n.d.	
Italy 1997	EC	4	0.25-0.32	0.021	0	0.29	0.15	0.44	Sutcliffe, 1998d
					3	<0.05	<0.05	0.05	
					7	<0.05	<0.05	<u><0.05</u>	
					14	n.d.	n.d.	<0.05	
					21	n.d.	n.d.	n.d.	
Italy 1997	EC	4	0.26-0.32	0.021	0	0.23	0.1	0.33	Sutcliffe, 1998d
					3	0.06	<0.05	0.09	
					7	<0.05	<0.05	<u><0.05</u>	
					14	<0.05	<0.05	<0.05	
					21	n.d.	n.d.	n.d.	
Spain 1992	EC	1	0.26	0.026	0			0.27	Conraux, 1993j
					15			<0.04	

CROP Country Year	Application				PHI, days	Dinocap, mg/kg			Reference Comments
	Form	No	kg ai/ha	kg ai/hl		2.4-	2.6-	Total	
					22			<0.04	
					29			<0.04	
		2	0.26	0.026	0			0.71	
					15			0.24	
					22			0.05	
					29			<0.04	

Cucumbers. Two protected field trials were carried out in Southern France in 1996, where the EC formulation was sprayed 6 times on cucumber plots (8-9.5 x 10 m) almost to run-off at intervals of 10-11 days. The first applications were made when the first flowers opened or first fruits developed, and the last near ripening. The SAIs were 327-341 days (Lees, 1998e).

Protected field trials were conducted with dinocap EC in Spain in 1993 and 1996. In 1993 plants were treated with 3 sprays at a rate of 0.39 kg ai/ha, with spray volumes of 1200-2030 l/ha and application intervals of 7 days. Samples were taken 0, 3, 7 and 14 days after the last treatment. No residues above the LOD (0.04 mg/kg) were detected in any of the samples. Samples were stored at -18ºC for 42 days before analysis (Jousseaume, 1994a). In 1996 3-3.8 x 10 m plots were sprayed 5 or 6 times almost to run-off at intervals of 10-14 days, from flowers developing to fruits developing. Samples were stored for 305-348 days before analysis. The reported LOD was 0.05 mg/kg and the mean recovery 84-88% (Lees 1998e).

The results are shown in Table 41.

Table 41. Residues of dinocap in cucumbers from protected trials. Underlined residues are from trials according to GAP.

Country Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
France 1996	EC	6	0.14-0.21	0.021	0	<0.05	<0.05	0.05	Lees, 1998e
					3	<0.05	n.d	<u><0.05</u>	
					7	n.d.	n.d.	n.d.	
France 1996	EC	6	0.16-0.18	0.021	0	<0.05	<0.05	<0.05	Lees, 1998e
					3	<0.05	n.d.	<u><0.05</u>	
					7	n.d.	n.d.	n.d.	
Spain 1993	EC	3	0.39	0.019	0			<0.04	Jousseaume 1994b
					3			<0.04	
					7			<u><0.04</u>	
					14			<0.04	
		2	0.39	0.019	7			<0.04	
Spain 1996	EC	6	0.28-0.63	0.021	0	0.07	<0.05	0.09	Lees, 1998e
					3	<0.05	<0.05	0.05	
					7	<0.05	<0.05	<u><0.05</u>	
Spain 1996	EC	5	0.47-0.74	0.021	0	0.05	<0.05	0.08	Lees, 1998e
					3	0.05	<0.05	0.08	
					7	n.d	n.d.	n.d.	

<u>Melons</u>. In two trials in France in 1993 the EC or WP formulation was applied four times to triplicate plots (10 m^2) with spray volumes of 400 l/ha. The last applications were made at maturity. Samples were stored at -18ºC for 174 days before analysis. (Conraux, 1994a).

In one field trial in Greece in 1997 there were six applications at intervals of 10 days, the first at 3-4 leaves unfolded and the last when the fruits reached final size. The SAI was 134 days (Sutcliffe, 1998c).

Field trials were conducted in Italy from 1991 to 1995. In 1991 critical information was not submitted (Pessina, 1993b).

In two other trials in 1992 the EC formulation was applied three times to plots of 100 or 200 m^2 at 7-day intervals with a knapsack sprayer. Spray volumes were 600 l/ha. Samples were harvested 0, 7 and 14 days after the last treatment and stored frozen for 96-150 days before analysis (Pessina, 1993h). In two field trials in 1993 the EC or WP formulation was sprayed 3 times at 7-day intervals on 50 m^2 plots at fruit ripening with spray volumes of 920 to 990 l/ha. Samples were stored at -20ºC for 6-7 months before analysis. The reported LOD was 0.04 mg/kg and recoveries ranged from 86 to 114% (Pessina, 1994a). In two trials in 1995 on different varieties the EC formulation was applied six times at a higher rate than GAP, the first application in an open glasshouse and the last in the field at 10% ripeness, at intervals of 10-14 days. Samples were frozen for 6 months before analysis (Pessina, 1996).

Field trials were carried out in Spain in 1991 (2), 1992 (2) and 1997 (1). In 1991 melons were sprayed with the EC formulation at 0.175 kg ai/ha and a spray volume of 825 l/ha. Samples were stored at -18ºC for 20-22 months before analysis. Jousseaume (1993) used a method that measured only phenyl

crotonates. The samples were re-analysed by Conraux (1993a). The residues were all below the LOD (0.04 mg/kg).

In 1992 dinocap was applied once or twice to melon plots (20 m^2) with spray volumes of 1000 l/ha. Samples were stored for 272 days at -18ºC before analysis. The reported LOD was 0.04 mg/kg and the mean recovery 85%. No residues above the LOD were found in any of the samples taken from 7 to 21 days after the last treatment (Conraux, 1993l). In 1997 (glasshouse) five sprays were applied, the first when flowers were visible and the last when fruits reached maturity. The SAI was 137 days (Sutcliffe, 1998c).

The results are shown in Table 42.

Table 42. Residues of dinocap in melons. Underlined residues are from trials according to GAP.

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg	Reference
		Form	No	kg ai/ha	kg ai/hl			
France 1993	F	EC	4	0.175	0.044	0	<0.04	Conraux, 1994a
						4	<u><0.04</u>	
	F	WP	4	0.175	0.044	0	<0.04	
						4	<u><0.04</u>	
Greece 1997	F	EC	6	0.1-0.25	0.021	0	0.05	Sutcliffe, 1998c
						3	n.d.	
						7	n.d.	
Italy 1991	F	EC	3	<0.11	0.018	0	<0.04	Pessina, 1993b 3 replicates
						3	<0.04	
						7	<u><0.04</u>	
						14	<0.04	
Italy 1991	F	EC	3	<0.11	0.018	0	<0.04	Pessina, 1993b
						3	<0.04	
						7	<u><0.04</u>	
						14	<0.04	
Italy 1992	F	EC	3	<0.11	0.018	0	0.08	Pessina, 1993h
						7	<u><0.04</u>	
						14	<0.04	
Italy 1992	F	EC	3	<0.11	0.018	0	<0.04	Pessina, 1993h
						7	<u><0.04</u>	
						14	<0.04	
Italy 1993	F	WP	3	0.17-0.18	0.018	0	0.04 (<0.04-0.06)	Pessina, 1994a
						3	<0.04	
						7	<u><0.04</u>	
Italy 1993	F	EC	3	0.16-0.17	0.018	0	0.04	Pessina, 1994a
						3	<0.04	
						7	<u><0.04</u>	
Italy 1995	F	EC	6	0.29-0.32	0.032-0.063	0	<0.04	Pessina, 1996
Mirabella						3	<0.04	
						7	<0.04	
Italy 1995	F	EC	6	0.29-0.32	0.032-0.063	0	<0.04	Pessina, 1996a
Ferrara						3	<0.04	
						7	<0.04	
Spain 1991	F	EC	1	0.18	0.021	0	<0.04	Conraux, 1993a (re-analysed)
						1	<0.04	
						3	<0.04	

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg	Reference
		Form	No	kg ai/ha	kg ai/hl			
Spain 1991	F	EC	1	0.18	0.021	0	<0.04	Conraux, 1993a (re-analysed)
						13	<0.04	
Spain 1992	F	EC	2	<0.26	0.026	0	0.5	Conraux, 1993l
						7	<0.04	
						14	<0.04	
						21	<0.04	
			1	0.26	0.026	0	0.36	
						7	<0.04	
						14	<0.04	
						21	<0.04	
Spain 1997	G	EC	5	0.27-0.48	0.021	0	0.06	Sutcliffe, 1998c
						3	0.06	
						7	<0.05	

F: field
G: glasshouse

Summer squash. Summary information on two field trials in Southern France in 1991 was submitted. The EC formulation was sprayed once or twice on small plots (3-4 m^2) of different varieties. Samples were analysed three months after harvest (only total diphenyl crotonates were determined) and re-analysed 19 months later after storage at -18ºC for 22 months (Conraux, 1993c).

Two other field trials were carried out in France in 1992 with dinocap EC. In one 3 replicate plots of 5 plants were sprayed 5 times with volumes of 500 l/ha (Conraux, 1993k). In the other there were 4 sprays of 750 l/ha at a rate 0.35 kg ai/ha. Samples were stored below -18ºC for 226 days before analysis. No residues above the LOD (0.04 mg/kg) were detected in samples taken 3 and 7 days after the last treatment (Conraux, 1993f).

Two field trials were conducted in Italy in 1991. The EC formulation was sprayed 3 times with a volume of 600 l/ha. Only a summary was reported (Pessina, 1993c).

Two other trials were carried out at different locations in Italy in 1992 where the EC formulation was applied 3 times to plots of 100 m^2 and 200m^2, the first at flowering and the last at maturity with application intervals of 6 days and spray volumes of 600 l/ha. Samples were stored frozen for 5 to 7 months before analysis. The reported LOD was 0.04 mg/kg and recoveries 78 to 130% (Pessina, F., 1993i).

In two field trials in Italy in 1993 (Pessina, 1994b) the EC and WP formulations were sprayed 3 times to plots of 47 plants starting at the flowering stage at intervals of 7 days and spray volumes of 946-1013 l/ha. Samples were stored at about -20ºC for 3-4 months before analysis.

In Spain in 1993 the EC formulation was sprayed two or three times at intervals of 7 days by atomiser at spray volumes of 1388 l/ha on plots of 36 m^2 (Jousseaume, 1994d). The SAI was 210 days at -18ºC.

The results are shown in Table 43.

Table 43. Residues of dinocap in summer squash (zucchini). Underlined residues are from trials according to GAP.

Country Year	Application				Sample	PHI, days	Dinocap, mg/kg	Reference
	Form	No	kg ai/ha	kg ai/hl				
France 1991	EC	1	0.175	0.035	whole fruit	0	0.29	Conraux, 1993c
T 1						3	<0.04	
						7	<0.04	
						14	<0.04	
France 1991	EC	2	0.175	0.035	whole fruit	0	0.08	Conraux, 1993c
T 2						3	<0.04	
						7	<0.04	
						14	<0.04	
France 1992	EC	5	0.18	0.044	whole fruit	0	<0/04	Conraux, 1993k
						3	<0.04	
						7	<0.04	
France 1992	EC	4	0.35	0.046	whole fruit	0	0.11	Conraux, 1993f
						3	<0.04	
						7	<0.04	
Italy 1991	EC	3	0.11	0.018	fruit	0	0.06	Pessina, 1993c
T 1						3	<0.04	
						7	<0.04	
						14	<0.04	
Italy 1991	EC	3	0.11	0.018	fruit	0	<0.04	Pessina, 1993c
T 2						3	<0.04	
						7	<0.04	
						14	<0.04	
Italy FD'Albero 1992	EC	3	0.11	0.018	fruit	0	0.26	Pessina, 1993i
						3	<0.04	
						7	<0.04	
Italy Boara	EC	3	<0.11	0.018	fruit	0	0.04	Pessina, 1993i
1992						3	<0.04	
						7	<0.04	
Italy 1993	EC	3	0.18	0.018	fruit	0	0.07	Pessina, 1994b
						3	<0.04	
						7	<0.04	
	WP	3	0.19	0.018	fruit	0	0.08	Pessina, 1994b
						3	<0.04	
						7	<0.04	
Spain 1993	EC	3	0.39	0.028	fruit	0	0.32	Jousseaume, 1994d
						3	<0.04	
						7	<0.04	
						14	<0.04	
		2	0.39	0.028	fruit	7	<0.04	

Peppers. Trials were carried out with the EC formulation in Greece (one in 1997), Italy (3 in 1997) and Spain (1 in 1993 and 4 in 1996). In Greece 6 applications were made to a plot of 6 rows x 7 m in a glasshouse with spray volumes of 1500 l/ha and application intervals of 10 days. The reported LOD was 0.05 mg/kg and the recovery 80% (Fielden, 1998b).

In Italy two trials were under a tunnel and the third in a glasshouse. The EC formulation was sprayed 6 times almost to run-off on plots of 4-5 rows x 9-10 m every 14 days, starting when the plant organs began to develop and ending at maturity. The spray volume increased from 800 l/ha at the first application to 1500-3000 l/ha at the last. Samples were stored at -20ºC for 91-150 days before analysis (Fielden, 1998b).

In the field trial in Spain in 1993 the EC formulation was sprayed three times, first at flowering, with a volume of 980 l/ha at intervals of 14 days on a plot of 202 m^2. Samples were taken 7 days after the second treatment and 0, 3, and 7 days after the third, and stored at -18ºC for 192 days before analysis (Jousseaume, 1994e).

In 1996 protected plots (4 rows of 10 m) at different locations were sprayed 6 times at a higher rate than GAP, with application intervals of 10-14 days and spray volumes of 980-2500 l/ha. In three trials the first application was when the flowers opened and in the fourth 24 days earlier. At harvest, the fruits in trials 1, 2 and 4 had reached a typical size and in trial 3 they were ripening. Samples were stored at -20ºC for 228 to 409 days before analysis (Lees, 1998g). The results are shown in Table 44.

Table 44. Residues of dinocap in peppers. Underlined residues are from trials according to GAP.

Country Year	F/G/P	Application				PHI, days	Dinocap, mg/kg			Ref.
		Form	No	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
Greece 1997	G	EC	6	0.17-0.32	0.021	0	0.09	<0.05	0.13	Fielden, 1998b
						3	0.08	<0.05	0.06	
						7	0.07	<0.05	0.06	
Italy 1997	G	EC	6	0.17-0.72	0.021	0	0.09	<0.05	0.13	Fielden, 1998b
						3	<0.05	<0.05	0.12	
						7	<0.05	<0.05	0.12	
Italy 1997	P	EC	6	0.17-0.48	0.021	0	0.23	0.1	0.33	Fielden, 1998b
						3	0.15	0.09	0.23	
						7	<0.05	<0.05	0.06	
Italy 1997	P	EC	6	0.17-0.32	0.021	0	0.13	0.06	0.2	Fielden, 1998b
						3	0.05	<0.05	0.09	
						7	<0.05	<0.05	<0.05	
Spain 1993	F	EC	2	0.39	0.04	7[1]			0.04	Jousseaume, 1994e
			3	0.39	0.04	0			0.43	
						3			0.21	
						7			0.16	
Spain 1996	P	EC	6	0.27-0.54	0.021	0	0.23	0.11	0.34	Lees, 1998g
T1						3	0.1	0.06	0.16	
						7	<0.05	<0.05	0.05	
Spain 1996	P	EC	6	0.3-0.48	0.021	0	0.35	0.18	0.53	Lees, 1998g
T2						3	0.08	0.05	0.13	
						7	0.06	<0.05	0.11	
Spain 1996	P	EC	6	0.3-0.41	0.021	0	0.16	0.07	0.24	Lees, 1998g
T 3						3	0.06	<0.05	0.1	
						7	<0.05	<0.05	0.06	
Spain 1996	P	EC	6	0.19-0.34	0.021	0	0.07	<0.05	0.11	Lees, 1998g
T 4						3	0.1	<0.05	0.15	
						7	0.05	<0.05	0.07	

[1] After second of three treatments.

F: field; G: glasshouse; P: protected

Tomatoes. A field trial was conducted in Southern France in 1997. The EC formulation was sprayed 4 times almost to run-off on a 108 m^2 plot, starting at flowering, at intervals of 10 days and spray volumes of 1300-1700 l/ha. Samples were stored at -20ºC for a maximum of 133 days before analysis. Samples from day 7 were processed to juice, purée, preserves and ketchup (Howie, 1998).

In a field trial in Italy in 1992 the EC formulation was applied three times to a commercial variety, starting at fruit enlargement, with 7-day application intervals and spray volumes of 600 l/ha. The reported LOD was 0.04 mg/kg and recoveries ranged from 73 to 120% (Pessina, 1993k).

Two other field trials were carried out in Italy in 1993 on commercial tomato plots (37 m^2 and 20 m^2). Three applications of the EC or WP formulation with spray volumes of 900-100 l/ha were made, starting at the change of fruit colour at intervals of 7 days. Samples were stored at -20ºC less than 5 months before analysis (Pessina 1994c).

Two other field trials were conducted in Spain in 1991 with 1 application of the EC formulation to Cristina and Bornia varieties with spray volumes near 1000 l/ha. The plot sizes were 30 m^2. Samples were first analysed by a method that measures only phenyl crotonate esters (Jousseaume, 1993e), but re-analysed by the Brackett method where the reported LOD was 0.05 mg/kg and the recovery 74.9%. Samples were stored at -18ºC for 12 months before analysis (Conraux, 1993e).

In two other fields trials in Spain in 1991 the EC formulation was applied once or twice to plots of 30 m^2 at 0.26 kg ai/ha and spray volumes of 1000 l/ha with an application interval of 7 days. Samples were stored at -18ºC for a maximum of 343 days before analysis (Conraux, 1993o).

Two indoor trials with 3 applications of the EC formulation at intervals of 7 days were conducted in Spain in 1993. In one dinocap was applied to a plot of 20 x 1.6 m with spray volumes of 1000-1500 l/ha. Summary details were submitted. The samples were stored below -18ºC for 42 days before analysis (Jousseaume, 1994b).

In the other indoor trial the plots were 26 m^2 and spray volumes 1100 l/ha. Samples were stored at -18ºC for 79 days before analysis. The reported LOD was 0.04 mg/kg and the mean recovery 72.7% (Jousseaume, 1994c).

None of the trials complied with GAP. The results are shown in Table 45.

Table 45. Residues of dinocap in tomatoes.

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg	Reference, Comments
		Form	No	kg ai/ha	kg ai/hl			
France 1997	F	EC	4	0.29-0.36	0.021	0	0.08	Howie, 1998
South						3	0.06	
						7	<0.05	
Italy 1992	F	EC	3	0.11	0.018	0	0.08	Pessina, 1993k
						7	<0.04	
						14	<0.04	
Italy 1993	F	WP	3	0.18	0.018	0	0.24	Pessina, 1994c
						3	0.07	
						7	<0.04	
Italy 1993	F	EC	3	0.17	0.018	0	0.09	Pessina, 1994c
						7	<0.04	

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg	Reference, Comments
		Form	No	kg ai/ha	kg ai/hl			
						14	<0.04	
Spain 1991	F	EC	1	0.26	0.026	0	0.29	Jousseaume, 1993b
						3	<0.04	Re-analysed Conraux, 1993e
Spain 1991	F	EC	1	0.26	0.026	0	0.11	Jousseaume, 1993b
						3	<0.05	Re-analysed Conraux, 1993e
Spain 1991	F	EC	1	0.26	0.026	0	0.11	Conraux, 1993o
						3	0.05	
						8	0.04	
						15	<0.04	
		EC	2	0.26	0.026	0	0.26	
						3	0.1	
						8	<0.04	
						15	<0.04	
Spain 1993	G	EC	2	0.39	0.025	8	0.18	Jousseaume, 1994b
			3	0.39	0.025	0	<0.04	
						3	0.21	
						7	0.08	
						14	<0.04	
Spain 1993	G	EC	1	0.39	0.036	0	0.06	Jousseaume, 1994c
			2	0.39	0.036	7	<0.04	
			3	0.39	0.036	0	0.09	
						3	0.06	
						7	<0.04	
						14	<0.04	

Animal feeding studies

No information.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

Processing studies were conducted on apples, grapes, peaches, strawberries and tomatoes.

Apples. In two trials in France in 1997 (one at a twofold rate), unwashed apples harvested 14 days after the last treatment were processed into juice and purée. Filtered and decanted apple juice was heated to 88-90ºC and sterilized in glass jars in boiling water for 5 minutes. For apple purée 5 kg of apples were blanched, crushed and sieved, sugar was added and dissolved by heating, and the purée was heated in glass jars at 80-85ºC. Samples were analysed by GLC with an ECD. The reported LOD for juice and purée was 0.05 mg/kg and the mean recoveries were 77% for juice and 88% for purée. Wet and dry pomace were not analysed. The SAI was 246 days (Lees, 1998c).

Two other studies were carried out with apples from two sites in the UK where apple trees were treated according to GAP. The procedures were reported as typical of processes that would be used for commercial manufacture. For the preparation of juice, washed apples were milled and pressed, the weight of extracted juice was recorded and the juice canned and pasteurized for 10 minutes at 100ºC. The cans were cooled and frozen at -18ºC. The SAI was 100 days for purée and 58 days for juice. Pomace was collected and frozen at -18ºC.

Processing to purée and juice reduced the residues since none were detected in any analysed samples. There was no concentration in pomace. The results are shown in Table 46.

Table 46. Residues of dinocap in apples and processed products.

Country Location Year	kg ai/hl/kg ai/ha	No. of applicn.	PHI, days	Sample	Dinocap, mg/kg	Reference
France St.Porchaire 1997	0.021 kg ai/l	6	14	whole fruit	<0.05	Lees, 1998c
				juice	n.d.	
				purée	n.d.	
France Villemade 1997	0.021 kg ai/hl	6	14	whole fruit	0.09	Lees, 1998c
				juice	n.d.	
				fruit	n.d.	
U.K. Nottinghamshire 1997	0.36-0.38 kg ai/ha	10	14	whole fruit unwashed	0.06	Lees, 1998h
				pomace	0.06	
				juice	n.d.	
				purée	n.d.	
UK Gloucestershire 1997	0.46-0.5 kg ai/ha	10	14	whole fruit unwashed	<0.05	Lees, 1998h
				pomace	<0.05	
				juice	n.d.	
				purée	n.d.	

Grapes. Residues of dinocap in must and wine from a Merlot grape trial in France in 1992 were reported, but no information about the vinification process was submitted. Must and wine samples were stored for 351 days at -18ºC before analysis, The LOD for all samples was 0.04 mg/kg and the mean recoveries 94.8 and 85.9% for must and wine respectively (Conraux, 1994b).

Two vinification trials in 1991, one in 1992 and three in 1993 were conducted in Italy with 6-7 applications at rates ranging from 0.11 to 0.28 kg ai/ha. No information on the vinification process was reported for the 1992 trial.

In 1991 white grapes were cooled at 2ºC and pressed, and the must was clarified. After remixing the must was kept 12 hours at 8ºC, then fermented with native yeast under controlled temperature. At the end of the fermentation the alcohol concentration was adjusted. Red grapes were stored at room temperature and then pressed. The must was separated and fermented with native yeast under controlled temperature, no higher than 25ºC. The fermented wine was filtered (Pessina, 1993e)

In 1993 a simple vinification procedure was adopted to define the effects of processing on residue levels. About 200 kg of grapes were divided into three containers and processed separately. The grapes were pressed and SO_2 was added. During fermentation the mixture was aerated twice a day. The fermented wine was kept 10 days in a refrigerator at -2ºC to precipitate tartrates. The wine was bottled after a month. Samples of must, wine and lees were analysed by GLC with an NPD, with an LOD of 0.04 mg/kg for all samples and mean recoveries of 108%, 97% and 98% for grapes, must and wine respectively (Pessina, 1994e).

Samples taken at a 21-day PHI from trials in Germany in 1996 were processed into must and young and mature wine according to standard commercial procedures in a pilot plant (Lees, 1998a). Samples were analysed by GLC with an ECD. The LOD was 0.05 mg/kg and recoveries were 76%, 74% and 91% for grapes, must and wine respectively. The SAI for must and wine was 358 days.

The results are shown in Table 47.

Table 47. Residues of dinocap in grapes and vinification products.

Country Year Variety	Application		PHI, days	Total dinocap, mg/kg					Ref.
	No	kg ai/hl		Grapes	Must	Young wine	Mature wine	Lees	
France 1992	6	0.14	14	0.1 whole bunch	<0.04		<0.04		Conraux, 1994b
Italy 1991	6	0.018	20	<0.05	<0.05		<0.05		Pessina, 1993e
Italy 1991	7	0.011	48	<0.05	<0.05		<0.05		Pessina, 1993e
Italy 1992		0.018	20	<0.04	<0.04		<0.04	<0.04	Pessina, 1993g
Italy 1993 Barbera	6 WP	0.022	20	<0.04	<0.04		<0.04	<0.04	Pessina, 1994e
Italy 1993 Pinot nero	6 WP	00.22	20	<0.04	<0.04		<0.04	<0.04	
Italy 1993 Pinot nero	6 EC	0.022	20	<0.04	<0.04		<0.04	<0.04	
Italy 1993	6 EC	0.21	20	<0.04	<0.04		<0.04	<0.04	
Germany 1996	8	0.063	21	0.67	<0.05	n.d.	n.d.		Lees, 1998a
Germany 1996	8	0.021	21	0.33	<0.05	n.d.	n.d.		Lees, 1998a

No residues were found above the LOD in the must or wine in any of trials where grapes were treated at or above the recommended rate. Residues in pomace, which can be used as animal feed, were not determined.

Peaches. Peaches from two trials at the recommended rate (0.021 kg/hl) were processed into juice and preserved fruit in Italy in 1997.

Control and treated peaches (3 and 6 kg) were blanched for 2 minutes at 85-90ºC, then peeled and sliced. A mixture of water and sugar was added and the mixture was sterilized in glass jars at 115ºC, then cooled and refrigerated or frozen.

To prepare juice 14.6 kg of peaches were cut, destoned and sieved to extract the juice (3.5 kg). In another trial 12.9 kg of peaches were cut, ground and sieved to obtain 3.7 kg of juice. The juice was sterilized.

The residues in the raw peaches and the processed products were all below the LOD. The results are shown in Table 48.

Table 48. Residues of dinocap in peaches and their processed products (Sutcliffe, 1998d).

Country Year	Application		PHI, days	Sample	Residues, mg/kg
	No	kg ai/hl			
Italy 1997	4	0.021	14	whole fruit	<0.05
				juice	<0.05
				Preserved fruit	n.d
Italy 1997	4	0.021	14	whole fruit	<0.05
				juice	n.d.
				Preserved fruit	n.d.

Strawberries. In two trials in the UK in 1996 strawberries picked 3 days after treatment according to GAP were processed to jam and preserved fruit. For the preparation of jam 2-3 kg of strawberries were washed for at least 2 minutes under a spray of potable water, then boiled with sugar (3 kg), water and pectin (16-17 g) in a steam pan until the soluble solids reached a concentration of approximately 63º Brix. Citric acid was added.

To prepare preserved fruit about 5 kg of strawberries were sorted, freed from foreign material and rotten fruit and washed. The strawberries were filled into glass jars, and water at 92ºC was added before pasteurisation at an initial temperature of 55-60ºC increasing to 90ºC.

After processing all samples were transferred to frozen storage at -18ºC for 319 days before analysis by GLC with an ECD. The LOD was 0.05 mg/kg and the mean recovery from jam and preserved fruit 74% (Lees, 1998f). The results are shown in Table 49.

Table 49. Residues of dinocap in strawberries and their processed products (Lees, 1998f).

Country Year	Application			PHI, days	Sample	Dinocap, mg/kg	Processing factor
	Form	No.	kg ai/hl				
UK 1996	EC	6	0.027	3	whole fruit	0.23	
					jam	0.08	0.35
					preserved fruit	<0.05	0.22
UK 1996	EC	6	0.027	3	whole fruit	0.31	
					jam	0.07	0.23
					preserved fruit	0.11	0.35

The average processing factor for jam and preserved strawberries was 0.29.

Tomatoes. In a trial in France in 1997 tomatoes treated with the EC formulation were processed into juice, purée, preserved tomatoes and ketchup. To prepare juice, crushed tomatoes were sieved and cooking salt was added. The juice was sterilized at 115ºC for 2 minutes in glass bottles and frozen at -20ºC for 126 days until analysis. To prepare purée, the cut tomatoes were reduced in a double saucepan

to 11º Brix, sieved, and sterilized in glass bottles. The bottles were stored at -20ºC for 112 days before analysis.

Some of the purée was reduced again to prepare ketchup. Preserved tomatoes, peeled tomatoes and juice were sterilized for 2 minutes at 115ºC in glass bottles. Samples were frozen at -20ºC for 97 days until analysis by GLC with an ECD. The LOD was 0.05 mg/kg and mean recoveries were 86% for juice, 77% for purée, 80% for ketchup and 92% for preserved tomatoes (Howie, 1998a).

The residues were below the LOD in the raw tomatoes and undetectable in the products. The results are shown in Table 50.

Table 50. Residues of dinocap in tomatoes and their processed products (Howie, 1998a).
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Country Year	Application			PHI, days	Sample	Dinocap, mg/kg
	Form	No.	kg ai/hl			
France 1997	EC	4	0.021	7	raw tomatoes	<0.05
					juice	n.d.
					purée	n.d.
					preserved tomatoes	n.d.
					ketchup	n.d.

Residues in the edible portions of food commodities

No data were provided except those included in the processing trials. The residues in most of the fractions were at or below the LOD.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The results of monitoring carried out in the UK in 1989-1991 were reported to the Meeting. Dinocap was not found above the reporting limit. The results are shown in Table 51.

Table 51. UK monitoring data for dinocap, 1989-91.

Commodity	Reporting limit, mg/kg	Samples	
		1989-90	1991
Dessert apples	0.1-1	40 UK produced	25 UK produced
		63 imported	36 imported
French beans	0.05	4 UK produced	
		20 imported	
Runner beans	0.2		7 UK produced
			1 imported
			3 unknown
Brussels sprouts	0.05	30 UK produced	
		4 imported	
		1 unknown	
Green cabbage	0.02		17 UK produced
			5 imported
Calabrese	0.02		26 UK produced

Commodity	Reporting limit, mg/kg	Samples	
		1989-90	1991
			23 imported
Cauliflower	0.02		17 UK produced
			4 imported
Cucumber	0.05	36 UK produced	
		37 imported	
Gooseberries	0.01	7 UK produced	
		1 imported	
Grapes	1	65 imported	
Greengages	1	3 UK produced	
Melons	0.01	25 imported	
Nectarines	1	24 imported	
Peaches	1	23 imported	
Pears	0.5	21 UK produced	
		24 imported	
Tomatoes	1	22 UK produced	
		23 imported	

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country	Commodity	MRL, mg/kg
Austria	Apple	1
	Cucurbits	1
	Grapes	1
	Pepper	1
	Tomatoes	1
	Stone fruits	1
	Strawberry	1
Australia	Apple	0.1
	Cucurbits	0.1
	Grapes	0.1
	Stone fruits	0.1
	Strawberry	0.1
Belgium	Apple	1
	Cucurbits	1
	Grape	1
	Pepper	1
	Tomatoes	1
	Stone fruits	1
	Strawberry	1
Canada	Apple	0.1
	Cucurbits	0.1
	Grapes	0.1
Denmark	Berries and small fruits	0.1
	Leafy vegetables	0.1
	Pome fruits	0.1
	Other fruits	0.1
	Stone fruit	0.1
	Potatoes	0.1
Finland	Apples	0.5

Country	Commodity	MRL, mg/kg
	Cucurbits	0.5
	Grape	0.5
	Pepper	0.5
	Stone fruit	0.5
	Strawberry	0.5
France	Fruit and Vegetables	0.1
Germany	Cucumber	1
	Grape	1
	Melon	1
	Pome fruit	1
	Stone fruit	0.1
	Strawberry	0.1
Hungary	Apple	0.2
	Cucurbits	0.2
	Grape	0.2
	Pepper	0.2
	Stone fruit	0.2
	Strawberry	0.2
Italy	Artichoke	1
	Cardoon	1
	Carrot	1
	Celery	1
	Chard	1
	Fennel	1
	Fruits	1
	Lettuce	1
	Maize	1
	Vegetables	1
	Wheat	0.05
Luxembourg	Fruit and Vegetables	1
	Other foods of vegetable origin	0.05
Netherlands	Apples	0.5
	Fruiting Vegetables	0.1
	Other food	0.05
New Zealand	Apple	1
	Cucurbits	1
	Grape	1
	Pepper	1
	Stone fruits	1
	Strawberry	1
South Africa	Apple	1
	Cucurbits	1
	Grape	1
	Peach	1
	Pepper	1
Spain	All plant products	0.1
Switzerland	Apple	0.05
	Cucurbits	0.05
	Grape	0.05
	Pepper	0.05
	Stone fruits	0.05
	Strawberry	0.05
Yugoslavia	Apple	0.1
	Cucurbits	0.1
	Grape	0.1

Country	Commodity	MRL, mg/kg
	Pepper	0.1
	Stone fruits	0.1
	Strawberry	0.1
U K	Apple	0.1
	Strawberry	0.5
USA	Apple	0.1
	Grape	0.1

APPRAISAL

Dinocap is a contact fungicide used to control powdery mildew on many crops and is also used as a non-systemic acaricide. It has been evaluated several times by the JMPR. In 1992 the JMPR recommended withdrawal of the temporary MRLs and in 1993 the CAC agreed to delete dinocap from the Codex list. In the present evaluation dinocap is therefore considered as a new compound.

Dinocap is marketed as WP and EC formulations, and is also formulated with other fungicide such as myclobutanil and fenbuconazole.

Dinocap is composed of a mixture of six isomeric dinitrooctylphenyl crotonates, three isomers of 2,4-dinitro-6-octylphenyl crotonate (2,4-DNOPC) and three of 2,6-dinitro-4-octylphenyl crotonate (2,6-DNOPC), where “octyl” is a mixture of 1-methylheptyl, 1-ethylhexyl and 1-propylpentyl groups. The ratio of the 2,4-DNOPC to the 2,6-DNOPC isomers in technical dinocap is approximately 2:1, and that of the octyl isomers 1:1:1.

The metabolic degradation of dinocap has been studied in rats and mice with 2,4-DNOPC uniformly labelled with ^{14}C in the aromatic ring.

In an early feeding study with rats, radioactivity was rapidly excreted in the faeces and urine. Another study with male mice and rats showed different metabolite profiles in the two species and it was also observed that in mice but not in rats the proportion of the administered radioactivity excreted in the urine decreased with increasing dose. Metabolites in the faeces and urine samples were characterized by HPLC with UV detection.

In a study to characterize the urinary metabolites in rats and mice after the oral administration of labelled 2,4-DNOPC, the DNOPC was rapidly metabolized with the rats excreting approximately 30.9% and mice approximately 58.3% of the administered ^{14}C in the urine over a 4-day period: in both species, more than 90% of the total was excreted within 24 hours. Twelve metabolites in rats and 13 in mice were identified. In both species the pattern of metabolites was consistent with a metabolic pathway involving hydrolysis of the crotonate ester, β- or α-oxidation of the methylheptyl group and β-oxidation, followed in rats only by reduction of the nitro groups and *N*-acetylation. Although there were qualitative and quantitative differences in the metabolic profile in rats and mice, the main metabolites in the urine of both species were the same, namely 6-(4-carboxy-1-methylbutyl)-2,4-dinitrophenol and 6-(3-carboxy-1-methypropyl)-2,4-dinitrophenol.

In cows dosed with radiolabelled 2,4-DNOPC at levels equivalent to 0.1, 0.3 and 1 ppm in the diet the main route of elimination was in the faeces with small amounts in the urine. No radioactive residues were detectable in the milk or tissues at any dosing level.

Bluegill sunfish were exposed to concentrations of 1 or 0.2 µg/l of [^{14}C]2,4-DNOPC in water tanks for 28 days, followed by a depuration period of 14 days. Bioconcentration was observed with accumulation increasing during the first 3 days, after which a steady level was reached and maintained until the end of the exposure period. Loss of residue during depuration was rapid. At the end of the depuration period more than 90% of the radioactivity in whole fish had been eliminated. The half-lives calculated for the ^{14}C in whole fish were 0.6 and 0.9 days for the low and high dose respectively.

The fate of residues in plants was studied in apples, cucumbers and squash with radiolabelled 2,4-DNOPC. Studies on apples showed that more than 92% of the radioactivity in the fruit was associated with the peel. Two groups of compounds, the parent 2,4-DNOPC isomers and the corresponding phenols 2,4-DNOP, were identified in the fruit. The phenol metabolites represented 2-4% of the total radioactivity at all sampling intervals. The calculated half-life of 2,4-DNOPC was 5.2 days. The relatively constant concentration of the phenols throughout the sampling period showed that they did not accumulate. They appeared to be metabolized to more polar compounds.

In another study on apples, peel samples were extracted with methanol, partitioned with hexane and analysed by TLC, HPLC and GC-MS. Five minor unknown compounds were isolated from the peel, each of which accounted for less than 0.5% of the total residue. The results suggest that photolysis is a potential degradation pathway for 2,4-DNOPC.

In cucumbers, the metabolism of 2,4-DNOPC produced 28 metabolites, but only the parent mixture and 2,4-DNOP were identified. 2,4-DNOPC dissipated rapidly from cucumber leaves and stems.

In squash the residues in mature fruit were mainly associated with the peel. Six unidentified metabolites were found in the fruit and 10 in the leaves at low concentrations.

The half-lives of the total radioactive residues on cucumber and squash leaves were 11.8 and 8 days respectively.

Dinocap metabolites from squash and cucumber were very similar in their TLC behaviour and more similar to rat faecal metabolites than to urinary metabolites.

In summary, plant metabolism studies indicated that the metabolic pathways of dinocap in crops are complex, resulting in a large number of metabolites present at low concentrations. The isolation of sufficient quantities of most of the metabolites to allow identification was not possible. The only significant metabolite found was 2,4-DNOP. Residues are associated with the peel and it was found that dinocap is rapidly degraded on fruit and leaf surfaces, suggesting that photolysis is a significant pathway of degradation.

Four studies were carried out to determine the rate of dissipation of dinocap in different soils. A study with two standard soils and one agricultural soil showed that dinocap was slowly degraded in the standard soils but readily degraded to CO_2 in a typical agricultural soil. It can be concluded that moisture and microbial activity play an important role in the degradation of dinocap in soil.

The route and rate of degradation of 2,4-DNOPC was also investigated in sandy loam, silty loamy sand, loamy sand and clay loam at two temperatures. 2,4-DNOPC was degraded rapidly in all the soils at rates which appear to be dependent on the soil pH rather than other characteristics, indicating that chemical hydrolysis to 2,4-DNOP is a major route of degradation. The half-life ranged from 4.1 days at pH 7.1 to 24 days at pH 4.8 at 20ºC.

The degradation of 2,4-DNOPC and 2,6-DNOPC was studied in a sandy loam soil (pH 5.8) in aerobic conditions. Both were degraded rapidly, the 2,6- isomers more rapidly than the 2,4-. Calculated half-lives were 10 and 4.5 days for 2,4- and 2,6-DNOPC respectively. The main degradation products were 2,4- and 2,6-DNOP. After 120 days of incubation significant mineralization was observed (22.4% of the applied 2,4-DNOPC and 36.7% of the 2,6-DNOPC).

A study of the adsorption and desorption of [^{14}C]2,4-DNOPC in four different agricultural soils showed that it was strongly adsorbed in the soils studied and could be classified as having very low mobility in soil.

The leaching behaviour of [^{14}C]dinocap was studied in five different fresh soils, in sandy loam soil after ageing for 30 days and in silt loam after ageing for 102 days before leaching. Radioactivity was detectable in the leachate from only two of the fresh soils (silt loam and clay loam). Between 74% and 99% of the applied radioactivity was recovered in the top layers of all the soils. It can be concluded that it is very unlikely that dinocap or its degradation products could be leached even under exaggerated laboratory conditions.

The octanol/water partition coefficient was determined for 2,4- and 2,6-DNOPC and their phenol metabolites. The coefficients showed that DNOPC isomers are fat-soluble (log P_{ow} 2,4-DNOPC 6.55, log P_{ow} 2,6-DNOPC 6.45).

The rates of hydrolysis of the isomeric forms of DNOPC and the corresponding phenols were determined in buffer solutions at pH 4, 7 and 9 at 20º and 30ºC. It was concluded that hydrolysis of the crotonates was highly dependent on pH and temperature, being more rapid at basic pH. Degradation of the phenols was found to be negligible at all pH values and temperatures.

The photolysis of 2,4-DNOPC was investigated in a pH 5 aqueous buffer solution irradiated with a xenon arc for 367 hours. Degradation was biphasic with initial and terminal half-lives equivalent to 4.9 and 57.2 hours of summer sunlight. The major degradation product was $^{14}CO_2$. The free phenol 2,4-DNOP was an important initial product. In another study the aqueous photolysis of the isomeric forms of DNOPC and DNOP was measured in sterile, aqueous buffer (50 µg/l, pH 4) irradiated with a xenon arc for up to 10 hours for DNOPC and 96.1 hours for DNOP. The half-life was 0.63 and 0.73 days for 2,4- and 2,6-DNOPC respectively and 8.7 and 20.8 days for 2,4- and 2,6-DNOP. The only photodegradation product of DNOP identified was CO_2. Other photodegradation products were not resolved by HPLC.

The aerobic aquatic degradation of [^{14}C]2,4-DNOPC was studied in two water/sediment systems from natural environment sites at 20ºC in the dark. There was rapid transfer of radioactivity from water to sediment and an apparent rapid degradation of DNOPC to DNOP, which was further degraded to CO_2. At the end of the 100-day study 40.7% to 78.4% of the applied radioactivity was associated with sediments and 6.4 to 11.8% with the water phases.

Analytical methods for the determination of residues of dinocap have been developed for several crops and their processed products, and for soil and water. All the methods are similar. They include extraction with methanol, either by Soxhlet or maceration with the solvent. Juices and wine are simply diluted with methanol. The dinocap isomers are converted to the corresponding phenols by basic hydrolysis, and the extracts partially purified by partition into hexane. After solvent evaporation the residue is taken up in diethyl ether, methylated with diazomethane, and purified by silica gel column chromatography. The methylated phenols are determined by GLC with an ECD or NPD, the sum of the peak areas or heights being measured. The method was validated for many crops. The mean recoveries of dinocap from fruit

were above 70% with reported LODs of 0.05 mg/kg. Crop samples were fortified with 2,4-DNOPC and 2,6-DNOPC and the analytical standards were the methyl esters of 2,4-DNOP and 2,6-DNOP.

In studies of the storage stability of residues in frozen analytical samples of apples and grapes stored for 24 months, the residues in grapes showed good stability, but there was a marked decrease of the dinocap residue during the storage of apples. In another study, the storage stability of dinocap at levels of 1 mg/kg was determined in cucumbers, tomatoes, peaches, apples and strawberries over a period of 9 months in the dark at approximately –20ºC. Dinocap residues were found to be stable in all the crops for at least 9 months. The analytical method for apples was modified slightly by increasing the volume of the extraction solvent. This modification improved the extraction efficiency. It was reported that studies on cucumbers, peaches, apples and strawberries would be continued for a total of 24 months.

The results of metabolism studies showed that the dinocap isomers are readily hydrolysed to the corresponding phenols. The analytical methods used in residue trials quantify residues of dinocap and their phenol metabolites as the methylated phenols and express the results as dinocap. The Meeting concluded that the residues should be defined as the sum of dinocap isomers and the dinocap phenols, expressed as dinocap.

Dinocap is fat-soluble but metabolism, feeding and bioaccumulation studies showed that residues do not accumulate in tissues. This is probably because dinocap is rapidly degraded and the metabolites that constitute the main residues are not fat-soluble.

Residues resulting from supervised trials

Data from trials on apples, grapes, strawberries, stone fruits and cucurbits in European countries were evaluated.

Residues of 2,4- and 2,6-DNOPC in the trials were calculated from the sum of 6 peak areas or heights. The residues of the two groups of isomers were generally recorded separately and their sum expressed as dinocap. If the calculated concentration of each isomeric group was <0.05 mg/kg the total dinocap residue was recorded as <0.05 mg/kg.

Apples. Trials in France, Greece, Italy and the UK were reported. In two trials in France and two in Greece according to GAP the residues were <0.05 mg/kg. Six trials according to Italian GAP yielded total residues between <0.04 and 0.09 mg/kg. In the UK, 18 trials complied with GAP, with residues from <0.05 to 0.08 mg/kg.

The dinocap residues in rank order (median underlined) were <0.04 (2), <0.05 (18), 0.05, 0.05, 0.06, 0.07, 0.08 (3) and 0.09 mg/kg. The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.05 mg/kg for apples.

Grapes. Numerous field trials on vines in France, Germany, Greece, Italy and Portugal were reported to the Meeting. Ten of thirteen trials in France were according to GAP: the residues ranged from <0.05 to 0.59 mg/kg. Six field trials in Germany complied with French GAP, with residues from 0.22 to 0.67 mg/kg. In two field trials in Greece according to Italian GAP the residues were 0.1 and 0.2 mg/kg. In sixteen trials in Italy and three in Portugal complying with the national GAP the residues ranged from <0.04 to 0.3 mg/kg.

The residues of dinocap in rank order (median underlined) were <0.04 (7), <0.05 (7), 0.06, 0.08, 0.09, 0.1, 0.11, 0.14, 0.18, 0.2 (2), 0.22 (2), 0.26, 0.28, 0.3 (2), 0.35, 0.36, 0.42, 0.43, 0.46, 0.5, 0.59 and 0.66 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.105 mg/kg.

Strawberries. Trials were conducted in France, Italy, Spain and the UK. In four French trials complying with French GAP the residues were 0.05-0.33 mg/kg. Two Spanish trials complying with GAP gave residues below the LOD of 0.04 mg/kg. In ten trials in the UK according to GAP (5 applications, 0.49 kg ai/ha, 7 days PHI) the residues ranged from <0.05 to 0.33 mg/kg.

The dinocap residues in rank order (median underlined) were <0.04 (2), <0.05, 0.05, 0.05, 0.06 (4), 0.08, 0.09, 0.14, 0.21, 0.32 and 0.33(2) mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg and an STMR of 0.06 mg/kg.

Stone fruits. A single trial in Italy on apricots according to GAP, with residues at 21 days PHI below the LOD (0.04 mg/kg) was insufficient to estimate a maximum residue level.

Residues in a trial on peaches in Greece complying with GAP were below the LOD (0.05 mg/kg). Six of nine trials in Italy complied with French GAP (0.018 kg ai/hl, 7 days PHI), giving residues from <0.04 to 0.09 mg/kg. In two trials in Spain according to GAP the residues were <0.04 and 0.05 mg/kg. The dinocap residues in peaches in rank order (median underlined) were <0.04 (5), <0.05 (3), 0.05 and 0.09 mg/kg.

The Meeting estimated a maximum residue level of 0.1 mg/kg and an STMR of 0.05 mg/kg.

Cucumbers. Two protected trials in France and three in Spain according to GAP gave residues below the LOD (0.05 and 0.04 mg/kg). The residues were <0.04 (3) and <0.05 (2).

Melons. Several field trials were carried out in France, Greece, Italy and Spain, and one indoor trial in Spain. In two trials in France at a higher spray concentration than the recommended GAP (0.18 kg ai/hl, 3 day PHI) the residues were below the LOD (0.04 mg/kg). In one trial in Greece, 6 trials in Italy and two in Spain according to GAP the residues were all <0.04 or <0.05 mg/kg. In summary, dinocap residues in melons from 9 trials according to GAP and 2 at a higher rate were all below the LOD.

Summer squash. Residues in three trials in France, 4 in Italy and 2 in Spain according to national GAP were all below the LOD.

The use patterns on cucumbers, melons and summer squash are similar. The residues in all these crops were below the LOD, which is consistent with the results of metabolism studies. The Meeting therefore estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.05 mg/kg for cucurbits.
Peppers. Eight protected trials carried out on peppers in Greece, Italy and Spain complied with Greek GAP (0.018 kg ai/hl, 7 days PHI). The residues in rank order (median underlined) were <0.05, 0.05, 0.06, 0.06, 0.06, 0.07, 0.11 and 0.12 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.06 mg/kg for peppers.

Tomatoes. Field and protected trials were conducted in Southern France, Italy and Spain. There is no GAP for tomatoes in France or Italy and all the trials were at much higher application rates than allowed by GAP in Spain (0.011 kg ai/hl, 7 days PHI) and shorter PHIs than GAP in Greece.

As no trials according to GAP were reported, the Meeting could not estimate a maximum residue level.

Processing studies

Apples. Unwashed apples from 2 trials in France with sprays of 6 x 0.021 kg ai/hl and 14 days PHI were processed to juice and purée. Residues were not detected in the processed commodities. In two studies in the UK apples treated according to GAP were processed according to commercial practice to juice, purée and pomace. Dinocap residues were not detected in the juice or purée and residues in the pomace were similar to those in the raw commodity.

The data indicated that there is no concentration of residues in apple juice. On the basis of the STMR of 0.05 mg/kg for apples, the Meeting estimated an STMR of 0.05 mg/kg for apple juice.

Grapes. Data from processing studies in France and Germany indicated that residues of dinocap decreased in wine and must and were below the LOD or not detected. Studies with higher residue levels in the raw grapes in Germany showed a processing factor of 0.07 for both must and wine. The Meeting therefore estimated STMRs for must and wine of 0.007 mg/kg, derived from the STMR for grapes of 0.105 mg/kg.

Peaches. Peaches treated according to GAP in two trials in Italy were processed into juice and preserves. Residues in the raw peaches were below the LOD and no concentration was detected in the processed commodities.

Tomatoes. Tomatoes from one supervised trial were processed into juice, purée, preserve and ketchup. Residues of total dinocap in the tomatoes were below the LOD (0.05 mg/kg) and residues were not detected in the processed commodities.

The Meeting could not calculate processing factors for peaches and tomatoes since the residues in the raw commodities were below the LOD.

Strawberries. Two processing trials in the UK showed that residues do not concentrate in strawberry jam or preserved strawberries. The average processing factor was 0.29 for both commodities. On the basis of an STMR of 0.06 mg/kg for strawberries, the Meeting estimated an STMR of 0.017 mg/kg for strawberry jam and preserved strawberries.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and for the estimation dietary intake: sum of dinocap isomers and dinocap phenols, expressed as dinocap.

Commodity		Recommended MRL, mg/kg		STMR
CCN	Name	New	Previous	
FP 0226	Apple	0.2	-	0.05
JF 0026	Apple juice			0.05
VC 0045	Fruiting vegetables, Cucurbits	0.05*	-	0.05
FB 0269	Grapes	1	-	0.105
	Grape must			0.007
FB 0275	Strawberry	0.5	-	0.06
	Strawberry jam and preserved			0.017
FS 0247	Peach	0.1	-	0.05
VO 0051	Peppers	0.2	-	0.06
	Wine			0.007

*At or about the limit of determination.

FURTHER WORK OR INFORMATION

Desirable

1. Processing studies with raw commodities containing dinocap residues at higher concentrations.

2. Animal feeding studies

3. Final report of the completed study of the storage stability of residues in analytical samples that was reported to be in progress.

DIETARY RISK ASSESSMENT

STMRs have been estimated for apples, grapes, strawberries, peaches, peppers and cucurbits. The International Estimated Daily Intakes of dinocap for the five GEMS/Food regional diets were in the range of 0 to 1% of the ADI. The Meeting concluded that the intake of residues of dinocap resulting from its uses that had been considered by the JMPR is unlikely to present a public health concern.

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DISULFOTON (074)

EXPLANATION

Residue aspects of disulfoton were reviewed by the JMPR in 1973, 1975, 1979, 1981, 1984, 1991 and 1994. At the 1996 CCPR MRLs set "at or about the limit of determination" were amended from 0.01 to 0.02 mg/kg after a recommendation from the Ad Hoc Working Group On Methods of Analysis (ALINORM 97/24 para. 52). Several delegations expressed concern at the high levels of estimated intakes relative to the ADI and it was noted that processing data were not available for refinement of the estimation of intake. The Committee requested revised intake calculations and decided to keep all other proposals at step 7C (ALINORM 97/24, paras. 53 and 54).

In 1997, the CCPR was informed that additional data would be available for the 1998 JMPR and disulfoton MRLs were kept at Step 7B pending the 1998 evaluation. The present Meeting received new residue data on lima beans, cotton, lettuce and potatoes, as well as reports of recent processing studies on coffee, cotton seed, maize, sorghum and wheat. Processing data on potatoes were also submitted, although minimal information was provided on the field conditions and the analytical methods used. The Meeting received summaries of data reviewed in the previous monographs on disulfoton for the estimation of STMRs and refinement of the dietary intake calculations.

IDENTITY

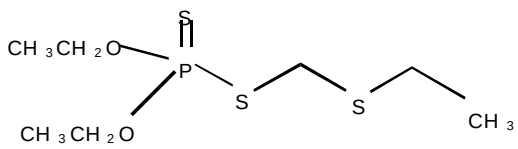
ISO Common name: disulfoton

Chemical name
IUPAC: *O*,*O*-diethyl *S*-2-ethylthioethyl phosphorodithioate
CA: *O*,*O*-diethyl *S*-[2-(ethylthio)ethyl] phosphorodithioate

CAS no: [298-04-4]

Synonyms: disyston

Structural formula:



Molecular formula: $C_8H_{19}O_2PS_3$

Molecular weight: 274.4

Physical and chemical properties

Pure active ingredient

Appearance: colourless oil with a characteristic odour

Vapour pressure: 7.2 mPa (20°C), 13 mPa (25°C), 22 mPa (30°C)

Melting point: <–25°C

Boiling point: 128°C at 1 mm Hg

Octanol/water partition coefficient: log P_{ow} = 3.95

Solubility: water 12 mg/l (20°C). Readily miscible with *n*-hexane, dichloromethane, isopropanol, toluene.

Specific gravity: 1.144 g cm^{-3} (20°C)

Hydrolysis: Hydrolysed in alkaline media. Half-life at 22°C: 133 days (pH 4), 169 days (pH 7), 131 days (pH 9)

Photolysis: Half-life 1-4 days

Formulations

Disulfoton is formulated as granules (GR) 5%–15%, as an emulsion concentrate (EC) 960 g/l and a suspension concentrate (SC) 720 g/l.

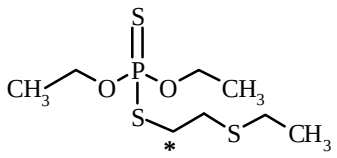
METABOLISM AND ENVIRONMENTAL FATE

Plant metabolism

The metabolism of disulfoton in cotton plants, lemon trees, beans and alfalfa plants was reviewed in previous monographs. In many of the studies, [^{32}P]disulfoton was used, and metabolites which did not contain the phosphorus label were not identified or fully characterized.

In earlier studies, the transformation of unlabelled disulfoton applied as a seed dressing to cotton, as a foliar spray to lettuce, and as soil and foliar applications to asparagus was investigated (JMPR, 1991).

New studies describing the metabolism of [^{14}C]disulfoton in lettuce, potatoes, wheat and soya beans have been provided by the manufacturer. The position of the ^{14}C label is indicated by an asterisk in the structural formula below.



* label position

[^{14}C]disulfoton was applied to soil at a rate of 3.2 kg ai/ha before planting lettuce (Fought, 1994c). Plants were harvested 49 days after planting (normal harvest). The total radioactive residue (TRR) in lettuce was 3.74 mg/kg disulfoton equivalents. Soil samples (2.5 cm depth) were taken at planting and at harvest; the total radioactive residues were 10 and 2.52 mg/kg disulfoton equivalents at planting and harvest respectively.

Acidic methanol (1% TFA/MeOH[N1]) extracted 93% of the TRR from homogenised lettuce. Approximately 84% of the TFA/MeOH extract was soluble in acetonitrile and 9% was soluble in water. The remaining filter cake contained 7% of the TRR, of which only 1% remained after consecutive acidic and basic hydrolyses.

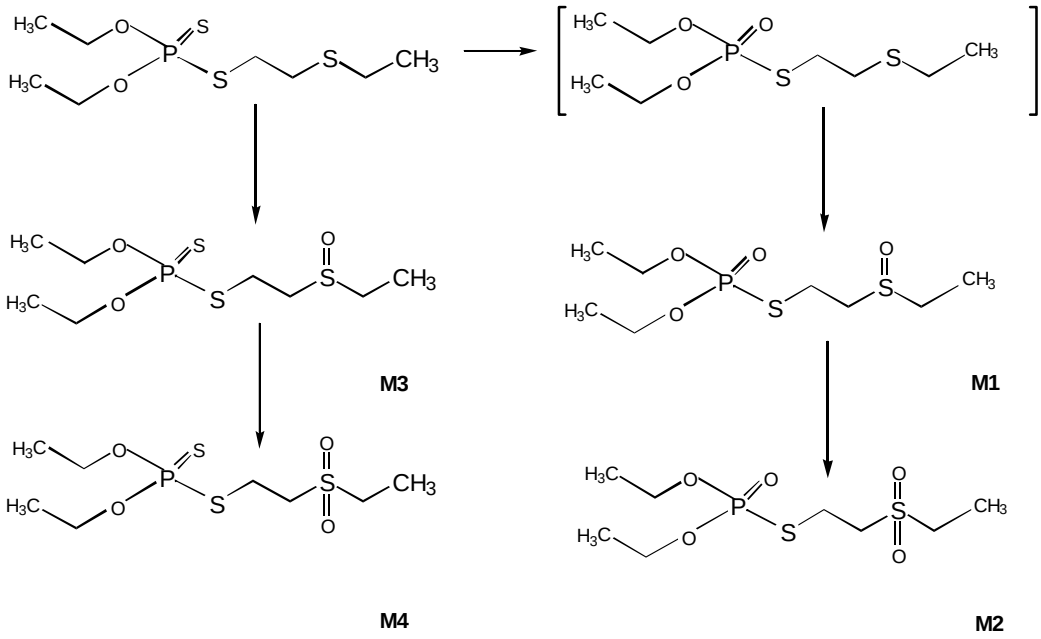
The main metabolites in mature lettuce, identified by HPLC, were disulfoton sulfone (M4), disulfoton oxygen analogue sulfone (M2), disulfoton oxygen analogue sulfoxide (M1) and disulfoton sulfoxide (M3) at 26, 23, 6 and 5% of the total radioactivity respectively, a total of 60%, The details are shown in Table 1. The structures of the major metabolites are shown in Figure 1.

Table 1. Distribution of radioactive residues in mature lettuce 49 days after planting in soil treated with [^{14}C]disulfoton at the rate of 3.2 kg ai/ha.

Compound	Metabolites in extracted fractions, % of TRR and (mg/kg as disulfoton)			
	Acetonitrile	Aqueous	Acidic	Total
M1 disulfoton oxygen analogue sulfoxide	6 (0.22)	<1 (<0.04)		6 (0.22)
M2 disulfoton oxygen analogue sulfone	22 (0.82)	1 (0.04)		23 (0.86)
M3 disulfoton sulfoxide	5 (0.19)	<1 (0.04)		5 (0.19)
M4 disulfoton sulfone	25 (0.94)	1 (0.04)		26 (0.98)
5		< 1 (<0.04)		
6 M5 (tentative identification)	1 (0.04)	1 (0.04)		2 (0.08)
7 M9 (tentative identification)	1 (0.04)			1 (0.04)
8	1 (0.04)			1 (0.04)
9	1 (0.04)		1 (0.04)	2 (0.07)
10	2 (0.07)		1 (0.04)	3 (0.11)
11 M6 (tentative identification)	<1 (<0.04)			<1 (<0.04)
12	7 (0.26)	2 (0.07)		9 (0.33)
13	12 (0.45)	3 (0.11)	<1 (<0.04)	15 (0.56)
14 M7 (tentative identification)	1 (0.04)	1 (0.04)		2 (0.07)
15			1 (0.04)	1 (0.04)
Total				96 (3.59)

Metabolites 12 and 13, which were not identified, accounted for 24% of the total extractable radioactivity. Four metabolites which totalled 6% of the TRR were tentatively identified as 2-(ethylsulfonyl)ethanol (M5), 2-(ethylthio)ethanesulphonic acid (M9), 1-(ethylsulfonyl)-2-(methylthio)ethane (M6) and 1-(ethylsulfinyl)-2-(methylsulfinyl)ethane (M7). Disulfoton and disulfoton oxygen analogue [N2]were not detected.

Figure 1. Disulfoton metabolism in lettuce.



Disulfoton oxygen analogue is shown as an intermediate as it was not identified in the study.

The storage stability of the total radioactive residue in lettuce was investigated by HPLC. Ethyl acetate extracts prepared immediately after harvest and after 13 months frozen storage were compared. Ethyl acetate extracted 58% of the TRR after harvest and 65% after storage. Analysis of the extracts showed that the relative amounts of the main metabolites were the same, although the extracted proportion of the TRR had changed slightly. The results showed that the metabolites extracted at harvest were stable in the freezer for 13 months and that the total radioactivity was also stable.

[^{14}C]disulfoton was applied to soil at a rate of 7.87 kg ai/ha (1.76 times the maximum recommended US rate) before planting potatoes, and two foliar applications were made 33 and 69 days after planting at a rate of 2.24 kg ai/ha, twice the label rate (Fought *et al.*, 1994b). Plants were grown under field conditions for 2 months, then moved to a greenhouse for 3 months. Potatoes were harvested 99 days after planting and soil samples (5 cm depth) were taken at planting and at harvest.

The total radioactive residues were 12 and 0.97 mg/kg disulfoton equivalents at planting and harvest respectively in the soil, and 3.71 mg/kg in the tubers. Acid methanol extracted 91% of the TRR in tubers, with 9% remaining in the filter cake. The extracted material was largely soluble in acetonitrile (78% of the TRR) with 13% water-soluble.

Disulfoton sulfone (M4), sulfoxide (M3), oxygen analogue sulfone (M2) and oxygen analogue sulfoxide (M1) accounted for 2% of the TRR. The hydrolysis products 1-(ethylsulfinyl)-2-(methylsulfinyl)ethane (M7), 1-(ethylsulfonyl)-2-(methylthio)ethane (M6) and 2-(ethylsulfonyl)ethanol (M5) constituted 4, 1 and 11% of the TRR respectively.

The storage stability of the acidic methanol extracts of potato tubers was investigated by determining the total radioactivity in samples prepared after harvest and after 8 months of frozen storage. Ninety two per cent of the TRR was extracted at harvest and 91% after storage. Disulfoton and the main metabolites M1, M2, M3 and M4 were not detected.

The radioactive residue in the tubers was further examined by extraction with acetonitrile/H_2O followed by dilute HCl (Hall and Hartz, 1996b). Soxhlet extraction and ion-exchange chromatography were employed before identification by GC-MS and thermospray MS. This solvent combination extracted 99% of the TRR, of which 75% was identified as shown in Table 2.

Table 2. Compounds identified in radioactive residues extracted from potato tubers after a soil treatment (7.87 kg ai/ha) and two foliar applications (2.24 kg ai/ha) of [^{14}C]disulfoton.

Compound	% of TRR	mg/kg
Sulfinyl lactate conjugate of 2-(ethylsulfonyl)ethylene (M18)	53	2.27
Cysteine conjugate of 2-(ethylsulfonyl)ethylene (M16)	9	0.40
Thiolactate conjugate of 2-(ethylsulfonyl)ethylene (M17)	7	0.28
Disulfoton oxygen analogue sulfoxide (M1)	<1	0.015
Disulfoton oxygen analogue sulfone (M2)	<1	0.032
Disulfoton sulfone (M4)	<1	0.003

The results show that the organophosphorus triesters M1-M4 constituted only a small proportion of the radioactive residues in the tubers. Most of the radioactivity is incorporated in amino acid conjugates of 2-(ethylsulfonyl)ethylene which may be formed by β-elimination from disulfoton oxygen analogue sulfone. Both 2-(ethylsulfonyl)ethylene and 2-(ethylsulfonyl)ethanol were tentatively identified at 5% of the TRR. The metabolic pathways proposed for disulfoton in plants are shown in Figure 2.

Wheat was planted in soil treated with [^{14}C]disulfoton at the rate of 0.97 kg ai/ha (Fought *et al.*, 1994d). At 37 and 63 days after planting, two foliar sprays were applied at a rate of 0.85 kg ai/ha. The plants were grown under field conditions for 2 months, then transferred to a greenhouse for another month. Soil samples (2.5 cm depth) were taken at the time of treatment and at harvest. Immature plants were sampled immediately before the first foliar application 37 days after planting. Mature plants were harvested 90 days after planting and grain and chaff were separated for analysis. Plants which were left to dry were collected as straw and forage 104 days after planting.

The forage samples included chaff separated from the wheat heads. The TRR in the samples are shown in the Table.

Interval	Sample	Disulfoton equivalents, mg/kg
Planting	Soil	3.05
Immature	Plants	4.62
Harvest	Soil	0.65
	Grain	2.80
	Forage	36.2
	Straw	40.2

Grain, forage and straw samples were extracted with 1% TFA/MeOH and immature plants with acetone. The proportion of the radioactivity extracted varied as shown. The organophosphorus triesters accounted for a small proportion of the total radioactivity in all the samples, as shown in Table 3.

Sample	Fraction	% of TRR
Wheat grain	TFA/MeOH + CH_3CN	45
	Filter cake	55
Wheat forage	TFA/MeOH + CH_3CN	75
	Filter cake	23
Wheat straw	TFA/MeOH + CH_3CN	76
	Filter cake	23
Immature wheat	acetone	61
	Filter cake	39

Table 3. Distribution of residues in immature wheat, grain, straw and forage after a soil treatment at 0.97 kg ai/ha and two foliar applications at 0.85 kg ai/ha.

Metabolite	^{14}C, % of TRR and (mg/kg as disulfoton)			
	Immature wheat	Wheat grain	Wheat forage	Wheat straw
M1 disulfoton oxygen analogue sulfoxide	1 (0.05)	1 (0.03)	5 (1.88)	6 (2.41)
M2 disulfoton oxygen analogue sulfone	14 (0.65)	<1 (0.1)	8 (2.97)	8 (3.21)
M3 disulfoton sulphoxide	<1 (0.02)	1 (0.03)	6 (2.21)	2 (1.00)
M4 disulfoton sulfone	6 (0.28)	1 (0.03)	4 (1.45)	4 (1.81)

The triesters constituted 23% of the TRR in wheat forage, 20% in wheat straw, 21% in immature wheat and <4% in wheat grain. 2-(ethylsulfonyl)ethanol was tentatively identified at 42% or 1.18 mg/kg in wheat grain and at 5% or 1.81 mg/kg in wheat forage. The remaining radioactivity was characterized as a mixture of polar compounds of low molecular weight.

The storage stability of the radioactive residues in wheat forage was determined by comparing the extracts of forage prepared after harvest and 12 months later. TFA/MeOH extracted 79% of the TRR after harvest and 76% after 12 months of frozen storage. Four metabolite peaks were identified, together with a peak containing polar compounds.

Metabolite	% of TRR	
	Harvest	12 Months
Disulfoton oxygen analogue sulfoxide	7	5
Disulfoton oxygen analogue sulfone	12	8
Disulfoton sulfoxide	10	6
Disulfoton sulfone	9	5
Polar compounds	41	52

The percentages of the four metabolites were comparable after 12 months storage, while the percentage of polar compounds increased. Wheat forage, straw and grain were extracted with 1% TFA/MeOH 7 and 12 months after harvest. The proportions of the TRR extracted were similar: 77% from forage, 75% from straw and 49% from grain after 7 months; 79% from forage, 77% from straw and 45% from grain after 12 months.

Soya beans were planted in soil treated with [^{14}C]disulfoton at the rate of 1.84 kg ai/ha, grown under field conditions for 2 months then transferred to a greenhouse for another month (Fought *et al.*,1994a) Soil samples (5 cm depth) were collected at the time of treatment and at harvest. Some mature plants were harvested 85 days after planting for collection of bean, hull and forage samples. The remaining plants were left to dry for 2 weeks and collected as hay. The TRR in the various samples is shown below.

Time of sampling	Sample	disulfoton equivalents, mg/kg
Planting	Soil	2.88
Harvest	Soil	0.32
	Beans	1.39
	Hulls	8.05
	Forage	27.0
	Hay	43.7

Extraction with 1% TFA/MeOH followed by acid hydrolysis released a high proportion of the radioactivity:

Sample	% of TRR extracted		
	TFA/MeOH + CH_3CN	HCl	Filter cake
Beans	67	25	5
Hulls	79	18	1
Forage	93	5	1
Hay	85	12	1

Less than 4% of the extracted ^{14}C was in the triesters, as shown in Table 4.

Table 4. Distribution of radioactivity in soya beans, hulls, forage and hay after a soil treatment at 1.84 kg ai/ha.

Metabolite	% of TRR and (mg/kg as disulfoton)			
	Beans	Hulls	Forage	Hay
M1 disulfoton oxygen analogue sulfoxide	<1 (0.01)	<1 (0.01)	<1 (0.02)	<1 (0.01)
M2 disulfoton oxygen analogue sulfone	<1 (0.01)	<1 (0.01)	<1 (0.04)	<1 (0.01)
M3 disulfoton sulphoxide	<1 (0.01)	<1 (0.01)	<1 (0.02)	<1 (0.02)
M4 disulfoton sulfone	<1 (0.01)	<1 (0.01)	<1 (0.01)	<1 (0.02)

2-(ethylsulfonyl)ethanol was tentatively identified at 6% of the TRR in hay, 4% in hulls, 26% in beans and 7% in forage.

The storage stability of the TRR in the soya bean forage was investigated. TFA/MeOH extracted 93% of the TRR both immediately after harvest and after 9 months of frozen storage. The chromatographic profile was similar in both extracts. Neither disulfoton nor the triester metabolites were detected.

Identification of the other metabolites in the beans and forage was facilitated by Soxhlet extraction of the residual solids with CH_3CN and water, followed by base extraction and ion exchange chromatography (Hall and Hartz, 1996a). The procedure extracted 94% and 66% of the TRR from the forage and beans respectively, of which 89% and 40% were positively identified (Table 5).

Table 5. Distribution of metabolites in soya beans and soya bean forage after a soil treatment at 1.84 kg ai/ha. The main identified components of the TRR were 2-(ethylsulfonyl)ethanol in the forage and 2-(ethylsulfonyl)acetic acid in the beans.

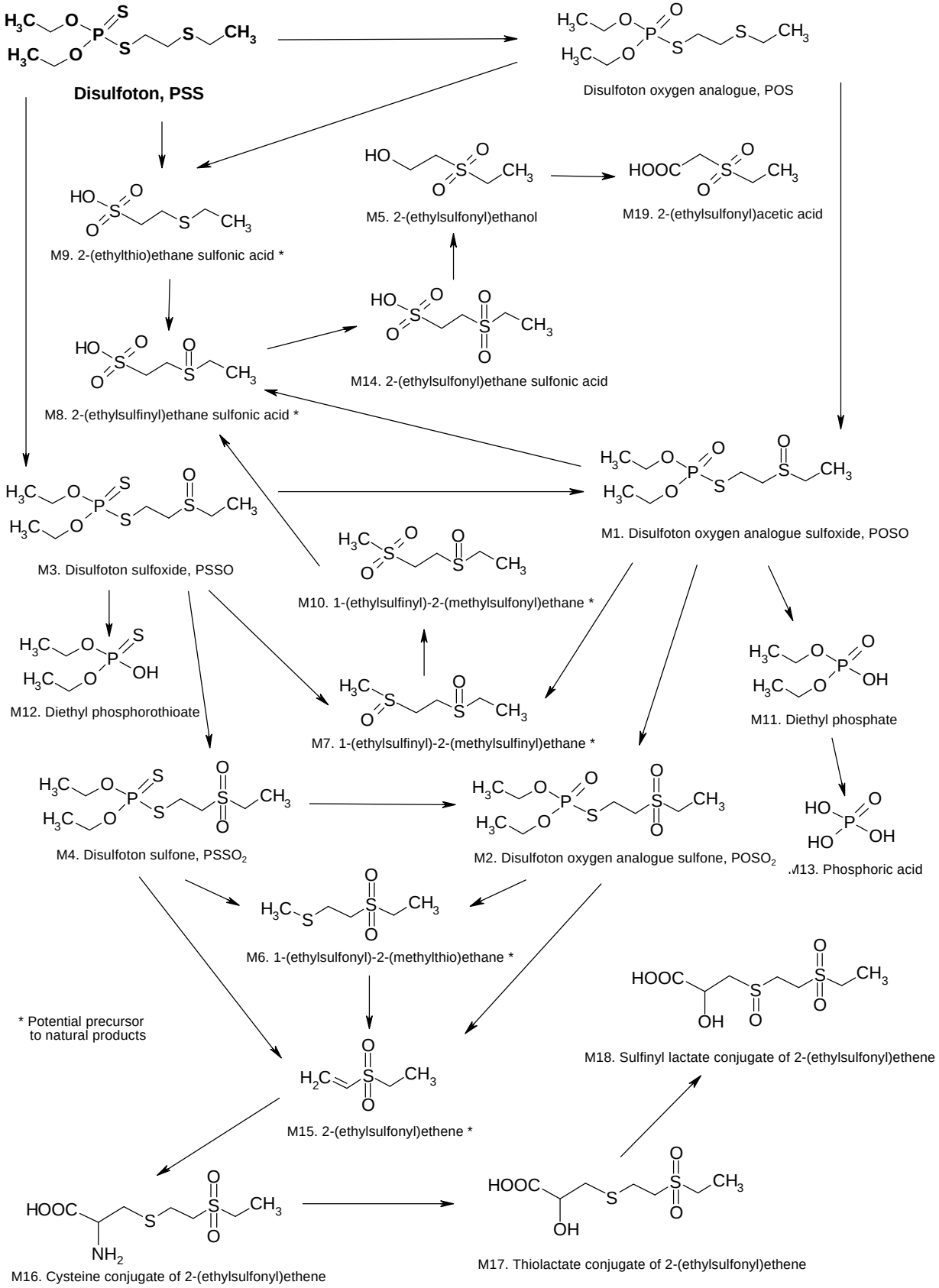
Metabolite	% of TRR and (mg/kg as disulfoton)	
	Soya beans	Soya bean forage
M18 2-(ethylsulfinyl)ethylsulfonic acid	<1 (0.01)	10 (2.21)
M19 2-(ethylsulfonyl) acetic acid	39 (0.51)	22 (5.08)
M5 2-(ethylsulfonyl)ethanol	–	58 (13.09)

In summary triester is similar in all the crops and four common metabolites were identified and characterized: disulfoton sulfoxide, disulfoton oxygen analogue sulfoxide, disulfoton sulfone, and disulfoton oxygen analogue sulfone. Neither unchanged disulfoton nor disulfoton oxygen analogue were detected in any of the reported studies, so the inclusion of the oxygen analogue (demeton-S) in the residue definition is of questionable practical importance. Cleavage of the triesters led to the formation of sulfonyl and sulfonic acid products. The single metabolite common to lettuce, wheat, potatoes and soya beans was 2-(ethylsulfonyl)ethanol. Derivatives or precursors of this compound such as 2-(ethylsulfonyl)acetic acid, 2-(ethylsulfinyl)ethanesulfonic acid, 2-(ethylsulfonyl)ethanesulfonic acid and 1-(ethylsulfinyl)-2-(methylsulfonyl)ethane were tentatively identified in various crops and crop parts. In potatoes, conjugation with glutathione followed by reduction and deamination of the conjugate was observed in addition to the common hydrolytic and oxidative pathways.

In reported metabolism studies on cotton with [^{32}P]disulfoton (Bull, 1965), hydrolytic products such as phosphoric acid, *O*,*O*-diethyl hydrogen phosphorothioate and diethyl phosphate

were identified in addition to disulfoton sulfone and sulfoxide, and disulfoton oxygen analogue sulfone and sulfoxide. These are also included in Figure 2.

Figure 2. Proposed metabolic pathways of disulfoton in plants.



METHODS OF RESIDUE ANALYSIS

Analytical methods

Enforcement methods

In a regulatory method reported by The Netherlands (Netherlands, 1966) disulfoton and its oxidized metabolites are all determined by gas chromatography with an ion trap or nitrogen-phosphorus detector. The limit of determination is 0.01-0.05 mg/kg for a variety of food samples. The mean recoveries of disulfoton and disulfoton sulfone in lettuce were reported as 76 and 94% respectively, with fortification at 0.29 mg/kg (n = 10) of each compound. In potatoes the limit of determination was 0.01 mg/kg with 115% recovery at 0.1 mg/kg. The compound used in the determination was not specified.

Specialised methods

Three specialised methods of analysis were reported by the manufacturer. In method 00043 (Thornton, 1967, revised 1978) disulfoton and its metabolites are quantified by gas chromatography with a KC1 flame ionization detector. The method involves extraction and precipitation to remove interfering plant products, followed by oxidation with $KMnO_4$ to convert disulfoton and its oxon and their sulfoxides to the corresponding sulfones. This method was reported in the 1973 monograph and the 1991 periodic review. Recoveries were determined with added disulfoton and the oxon sulfoxide and sulfone at 0.1 mg/kg each in maize kernels, molasses, potatoes, sorghum fodder, sorghum grain, soya beans, strawberries, sugar, sugarcane and wheat grain, at 0.4 mg/kg in wheat straw, and at 0.5 mg/kg in cotton seed. Recoveries ranged from 73 to 114% for disulfoton, 73 to 122% for disulfoton oxygen analogue sulfoxide and 90 to 108% for the sulfone. The limit of determination was 0.1 mg/kg, and the limit of detection was reported as 0.02 mg/kg.

A rapid screening method for the determination of disulfoton and the same metabolites in alfalfa and wheat was subsequently reported (Thornton, 1974). It is a modification of the procedure described above in which some of the clean-up steps have been amended. Recoveries [N3] with fortification at 1 mg/kg were in the range 80-100%. The limit of determination is in the range 0.1-0.2 mg/kg.

A modified method for the determination of disulfoton and the same metabolites in cotton seed was described by Seym (1996a). The modification of the Thornton procedure includes an extra partitioning step with hexane and CH_3CN before oxidation with $KMnO_4$. Cotton seed was fortified with mixtures of disulfoton, disulfoton sulfoxide, disulfoton sulfone, disulfoton oxon, disulfoton oxon sulfoxide and disulfoton oxon sulfone at 0.01, 0.02 or 0.1 mg/kg of each compound, giving total concentrations of 0.06, 0.12 and 0.6 mg/kg. Recoveries ranged from 75 to 103% at 0.06 mg/kg, 63 to 85% at 0.12 mg/kg and 75 and 90% at 0.6 mg/kg. The limit of determination was 0.01 mg/kg for each compound or 0.06 mg/kg for the mixture.

Fortification level, mg/kg	Recovery, %
0.06 (0.01 mg/kg of each compound)	75, 84, 103
0.12 (0.02 mg/kg of each compound)	63, 72, 75, 76, 81, 85
0.6 (0.1 mg/kg of each compound)	75, 90

Stability of pesticide residues in stored analytical samples

The storage stability of disulfoton and its oxidized metabolites in a range of crops and processed commodities was investigated by Wiedmann and Koch (1994). Samples of alfalfa forage and hay, broccoli, dry coffee beans, cotton seed, lettuce, peanut meal, oil and soapstock, green peas, potatoes, sorghum, strawberries, sweet corn, tobacco, tomatoes and juice, pomace and ketchup, and wheat grain, bran, flour, shorts, forage and straw were fortified with a mixture of disulfoton, its sulfone and sulfoxide or of disulfoton oxygen analogue and its sulfone and sulfoxide. Each sample contained

0.5 mg/kg disulfoton equivalents of each compound, totalling 1.5 mg/kg of the P=S compounds (disulfoton, disulfoton sulfoxide and disulfoton sulfone) or the P=O compounds (disulfoton oxon and its sulfoxide and sulfone). Samples were stored at –22°C and analysed after 0, 6, 12, 16 and 24 months[N4]. The limit of determination was 0.01 mg/kg. Recoveries of the P=S compounds ranged from 74 to 113% and of the P=O compounds from 74 to 116%.

After 24 months of frozen storage, no decomposition of the P=S compounds was found in alfalfa forage or hay, broccoli, lettuce, peanut oil, green peas, potatoes, sorghum, strawberries, sweet corn, tobacco, tomato juice, ketchup or pomace, or wheat flour, shorts, grain, forage or straw. Coffee beans, cotton seed, peanut meal and wheat bran showed <9% decomposition of the P=S compounds.

No decomposition of the P=O compounds was found in broccoli, lettuce, green peas, sorghum, strawberries, tomatoes (whole or juice), or wheat flour, shorts or straw after 24 months. Less than 25% decomposition was found in alfalfa forage and hay, coffee beans, peanut meal and oil, potatoes, sweet corn, tobacco, tomatoes (whole, ketchup and pomace), and wheat bran, grain and forage. There was 37% decomposition in cotton seed.

In a subsequent study (Lemke, 1996) the stability of the disulfoton P=S and P=O compounds in the same commodities was investigated for 36 months of frozen storage[N5], with analyses by the revised method of Thornton (1978). The extent of decomposition is shown in Table 6.

Table 6. Decomposition of disulfoton P=S and P=O compounds in various commodities after 36 months of frozen storage.

% Decomposition of P=S compounds	Sample
0	Alfalfa (forage and hay), broccoli, coffee beans, sweet corn, cotton seed, lettuce, green peas, strawberries, wheat grain, bran, flour, forage, straw and shorts
1	Peanut meal, tomato pomace,
3	Tobacco
4	Tomato juice
6	Peanut oil
8	Sorghum grain, tomato ketchup
9	Potato tubers
18	Peanut soapstock
% Decomposition of P=O compounds	Sample
0	Alfalfa hay, broccoli, cotton seed, green peas, strawberries, tomatoes (whole, juice, ketchup, pomace), wheat flour, bran, shorts, forage and straw
2	Alfalfa forage, peanut oil,
3	Lettuce
4	Coffee beans
5	Peanut meal
6	Wheat grain
11	Sweet corn
19	Tobacco
22	Potato tubers
37	Peanut soapstock

The greatest degradation of both P=S and P=O compounds was in peanut soapstock.

The storage stability of disulfoton and its metabolites in processed potato products was reported by Lenz (1996). Potato chips, flakes, wet and dry peel were fortified with 1.5 mg/kg of a mixture of the P=S compounds (disulfoton, its sulfoxide and sulfone) and 1.5 mg/kg of the P=O

compounds (the corresponding oxons) and stored at –22°C for 13 months. Wet potato peel was analysed after 24 months storage. The revised method of Thornton (1978) was used.

After 13 months storage the P=S compounds had decomposed by 2% in wet potato peel, 3% in dry peel, 5% in chips, and 23% in flakes, and the P=O compounds by 0% in wet peel, 4% in dry peel, 8% in chips and 17% in flakes. The limit of determination was 0.3 mg/kg for both P=S and P=O mixtures.

USE PATTERN

Disulfoton is a systemic pre-emergent and post-emergent insecticide used for the control of a variety of insect pests such as aphids, mites, leafhoppers, leafminers, nematodes, thrips and beetles. The active ingredient is formulated as granules, EC and SC formulations, and generally applied to the soil at planting as a soil injection, or at sowing in-furrow, as a side-dressing (*i.e.* at the side of the furrow), or as a broadcast spray . Foliar sprays may be applied after planting (pre-emergent) or at a post-emergence stage of growth. Information on registered use patterns was provided by the manufacturer and the UK and German governments.

On US labels, soil applications are expressed as lb product/acre and also as oz product/1000 square foot of row or 1000 ft of row. Row spacing rate charts are included to allow the grower to calculate the amount of product to be applied in accordance with the corresponding row spacing. As the rates applied in the residue trials are expressed as lb product/acre and these rates are also shown on the labels provided, only these rates are shown in the GAP Table. Row spacing rates are shown in the footnotes to the Table.

Table 7. Registered uses of disulfoton on vegetables and cereals.

Crop	Country	Form	Application				PHI,
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	days
Barley	Canada	GR 15%	Soil treatment	1.12		1-2	60
Barley	USA	EC 960 g/l	Soil injection	1.12[1]		1 [2]	60[3]
			Foliar application	0.56-1.12[4]		1	30
Barley	USA	GR 15%	Drilling or broadcast[5]	1.12		1-2[6]	60, 30[7]
Beans	Canada	GR 15%	Soil treatment, side-dressing	1.12-2.25		1	60
Beans	Japan	GR 50 g/kg		2.0		1	60
Beans	USA	GR 15%	In soil band at planting	1.12-2.23[8]		1	60
Beans	USA	EC 960 g/l	Soil injection or side-dressing	1.12-2.24		1	60
Beans	Japan	GR 5%	In furrow	2.0		1	60
Beans (French and runner))	UK	GR 10.7%	Soil application	1.18		1	42
Broad beans	UK	GR 10.7%	Foliar	0.909		1	42
Broccoli	Canada	GR 15%	Soil treatment, side-dressing	1.12		1	42

[1] 7.1 g ai/1000 ft of row;
[2] Maximum application 2.24 kg ai/ha/season, soil + foliar.
[3] 30 days withholding period for forage.
[4] Low rate up to tillering and higher rate after tillering.
[5] Drilling or broadcast at planting or broadcast post-emergent.
[6] 21 day re-treatment interval
[7] 30 days grazing withholding period.
[8] 25.5-51 g ai/1000 ft of row

Crop	Country	Form	Application				PHI,
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	days
Broccoli	USA	GR 15%	In soil bed[9]	1.12[10]		1	14
Broccoli	USA	EC 960 g/l	Side-dressing	1.12		1	14
Broccoli	Mexico	GR 100 g/kg	Band application to soil	1.0		1	na
Broccoli	UK	GR 5%	Soil application	2.92		1	42
Broccoli	UK	GR 6.2%	Soil application	3.48		1	42
Brussels sprouts	USA	GR 15%	In soil bed or soil band	1.12[11]		1-2	30
Brussels sprouts	USA	EC 960 g/l	Side-dressing or injection to soil	1.12		1-2	30
Brussels sprouts	UK	GR 5%	Soil application	2.92		1	42
Brussels sprouts	UK	GR 6.2%	Soil application	3.48		1	42
Brussels sprouts	UK	GR 10.7 %	Soil application	1.5		1	42
			Foliar	1.5		1	
Cabbage	Canada	GR 15%	Soil treatment, side-dressing	1.12		1	42
Cabbage	USA	GR 15%	In soil bed or in soil band	1.12-1.70[12]	No high rate in label.	1	42
Cabbage	UK	GR 5%	Soil application	2.92		1	42
Cabbage	UK	GR 6.2%	Soil application	3.48		1	42
Cabbage	USA	EC 960 g/l	Side-dressing or soil injection	1.12-2.24		1	42
Cabbage	UK	GR 10.7%	Soil application	1.5		1	42
			Foliar	1.5			
Cabbage	Mexico	GR 100 g/kg	Band application	1.0-1.5			na
Cabbage	Japan	GR 5%	In furrow	1.5-3.0		1	na
Calabrese	UK	GR 5%	Soil application	2.92		1	42
Carrot	UK	GR 10.7%	Soil application	2.25		1	42
			Foliar	1.18			
Cauliflower	Canada	GR 15%	Soil treatment, side-dressing	1.12		1-2	30
Cauliflower	USA	GR 15%	In soil bed or soil band	1.12[13]		1-2	40
Cauliflower	USA	EC 960 g/l	Side-dressing or injection to soil	1.12		1-2	40
Cauliflower	Mexico	GR 100 g/kg	Soil treatment	1.0		1	na
Cauliflower	UK	GR 5%	Soil application	2.92		1	42
Cauliflower	UK	GR 6.2%	Soil application	3.48		1	42
Cauliflower	UK	GR 10.7%	Soil application	1.5		1	42
			Foliar	1.5		1	
Celery	UK	GR 10.7%	Soil application	2.25		1	42
Coffee	USA[14]	GR 15%	Under tree canopy	4.3-8.6 kg ai/ha[15]		2	90
Coffee	South Africa	GR 5%		3.3-6.6		1	90
Coffee	South Africa	50 g/kg	Under trees	5.5		1	90
Coffee	Brazil	75 g/kg	Under trees	2.25-5.25		1	90

[9] In soil bed or over the plants after emergence or side of the furrow after planting.
[10] 31.5 g ai/1000 ft of row
[11] 31.5 g ai/1000 ft of row
[12] 48 g ai/1000 ft of row
[13] 31.5 g ai/1000 ft of row.
[14] For Puerto Rico only.
[15] 0.3-0.6 g ai/ft of tree; 2 m trees and 2200 trees/ha.

Crop	Country	Form	Application				PHI,
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	days
Coffee	Honduras	80 g/kg	Under trees	4.8-7.2		1-3	na
Corn	Canada	GR 15%	Band application, soil treatment	1.12		1	100
Corn	USA	EC 960 g/l	Band application	1.12		1[16]	28
			Foliar	0.56-1.12		1	28
Cotton	Greece	GR 100 g/kg (10 GR)	At planting	1.0-1.5		1	60
Cotton	USA	GR 15%	In furrow	0.67-1.12[17]		1[18]	28
Cotton	USA	EC 960 g/l	In furrow or soil injection	0.66-1.12		1-2[19]	28
			Post-planting in furrow	2.24			90
			Foliar	0.22-0.63		1-3	
Cotton	Mexico	GR 100 g/kg	In furrow	1.2-2.0		1	na
Field beans	UK	GR 10.7%	Foliar	1.18		1	42
Herbs (various)	UK	GR 10.7%	Soil application, drilling	1.18		1	42
Kohlrabi	UK	GR 5%	Soil application	2.92		1	42
Lettuce	Canada	GR 15%	Side-dressing, soil treatment	1.12-2.25		1	na
Lettuce	USA	GR 15%	In soil band	1.12-2.8[20]		1	NS
Lettuce	USA	EC 960 g/l	Side-dressing or soil injection	1.12-2.24		1	60
Marrow	UK	GR 10.7%	Soil application	1.18		1	42
Oats	Canada	GR 15%	Soil treatment	1.12		1-2	60
Onion	Japan	GR 5%	In furrow	2.0		1	na
Parsley	UK	GR 10.7%	Drilling in soil	1.18		1	42
Parsnip	UK	GR 10.7%	Soil application	1.18		1	42
			Foliar	1.18			
Peanut	USA	GR 15%	In furrow	1.12-2.23[21]		1	80
Peas	Canada	GR 15%	In furrow spray, soil treatment	1.12-2.62		1	50
Peas	USA	GR 15%	Drilling or broadcast	1.12-2.80		1	50
Peas (and lentils)	USA	EC 960 g/l	Side-dressing or soil injection; in furrow spray	1.12-2.80		1	50
Pecans	USA	GR 15%	Band around tree	1.68-3.36		1[22]	80
Pecans	USA	EC 960 g/l	Band application to soil	1.68-3.36		1	80
			Foliar	0.84-1.68		3[23]	30
Peppers	USA	GR 15%	In soil band	1.12-2.23[24]		1	90
Pineapple	Honduras	80 g/kg	Soil treatment	4.8-7.2		1-3	90
Pineapple	Japan	GR 5%	Soil treatment	2.0-2.5		1-3	120
Pineapple	France	GR 5%	Soil treatment	0.5 g ai/plant		1	na

[16] Apply one soil and one foliar treatment per season.
[17] For a 40 inch row spacing; 21-34 g ai/1000 sq. ft of row or 5 to 8 oz for any row spacing.
[18] On irrigated cotton, two treatments may be necessary, soil incorporated side-dress application; re-treatment interval of 21 days.
[19] Maximum of 3 applications of disulfoton per season. If soil treatments, then foliar application is not recommended. If foliar applications then soil treatment within the same season is not recommended. Last foliar application should be before bloom.
[20] 17-34 g ai/1000 ft of row.
[21] 31.5-62.5 g ai/1000 sq. ft of row.
[22] One application per season in six foot bands around the tree.
[23] No more than 3 applications per season; by aircraft 0.84-1.12 kg ai/ha.
[24] 28.5-56.5 g ai/1000 ft of row.

Crop	Country	Form	Application				PHI,
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	days
Potato	Canada	GR 15%	In furrow, soil treatment	1.16		1	90
			Side-dressing, soil treatment	1.16		1	
			In furrow	2.25-3.38		1	90
Potato	Greece	GR 100 g/kg		1.5-2.5		1	60
Potato[25]	USA	GR 15%	In furrow or soil band	2.27-3.44[26]		1	75
			Broadcast	3.36-4.48		1	
Potato	USA	EC 960 g/l	Broadcast, pre-planting	3.36-4.48[27]			
			Soil injection, side-dressing; in furrow	2.24-3.36			75
			Foliar	0.42-1.12		1-3[28]	30
			Foliar	3.36		1	60
Potato	South Africa	GR 5%	In furrow	1.0		1	90
Potato	Mexico	GR 100 g/kg	In furrow	2.0-3.0		1	na
Potato	Japan	GR 5%	In furrow	2.0		1	na
Potato	UK	GR 10.7%	Soil application	1.7		1	42
Radish (Japanese)	Japan	GR 5%	In furrow	1.5-2.0		1	na
Sorghum	USA	GR 15%	In furrow or	0.84-1.12[29]		1	30
			band in soil				
			Post-planting	1.12		1	
Sorghum	USA	EC 960 g/l	In furrow or soil band	0.84-1.12		1-2	34[30]
			Side-dressing in soil	1.12		1	
			Foliar	0.28-0.56		1-2	7
			Foliar[31]	0.28-0.56		1-3	34
Soya beans	USA	GR 15%	In furrow or band	1.12[32]		1	75
Strawberry	UK	GR 10.7%	Foliar	1.18		1	42
Sugar beet	UK	GR 10.7%	Foliar	1.18		1	42
				0.59		2	
Sugar beet	UK	GR 5%	In furrow, soil treatment	1.0		1	30
			Foliar	1.0			30
Tomatoes	USA	EC 960 g/l	In furrow or side-dressing in soil; broadcast spray	1.12-3.36		1-2	30
Tomatoes	Mexico	GR 100 g/kg	In furrow	1.0-3.0		1	na
Tomatoes	Japan	GR 5%	Side-dressing; soil treatment	1.5-3.0		1	na
Wheat	Canada	GR 15%	Soil treatment	1.12		1	na
Wheat	USA	GR 15%	Drilling or broadcast	0.5-1.12[33]		1	75
Wheat	USA	EC 960 g/l	Soil injection	1.12		1	
			Foliar[34]	0.28-0.84		1-3	30

[25] Maximum of 2 applications per season, 1 in furrow and 1 broadcast.
[26] 63.8-97.8 g ai/1000 ft of row.
[27] Maximum of 2 soil applications per season regardless of method of application or formulation used.
[28] No more than 3 sprays per season.
[29] 25.5-34 g ai/1000 sq. ft of row.
[30] With a maximum of 2 soil applications-34 days for harvest and 45 days for fodder; maximum of 3 foliar applications and 2 soil treatments-34 days for harvest and 60 days for fodder.
[31] At 50% seed head.
[32] 34 g ai/1000 sq. ft of row.
[33] Rate ranges from 0.5 to 1.12 kg ai/ha in relation to row spacing.; 7.1 g ai/1000 ft of row.
[34] 1 fall application and 1-2 spring applications; 30 days re-treatment interval.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Data from supervised trials which have not previously been evaluated on lima beans, cotton, lettuce and potatoes are shown in Tables 8-11.

Table 8	Lima beans. *USA.*
Table 9	Cotton. *Greece.*
Table 10	Lettuce. *USA.*
Table 11	Potatoes. *Netherlands.*

Data which were reviewed in the 1991 and 1994 monographs are interpreted in the light of current GAP in Tables 12-30.

Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the limit of detection, to 1 significant figure. Although trials included control plots, residues in the untreated samples are not reported unless they exceeded the limit of determination. Residues from trials according to GAP are underlined; those used to estimate STMRs are double underlined. All analyses were conducted according to the revised method of Thornton (M00318, 1978) unless otherwise stated. All residues, unless otherwise stated, are defined as the sum of disulfoton sulfone, disulfoton sulfoxide, disulfoton oxygen analogue sulfone and disulfoton oxygen analogue sulfoxide, expressed as disulfoton.

Lima beans. A double side-dress pre-emergent application of disulfoton was made at 2.3 kg ai/ha (Anon., 1976a). Minimal field details were reported. The results are shown in Table 8. There was little rainfall during the trials and the crops were furrow irrigated. Samples of pods and beans were taken at normal harvest intervals of 105 and 106 days after treatment. The method of Thornton (M00034) was used to determine the residues and recoveries of 70 to 118% were reported from fortification with disulfoton, disulfoton oxygen analogue sulfone and sulfoxide at concentrations of 0.1 and 0.5mg/kg.

Cotton. The results of trials in Greece are shown in Table 9 (Seym, 1996b,c). Disulfoton was applied at sowing at 1 kg ai/ha by granule spreader in combination with a tractor and seeder. Trial plots ranged from 1786 to 3836 m^2 and 494 to 2074 m^2 in the 1993 and 1994 trials respectively. Irrigation methods where stated, included gun pump and drip irrigation. Samples were taken 150 to 169 days after treatment (80-90% bolls open). After sampling, the bolls were delinted and stored at −18°C for 4 to 10 months before analysis.

Lettuce. The results of six US trials are shown in Table 10 (Duah, 1997a). In each trial a single side-dress was applied at sowing at a rate equivalent to 1.1-2.2 kg ai/ha[N6] by injector shanks mounted in front and on each side of the planter. The trial plots ranged from 88 to 333 m^2 and irrigation was predominantly by sprinkler and furrow. Control and treated samples of head lettuce (with wrapper leaves) were harvested between 62 and 116 days after planting, and the leaf lettuce between 60 and 90 days after planting. The intervals between harvest and analysis were typically 3 to 7 months. All samples were homogenised and stored at –15°C; the storage stability of analytical samples of lettuce was reported independently (Lemke, 1996).

Potatoes. Trials in The Netherlands and the USA were reported by the government of The Netherlands. Disulfoton was applied at planting at 1.5 kg ai/ha to the soil and tubers were harvested after 113 days. No field or climate details were reported. A published analytical method (Dutch) was also provided. The results are shown in Table 11.

Table 8. Disulfoton residues in lima beans resulting from a double side-dress application of disulfoton at planting, USA, California, 1975.

Variety	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha[1]	kg ai/hl	No.[2]				
Mezcla	GR 15%	2.3		1	78 93 106 106 106	vines beans pods	<0.01 <0.01 <0.01 <0.01 <0.01	Exp. 461-470-75H (Anon. 1976a). 50690
Sutter pink	GR 15%	2.3		1	105	beans, dry	<0.01	Exp. 461-477-75H 50692
Mezcla	GR 15%	2.3		1	78 93 106	vines	0.07 0.11 <0.01	Exp. 461-467-75H 50691

[1] 3 gallons of spray /1000 ft of row; 30 inch row spacing, 4 rows/plot, 50 foot long plot.
[2] Double side-dress applied at pre-emergence stage.

Table 9. Disulfoton residues in cotton seed resulting from supervised trials according to GAP in Greece.

Location year, (variety)	Application[1]				PHI, days	Residues, mg/kg	Reference
	Form.	kg ai/ha	kg ai/hl	No.			
Alexandria 1993 (Corina)	10 GR	1.0		1	163	<0.12	RA-2037/93 300683
Corifi 1993 (Corina)	10 GR	1.0		1	153	<0.12	RA-2037/93 303720
Larisa), 1993 (Acala-Zeta)	10 GR	1.0		1	169	<0.12	RA-2037/93 303739
Agios Dimitrios), 1993 (Zeta 2)	10 GR	1.0		1	154	<0.12	RA-2037/93 303742
Nikea 1994 (Acala SJ-2)	10 GR	1.0			158	<0.06	RA-2053/94 402044
Girtoni 1994 (Acala SJ-2)	10 GR	1.0			158	<0.06	RA-2053/94 402052
Petra 1994 (Zeta 2)	10 GR	1.0			150	<0.06	RA-2053/94 402060
Nisi 1994 (Corina)	10 GR	1.0			155	<0.06	RA-2053/94 402079

[1]Application was by granule spreader whereby the product is applied simultaneously with the seed in the row.

Table 10. Disulfoton residues in lettuce (head and leaf), resulting from soil application in supervised trials in the USA.

State, year (variety)	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	kg ai/hl	No.				
California 1995, (Salad bowl)	EC 960 g/l	1.1	1.8	1	60	Lettuce, leaf	1.09 1.15	Rep. 107520 FCA-D1004-95H
California 1995 (Green supreme)	EC 960 g/l	1.1	0.29	1	90	Lettuce, leaf	<0.05 <0.05	Rep. 107520 458-DI005-95H
Florida 1996 (Slobolt)	EC 960 g/l	1.1	2.3	1	73	Lettuce, leaf	0.57 0.59	Rep. 107520 VBL-DO006-95H
California 1995, (Great Lakes 6)	EC 960 g/l	1.1	1.8	1	97	Lettuce, head	0.22 0.15	Rep. 107520 FCA-DI001-95H

Arizona 1995 (Empire)	EC 960 g/l	1.2	0.25	1	116	Lettuce, head	<0.05 <0.05	Rep. 107520 458-DI002-95H
Florida 1996 (South Bay)	EC 960 g/l	1.2	2.0	1	62	Lettuce, head	≤0.05 ≤0.05	Rep. 107520 VBL-DI003-95H

Table 11. Disulfoton residues in potatoes resulting from soil applications in The Netherlands and the USA.

Country, year, (variety)	Application				PHI, days	Residues, mg/kg	Reference
	Form.	kg ai/ha	kg ai/hl	No.			
Netherlands, 1971 (Bintjie).	–	1.5		1	113	0.05, 0.10, 0.03, <0.01 *c* 0.02	Report R 3957 (1973)
USA (California) 1995 (Green supreme)	–	1.5		1	113	<0.01, <0.01, 0.10, 0.21 *c* 0.12	

Interpretation Tables derived from new and previously reported data

Data which were evaluated by the JMPR in 1991 and 1994 (and in the case of rice in 1973) as well as those in Tables 8-11 above are interpreted in Tables 12-30.

Table 12. Interpretation table for disulfoton residues in barley from trials reported in Table 2 1991 and Table 5 1994. The trials were with soil and foliar applications in the USA and foliar sprays in Canada.

Country,	Application				PHI,	Residues,	
Year,	Form.	kg ai/ha	kg ai/hl	No.	days	mg/kg	Report No.
Canadian GAP		1.12		1-2	60		
Canada 1976	720 EC	1.12 foliar		2	30	0.01	49085 (1991)
US GAP	EC	0.56-1.12		1	30		
USA 1976	720 EC	1.12		2	29	0.06	49263 (1991)
				2	31	0.09	49262 (1991)
				2	30	0.02	49087 (1991)
				2	30	0.14 c 0.11	49088 (1991)
				2	30	≤0.01	49089 (1991)
				2	30	0.01	49090 (1991)
				2	30	≤0.01	50841 (1994)
				2	30	0.04	49091 (1991)
				1	74	<0.01	49230 (1991)
				1	154	<0.01	49201 (1991)
USA 1976	960 EC	1.12		2	31	0.10	68995 (1991)
					31	0.10	68996 (1991)
	720 EC	1.12		2	32	≤0.01	49264 (1991)
	720 EC	0.56 + 1.12		1 + 1	30	0.19 c 0.11	49261 (1994)
USA 1989[1]	15 GR + 960 EC	1.12 + 0.84		1 + 2	30	≤0.01	99130 (1991)
	15 GR + 960 EC	1.12 + 0.84		1 + 2	31	0.03	99130 (1991)
US GAP	GR/EC	1.12		1-2	60		
USA 1976	720 EC	1.12		1	74	≤0.01	49230 (1991)
USA 1976	15 GR	1.12		1	80	0.01	49203 (1991)
USA 1976	15 GR	1.12		1	74	≤0.01	49202 (1991)
USA 1976	960 EC	1.12		2	59	≤0.02	91478 (1991)
				2	62	≤0.02	91478 (1991)

Country,	Application				PHI,	Residues,	
Year,	Form.	kg ai/ha	kg ai/hl	No.	days	mg/kg	Report No.
				2	63	≤0.02	91478 (1991)
USA 1976	15 GR	1.12		2	61	0.02	49204 (1991)
		1.12		2	83	0.03	49200 (1991)
	15 GR	1.12		1	79	<0.01	49265 (1991)
	15 GR	1.12		2	61	≤0.01	49205 (1991)
	15 GR	1.12		2	62	≤0.01	49266 (1991)

[1]In-furrow at planting plus a ground application and a foliar application.

Table 13.Interpretation table for disulfoton residues in beans (lima beans, kidney beans and snap beans) from trials reported in Table 2 1991, Table 3 1994 and Table 8 1998 (shaded). Trials were with a soil application at planting, a soil injection or side-dress in the USA and an in-furrow treatment in Japan. Beans were analysed.

Country, Year, Type of bean	Application				PHI, days	Residues, mg/kg	Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
US GAP	EC/GR	1.12-2.24		1	60		
USA 1975	15 GR	2.3		1	106	≤0.01	461-470-75H
		2.3		1	105	≤0.01	461-477-75H
USA 1975		1.5		1	105	≤0.01	50692 (1994)
USA 1976	15 GR	3.16		1	86	0.03	49327 (1994)
USA 1976	960 EC	3.16		1	86	<0.01	49329 (1994)
USA 1976	960 EC	3.16		1	66	≤0.01	49208 (1991)
Dry beans		3.48		1	59	≤0.01	49328 (1991)
		2.18		1	60	≤0.01	49207 (1991)
	15 GR	3.16		1	66	≤0.01	49282 (1991)
		3.48		1	59	≤0.01	49288 (1991)
USA 1976	960 EC	3.87		1	70	0.02	49280 (1991)
Lima beans	15 GR	3.87		1	70	0.01	49281 (1991)
USA 1976	960 EC	3.48		1	52	0.10	49283 (1991)
Snap beans		1.55		1	60	≤0.01	49289 (1991)
		3.48		1	61	≤0.01	49284 (1991)
		3.16		1	63	0.04	49146 (1991)
		3.16		1	65	0.11	49279 (1991)
	15 GR	3.48		1	52	0.11	49212 (1991)
		1.55		1	60	≤0.01	49290 (1991)
		3.48		1	61	≤0.01	49285 (1991)
		3.16		1	63	0.14	49145 (1991)
		3.16		1	64	0.06	49715 (1991)
Japanese GAP	GR	2.0		1	60		
Japan 1972	5 GR	2.0		2	68	≤0.01	36/72 (1991)
Kidney beans		4.0		2	68	<0.01	
		2.0		2	62	≤0.01	
		4.0		2	62	<0.01	

Table 14. Interpretation table for disulfoton residues in brassica vegetables from trials reported in Table 2 1991 and Tables 2 and 3 1994. Trials were with a soil treatment or side-dress in the USA and an in-furrow treatment in Japan.

Crop	Application				PHI,	Residues,	Reference
Country, Year,	Form.	kg ai/ha	kg ai/hl	No.	days	mg/kg	Report No.
BROCCOLI							
US GAP	GR/EC	1.12		1	14		
Canadian GAP	GR	1.12		1	42		
USA 1987	960 EC	1.12 + 1.68		1 + 1	14	<0.02	91147[1] (1991)
					30	<0.02	
	960 EC	1.12 + 1.68		1 +1	14	0.05	
					41	<0.02	
	960 EC	1.12 + 2.04		1 + 1	15	0.03	
					29	0.11	
	15 GR + 960 EC	1.12 + 2.04		1 + 1	14	0.03	
					41	<0.02	
	15 GR + 960 EC	1.12 + 2.04		1 + 1	15	0.06	
					29	0.09	
	15 GR	1.12 + 2.04		1 + 1	14	<0.02	
					30	<0.02	
CABBAGE, head							
US GAP	EC	1.12-2.24		1	42		
	GR	1.12-1.70		1	42		
Canadian GAP	GR	1.12		1	42		
USA 1987	960 EC	1.12 + 1.72		1 + 1	30	0.09	91152[2] (1991)
					42	0.17	
	960 EC	1.12 + 3.16		1 + 1	31	0.02	
					42	<0.02	
		1.12 +1.30		1+ 1	39	<0.02	
					51	<0.02	
		1.12 + 1.72		1 + 1	32	<0.02	
					41	0.02	
		1.12		2	30	<0.02	
					42	<0.02	
	15 GR + 960 EC	1.12 + 3.16		1 + 1	31	0.03	
					42	<0.02	
	960 EC + 15 GR	1.12 + 1.30		1 + 1	39	<0.02	
					51	<0.02	
	15 GR	1.12 + 1.72		1 + 1	30	0.23	
					42	0.17	
	15 GR	1.12 + 1.72		1 + 1	32	<0.02	
					41	0.03	
	15 GR	1.12 + 1.48		1 + 1	30	<0.02	
					42	<0.02	
	960 EC	1.12 + 3.16		1 + 1	29	0.07	
					43	0.02	
	960EC	1.12 + 1.72		1 + 1	30	0.12	
					42	0.06	
	15 GR + 960 EC	1.12 + 3.16		1 + 1	15	0.11	
					29	0.03	
	15 GR	1.12 + 1.72		1 + 1	30	0.32	
					42	0.08	

Crop	Application				PHI,	Residues,	Reference
Country, Year,	Form.	kg ai/ha	kg ai/hl	No.	days	mg/kg	Report No.
Japanese GAP	GR	1.5-3.0		1	na		
Japan 1972	5 GR	2		1	57	0.073	27/72 (1991)
		4		1	57	0.096	
		2		1	69	0.072	28/72 (1991)
		4		1	69	0.063	
CAULIFLOWER							
US GAP	EC\GR	1.12		1-2	40		
Canadian GAP	GR	1.12		1-2	30		
USA 1987	960 EC	1.12		3	30	0.01	91154[3] (1991)
					40	0.31	
		1.12 + 1.68		1 +2	30	<0.01	
					40	<0.01	
		1.12 + 1.0		1 + 2	38	<0.01	
	15 GR	1.12		3	30	0.02	
					40	0.04	
	15 GR	1.12 + 1.68		1 + 2	30	<0.01	
					40	<0.01	
	15 GR	1.12		3	30	<0.01	
					40	0.01	
	15 GR	1.12 + 1.0		1 + 2	28	0.05	
					38	0.01	

[1]One soil spray followed by one side-dress spray.
[2]One soil broadcast followed by one side-dress spray.
[3]One broadcast application followed by two side-dress sprays.

Table 15. Interpretation table for disulfoton residues in coffee beans from trials reported in Table 2 1991. Trials were with soil application under the tree canopy.

Country, Year,	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
Puerto Rico GAP		4.3-8.6[1]		1-2	90		
(USA use pattern)		g ai/tree					
Puerto Rico 1986	GR	7.2		1	89	0.09 berries	91497 (1991)
						0.10 beans	
		28.8[2]		1	89	05 berries	
						0.2 beans	
		72.2[3]		1	89	0.28 berries	
						0.17 beans	

[1]Calculated from tree height of 2m, assuming 2200 trees/ha (0.3-0.6 g ai/30 cm of tree height).
[2]2.4 g ai/30 cm tree height, fourfold rate.
[3]6 g ai/cm tree height, tenfold rate.

Table 16. Interpretation table for disulfoton residues in cotton seed from trials reported in Table 2 1991, Table 11 1994 and Table 9 above (shaded). Trials were with applications at planting or before planting and post-plant in the USA and at planting in Greece.

Country, year,	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			

Country, year,	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
Greek GAP	GR	1.0-1.5		1	60[1]		
Greece 1993	10 GR	1.0		1	163	<0.12	RA-2037/93
					153	<0.12	
					169	<0.12	
					154	<0.12	
Greece 1994	10 GR	1.0		1	158	<0.06	RA-2037/94
					158	<0.06	
					150	<0.06	
					155	<0.06	
US GAP	EC	0.63-1.12		1			
		0.21-0.63		1-3			
		2.24		1	90		
		1.12		1	28		
	GR	0.67-1.12		1	28		
USA 1967	SC≡EC	2.24		1	127	0.1	21636[2]
		2.24		1	105	<0.03	21637[2]
		6.72		1	136	0.02	21639[2]
		4.48		1	110	0.02	21640[2]
		2.24		1	110	0.05	21641[2]
		2.24		1	145	<0.03	21642[2]
		2.24		1	88	<0.02	21643[2]
		2.24		1	133	<0.04	21644[2]
USA 1969	LC≡EC	1.12		3	99	<0.11 c 0.10	24014[3] (1994)
		1.12		3	89	0.04	24019[3] (1994)
		1.12		3	94	<0.05	24023[3] (1994)
		1.12		3	111	0.03	24029[3] (1994)
		1.12		3	88	0.12	24030[3] (1994)
		1.12		3	94	<0.05	24042[3] (1994)
		1.12		3	111	0.03	24044[3] (1994)
		1.12		3	88	0.12	24045[3] (1994)
		1.12		3	89	0.04	24046[3] (1994)
		0.5 + 1.12		1 + 3	45	<0.03	24018[4] (1994)
		0.5 + 1.12		1 + 3	33	0.03	24021[4] (1994)
		0.5 + 1.12		1 + 3	90	<0.06	24022[4] (1994)
		0.5 + 1.12		1 + 3	90	<0.06	24041[4] (1994)
		0.5 + 1.12		1 + 4	95	0.10	24020[4] (1994)
		0.5 + 1.12		1 + 4	95	0.10	24040[4] (1994)
USA 1972	15 GR	2.24		2	28	<0.19	33227[5] (1994)
		1.12		2	28	<0.19	
		2.24		2	28	<0.19	33228[5] (1994)
		1.12		2	28	<0.19	
USA1979	5 GR	2.3 + 3.68		1 + 1	119	<0.01	67811 ?
USA1979	5 GR	2.3 + 3.68		1 + 1	119	0.02	67812 ?
USA 1985	15 GR +	1.12 + 0.22		1 + 3	31	<0.01	87300 (1991)
	960 EC				35	<0.01	
		1.12 + 0.22		1 + 3	28	<0.01	87301 (1991)
					35	<0.01	
		1.12 + 0.22		1 + 3	35	<0.01	87302 (1991)
		1.12 + 0.22		1 + 3	28	<0.01	87363 (1991)
					35	<0.01	
	960 EC	1.12 + 0.22		1 + 3	31	<0.01	87303 (1991)

Country, year,	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
					35	≤0.01	
		1.12 +0.22		1 + 3	28	≤0.01	87304 (1991)
					35	≤0.01	
		1.12 + 0.22		1 + 3	35	≤0.01	87305 (1991)
		1.12+ 0.22		1 + 3	28	≤0.01	87364 (1991)
					35	≤0.01	
USA 1987	960 EC + 15 GR+ 15 GR	0.5 + 0.93 + 1.12		1 + 1 +2	27	≤0.01	91487[6] (1991) 354-DI092-86D
		0.5 + 0.97 + 1.16		1 + 1 +2	38	0.43	BMS-DI095-86D[6] (1991)
		0.5 + 0.98 + 1.17		1 + 1+ 2	27	≤0.01	RTX-DI096-86D[6] (1991)
		0.5 + 0.92 + 1.13		1 + 1+ 2	28	0.05	458-DI093-86D[6] (1991)
		0.5 + 0.97 + 1.16		1 + 1 + 2	28	≤0.01	456-DI094-86D[6] (1991)
		0.5 + 0.93 + 2.24		1 + 1 + 2	47	≤0.01	354-DI097-86D[6] (1991)
		0.5 + 0.97 + 2.32		1 + 1+ 2	92	≤0.01	BMS-DI100-86D[6] (1991)
		0.5 + 0.97 + 2.34		1 + 1 + 2	83	≤0.01	RTX-DI101-86D[6] (1991)
		0.5 +0.92 + 2.26		1 + 1 + 2	90	0.05	458-DI098-96D[6] (1991)
		0.5 + 0.97 + 2.32		1 + 1 + 2	90	0.02	456-DI099-86D[6] (1991)

[1]From planting to harvest.
[2]Side-dress spray at squaring.
[3]Foliar spray.
[4]Seed treatment at 0.5 kg ai/100 kg seed plus 3 or 4 foliar treatments at 1.12kg ai/ha.
[5]In-furrow plus band side-dress.
[6]Seed treatment at 0.5 kg ai/100 kg seed, plus in-furrow application at planting and side-dress application post-emergent.

Table 17: Interpretation table for disulfoton residues in garden peas from trials reported in Table 2 1991 and Table 4 1994. Trials were with in-furrow and side-dress applications, USA.

Country, year,	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
US GAP	GR	1.12-2.8		1	50		
	EC	1.12-2.24		1	50		
Canadian GAP	GR	1.12-2.62		1	50		
1976 (peas)	720 EC	2.8		1	49	≤0.01	49209[1] (1991)
					59	≤0.01	
					69	<0.01	
					79	<0.01	
	720 EC	2.8		1	56	≤0.01 peas	49210[1] (1991)
						≤0.01 pods	
					78	<0.01 peas	
						<0.01 pods	
	720 EC	2.8		1	33	0.02 peas	49298[1] (1991)
						<0.01 pods	
				1	50	≤0.01 peas	
						0.02 pods	

Country, year,	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
					60	≤0.01 peas	
						0.08 pods	
					71	<0.01 peas	
						0.03 pods	
	720 EC	2.8		1	49	≤0.01	50840[1] (1991)
	15 GR	2.8		1	60	≤0.01	49299[1] (1991)
	15 GR	2.8		1	33	0.04 peas	49300[1] (1994)
						0.10 pods	
	15 GR	2.8		1	56	≤0.01 peas	49301[1] (1991)
						≤0.01 pods	
					70	<0.01 peas	
						<0.01 pods	
					78	<0.01 peas	
						<0.01 pods	
					85	<0.01 peas	
						<0.01 pods	
	15 GR	2.8		1	49	≤0.01	49302[1] (1991)
					59	≤0.01	
					69	<0.01	
					79	<0.01	
1976	15 GR	2.8		1	67	<0.01 pods	50670[1] (1991)
1978	720 EC	2.8		1	81	<0.01 peas	65779[1] (1994)
						<0.01 pods	
1969	720 EC	3.36		3	29	1.06	24138[2] (1994)
(Southern peas)[3]	720 EC	2.24		2	30	0.28	24139[2] (1994)
	720 EC	2.24		2	30	0.04	24140[2] (1994)
	720 EC	3.36		2	28	1.48	24141[2] (1994)
	720 EC	2.24		2	28	0.24	24150[2] (1994)
	720 EC	2.24		2	28	0.24	24151[2] (1994)
	10 GR	3.36		2	30	0.23	24193[2] (1994)
	10 GR	2.24		2	28	0.31	24205[2] (1994)
	10 GR	3.36		2	30	<0.02	24188[2] (1994)
	10 GR	2.24		2	30	<0.02	24204[2] (1994)

[1]Double side-dress, early post-emergent.
[2]Side-dress at planting and post-emergent.
[3]Black-eyed or Southern peas (green peas).

Table 18. Interpretation table for disulfoton residues in lettuce from trials reported in Table 10 above and Table 2 1991. Trials were with soil side-dress applications in the USA.

Country, year,	Application				PHI, days	Residues, mg/kg	Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
US GAP	960 EC	1.12-2.24		1	60		
1985	960 EC	1.1		1	60	0.11	91473
leaf lettuce		2.23		1	59	≤0.03	
		2.44		1	50	0.56	
		1.05		1	61	≤0.03	
		2.92		1	60	0.06	
1985	960 EC	1.1		1	61	0.64	
head lettuce		2.23		1	62	≤0.03	
		2.44		1	60	0.44	
		2.92		1	59	0.10	

		1.05		1	61	0.04	
1995	960 EC	1.1		1	60	1.09, 1.15	107520
leaf lettuce		1.14		1	73	0.57, 0.59	
1995	960 EC	1.21		1	62	<0.05, <0.05	
head lettuce							

Table 19. Interpretation table for disulfoton residues in maize from trials reported in Table 2 1991 and Table 6 1994. Trials were with side-dress applications and foliar sprays in the USA.

Country, year,	Form.	Application kg ai/ha	kg ai/hl	No.	PHI, days	Residues, mg/kg	Reference Report No.
US GAP	EC	1.12		1[1]	28		
		0.56-1.12		1	28		
Canadian GAP	GR	1.12		1	100		
1975	720 EC	1.12		3	35	<0.01	44179[2] (1991)
	720 EC	1.12		3	24	<0.01	44181[2] (1991)
	720 EC	1.12		3	29	<0.01	44183[2] (1991)
	720 EC	1.12		3	28	<0.01	44184[3] (1991)
					42	0.07	
	720 EC	1.12		3	28	<0.01	49307[4] (1991)
					35	<0.01	
	720 EC	1.12		3	21	<0.01	49476[4] (1991)
					28	<0.01	
	720 EC	1.12		3	21	<0.01	53294[4] (1994)
					28	<0.01	
					35	<0.01	
					42	<0.01	
	720 EC	1.12		3	21	<0.01	53298[4] (1994)
					28	<0.01	
					35	<0.01	
					42	<0.01	
	720 EC	1.12		3	21	<0.01 *c*	53297[5] (1994)
						0.05	
					28	<0.01	
1987	960 EC	1.46 + 1.12		1 + 1	27	<0.02	91482 (1991) 255-DI068-86D[6]
					45	<0.02	
	960 EC	1.22 + 1.12		1 + 1	28	<0.02	HIN-DI069-86D[6]
					45	<0.02	
	960 EC	1.22 + 1.12		1 + 1	27	<0.01	STF-DI070-86P[6]
					47	<0.01	
	960 EC	1.46 + 1.12		1 + 1	29	<0.02	251-DI066-86D[6]
					45	<0.02	
	960 EC	1.46 + 1.12		1 + 1	28	<0.02	252-DI067-86D[6]
					45	<0.02	

[1]One soil and one foliar treatment per season.
[2]Foliar spray.
[3]ULV aerial application.
[4]Foliar spray.
[5]Topical pre-emergent.
[6]Side-dress and foliar spray.

Table 20. Interpretation table for disulfoton residues in oats from trials reported in Table 2 1991. Trials were with a broadcast spray at planting or broadcast sprays both pre- and post-emergent in the USA.

Country, year,	Form.	Application kg ai/ha	kg ai/hl	No.	PHI, days	Residues, mg/kg	Reference Report No.
Canadian GAP	GR	1.12		1-2	60		

Country, year,	Application				PHI,	Residues,	Reference
	Form.	kg ai/ha	kg ai/hl	No.	days	mg/kg	Report No.
USA 1976	15 GR	1.12		2	61	<0.01	49214[1]
	15 GR	1.12		2	62	<0.01	49215[1]
	15 GR	1.12		2	66	<0.01	49216[1]
	15 GR	1.12		1	79	<0.01	49215[1]
	720 EC	1.12		1	79	<0.01	49297[2]
	720 EC	1.12		1	80	<0.01	49314[2]

[1]Broadcast application pre- and post-emergent.
[2]Broadcast spray incorporated at planting.

Table 21. Interpretation table for disulfoton residues in peanuts from trials reported in Table 2 1991. Trials were with a side-dress and band application in the USA.

Country, year,	Application Form.	kg ai/ha	kg ai/hl	No.	PHI, days	Residues, mg/kg	Reference Report No.
US GAP	GR	1.12-2.23		1	80		
USA 1987	15 GR	1.72		2	62	0.02	91492
kernels					72	0.02	
	15 GR	2.26		2	60	0.09	91492
	15 GR	2.20		2	61	<0.01	91492
					75	<0.01	
	15 GR	2.29		2	85	<0.01	91492

Table 22. Interpretation table for disulfoton residues in pecan nuts from trials reported in Table 2 1991 and Table 12 1994. Trials were with foliar and aerial applications in the USA.

Year,	Application Form.	kg ai/ha	kg ai/hl	No.	PHI, days	Residues, mg/kg	Reference Report No.
US GAP	EC	1.68-3.36		1	80		
		0.84-1.68		1-3	30		
		0.84-1.12		1-3	30		
1971	720 EC	1.68		3	22	0.21	32688[1] (1994)
		1.12		3	22	0.08	32683[1] (1994)
		5.40		3	28	<0.05	32684[1] (1994)
		2.24		3	41	<0.1 (*c* = 0.1)	32685[1] (1994)
		3.58		3	30	<0.01	32686[1] (1994)
		2.24		3	28	0.22	32687[1] (1994)
		3.36		3	41	<0.11	32689[1] (1994)
		5.38		3	30	0.05	32690[1] (1994)
		3.36		3	28	0.43	32691[1] (1994)
		6.72		3	31	<0.08	32692[1] (1994)
		5.88-7.06		3	26	<0.03	32693[1] (1994)
1975	720 EC	1.12		3	31	<0.01 kernel 0.85 shell	44344[2] (1991)
		1.68		3	30	0.01 kernel <0.01 shell	44345[2] (1991)
		1.68		3	31	<0.01 kernel <0.01 shell	44346[2] (1991)
		1.12		4	30	<0.02 kernel 0.03 shell	44347[2] (1991)
s		1.12		3	30	<0.01 kernel <0.01 shell	44348[2] (1991)

[1]Foliar spray. [2]Aerial spray.

Table 23. Interpretation table for disulfoton residues in pineapples from trials reported in Table 2 1991 from Martinique and Brazil.

Country, year,	Application Form.	kg ai/ha	kg ai/hl	No.	PHI, days	Residues, mg/kg	Reference Report No.
French GAP	GR	0.025[1]		1	na		
Martinique 1966	5 GR	0.025[1,2]		1	92	<0.1	4/66
	5 GR	0.025[1]		1	61	<0.1	
	5 GR	0.025[1]		1	29	<0.1	
Honduras GAP	GR	4.8-7.2		1-3	90		
	GR	2.5-3.0 (0.1[1])		1	na		
Brazil 1983	2.5 GR	0.075[1]		1	90	<0.1	65780

Country, year,	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
	2.5 GR	0.075[1]		1	60	<0.1	
	2.5 GR	0.15[1]		1	90	<0.1	
	2.5 GR	0.15[1]		1	60	<0.1	

[1]g ai/plant [2]Spread into the upper leaves and on the bottom of the stigma.

Table 24. Interpretation Table for disulfoton residues in potatoes from trials reported in Table 2 1991 and Table 11 1998 (shaded). Trials were with in-furrow, side-dress and band applications in the USA and a broadcast application in Japan.

Country, year,	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
US GAP	EC	3.36-4.48[1]		1-2			
		2.24-3.36[2]		1-2	75		
		0.42-1.12[3]		1-3	30		
		3.36[4]		1	60		
	GR	2.27-3.44[5]		1-2			
		3.36-4.48[6]		1			
USA 1968	720 SC	3.36		2	60	0.11	21980[7] (1991)
		3.36		2	63	0.31	21990[7] (1991)
		3.36		2	61	<0.02	21992[8] (1991)
USA 1967	10 GR + 720 SC	3.36 + 3.36		1 + 1	60	0.15	21576[9] (1991)
					87	0.08	
	10 GR + 720 SC	3.36 + 3.36		1 + 1	60	0.07	21588[9] (1991)
					87	0.16	
USA 1968	10 GR + 720 SC	3.36 + 3.36		1 + 1	60	0.07	21959[7] (1991)
	10 GR + 720 SC	3.36 + 3.36		1 + 1	60	0.01	21961[7] (1991)
	10 GR	3.36		2	63	<0.01	21989[7] (1991)
	10 GR	3.36		2	60	0.09	21993[7] (1991)
					90	0.20	
USA 1973	15 GR	1.12 + 3.36		1 + 1	78	0.13, 0.23	39081[10] (1991)
USA 1986	15 GR	3.36		2	75	<0.01	91467[11] (1991)
	15 GR	3.36		2	64	0.06	91467[12] (1991)
					77	<0.01	
Japanese GAP	GR	2.0		1	na		
Japan 1971	5 GR	2.0		1	85	0.04	90/71[13] (1991)
	5 GR	2.0		1	105	0.07	
	5 GR	2.0		1	85	0.12	
	5 GR	2.0		1	105	0.10	
Netherlands 1971		1.5		1	113	0.05, 0.10, 0.03, <0.01 c 0.02	R 3957 (1998)
USA 1995		1.5		1	113	<0.01, <0.01, 0.10, 0.21 c 0.12	

[1]Pre-plant broadcast application. [2]In-furrow, soil injection or side-dress at planting.
[3]Foliar spray. [4]Foliar spray.
[5]In-furrow application. [6]Broadcast application.
[7]In-furrow, side-dress application. [8]Double band, side-dress application. (Continued)
[9]At planting, side-dress spray. [10]Post-emergent band application (side-dress).

[11]Soil application.
[12]Post-emergent aerial application.
[13]Broadcast application.

Table 25. Interpretation table for disulfoton residues in Japanese radishes from trials reported in Table 2 1991. Trials were with an in-furrow application in accordance with GAP in Japan.

Country, year,	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
Japanese GAP	GR	1.5-2.0		1	na		
Japan 1977	5 GR	1.0		1	61	0.05	N463/76
					67	0.01	
	5 GR	1.5		1	61	0.12	
					67	0.10	
	5 GR	1.0		1	56	0.02	N 465/76
					63	0.05	
	5 GR	1.5		1	56	0.14	
					63	0.08	
	5 GR	1.0		1	61	0.02	N 467/76
					68	0.02	
	5 GR	1.5		1	61	0.02	
					68	0.03	
	5 GR	1.0		1	75	0.004	N 469/76
					82	0.004	
	5 GR	1.5		1	75	0.004	
					82	0.004	
Japan 1978	5 GR	1.0		1	102	0.008	N 569.78
					112	0.01	
	5 GR	1.5		1	102	0.02	
					112	0.02	

Table 26. Interpretation table for disulfoton residues in rice from trials reported in Table 1 1973.

Year	Application				PHI, days	Residues, mg/kg	Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
Japanese GAP	GR	2 0-3.0		1-2	50		
1971	5 GR	3.0		1	119	<0.01	20/71
	5 GR	3.0		1	139	<0.01	19/71
1972	5 GR	3.0		1	90	<0.01	34/72

Table 27. Interpretation table for disulfoton residues in sorghum from trials reported in Table 2 1991 and Tables 7 and 8 1994. Trials were with in-furrow, side-dress and foliar applications in accordance with GAP in the USA.

Year	Application				ssPHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
US GAP	GR	0.84-1.12[1]		1	30		
1969	10 GR	1.12		1	32	0.02	24049
	10 GR	1.12		1	33	0.04	24051
	10 GR	1.12		1	30	0.01	24052
	10 GR	1.12		1	35	0.04	24053
	10 GR	1.12		1	29	0.02	24054
	10 GR	1.12		1	30	<0.01	24055
	10 GR	1.12		1	32	0.08	24056

Year	Application				ssPHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
1969	10 GR	1.12		3	30	<0.01	24048
1971	15 GR	1.12		3	30	<0.02	33159
1971	15 GR	1.12		3	30	0.02	33154
1971	15 GR	1.12		4	30	<0.05	33155
1971	15 GR	1.12		3	47	0.09	33161
1975	15 GR	1.22 + 1.12		1 + 3	33	0.01	49466
1975	15 GR	1.22 + 1.12		1 + 3	33	0.01	49466
1972	15 GR	1.68		4	30	<0.05	33153
1972	15 GR	1.68		4	29	0.04	33157
1972	15 GR	1.68		3	30	0.06	33160
US GAP	EC	0.84-1.12[2]		1			
		1.12[3]		1			
		1.12[4]		1			
		0.28-0.56		[5]	34		
		0.28-0.56		1-2	7		
		0.28-0.56		3	34		
1987	960 EC	1.12		2	7	0.24	353-DI064-86D
					14	0.04	(OK)[6]
	960 EC	1.12		2	7	0.15	353-DI065-86D
					14	0.08	(OK)[6]
	960 EC	1.12		2	5	1.46	352-DI062-86D
					13	0.87	(TX)[6]
	960 EC	1.12		2	5	3.67	352-DI063-86D
					13	2.52	(TX)[6]
1968	720 EC	0.56		1	35	<0.01	23397[7]
1968	720 EC	1.12		2	7	0.28	23969[7]
	720 EC	1.12		2	7	<0.01	23970[7]
	720 EC	1.12		2	7	0.09	23973[7]
	720 EC	1.12		2	7	0.73	23974[7]
	720 EC	1.12		2	7	0.39	23975[7]
	720 EC	1.12		2	7	0.56	23976[7]
1971	720 EC	1.12 + 1.12+ 0.56		1 + 1+ 3	34	<0.01	29388[8]
	720 EC	1.12 + 1.12 + 0.56		1 + 1+ 3	46	<0.01	29391[8]
	15 GR + 15 GR	1.12 + 1.12		1 + 3	29	0.10	33158[9]
1975	15 GR + 15 GR	1.46 + 1.12		1 + 2	29	0.08	49934[10]
	720 EC	1.46 + 1.12		1 + 2	29	0.23	49936
1970	720 EC 15 GR 720 EC	1.12 + 1.12 + 0.56		1 + 1 + 3	34	<0.01	29839[11]

[1]In furrow or band in soil at planting.
[2]At planting in-furrow application.
[3]At planting band application.
[4]Post planting side-dress application.
[5]Any soil plus any foliar application.
[6]Foliar spray, ground or aerial application.
[7]Foliar spray.
[8]In-furrow side-dress and foliar spray.
[9]Pre-emergent band application and broadcast.
[10] Side-dress and foliar application.
[11]In-furrow and side-dress and foliar spray.

Table 28. Interpretation table for disulfoton residues in sugar beet from trials in the USA reported in Table 2 1991. Trials were with in-furrow and foliar sprays and topical applications.

Country, year	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
Chile GAP	GR	1.0		1	30		
USA 1970	10 GR + 720 SC	1.7 + 1.12		1 + 5	15	0.03	27025[1]
	10 GR + 720 SC	1.7 + 1.12		1 + 5	15	<0.01	27077[2]
	10 GR + 720 SC	1.12		6	15	0.01	27078[3]
	15 GR + 720 SC	1.8 + 1.12		1 + 5	15	0.02	26974[3]
	15 GR + 720 SC	1.8 +1.12		1 + 5	15	<0.03	26975[3]
	15 GR + 720 SC	1.3 + 1.12		1 + 5	21	0.01	27023[3]
	15 GR + 720 SC	1.7 + 1.12		1 + 5	15	0.01	27024[3]
	15 GR + 720 SC	1.7 + 1.12		1 + 5	15	0.04	27075[3]
					31	0.06	
	15 GR + 720 SC	1.10 + 1.12		1 + 3	28	0.02	50671[4]
	15 GR + 15 GR	1 64 + 1.12		1 + 3	29	<0.01	49295[4]
	15 GR + 15 GR	1.64 + 1.12		1 + 3	30	<0.01	49296[4]
					40	0.03	
	15 GR + 15 GR	1.50 + 1.12		1 + 3	28	0.06	50833[4]
					40	0.01	
	15 GR + 15 GR	1.50 + 1.12		1 + 3	31	0.06	53066[4]

[1]In-furrow and foliar sprays.
[2]Soil band and foliar sprays.
[3]In-furrow and topical application over the row.
[4]In-furrow and topical applications over the row.

Table 29. Interpretation table for disulfoton residues in tomatoes from trials reported in Table 2 1991. Trials were with drip and side-dress applications in accordance with GAP in the USA and Japan.

Country, year,	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
US GAP	EC	1.12-3.36		1-2	30		91474
USA 1987	960 EC	1.46		2	14	0.02	456-DI109-86D
					20	<0.01	(1991)
					27	<0.01	
	960 EC	2.09		2	14	0.36	457-DI110-86D
					21	0.01	(1991)
					28	0.02	
	720 EC	1.46		2	14	<0.01	458-DI111-86D
					21	<0.01	(1991)
					28	<0.01	
Japanese GAP	GR	1.5-3.0		1	na		
Japan 1977	5 GR	0.05[1]		1	70	<0.01	N 476/76
	5 GR	0.1[1]		1	70	<0.01	N 476/76
	5 GR	3.0 + 0.1[1]		1 + 1	30	0.05	N 476/76
					41	0.05	
	5 GR	0.05[1]		1	38	0.03	N 477/76
	5 GR	0.1[1]		1	38	0.05	
	5 GR	3.0 + 0.1[1]		1 + 1	33	0.04	N 477/76

[1]g ai/plant.

Table 30. Interpretation table for disulfoton residues in wheat from trials reported in Table 2 1991 and Tables 9 and 10 1994. Trials were with in-furrow and foliar applications according to US GAP.

Country, year	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
US GAP	EC	1.12		1[1]	na		
		0.28-0.84		1-3[2]	30		
	GR	1.12		1[3]	75		
USA 1967	720 SC	1.12		1	29	<0.01	21416[4] (1994)
USA 1968	720 EC	0.84		2	30	<0.02	23115[4] (1994)
	720 SC	0.84		2	29	<0.1	23117[4] (1994)
	720 SC	0.84		3	33	0.14	23118[4] (1994)
USA 1970	720 SC	0.28 + 0.56 + 1.12		2 + 1 + 1	30	<0.01	26557[4] (1994)
	720 LC	0.28 + 0.56 + 1.12		2 + 1 + 1	30	0.02	26579[4] (1994)
	720 LC	0.28 + 0.56 + 1.12		2 +1 +1	30	0.24	26580[4] (1994)
	720 LC	0.28 + 0.56 + 1.12		2 + 1 + 1	30	0.18	26581[4] (1994)
	720 LC	0.28 + 0.56 + 1.12		2 + 1 + 1	30	0.02	26582[4] (1994)
	720 LC	0.28 + 0.56 + 1.12		2 + 1 +1	29	0.01	26583[4] (1994)
	720 LC	0.84 + 1.12		2 + 2	30	<0.01	26895[4] (1994)
	720 LC	0.84 + 1.12		2 + 2	29	0.05	26896[4] (1994)
	720 LC	0.28 + 0.56 + 1.12		2 + 1 + 1	29	0.27	26905[4] (1994)
	720 LC	0.84 + 1.12		2 + 2	30	0.02	26944[4] (1994)
	720 LC	0.84 + 1.12		2 + 2	30	0.01	26945[4] (1994)
	720 LC	0.28 + 0.56 + 1.12		2 + 1 + 1	33	0.02	26946[4] (1994)
	720 LC	0.84 + 1.12		2 + 2	33	0.04	26947[4] (1994)
	720 LC	0.84 + 1.12		2 + 2	30	<0.01	26954[4] (1994)
	720 LC	0.84 + 1.12		2 + 2	30	0.19	26956[4] (1994)
	720 LC	0.84 + 1.12		2 + 2	29	0.05	26961[4] (1994)
	720 LC	0.84 + 1.12		2 + 2	33	0.03	26962[4] (1994)
	720 LC	0.28 + 0.56 + 1.12		2 + 1 +1	33	0.04	26963[4] (1994)
USA 1988	960 EC	0.84		2	31	<0.01	87173[4] (1991)
				2	31	<0.01	
				2	31	<0.01	
				2	31	<0.01	
				2	31	<0.01	
				2	31	<0.01	
				2	31	<0.01	
USA 1987	15 GR + 960 EC	1.12 + 0.84		1 + 2	26	<0.02	91477[5] (1991)
	15 GR + 960 EC	1.12 + 0.84		1 + 2	29	<0.02	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	30	0.02, <0.02	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	32	<0.02	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	37	<0.02	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	38	<0.02	

Country, year	Application				PHI, days	Residues, mg/kg	Reference Report No.
	Form.	kg ai/ha	kg ai/hl	No.			
	15 GR + 960 EC	1.12 + 0.84		1 + 2	31	<0.02	
	960 EC	0.84		2	28	<0.02	
	960 EC	0.84		2	31	<0.02	
USA 1989	15 GR + 960 EC	1.12 + 0.84		1 + 2	30	<0.01	99130[5] (1991)
winter wheat	15 GR + 960 EC	1.12 + 0.84		1 + 2	30	0.03	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	31	<0.01	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	31	<0.01	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	30	<0.01	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	31	0.01	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	30	0.01	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	27	<0.01	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	29	<0.01	
	15 GR + 960 EC	1.12 + 0.84		1 + 2	29	0.01	
	15 GR + 960 EC	1.12 + 0.84		1 + 2			
USA 1975	15 GR	1.12		2	26	0.16	43155[6] (1994)
	15 GR	1.12		2	26	<0.05	43615[6] (1994)
	15 GR	0.56		2	26	0.05	43617[6] (1994)
	15 GR	1.12		2	26	<0.05	43621[6] (1994)
Canada 1989	720 LC	0.84		1	30	<0.01	99215[4] (1994)
	720 LC	0.84		1	30	<0.01	
	720 LC	0.84		1	30	<0.01	
	720 LC	0.84		1	30	0.11	

[1]Soil injection.
[2]Foliar sprays; 1 autumn and 2 spring applications.
[3]Drilling or broadcast.
[4]Foliar spray.
[5]Soil broadcast or in-furrow and aerial or ground foliar sprays.
[6]Broadcast application.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

The Meeting received information on the fate of disulfoton during the processing of coffee, cotton seed, maize, potatoes, sorghum and wheat.

In the trials reported by the manufacturer, processing factors are calculated on the basis of average residues in the raw agricultural and processed commodities. All analyses were by the revised

method 00318 of Thornton (1978) in which residues are oxidized to disulfoton sulfone and disulfoton oxygen analogue sulfone.

Coffee. Disulfoton 15 GR was applied at a rate 3 g ai/30 cm tree height (112 g product/tree, 16.8 g ai/tree) to the soil around coffee trees at the time of berry filling (Duah 1997b). The application rate was approximately 5 times the maximum label rate. Trees were 4-5 years old and the plot was 633 m^2. The beans were harvested 89 days after treatment and the skin, pulp and endocarp were removed to leave the green beans. Samples were removed for analysis and the remaining beans were processed into roasted beans and instant coffee. Samples of green and roasted beans, and instant coffee were analysed for disulfoton residues. The limit of determination was 0.1 mg/kg.

Table 31. Disulfoton residues in coffee beans and their processed products after a single soil treatment at 112 g ai/tree.

Sample	Residues, mg/kg[1]	Processing factor
Coffee beans (green)	0.289, 0.298, 0.302	
Roasted coffee beans	<0.1, <0.1, <0.1, <0.1, <0.1, <0.1	<0.3
Instant coffee	<0.1, <0.1, <0.1	<0.3

[1]Replicate samples analysed.

Recoveries were 87 to 106% from green coffee beans, 77 to 109% from roasted coffee beans and 73 to 100% from instant coffee over all the individual components of the residue definition. Overall, recoveries from instant coffee were lower (average 78%) for each compound at 0.1 mg/kg.

Cotton. In a US processing study (Freeseman, 1997), disulfoton was applied in-furrow at a rate equivalent to 5.48 kg ai/ha[N7]. 24 days after planting (1st leaf stage), a soil injection at 10.92 kg ai/ha was applied on each side of the row, and 51 days after planting (6-8 leaf stage), a foliar spray was applied at 3.15 kg ai/ha. Two additional foliar sprays were applied at 7-day intervals, with the final spray at squaring, 111 days before harvest. Each individual treatment was 5 times the maximum recommended rate. GAP in the USA dictates that soil and foliar treatments are not both made within the same crop year, so the treatment regime was exaggerated. The cotton was mechanically harvested and ginned and the seed was processed into meal, hulls and refined, bleached and deodorised oil. Undelinted seed samples were stored frozen for 12 months and the processed commodities for 9, 8 and 7 months before analysis. The storage stability of disulfoton residues in undelinted cotton seed was reported by Wiedmann and Koch (1994) and Lemke (1996). The residues found in the cotton seed and processed products are shown in Table 32. As all the residues were below the LOD, processing factors could not be calculated.

Table 32. Residues in cotton seed and processed commodities after an in-furrow treatment (5.48 kg ai/ha), soil injection (10.92 kg ai/ha) and three foliar sprays (3.15 kg ai/ha).

Sample	Residues[1], mg/kg
Undelinted cottonseed	<0.025, <0.025, <0.025
Hulls	<0.025, <0.025, <0.025
Meal	<0.025, <0.025, <0.025
Refined, bleached, deodorised oil	<0.025, <0.025, <0.025

[1]Replicate samples analysed. Limit of determination = 0.025 mg/kg

Recoveries were determined with fortification either with individual compounds or mixtures of the three P=S and three P=O compounds. Recoveries were 76 to 112% from undelinted cotton

seed, 84 to 112% from hulls, 72 to 92% from meal and 72 to 112% from oil. The limit of determination was 0.025 mg/kg.

Maize. In a US processing study (Duah, 1997c), disulfoton was applied as a band at planting at a rate equivalent to 6.72 kg ai/ha, and 7 days before harvest a foliar spray was applied at 5.6 kg ai/ha. Both applications were 5 times the US label rate. Mature maize was mechanically harvested 7 days after the foliar application and immediately frozen. All commodities were stored and analysed within 6 months of harvest. The maize was used to generate aspirated grain fractions and starch, grits, meal, flour, refined, bleached and deodorised (RBD) wet and dry milling oil. The grain, aspirated fractions and processed commodities were analysed for disulfoton residues with the results shown in Table 33.

Table 33. Disulfoton residues in maize and its processed commodities from a band application of 6.72 kg ai/ha at planting and a foliar spray of 5.6 kg ai/ha 7 days before harvest.

Sample	Residues, mg/kg[1]	Processing factor
Grain	0.38, 0.45, 0.40	
Aspirated grain fractions	3.31, 6.19, 3.13, 4.34	10.3
Starch	<0.1, <0.1, <0.1	<0.25
Grits	<0.1, <0.1, <0.1	<0.25
Meal	<0.1, <0.1, <0.1	<0.25
Flour	<0.1, <0.1, <0.1	<0.25
RBD wet milling oil	<0.1, <0.1, <0.1	<0.25
RBD dry milling oil	<0.1, <0.1, <0.1	<0.25

[1]Replicate samples analysed. Limit of determination = 0.1 mg/kg based on total residues.

The results show concentration of residues from processing of the RAC to aspirated grain fractions by a factor of about 10. On further processing, no residues above the limit of determination were found in any of the products.

Residues in sweet corn were stable during 6 months of frozen storage (Wiedmann and Koch, 1994). No data were available on the storage stability of processed maize commodities.

Recoveries in the individual commodities were determined by fortification separately with disulfoton, disulfoton sulfone and sulfoxide, and disulfoton oxygen analogue, and its sulfone and sulfoxide, and mixtures of the three P=S compounds and of the three oxons. Fortification concentrations were 0.1 mg/kg of the individual compounds and 0.2 and 0.45 mg/kg of the three-compound mixtures in all commodities except aspirated grain fractions where 3 and 6 mg/kg concentrations were used.

Potatoes. A Canadian and several US processing studies were reported (Anon., 1968). Potatoes were treated with 10% GR at 48, 64 or 72 oz/acre, either as an in-furrow plus side-dress or a band spray at planting followed by a side-dress. The tubers were harvested 60 or 87 days after planting. Field details and validation data were not reported. The results are shown in Table 34.

Table 34. Processing data for potatoes not previously reviewed.

Sample	Residues, mg/kg	Processing factor	Report
Whole potato, raw	0.15, 0.08		21576
Peel, raw	0.13, 0.10	0.87, 1.25	
Potato, peeled, raw	0.23, 0.09	1.53, 1.13	
Potato, peeled, boiled	0.05, 0.05	0.33, 0.63	
Whole potato, raw	0.04		21998
Peel, raw	0.07	1.75	
Potato, peeled, raw	0.05	1.25	
Potato, peeled, boiled	<0.01	0.25	
Whole potato, raw	<0.02		21989
Peel, raw	0.35	17.5*	
Potato, peeled, raw	0.09	4.5*	
Potato, peeled, boiled	<0.02	1	
Whole potato, raw	0.15		21984
Peel, raw	0.05	0.33	
Potato, peeled, raw	0.03	0.2	
Potato, peeled, boiled	0.03	0.2	
Whole potato, raw	0.27		21980
Peel, raw	0.73	2.7	
Potato, peeled, raw	0.31	1.15	
Potato, peeled, boiled	0..08	0.3	
Whole potato, raw	<0.02		21962
Peel, raw	<0.02	1	
Potato, peeled, raw	<0.01	0.5	
Potato, peeled, boiled	<0.01	0.5	
Whole potato, raw	<0.01		21961
Peel, raw	<0.02	2	
Potato, peeled, raw	<0.01	1	
Potato, peeled, boiled	<0.01	1	
Whole potato, raw	0.08		21960
Peel, raw	0.07	0.88	
Potato, peeled, raw	0.07	0.88	
Potato, peeled, boiled	0.01	0.13	
Whole potato, raw	0.07		21959
Peel, raw	<0.02	0.29	
Potato, peeled, raw	<0.01	0.14	
Potato, peeled, boiled	<0.01	0.14	
Whole potato, raw	0.02		21602
Peel, raw	0.06	3	
Potato, peeled, raw	0.02	1	
Potato, peeled, boiled	0.09	4.5*	
Whole potato, raw	0.07, 0.16		21588
Peel, raw	0.15, 0.08	2.14, 0.5	
Potato, peeled, raw	0.08, 0.05	1.14, 0.31	
Potato, peeled, boiled	0.05, 0.02	0.71, 0.13	

*Outliers. Not included in the calculation of the average processing factor.

In a recent potato processing study (Harbin 1997a), disulfoton was applied in-furrow at planting at a rate equivalent to 16 kg ai/ha, and foliar applications were made at the rate of 5.4 kg ai/ha 61, 75 and 89 days after planting. All application rates were five times the maximum US GAP. Mature tubers were harvested 30 days after the final foliar application. Samples were taken for analysis and the remainder were processed into granules, chips, wet peel and dry peel; the dry peel was not analysed. The tubers were stored frozen for 711 days; granules and chips for 399 days, and

wet peel samples for 731 days. The residues in potato tubers were shown to be stable for 24 months, and in chips, granules and wet peel for 13 months (Wiedmann and Koch, 1994; Lemke, 1996; Lenz, 1996).

Table 35. Residues in potato tubers and processed commodities after an in-furrow treatment at 16 kg ai/ha and three foliar sprays at 5.4 kg ai/ha.

Sample	Residues, mg/kg[1]	Processing factor
Tubers	0.37, 0.34, 0.40	
Granules	0.66, 0.48, 0.43	1.4
Chips	0.22, 0.21, 0.18	0.54
Wet peel	0.56, 0.65, 0.71	1.7

[1]Replicate samples analysed. LOD = 0.1 mg/kg in tubers and [0.25 mg/kg in processed commodities.

Recoveries of disulfoton at fortification levels of 0.25 mg/kg were 93 to 95% from tubers, 87 to 92% from granules, 76 to 82% from chips and 86 to 90% from wet peel, and at 0.1 mg/kg recoveries of disulfoton, disulfoton sulfoxide and sulfone from tubers were 83, 79 and 88% respectively. Recoveries of disulfoton oxygen analogue sulfoxide at 0.25 mg/kg were 119 to 122 % from tubers, 100 to 110 % from granules, 98 to 106% from chips and 112 to 118% from wet peel. At 0.1 mg/kg recoveries of disulfoton oxygen analogue, its sulfoxide and sulfone from tubers were 105, 96 and 109% respectively.

Sorghum. Disulfoton was applied at planting in-furrow at a rate equivalent to 3.66 kg ai/ha, and as a side-dress application at the same rate 111 days after planting (Harbin, 1997b). Three foliar sprays were applied at 1.7 kg ai/ha 125, 138 and 152 days after planting (at ripening). All the applications were 3 times the maximum US label rate.

Sorghum was mechanically harvested 161 days after planting or 8 days after the final foliar application. Mature grain was sampled for analysis and the remaining grain processed into aspirated grain fractions. The grain and aspirated fractions were stored frozen for 15 months and 4 months respectively before analysis. Residues of disulfoton were shown to be stable for 24 months of frozen storage without any degradation (Wiedmann and Koch, 1994). The residues in the grain and aspirated grain fractions are shown in Table 36.

Table 36. Disulfoton residues in sorghum grain and aspirated grain fractions after an in-furrow treatment and a side-dress application at 3.66 kg ai/ha and three foliar sprays at 1.7 kg ai/ha.

Sample	Residues, mg/kg[1]	Processing factor
Sorghum grain	1.57, 1.34, 1.68	
Aspirated grain fractions	3.95, 4.04, 4.07	2.7

[1]Replicate samples analysed. Limits of determination 0.25 mg/kg in grain and 0.5 mg/kg in aspirated grain fractions.

Recoveries of disulfoton, its sulfoxide and sulfone at 0.25 mg/kg from sorghum were 99, 106 and 101% respectively, and for a mixture of the three compounds at 1.5 mg/kg 83, 80 and 116%. In aspirated grain fractions, recoveries were 94, 101 and 101% for disulfoton, its sulfoxide and sulfone at 1 mg/kg, and 82, 78 and 78% for the mixture of the three compounds at 3.75 mg/kg. Recoveries of disulfoton oxygen analogue, its sulfoxide and sulfone were 110, 99, 110% from grain at 0.25 mg/kg and 117, 97 and 118% from grain fractions at 0.5 mg/kg. Recoveries of a mixture of the three compounds at 0.45 mg/kg were 97, 114 and 123%.

Wheat. In a study by Harbin (1997c) disulfoton was applied at planting in-furrow at 6.53 kg ai/ha. Three foliar applications at 4.2 kg ai/ha followed 61, 75 and 89 days after planting. The wheat was harvested 120 days after planting or 31 days after the final foliar spray and immediately frozen. The total application of disulfoton was five times the maximum US rate. The wheat was processed into aspirated grain fractions, bran, flour, germ, middlings and shorts, with the results shown in Table 37.

Table 37. Disulfoton residues in wheat grain and processed products after an in-furrow application at 6.53 kg ai/ha and three foliar sprays at 4.2 kg ai/ha (Harbin, 1997c).

Sample	Residues, mg/kg[1]	Average residue, mg/kg	Processing factor
Grain	0.94, 0.98, 0.82, 0.79	0.88	
Bran	0.99, 0.73, 0.78	0.83	0.94
Flour	0.18, 0.16, 0.16	0.17	0.19
Germ	1.91, 1.85, 1.84	1.87	2.1
Middlings	0.37, 0.30, 0.42	0.36	0.41
Shorts	0.90, 0.96, 1.08	0.98	1.1
Aspirated grain fractions	1.27, 1.09, 1.19	1.18	1.3

[1]Residues in replicate samples. The limit of determination for grain and all processed commodities was 0.25 mg/kg for all analytes.

Recoveries of disulfoton, disulfoton sulfoxide and disulfoton sulfone ranged from 71 to 91%, 75 to 107% and 78 to 96% respectively from all samples over the fortification range 0.25-0.5 mg/kg. Mixtures of the three compounds at total concentrations of 0.75 to 1.50 mg/kg were used to fortify grain, bran, germ, shorts and aspirated grain fractions. Recoveries of the mixtures ranged from 72 to 106%.

Recoveries of disulfoton oxygen analogue, its sulfone and sulfoxide were 82 to 103%, 77 to 114% and 74 to 99% respectively from all samples at 0.25 mg/kg. Recoveries of mixtures of the three compounds at total concentrations of 0.3 and 0.9 mg/kg were 75, 77 and 79% from germ and 87, 91 and 93% from shorts.

Processing data from the 1991 evaluation

The manufacturer provided information on processing data which had been reviewed in the 1991 monograph. Details of the trials are not repeated here but references and report numbers are given. The data are shown in Tables 38 to 42.

Table 38. Processing data for peanuts.

Sample	Residues, mg/kg	Processing factor	Reference
Peanut meat	0.01	-	Report 96726
Presscake	<0.01	<1	
Peanut oil, crude	0.06	6	Leslie, 1988
Peanut oil, refined	0.01	1	
Soapstock	0.02	2	

Table 39. Processing data for tomatoes.

Sample	Residues, mg/kg	Processing factor	Reference

Sample	Residues, mg/kg	Processing factor	Reference
Tomato	0.15		Report 91475
Juice	<0.05	<0.27	RTX-DI112-86P
Puree	0.18	1.2	Bailey, 1987a
Paste	0.26	1.73	
Pulp, wet	0.15	1	
Pulp, dry	0.19	1.27	

Table 40. Processing data for maize.

Sample	Residues, mg/kg[1]	Processing factor	Reference
Dry kernels	0.01		Report 91483
Flour	<0.01	<1	455-DI106-86P
Hulls	<0.01	<1	Bailey, 1987b
Meal	<0.01	<1	
Oil, crude	<0.01	<1	
Oil, refined	<0.01	<1	
Germ	<0.01	<1	
Grits	<0.01	<1	
Press cake	<0.01	<1	
Soapstock	<0.01	<1	

Table 41. Processing data for potatoes.

Sample	Residues, mg/kg[1]	Processing factor	Reference
Potato tuber	0.11		Report 91467/94417
Potato, dried	0.08	0.64	Calovich, 1987

Table 42. Processing data for wheat.

Sample	Residues, mg/kg	Processing factor	Reference
Grain	0.19		Report 94723
Low grade flour	0.03	0.16	STF-DI004-87P
Patent flour	0.01	0.05	Pither, 1988
Shorts	0.08	0.42	1991 JMPR
Bran	0.07	0.39	
Middlings	0.05	0.26	

The data reviewed in 1991 and at the present Meeting were combined to give the processing factors shown in Table 43.

Table 43. Collation of processing factors from 1991 and the present evaluation.

Sample	Processing Factor	Reference
Roasted coffee beans	<0.3	Report 107657 JMPR 1998
Instant coffee	<0.3	(Duah 1997b)
Cotton seed hulls	<1	Report 197541 (Freeseman, 1997)
Cotton seed meal	<1	JMPR 1998
Cotton seed oil, RBD	<1	
Maize aspirated grain fractions	10.3	Report 107691 (Duah, 1997c)
Starch	<0.25	JMPR 1998
Grits	<0.25	
Meal	<0.25	
Flour	<0.25	
RBD wet milling oil	<0.25	
RBD dry milling oil	<0.25	
Flour	<1	Report 91483 (Bailey, 1987b)
Hulls	<1	
Meal	<1	
Oil, crude	<1	
Oil, refined	<1	
Germ	<1	
Grits	<1	
Press cake	<1	
Soapstock	<1	
Potato granules	1.4	Report 107525 (Harbin, 1997a)
Potato chips	0.54	JMPR 1998
Wet peel	1.7	
Potato dried	0.64	Report 91467/94417 (Calovich, 1987)
Sorghum grain aspirated fractions	2.7	Report 107525 (Harbin, 1997b)
		JMPR 1998
Wheat bran	0.94	Report 107692 (Harbin, 1997c)
Flour	0.19	JMPR 1998
Germ	2.1	
Middlings	0.41	
Shorts	1.1	
Aspirated grain fractions	1.3	
Low grade patent flour	0.16	Report 94723 (Pither, 1988)
Patent flour	0.05	
Shorts	0.42	
Bran	0.39	
Middlings	0.26	
Peanut meat	1	Report 96726 (Leslie, 1988)
Presscake	<1	
Oil, crude	6	
Oil, refined	1	
Soapstock	2	
Tomato juice	<0.27	Report 91475 (Bailey, 1987a)
Purée	1.2	
Paste	1.73	

Sample	Processing Factor	Reference
Pulp, wet	1	
Pulp, dry	1.27	

The processing factors in Table 43 were used to estimate STMRs to refine the dietary intake calculations. Data from Table 34 (on potatoes) of the present monograph are not included as minimal details of the trials and analyses were reported.

Residues in the edible portion of food commodities

No information.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

National monitoring data were reported by The Netherlands.

Table 44. Monitoring data for disulfoton in The Netherlands (1994 to 1996).

Commodity	Samples analysed	Samples without residues (LOD = 0.02 mg/kg)	Samples with residues <MRL	Samples with residues >MRL	Mean, mg/kg	MRL, mg/kg
BERRIES AND SMALL FRUIT						
Grapes	667	667		6	<0.02[1]	0.02*
BULB VEGETABLES						0.02*
Onions (including pearl/cocktail onions)	97	96		1	<0.02[1]	0.02*
Shallots	18	17	1		<0.02[1]	0.02*
FRUITING VEGETABLES						
Tomatoes	1108	1108			<0.02	0.02*
Melons	390	390			<0.02	0.02*
LEAF VEGETABLES AND FRESH HERBS						
Iceberg lettuce	471	470		1	<0.02	0.02*

[1]For samples without residues (<LOD), half the LOD is taken for the calculation of the mean.
*Lower limit of determination (LOD).

NATIONAL MAXIMUM RESIDUE LIMITS

The national MRLs shown below were reported.

National MRLs

Country	MRL, mg/kg	Commodity
Argentina	0.4 0.5	Bean, dry Aubergine, cotton seed, cucumber, hops, lettuce, melon, peppers (sweet), potato, pumpkin, tomato
Australia	0.01 *0.02 0.02 0.5	Milk, milk products Eggs, poultry meat by-products Meat (mammalian), meat by-products, poultry meat Cotton seed, hops, potato, vegetables
Austria	0.1 10	Cereals, potato Hops
Belgium	*0.02 *0.05 0.05 0.1	All food of animal origin, other plant commodities Tea Cotton seed Wheat
Brazil	0.1 0.2 0.5	Coffee, peanut Cotton seed Beans, melon, watermelon, onion, potato, tomato
Canada	0.05 *0.1 0.2 0.5	Broccoli, cabbage, Asparagus, aubergine, barley, maize (corn), oats, peppers (sweet), wheat Potato Beans, lima beans, Brussels sprouts, cauliflower, lettuce (head), garden peas, spinach, tomato
EU[1] EU[2]	*0.02 0.02 T*0.02 *0.02 *0.05 0.1 0.2 3	Eggs, fat, meat, meat by-products, meat (preparations of) Milk, milk by-products Beans (dry), broccoli, Brussels sprouts, cabbage (head), cauliflower, celery, herbs, hops, kohlrabi, other legume vegetables, other stem vegetables, parsnip, pineapple, potato, squash (summer and winter), strawberry, Berries (wild), bulb vegetables, chicory (witloof), citrus fruit, corn (sweet), cucurbits (with edible peel), grapes, leafy brassicas, lettuce and similar, mushrooms, nuts, berries and other small fruit, other brassica vegetables, other cereals, other cucurbits, other oilseeds, other pulses, other root and tuber vegetables, other tropical and sub-tropical fruit, peas (without pods), pome fruit, carne fruit (rubus), solanacea, spinach and similar, stone fruit, watercress Cotton seed, tea Wheat Barley, sorghum Carrots
France	0.1	Pineapple
Germany	0.1 0.2 10	Cereals, other plant commodities Potato Hops
Italy	0.4	Aubergine, beans, beans (kidney), cabbage, maize/corn, melon, peas, potato, sugar beet, tobacco, watermelon
Japan	0.05 0.07 0.1	Fruit, pulses Rice Potato, vegetables
Luxembourg	0.02	All plant commodities
Malaysia	0.1 0.2 0.5	Coffee, nuts, pineapple, soya bean (dry) Cereals except corn Celery, maize/corn, potato, rice, sugar beet, vegetables
Mexico	0.1 0.3 0.75	Capsicum (pepper/chilli), soya bean Coffee, maize/corn, sorghum, sugar cane Asparagus, barley, beans, broccoli, Brussels sprouts, cabbage, cauliflower, chick-peas, cotton seed, lettuce, oats, peanut, pecan nut, pineapple, potato, rice, spinach, tomato, wheat
Netherlands	*0.05	Other plant commodities
New Zealand	<0.1[3]	Alfalfa, beans, brassica vegetables, carrot, cereals, forage crops, peas, potato
Paraguay	0.5	Garlic, onion, rice, tomato
South Africa	0.05	Wheat

Country	MRL, mg/kg	Commodity
	0.1	Coffee
	0.2	Cotton seed
	0.5	Criciferae, onion, potato, tomato
Spain	0.02	Cocoa, coffee, cola, forage crops (straw), fruit, fruit and vegetables (dry), nuts, other cereals, other oilseeds, pulses, spices, sugar beet, sugar cane, tea, tobacco, vegetables
	0.1	Cotton seed, maize/corn, sorghum
	0.5	Hops
UK[2]	*0.02	Almond, apple, apricot, artichoke, asparagus, aubergine, avocado, banana, beetroot, berries (wild),blackberry, boysenberry, buckwheat (common), cabbage (Chinese), cardoon, cashew nut, celeriac, cherry, chestnut, chicory (witloof), coconut, collard, cranberry, cress (garden), cucumber, cucurbits (with edible and inedible peel), currants (black, red, white), dates, dewberry, eggs, escarole, fat, fennel (common), figs, flax/linseed, fruit (wild), garlic, gherkin, gooseberry, grapes, grapefruit, hazelnut, horseradish, kiwifruit, kumquat, lamb's lettuce, leeks, lemons, lentils, lettuce, limes, litchi, macadamia nut, maize/corn, mandarins, mango, meat, meat (preparations of), melon, milk, milk products, millet (French), mushroom, mustard seed, nectarines, nut (para-), oats, olives, onion, oranges, other berry fruit, other brassica vegetables, other bulb vegetables, other citrus fruit, other leafy vegetables, other legume vegetables, other nuts, other oilseed, other pome fruit, other pulses, other root and tuber vegetables, other solanacea, other stem vegetables, other stone fruit, other tropical and sub-tropical fruit, parsnip (turnip-rooted), passionfruit, peas (garden, dry), peas (garden without pods), peach, peanut, peanut seed, pear, pecan nut, pepper (sweet), pistachio, pomegranate, poppy seed, pummelo, quince, radish, rapeseed, raspberry, rhubarb, rice, rutabaga, rye, salsify (black), sesame seed, shallot, soya seed, spinach, spring onion, sunflower seed, sweet corn, sweet potato, Swiss chard, tomato, topinambur, triticale, turnip (edible), walnut, watercress, watermelon, wine grapes, yams, zucchini
	0.05	Cotton seed
	0.1	Wheat
	0.2	Barley, sorghum
Uruguay	0.1	Tomato
	0.5	Garlic, onion, pepper (sweet), rice
USA[4]	0.1	Asparagus[5], pepper (sweet), soya bean
	0.25	Soya forage, soya hay
	0.3	Coffee, corn (sweet grain), maize/corn (grain), peanut hull, popcorn (grain), sugarcane, wheat (grain)
	0.5	Hops, sugar beet (root)
	0.75	Barley (grain), bean (dry), bean (kidney), bean (lima), broccoli, Brussels sprouts, cabbage, cauliflower, cotton seed, lettuce, oat (grain), peas (garden), peanut, pecan nut, pineapple, potato, rice, sorghum (grain), spinach, tomato
	2.0	sugar beet (leaves or top)
	5.0	Barley fodder, barley (green), barley straw, bean vines, clover (fresh), maize/corn fodder, maize/corn forage, oat fodder, oat (green), oat straw, peas (garden vines), peanut hay, pineapple bran, pineapple foliage, popcorn fodder, popcorn forage, rice straw, sorghum fodder, sorghum forage, sugar beet pulp (dry), sweet corn fodder, sweet corn forage, wheat fodder, wheat (green), wheat straw
	12	Clover hay

[1]Residue definition: sum of disulfoton and sulfones, expressed as disulfoton.
[2]Residue definition: sum of disulfoton, demeton-S and their sulfoxides and sulfones expressed as disulfoton.
[3]Generally <0.1 mg/kg; MRL not established.
[4]Residue definition: disulfoton and its cholinesterase-inhibiting metabolites.
[5]Regional tolerance in Idaho, Oregon, Washington and California.

APPRAISAL

Residue aspects of disulfoton were reviewed by the JMPR in 1973, 1975, 1979, 1981, 1984, 1991 and 1994. At the 1996 CCPR MRLs set "at or about the limit of determination" were amended from 0.01 to 0.02 mg/kg after a recommendation from the Ad Hoc Working Group On Methods of Analysis (ALINORM 97/24 para. 52). Several delegations expressed concern at the high levels of estimated intakes relative to the ADI and it was noted that processing data were not available for refinement of the estimation of intake. The Committee requested revised intake calculations and decided to keep all other proposals at step 7C (ALINORM 97/24, paras. 53 and 54).

In 1997, the CCPR was informed that additional data would be available for the 1998 JMPR and disulfoton MRLs were kept at Step 7B pending the 1998 evaluation. The present Meeting received new residue data on lima beans, cotton, lettuce and potatoes, as well as reports of recent processing studies on coffee, cotton seed, maize, sorghum and wheat. Processing data on potatoes were also submitted, although minimal information was provided on the field conditions and the analytical methods used. The Meeting received summaries of data reviewed in the previous monographs on disulfoton for the estimation of STMRs and refinement of the dietary intake calculations.

Plant metabolism

The metabolism of [^{14}C]disulfoton in lettuce, potatoes, wheat and soya beans was reported.

[^{14}C]disulfoton was applied to soil at a rate of 3.2 kg ai/ha before planting lettuce. Total radioactive residues of 3.7 mg/kg disulfoton equivalents were found in mature lettuce 49 days after treatment. Approximately 93% of the radioactivity was extracted with 1% trifluoroacetic acid in methanol (1%TFA/MeOH). Four major metabolites which were identified by HPLC accounted for a total of 60% of the radioactivity. The metabolites were disulfoton sulfone, disulfoton oxygen analogue sulfone, disulfoton oxygen analogue sulfoxide and disulfoton sulfoxide, which constituted 26, 23, 6 and 5% of the TRR respectively.

Potatoes were planted in soil treated with [^{14}C]disulfoton at a rate of 7.9 kg ai/ha. Two foliar sprays were applied 33 and 69 days after planting at a rate of 2.2 kg ai/ha. In tubers harvested 99 days after planting the total radioactive residues were 3.7 mg/kg as disulfoton. 1% TFA/MeOH extracted 91% of the total radioactivity in the tubers. The organophosphorus triesters (disulfoton sulfone and sulfoxide, disulfoton oxygen analogue sulfone and sulfoxide) constituted in total 2% of the TRR. Most of the radioactivity (69%) was incorporated into amino acid conjugates of 2-(ethylsulfonyl)ethylene which is formed from disulfoton oxygen analogue sulfone by hydrolysis and elimination of water.

Wheat was planted in soil treated with [^{14}C]disulfoton at a rate of 0.97 kg ai/ha. At 37 and 63 days after planting, two foliar sprays were applied at a rate of 0.85 kg ai/ha. Immature and mature plants were harvested 37 days (before the first foliar application) and 90 days after planting respectively. Straw and forage samples were collected 104 days after planting. The TRRs in grain, wheat forage and straw were 2.8, 36.2 and 40.2 mg/kg disulfoton equivalents respectively. Metabolites were identified and quantified by HPLC after extraction with 1% TFA/MeOH. The organophosphorus triesters in total were <4% of the TRR in grain, 23% in wheat forage and 20% in wheat straw.

Soya beans were planted in soil treated with [^{14}C]disulfoton at a rate of 1.8 kg ai/ha. Mature plants were harvested 85 days after planting and hay samples were collected 99 days after planting. The TRR in soya beans, forage and hay was 1.4, 27 and 43.7 mg/kg disulfoton equivalents respectively, of which 1% TFA/MeOH extracted 67, 93 and 85% respectively. The organophosphorus

triesters constituted less than 4% of the TRR in all of the samples. After further extraction, 39% of the TRR in the beans and 22% in the forage was identified as 2-(ethylsulfonyl)acetic acid. Another 58% of the TRR in the forage was identified as 2-(ethylsulfonyl)ethanol.

In summary, the metabolism studies indicated that there were common processes involved in the transformation of disulfoton in lettuce, potatoes, wheat and soya beans. The metabolism of disulfoton before hydrolysis of the triesters was similar in all the crops. Cleavage of the triesters led to the formation of alkylsulfonyl and sulfonic acid products such as 2-(ethylsulfonyl)ethanol and its oxidation product 2-(ethylsulfonyl)acetic acid. Both of these compounds were identified in soya beans and potatoes. Neither disulfoton nor its oxygen analogue (demeton-S) were identified in any of the metabolism studies; the inclusion of demeton-S in the residue definition was therefore questioned.

The question of including demeton-S in the residue definition was raised at the 1994 Joint Meeting and was discussed at the present Meeting in relation to the new crop metabolism studies provided. The Meeting agreed that although the disulfoton oxygen analogue was not isolated in any of the new metabolism studies reviewed and it would be oxidized to the corresponding sulfone in any determination of the total residue, there was no reason to remove it from the definition. The definition of the residue for compliance and MRLs and the estimation of dietary intake is *sum of disulfoton, demeton-S and their sulfoxides and sulfones, expressed as disulfoton.*

Analytical methods

Disulfoton is included in a multi-residue method reported by the government of The Netherlands. Recoveries from lettuce and potatoes were reported.

The determination of disulfoton in a number of types of sample was included in a general method. A rapid screening method for alfalfa and wheat was also reported. Recoveries were determined with mixtures of disulfoton, disulfoton oxygen analogue and their sulfones and sulfoxides and all recoveries were within acceptable limits (71 to 100%).

Stability of residues in stored analytical samples

The storage stability of disulfoton and its metabolites in a number of crops and processed commodities was investigated for periods up to 36 months. A loss of 37% of disulfoton oxygen analogue sulfone and sulfoxide was found in cotton seed after 24 months. In peanut soapstock losses of 18% of disulfoton sulfone and sulfoxide and 37% of disulfoton oxygen analogue sulfone and sulfoxide were found after 30 months. The Meeting considered that the reported losses were acceptable for storage periods up to 36 months.

Supervised residue trials

The manufacturer provided summaries of data reviewed in previous monographs on disulfoton (1991 and 1994) to estimate STMRs. These were combined with data from currently reviewed studies where appropriate. Only results from supervised trials conducted in accordance with GAP or current use patterns were used in the estimation of the STMRs.

<u>Dry beans</u> (Lima beans). The 1994 Meeting requested the provision of additional residue data reflecting GAP for beans. US GAP allows a maximum rate of 2.2 kg ai/ha to be applied as an in-furrow or side-dress application at planting. On registered US labels, a PHI of 60 days is indicated for beans. The 1994 monograph reported residues in lima beans and green vines of <0.01 and 0.06 mg/kg respectively, 92 days after a double side-dress application at 2.2 kg ai/ha. Data from the current evaluation were included in the estimation of a maximum residue level and an STMR for dry

beans. Although samples were harvested 105 and 106 days after treatment, the data were considered to be reflective of GAP for dry beans.

In US trials reported in the 1991 monograph application rates ranged from 1.6 to 3.9 kg ai/ha. GAP in Japan allows a maximum rate of application of 2 kg ai/ha with a PHI of 60 days. Data from four Japanese trials on kidney beans reviewed in 1991 were from treatments at 2 and 4 kg ai/ha, The residues in the beans were all <0.01 mg/kg 62 and 68 days after both treatments.

Residues reflecting GAP in the USA ranged from <0.01 to 0.14 mg/kg at pre-harvest intervals ranging from 52 to 106 days after treatment. The residues from the US and Japanese trials used to estimate the STMR were in rank order <0.01 (15), 0.01, 0.02, 0.04, 0.06, 0.10, 0.11 (2) and 0.14 mg/kg. The data do not support the existing MRL of 0.05 mg/kg for dry beans (Step 7B). The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.01 mg/kg for dry beans.

Cotton seed. Data from eight trials in Greece in 1993 and 1994 were reported. GAP in Greece allows application of disulfoton at rates of 1–1.5 kg ai/ha at planting with a PHI of 60 days. Cotton seed was harvested 150 to 169 days after planting (normal harvest) and the residues were below the limits of determination in all the samples of cotton seed. The limits of determination were 0.06 and 0.12 mg/kg based on fortifications with the six components of the defined disulfoton residue.

GAP in the USA allows an in-furrow treatment at 1.1 kg ai/ha, a post-planting in-furrow application at 2.2 kg ai/ha and up to three foliar sprays at 0.63 kg ai/ha. PHIs vary from 28 to 90 days according to the treatment regime. No more than three applications (soil and foliar) may be made. Residues reflecting GAP in the USA (1991 and 1994 evaluations) ranged from <0.01 to <0.19 mg/kg.

Residues resulting from GAP in the USA and Greece used in the estimation of the STMR were in rank order <0.01 (20), <0.02, 0.02, <0.03 (2), 0.03 (3), 0.04 (2), <0.05 (2), 0.05 (3), <0.06 (6), 0.10 (2), 0.11, <0.12 (4), 0.12 (2) and <0.19 (4) mg/kg.

The Meeting confirmed the previous recommendation for the draft MRL (Step 7B) of 0.1 mg/kg for cotton seed on the basis of the Greek and US data and estimated an STMR of 0.03 mg/kg.

Lettuce. Data from six US trials on head and leaf lettuce in 1995-6 were submitted for evaluation. GAP in the USA dictates a soil treatment at planting at 1.2-2.2 kg ai/ha and a PHI of 60 days. In the residue trials, disulfoton was applied as a single side-dress application at sowing at a rate of 1.1 or 1.2 kg ai/ha. Samples of leaf lettuce were taken 60 to 90 days after planting and head lettuce (with wrapper leaves) were sampled 62 to 116 days after planting. Residues in leaf lettuce ranged from <0.05 to 1.15 mg/kg and in head lettuce from <0.05 to 0.22 mg/kg. Five trials each on leaf and head lettuce in 1985 reported in the 1991 monograph were according to GAP and gave residues of <0.01-0.56 mg/kg in leaf and 0.01-0.64 mg/kg in head lettuce.

The residues resulting from US GAP from the 1985 and 1995-6 trials in rank order were leaf <0.03 (2), 0.06, 0.11, 0.56, 0.59 and 1.15 mg/kg; head <0.03, 0.04, <0.05 (2), 0.10, 0.44 and 0.64 mg/kg.

The Meeting confirmed the existing draft MRLs of 1 mg/kg for head lettuce and leaf lettuce and estimated STMRs of 0.11 and 0.05 mg/kg for leaf and head lettuce respectively.

Potatoes. Data were reported from two trials in The Netherlands (government submission). At planting, disulfoton was applied at a rate of 1.5 kg ai/ha and tubers were harvested after 113 days. There is no reported GAP for potatoes in The Netherlands. Field details were not reported although an analytical method was provided. The data could not be evaluated.

Data from the USA and Japan were evaluated in 1991. Residues from the US and Japanese trials used for the estimation of the STMR in rank order were <0.01 (3), 0.01, <0.02, 0.04, 0.06, 0.07 (3). 0.08, 0.09, 0.10, 0.11, 0.12, 0.13, 0.15, 0.16, 0.20, 0.23 and 0.31 mg/kg.

The Meeting confirmed the existing CXL of 0.5 mg/kg and estimated an STMR of 0.08 mg/kg for potatoes.

Processing studies

Processing studies on coffee, cotton seed, maize, potatoes and sorghum were reported.

In a coffee processing study, disulfoton was applied at a tenfold rate to the soil around coffee trees. Coffee beans were harvested and the initial preparation of the berries involved removal of the skin, pulp and endocarp to leave green beans. These were roasted and processed into instant coffee. Average residues in green coffee beans, roasted beans and instant coffee were 0.3, <0.1 and <0.1 mg/kg respectively. Processing factors for roasted coffee and instant coffee were both <0.3.

Cotton was treated at five times the maximum rate in a processing study with an in-furrow treatment at planting, a soil injection and three foliar sprays. The cotton was mechanically harvested and ginned. The resulting cotton seed was processed into meal, hulls and refined, bleached and deodorised (RBD) oil. The residues in the undelinted cotton seed, hulls, meal, and RBD oil were all <0.025 mg/kg. There was no concentration of disulfoton residues in any of the processed fractions. As residues were not detected in the raw agricultural commodity, processing factors could not be calculated.

Maize was treated with a band application at planting and a foliar spray 7 days before harvest at a total of approximately five times the recommended rate. Mature maize was mechanically harvested and processed into aspirated grain fractions (grain dust), starch, grits, meal, flour, and RBD oil produced by wet and dry milling. The average residues were 0.41 mg/kg in the grain, 4.24 mg/kg in aspirated grain fractions, and <0.1 mg/kg in grits, meal, flour, and RBD oil produced by wet and dry milling. The processing factors were 10.3 for the aspirated grain fractions and <0.25 for all the other fractions.

Two processing studies in potatoes were reported. In one the details were inadequate and the Meeting requested additional information to allow the study to be used for refining dietary intake calculations. In the second study an in-furrow treatment plus three foliar sprays were applied at five times the maximum recommended rate in the USA. Potatoes were harvested and processed into granules, chips, wet peel and dry peel. The average disulfoton residues, with processing factors in parentheses, were potatoes 0.37 mg/kg, granules 0.52 mg/kg (1.4), chips 0.2 mg/kg (0.54) and wet peel 0.64 mg/kg (1.7). Residues were concentrated in the granules and wet peel.

In a processing study on sorghum an in-furrow treatment, a side-dress application and three foliar sprays were applied at three times the recommended US rate. Sorghum was harvested and processed into aspirated grain fractions. The average residues in the sorghum grain and aspirated fractions were 1.5 and 4.0 mg/kg respectively, giving a processing factor of 2.7.

Wheat treated at three times the maximum recommended rate in the USA was harvested and processed into bran, flour, germ, middlings, shorts and aspirated grain fractions. The average residues, with processing factors in parentheses, were grain 0.88 mg/kg, bran 0.83 mg/kg (0.94), flour 0.17 mg/kg (0.19), germ 1.87 mg/kg (2.1), middlings 0.36 mg/kg (0.41), shorts 0.98 mg/kg (1.1) and aspirated grain fractions 1.18 mg/kg (1.3). Disulfoton residues were concentrated in the germ and aspirated grain fractions.

Estimation of STMRs for refinement of dietary intake calculations

Data evaluated by the 1991 and 1994 Meetings were combined with data supplied to the present Meeting for the estimation of STMRs to refine the dietary intake calculations.

US and Canadian data on barley were evaluated in 1991 and 1994. The residues in trials according to GAP in rank order were <0.01 (7), 0.01 (2), <0.02 (3), 0.02 (2), 0.03, 0.04, 0.06, 0.09 and 0.1 (2) mg/kg. The Meeting estimated an STMR of 0.02 mg/kg for barley.

Trials on broccoli in accordance with US and Canadian GAP were reviewed in 1991. The residues in rank order were <0.02 (6), 0.03 (2), 0.05, 0.06, 0.09 and 0.11 mg/kg. The Meeting estimated an STMR of 0.025 mg/kg.

Trials on head cabbage in the USA and Japan in accordance with GAP gave residues in rank order of <0.02 (12), 0.02 (3), 0.03, 0.06, 0.07 (3), 0.08, 0.09, 0.12, 0.17(2), 0.23 and 0.32 mg/kg. The Meeting estimated an STMR of 0.02 mg/kg for head cabbages.

Trials on cauliflower were reviewed in 1991. Although GAP in the USA and Canada allows a maximum of two sprays but three sprays were applied in the trials, the data were considered to be acceptable as the applications were made at an early stage of crop growth (pre-emergent and post-emergent). The residues in rank order were <0.01 (6), 0.01 (3), 0.02,0.03, 0.04, 0.05 and 0.31 mg/kg. The residue of 0.31 mg/kg was considered to be an outlier and was not used in estimating the STMR. The Meeting estimated an STMR of 0.01 mg/kg.

Three trials on coffee were reviewed in 1991. The rates of application were one, three and ten times the maximum recommended rate and the residues in the dry beans were 0.1-0.2 mg/kg. The Meeting could not estimate an STMR for coffee beans from only three results.

Residues in green peas and empty pods were reported in the 1991 and 1994 monographs. Data on Southern peas were not included in the estimation of the STMR as the trials were not compatible with current GAP in the USA. The residues in peas in six trials according to GAP were all <0.01 mg/kg and in the empty pods <0.01 (2), 0.02, 0.03 and 0.08 mg/kg. The Meeting estimated an STMR of 0.01 mg/kg for garden pea (shelled). As information on the weights of the whole pods in relation to the empty pods was not provided, an STMR for whole pods could not be estimated.

The 1994 Meeting considered the possibility of revising the maximum residue level of 0.01 mg/kg for maize estimated by the 1991 JMPR. The 1994 Meeting stated that the additional data provided since 1991 did not reflect GAP in the USA and that the MRL could not be set at 0.01* mg/kg as some residues had been determined at 0.01 mg/kg. Although GAP in the USA allows one soil treatment and a foliar spray, three sprays were applied in most of the trials reviewed in 1994. As the residues in most instances were below the limit of determination however, the present Meeting included the data from excessive treatments in estimating the maximum residue level and STMR. The residues in rank order were <0.01 (14), 0.01 and <0.02 (4) mg/kg. The Meeting estimated an STMR of 0.01 mg/kg and recommended a change in the existing MRL (Step 7B) from 0.01 mg/kg to 0.02* mg/kg.

Data on oats were reviewed in 1991. The results may be compared to Canadian GAP. Only three results may be strictly according to GAP, but as the treatment is either pre-emergent or early post-emergent, the data from all six trials could be considered for estimating an STMR. The Meeting concluded that on the basis of the recent studies of wheat metabolism where the four organophosphorus triesters constituted less than 4% of the TRR, and in view of the early application of the product, an STMR of 0 was appropriate.

Residues in peanut kernels were evaluated in 1991. The residues in four US trials reflecting GAP in rank order were <0.01 (2), 0.02 and 0.09 mg/kg. The Meeting estimated an STMR of 0.015 mg/kg for peanut.

Further information requested by the 1994 Meeting included additional residue data on pecans reflecting the higher aerial foliar application rates and data from soil applications according to GAP. The residues in trials reflecting GAP in rank order in the kernels were <0.01 (3), 0.01 and 0.02 mg/kg; and in whole nuts 0.08, 0.21 and 0.22 mg/kg. The Meeting concluded that there were enough trials reflecting GAP to estimate an STMR of 0.01 mg/kg for pecan kernels.

Data on pineapples from Martinique and Brazil were reviewed in 1991, in relation to GAP in France and Honduras. The residues in seven trials reflecting GAP were all <0.1 mg/kg at rates of 0.75 times to twice the maximum recommended rates. The Meeting estimated an STMR of 0 as the residues were below the limit of determination and were consistent with the results of recent metabolism studies.

Trials on Japanese radishes were reviewed in 1991. The residues in rank order were 0.004 (4), 0.008, 0.01, 0.02 (4), 0.03 (3), 0.06, 0.07, 0.10 (2), 0.12, 0.15 and 0.17 mg/kg. The Meeting estimated an STMR of 0.025 mg/kg for Japanese radish.

Data from the 1973 evaluation of disulfoton from Japan and the USA were submitted for the estimation of an STMR for rice. The Japanese data from only three trials. Twelve trials in the USA were reported but GAP was not identified and the residues were determined by a colorimetric method with a limit of quantification of 0.1 mg/kg. As recent GAP for the USA was not available and there were only three results from Japan, the Meeting could not estimate an STMR.

GAP for the treatment of sorghum in the USA allows a maximum of 2 soil treatments at 1.1 kg ai/ha followed by a maximum of three foliar applications at 0.56 kg ai/ha. The PHI for grain is 34 days after soil application and 7 days after foliar applications. Trials on sorghum were reviewed in 1991 and 1994. The residues resulting from excessive applications either at planting or post-planting were accepted for use in estimating an STMR, but those from excessive foliar treatments were not. As all the trials with foliar applications were either at twice the maximum recommended rate or with PHIs longer than 7 days, the foliar applications were not considered to reflect current GAP and the Meeting did not estimate an STMR for sorghum.

Trials on sugar beet reported in the 1991 monograph were with excessive treatment regimes. The data were originally evaluated against GAP from Chile, although the trials were conducted in the USA. The residues in rank order were <0.01 (3), 0.01 (4), 0.02 (2), <0.03, 0.03 (2), 0.04 and 0.06 (3) mg/kg. The Meeting considered that as recent GAP for sugar beet was not available and Chilean GAP could not be applied to the US trials, an STMR could not be estimated.

Residues in tomatoes were reported in 1991. The 1991 Meeting recommended an MRL of 0.1 mg/kg for tomatoes and the withdrawal of the MRL for vegetables. The residues in trials which reflect GAP in the USA and Japan were <0.01 (2), 0.02, 0.04 and 0.05 mg/kg. The Meeting considered that there were too few results to estimate an STMR.

Numerous trials on wheat were reviewed in 1991 and 1994. The residues in trials according to GAP in the USA and Canada in rank order were <0.01 (20), 0.01 (5), <0.02 (10), 0.02 (5), 0.03 (2), 0.04 (2), <0.05 (2), 0.05 (3), <0.1, 0.11, 0.14, 0.16, 0.18, 0.19, 0.24 and 0.27 mg/kg. The Meeting reaffirmed the existing draft MRL of 0.2 mg/kg and estimated an STMR of 0.02 mg/kg for wheat.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Note. The Meeting concluded that the dietary intake of disulfoton residues could in some circumstances exceed the ADI (see Dietary Risk Assessment below). As the present evaluation is not the first for disulfoton nor a full re-evaluation within the CCPR Periodic Review Programme however, the recommendations are for MRLs not MRLMs.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: sum of disulfoton, demeton-S and their sulfoxides and sulfones expressed as disulfoton.

Commodity		Recommended MRL, mg/kg		STMR, mg/kg
		New	Previous	
GC 0640	Barley	-	0.2	0.02
VD 0071	Beans (dry)	0.2	0.05	0.01
VB 0400	Broccoli	-	0.1	0.025
VB 0041	Cabbages, Head	-	0.2	0.02
VB 0404	Cauliflower	-	0.05	0.01
SO 0691	Cotton seed	0.1	0.1	0.03
VP 0529	Garden pea, shelled (succulent seeds)	-	0.02*	0.01
VL 0482	Lettuce, Head	1	1	0.05
VL 0483	Lettuce, Leaf	1	1	0.11
GC 0645	Maize	0.02*	0.01	0.01
CF 1255	Maize flour			0.0025
GC 0647	Oats	-	0.02*	0
SO 0697	Peanut	-	0.1	0.015
TN 0672	Pecan	-	0.1	0.01
FI 0353	Pineapple	-	0.1	0
VR 0589	Potato	0.5	0.5	0.08
VR 0591	Radish, Japanese	-	0.2	0.025
GC 0654	Wheat	-	0.2	0.02
CM 0654	Wheat bran			0.019
CF 1211	Wheat flour			0.004
CF 1210	Wheat germ			0.042

Collation of data for IEDI calculations

The STMRs and STMR-Ps estimated above are tabulated below for inclusion in the dietary intake refinement.

Commodity	MRL, mg/kg	STMR, mg/kg	STMR-P
Barley	0.2	0.02	
Beans, dry	0.2	0.01	
Broccoli	0.1	0.03	
Cabbages, head	0.2	0.02	
Cauliflower	0.05	0.01	
Coffee beans	0.2	–	
Coffee bean, roasted		–	
Coffee instant		–	
Cotton seed	0.1	0.03	
Cotton seed oil		0.03	0.03 × <1
Garden peas (pods)	0.1	–	
Garden peas (shelled)	0.02	0.01	
Lettuce, head	1	0.11	
Lettuce, leaf	1	0.10	
Maize/corn	*0.02	0.01	
Maize/corn flour		0.01	0.01 × 0.25
Oats	0.02	0	
Peanut	0.1	0.015	
Peanut oil, refined		0.02	0.02 × 1
Pecan nut	0.1	0.01	
Pineapple	0.1	0	
Potato	0.5	0.08	
Potato chips		0.08	0.08 × 0.67
Potato, peeled and boiled		0.08	0.08 × 0.44
Radish, Japanese	0.2	0.025	
Rice	0.5	–	
Sorghum	1	–	
Wheat	0.2	0.02	
Wheat flour		0.02	0.02 × 0.19
Wheat bran		0.02	0.02 × 0.94
Wheat germ		0.02	0.02 × 2.1

FURTHER WORK OR INFORMATION

Desirable

1. Details of the potato processing study (Anon., 1968) for consideration in the refinement of dietary intake calculations.

2. Additional residues data for rice and sorghum to allow the estimation of an STMR for the calculation of dietary intake.

DIETARY RISK ASSESSMENT

In the current evaluation STMRs were estimated for 18 commodities. Where consumption data were available these STMRs were used in the estimates of dietary intake together with the existing MRLs and draft MRLs for 9 other food commodities.[35]

The estimated daily intake exceeds the ADI for the five GEMS/Food regional diets by the following percentages: Middle Eastern 190%, Far Eastern 920%, African 440%, Latin American 280% and European 160%.

The Meeting concluded that the dietary intake of disulfoton residues may exceed the ADI for all the GEMS/Food regional diets. Since the compound is neither new nor being evaluated in the CCPR Periodic Review Programme, the recommended MRLs are not designated as MRLMs.

Since the commodities which made a large contribution to the intake are rice and sorghum, further consideration should be given to these commodities to allow refinement of the dietary intake estimate at the international level.

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[35] The commodity garden peas (whole pods) was not included in the dietary estimate as a consumption figure for whole pods was not available.

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Page: 589
[N1]Extraction using acetone and CH_2Cl_2 and hexane, as with analytical residue method, showed that 66% of TRR was identifed as the four metabolites; 21% M2, 33% M4, 5% M1 and 7% M3. These values were comparable to the TFA/MeOH extraction.
Page: 589
[N2]MnO_4 oxidation of the metabolites during work-up to identify the compounds.
Page: 595
[N3] Recoveries were not individually reported for disulfoton and the metabolites in the matrices concerned.
Page: 596
[N4]N=3 at each time point for each P=O or P=S sample.
Page: 596
[N5]N=2 at 36 months for each P=S and P=O mixture.
Page: 601
[N6]Stated as 1.2 oz ai/1000 row feet or 15.7 to 31.4 oz ai/acre.
Page: 619
[N7]6 oz ai/1000-row foot.

FOLPET (041)

EXPLANATION

Folpet was first evaluated in 1969 and has been reviewed several times since, most recently in 1993, 1994 and 1997 for residues. It was listed by the 1997 CCPR (29th Session, ALINORM 97/24A, Appendix III) for Periodic Review by the 1998 JMPR. Data was provided by the main manufacturer. and by the governments of Germany and The Netherlands.

Extensive information was reviewed by the 1997 JMPR, but is now also included in the present evaluation within the CCPR Periodic Review Programme.

IDENTITY

ISO common name: folpet

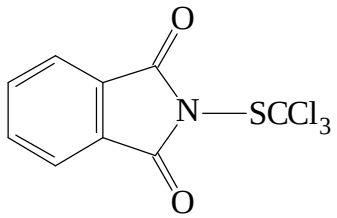
Chemical name
IUPAC: *N*-(trichloromethylthio)phthalimide
CAS: 2-[(trichloromethyl)thio]-1*H*-isoindole-1,3(2*H*)-dione

CAS No: [133-07-03]

CIPAC No: 75

Synonyms, trade names: Folpan, Folpet, Folpel, Phaltan

Structural formula:



Molecular formula: $C_9H_4Cl_3NO_2S$

Molecular weight 296.6

Physical state: amorphous powder

Formulations: SC, WP, WDG

Physical and chemical properties

Pure active ingredient

Melting point: 179-180°C (decomposition)

Henry's Law constant: 7.9×10^{-3} Pa. M^3/mole

Stability:	Stable in the dry state. Slowly hydrolysed by moisture at room temperature. Rapidly hydrolysed in concentrated alkalis and at elevated temperatures.
Vapour pressure	2.1×10^{-5} Pa (25°C)
Octanol/water partition coefficient:	1279 (25ºC)
Solubility	Water solubility: 0.59-0.80 mg/l at 25°C, 0.50 mg/l at 15°C (Schlesinger, 1987).
Specific gravity	1.72 g/cm^3
Hydrolysis (Weizman, 1985)	pH 4, half life 6.5 hours (25°), 1.06 hours (40°C) pH 7, half-life 0.70 hours (25°C), 10.7 minutes (40°C) pH 9, (25°C) too fast to measure with the standard methodology.
Photolysis	Stable under UV light or sunlight conditions

Technical material

Purity	minimum 92%. Not less than 880 g/kg (FAO specifications).
Specifications	FAO Specifications (FAO, 1988)

Formulations

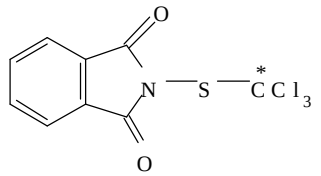
Folpet is available as a wettable powder, suspension concentrate (flowable) and water dispersible granules.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Information on the metabolism of folpet in a lactating goat was reported.

Tissues, milk, excreta and expired air residues were measured in a miniature lactating goat (22 kg bw) dosed orally by capsule for 3 consecutive days with [*trichloromethyl*-^{14}C]folpet at a rate equivalent to 20 ppm in the feed or a daily dose of 0.55 mg/kg bw (Corden, 1997a). The goat was housed in an enclosed metabolism chamber to allow collection of expired air, urine and faeces.



Folpet - position of label

The goat was milked twice daily. Approximately 23 hours after the final dose the goat was slaughtered and air was drawn through the metabolism chamber into potassium hydroxide traps to collect the expired CO_2.

Most of the radiolabel was rapidly excreted (Table 1). The liver (0.5% of total dose) accounted for most of the radiolabel in the tissues (0.8% of total dose) and contained the highest tissue residue (Table 2). Levels of ^{14}C in the milk had reached a plateau by 48 hours.

Table 1. Distribution of ^{14}C in the excreta, expired air, tissues and milk from a goat dosed with [*trichloromethyl*-^{14}C]folpet at a rate equivalent to 20 ppm in the feed for 3 days (Corden, 1997a).

Sample	^{14}C as % of total dose
Urine	10.2
Faeces	41.9
Expired air	31.4
Intestinal tract	16.9
Cage wash	0.2
Tissues	0.8
Milk	1.0
TOTAL	116.4%

Table 2. Residues of ^{14}C in the tissues and milk (expressed as folpet equivalents) from a goat dosed with [*trichloromethyl*-^{14}C]folpet equivalent to 20 ppm in the feed for 3 days (Corden, 1997a).

Sample	^{14}C as folpet mg/kg
Fat, subcutaneous	0.01
Fat, peritoneal	0.01
Muscle, fore-leg	0.03
Muscle, rump	0.04
Kidney	0.26
Liver	0.34
Milk, day 1	0.23
Milk, day 2	0.38
Milk, day 3	0.34

In another trial, residues in the tissues, milk and excreta of 2 lactating goats (60 and 50 kg bw) dosed orally for 6 consecutive days by capsule with [*trichloromethyl*-^{14}C]folpet or *[benzene*-^{14}C]folpet at a rate equivalent to 24 and 14 ppm respectively in the feed or with daily doses of 0.37 and 0.34 mg/kg bw (Corden, 1997b). The goats were again housed in metabolism chambers and milked twice daily. Approximately 23 hours after the final doses the goats were slaughtered.

From the goat dosed with *[benzene*-^{14}C]folpet 58% of the ^{14}C was excreted in the urine and 35% in the faeces. The label in the tissues and milk accounted for <0.1% of the total dose and its levels were higher in the kidneys and liver than in the other tissues (Table 3).

Thiazolidine was the main metabolite identified in the urine from the [*trichloromethyl*-^{14}C]folpet dosed goat and phthalamic acid and phthalimide the main metabolites in the urine and faeces from the *[benzene*-^{14}C]folpet dosed goat.

Table 3. Residues of folpet equivalents in the tissues and milk from a goat dosed with *[benzene*-^{14}C]folpet equivalent to 24 ppm in the feed for 6 days (Corden, 1997b).

Tissue and milk	^{14}C as folpet mg/kg
Fat, subcutaneous	0.004
Fat, peritoneal	<0.001
Muscle, fore-leg	0.003
Muscle, rump	0.003
Kidney	0.052

Tissue and milk	^{14}C as folpet mg/kg
Liver	0.022
Milk, day 1	0.004
Milk, day 2	0.006
Milk, day 3	0.005
Milk, day 4	0.005
Milk, day 5	0.005
Milk, day 6	0.006

^{14}C was incorporated into amino acids, cholesterol, phosphatidylcholine, choline chloride, glucose and other unknown components in the liver, kidneys and muscle of the [*trichloromethyl*-^{14}C]folpet dosed goat. In milk ^{14}C was incorporated into lactose and amino acids.

Phthalimide, phthalic acid and phthalamic acid were identified in the tissues and milk of the *[benzene*-^{14}C]folpet dosed goat (Table 4).

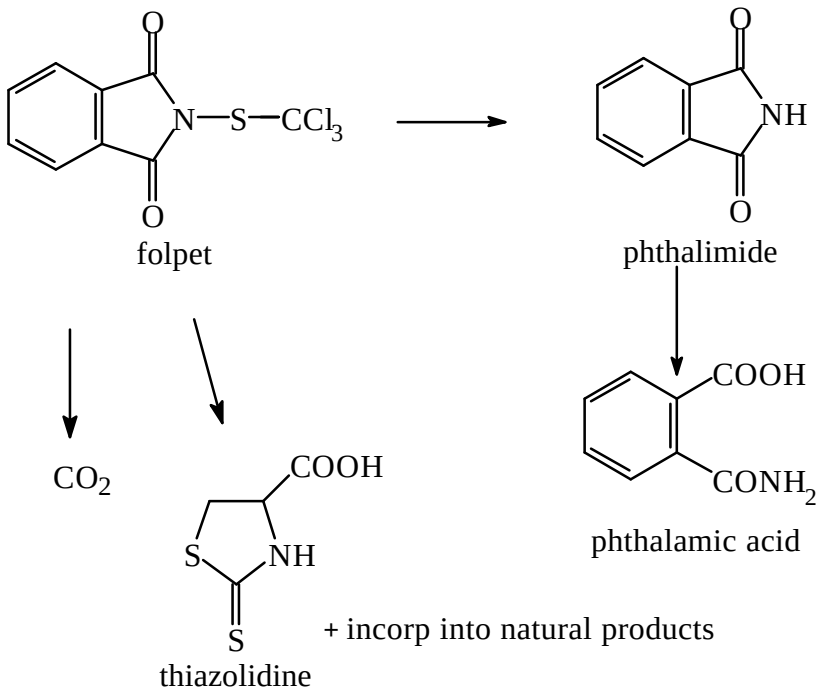
Table 4. Metabolites identified in the tissues and milk of a goat dosed with *[benzene*-^{14}C]folpet equivalent to 24 ppm in the feed for 6 days (Corden, 1997b).

Metabolite	Concentration, as folpet equivalents, mg/kg		
	liver	kidney	milk
Phthalamic acid	0.006	0.013	
Phthalimide	0.001	0.001	<0.001
Phthalic acid + phthalamic acid + phthalimide[1]		0.023	<0.001
TOTAL ^{14}C	0.022	0.052	0.006

[1] Components unresolved

Folpet is rapidly degraded in the goat, initially by loss of the $-CCl_3$. The carbon from the $-CCl_3$ becomes incorporated into thiazolidine and natural products. The benzene end of the molecule was metabolized to phthalimide and phthalamic acid. The proposed metabolic pathways in goats are shown in Figure 1.

Figure 1. Proposed metabolic pathways in goats.



Plant metabolism

The Meeting received information on the metabolism of folpet in tomato plants, winter wheat, grapes and avocados.

Tomatoes. Cheng (1980) treated the roots of tomato plants (7 weeks old) with 4 mg/l [*carbonyl*-^{14}C]folpet in 25 ml of a nutrient solution containing 0.25% acetone. The plants were treated while under a growth lamp and harvested after 1, 4, 7 and 11 days.

Methanol/water extracts of the roots and tops were analysed by TLC. One day after treatment about 85% of the ^{14}C in the nutrient solution had been absorbed into the plants and about 60% of the absorbed ^{14}C translocated to the tops. By the 11th day 93% had been absorbed from the nutrient solution and 90% of the ^{14}C in the plant was in the tops. The parent compound was a minor part of the residue in the plant.

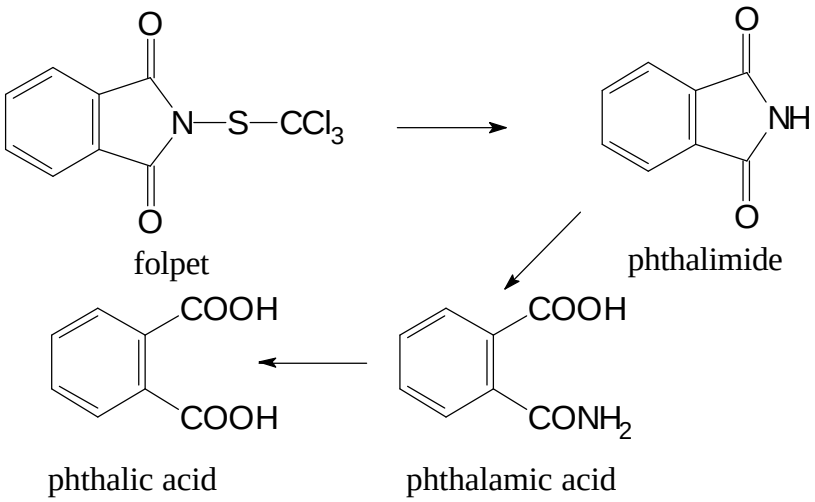
Table 5. Residues in tomato plants after exposure through the roots to a nutrient solution containing [*carbonyl*-^{14}C]folpet (Cheng (1980).

Compound	Compound as % of extractable ^{14}C in roots and tops							
	day 1		day 4		day 7		day11	
	top	root	top	root	top	root	top	root
Folpet	<0.1	0.2	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
Phthalimide	5.9	1.7	5.4	2.1	2.9	1.9	3.4	1.4
Phthalic acid + phthalamic acid	76	93	67	93	68	93	63	91
Unidentified[1]	15	2.3	25	2.8	26	3.0	30	5.1

[1] Three polar metabolites, possibly ring-hydroxylated phthalamic acid derivatives.

The TLC Rf values of phthalic acid and phthalamic acid were too close to be separated, but about 90% of the ^{14}C was estimated to be phthalamic acid from an autoradiogram.

Figure 2. Metabolism of folpet in tomato plants.



Crowe (1995) applied *[benzene-*^{14}C]folpet to winter wheat plants twice at a rate equivalent to 1.6 kg ai/ha and sampled the plants 1 day after each application, at maturity and at harvest. The ages of the plants at the two treatments, maturity and harvest were 190, 214, 258 and 269 days respectively.

Levels of ^{14}C were lower in the roots than the straw or grain at each sampling. Plant parts were not washed before measurements were made, so surface residues are included. Recovery of the ^{14}C in the extracts and the residue was high, particularly for straw and grain. Levels of ^{14}C were higher in the final stages of the crop because the plant had begun to dry out. The composition of the extractable residue is shown in Table 6.

Day	Total ^{14}C as folpet, mg/kg.		
	roots	straw	grain
191	0.03	4.5	3.2
215	0.23	9.4	7.5
258	0.63	13	10
269	0.74	15	24

The extracted straw from day 269 was treated with 1M HCl to release bound residues; phthalic acid (1 mg/kg) was released.

Table 6. Composition of the extractable residue in winter wheat straw and grain from plants treated with [*benzene-*^{14}C]folpet at 1.6 kg ai/ha on days 190 and 214 (Crowe, 1995).

Compound	^{14}C as parent or metabolite, mg/kg							
	day 191		day 215		day 258		day 269	
	straw	grain	straw	grain	straw	grain	straw	grain
Folpet	3.5	1.8	4.7	4.8	6.9	4.7	4.7	9.3
Phthalic acid	NDR	NDR	NDR	NDR	0.60	0.57	4.3	6.4
Phthalimide	0.41	0.80	0.98	1.2	0.76	0.98	1.5	3.1
Polar metab					0.43	0.49		
Unknown						0.29		

NDR: no detectable residues.

Folpet itself was the major component of the residue in all cases, but in the final stage the levels of phthalic acid + phthalimide exceeded those of folpet. Phthalamic acid was not mentioned in this study.

Mester (1994a) made 3 foliar applications at 1-month intervals of [*benzene*-^{14}C]folpet to Thomson Seedless grape vines, equivalent to 1.5 kg ai/ha for each application, and harvested grapes and leaves 25 days after the final application. O'Connor (1994) conducted the laboratory part of the study. Less than 1% of the ^{14}C in the grapes or leaves remained after washing and water/acetonitrile extraction. The water/acetonitrile extract was further divided into dichloromethane-soluble and water-soluble. The disposition of the radiolabel is shown in Table 7.

Table 7. Distribution of radiolabel in rinsing and extraction fractions from grapes and leaves of grape vines treated with 3×1.5 kg ai/ha [*benzene*-^{14}C]folpet and harvested 25 days after the final application (O'Connor, 1994).

Fraction	Grape		Leaf	
	^{14}C as % of total in grapes	^{14}C as folpet, mg/kg	^{14}C as % of total in leaves	^{14}C as folpet, mg/kg
Rinse	26%	2.0	87.8%	258
Organosoluble	19%	1.4	6.5%	19
Water-soluble	54%	4.1	4.6%	14
Unextracted residue	1.5%	0.11	1.1%	3.2
TOTAL	100%	7.6	100%	294

The identities of the components in the rinses and extracts are shown in Table 8. Folpet itself constituted 27% of the residue on the grapes, and phthalic acid and phthalimide 5.8% and 11% respectively. An unidentified compound in the water-soluble fraction accounted for 41% of the residue. HPLC showed that the material was very polar; on a reversed phase system it eluted with the solvent front. Attempts to identify the material by MS and various combinations of HPLC-MS were not successful. Acid hydrolysis yielded phthalic acid. The material was therefore identified as phthalic acid conjugates. Phthalamic acid was not considered as a possible metabolite in this study.

Table 8. Residues on grapes and leaves of grape vines treated with 3×1.5 kg ai/ha [*benzene*-^{14}C]folpet harvested 25 days after the final application (O'Connor, 1994).

Compound	Grapes Residue expressed as folpet, mg/kg			Leaves Residue expressed as folpet, mg/kg		
	rinse	organosoluble	water-soluble	rinse	organosoluble	water-soluble
Folpet	1.1	0.97		251	15	
Phthalic acid	0.16	0.28			2.2	4.8
Phthalimide	0.74	0.07		7.2	1.6	
Unidentified 1		0.11				
Unidentified 2			3.1			
Unidentified 3						6.7
Unidentified 4						2.0

Mester (1994b) made 3 foliar applications at 21-day intervals of [*benzene*-^{14}C]folpet to a small avocado tree in California, equivalent to 3.4 kg ai/ha for each application, and harvested fruit and leaves 21 and 97 days after the final application. Fruit were immature at 21 and mature at 97 days.

Toia and Collins (1994) conducted the laboratory part of the study. Aqueous rinsing released surface residues; samples were then thoroughly extracted with ethyl acetate. The distribution of

radiolabel in the fruit and leaf is shown in Table 9. The identities of the components in the rinses and extracts were examined by TLC and HPLC and are shown in Table 10.

Table 9. Distribution of radiolabel in rinses and extracts from avocado fruit and leaves from a tree treated with 3×3.4 kg ai/ha [*benzene*-^{14}C]folpet and harvested 21 and 97 days after the final application (Toia and Collins, 1994).

Fraction	^{14}C as folpet, mg/kg			
	Fruit		Leaf	
	21 days after treatment	97 days after treatment	21 days after treatment	97 days after treatment
Rinse	0.70	0.014	48	21
Ethyl acetate extract	8.8	14 (peel) 7.5 (pulp)	68	37
Residue after ethyl acetate extract	1.4	3.2 (peel) 0.66 (pulp)	20	15

Table 10. Components of the residue on avocado fruit and leaves from a tree treated with 3×3.4 kg ai/ha [*benzene*-^{14}C]folpet harvested 21 and 97 days after the final application (Toia and Collins, 1994).

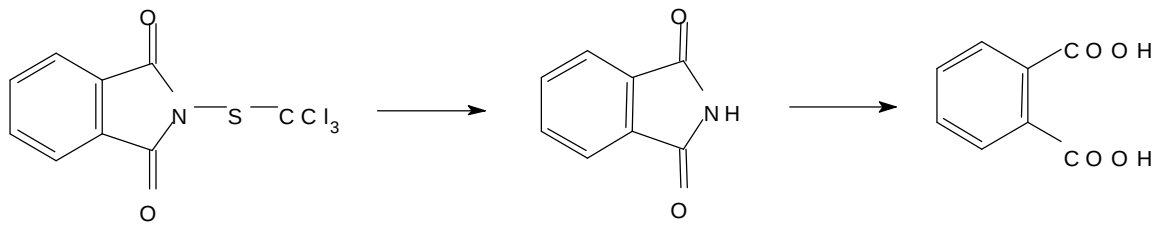
Compound	Residue expressed as folpet, mg/kg				
	Fruit			Leaf	
	21-day		97-day	21-day	
	rinse	extract	extract	rinse	extract
Folpet	0.29	0.25	0.026	24	54
Phthalimide	0.20	0.55	0.22	10.4	1.2
Phthalic acid	0.077	7.2	4.5	4.0	11
Polar materials	0.018	0.52	0.40	0.94	8.6
Others		0.59	0.34		0.78

Phthalic acid was the main component of the residue in the fruit, particularly in extracts. The extracts of the peel and pulp from 97-day fruit were examined separately; phthalic acid constituted 85% and 65% of the residues in the pulp and peel respectively, all expressed as folpet.

	Residue expressed as folpet, mg/kg on a whole fruit basis	
	Peel extracts	Pulp extracts
Folpet	0.022	0.004
Phthalimide	0.15	0.067
Phthalic acid	0.65	3.8
Polar compounds	0.017	0.38
Others	0.13	0.21

Folpet itself was mainly a surface residue. In the fruit harvested 21 days after the final application folpet accounted for 47% of the ^{14}C in the rinse, but only 2.7% of the ^{14}C extracted from the fruit. In the fruit harvested after 97 days the residue in the rinse was too low to identify individual components, but in the extracts of the mature fruit folpet accounted for only 0.5% of the ^{14}C.

Figure 2. Folpet metabolism in wheat, grapes and avocados.



Folpet phthalimide phthalic acid

METHODS OF RESIDUE ANALYSIS

Analytical methods

The analytical method of Schlesinger (1991) for folpet and phthalimide residues in non-oily crops was reviewed by the 1993 JMPR. Cowlyn (1996) described in detail the methods used in the supervised trials on apples, lettuce, melons, onions, strawberries and tomatoes, and summarized the validation data; the methods were developed from the Schlesinger method. Folpet was determined in the cleaned up extract by GLC with an ECD. The Schlesinger method, originally numbered FP/15/91, has been reissued as FP/15/93.

The region corresponding to the retention time of folpet in the chromatograms from control extracts was examined for potential interfering peaks. Freedom from peaks in the control was taken to imply specificity.

Recovery range	Number of values
50-59%	2
60-69%	13
70-79%	88
80-89%	98
90-99%	79
100-109%	45
110-119%	12
120-129%	3

Analytical recoveries of folpet by methods based on that of Schlesinger (1991), were obtained for various commodities during method validation and analysis of samples from supervised trials. The commodities tested were apple, apple juice, wet apple pomace, cranberry, cucumber, grape juice, grapes, lettuce, melons, must, onion, raisins, grape spirit, strawberry, tomato, tomato paste, tomato purée and wine. Recoveries were determined from 0.05 mg/kg up to 5 mg/kg for most substrates, and up to 20 or 50 mg/kg for some, and were found to be quantitative down to a level of 0.05 mg/kg, which is the limit of determination (LOD). Recoveries did not appear to depend on residue level or substrate. Over the 340 recovery tests the mean and median were 87% and 86% respectively.

De Paoli and Bruno (1995a, method MR 52) extracted tomatoes with dichloromethane and cleaned up the extract by passage through a chromatography cartridge. Folpet residues in the extract were measured by GLC with an ECD after the addition of ethion as an internal standard. Recoveries were 94-110% at 0.05 mg/kg (n = 3) and 97-106% at 0.20 mg/kg (n = 3). The LOD was 0.05 mg/kg. De Paoli and Bruno (1995b) also used method MR 52 for strawberry analysis. Recoveries were 72-80% at 0.10 mg/kg (n = 3) and 94-101% at 0.50 mg/kg (n = 3).

Grinbaum (1994) analysed grape samples for folpet and phthalimide after extracting the grapes with acetone and cleaning up the extract by solvent partition and column chromatography

(method FO 05/89). The folpet residues were measured by GLC with an ECD and the phthalimide by GLC with an NPD. Quantitative recoveries of both analytes were obtained at a level of 0.1 mg/kg and above. In 13 recovery tests on folpet at fortification levels of 0.10 to 3.0 mg/kg the mean recovery was 91% (range 75-114%). In 9 tests on phthalimide at fortification levels of 0.070 to 1.0 mg/kg the mean recovery was 90% (range 76-105%).

Williams (1996) tested the Schlesinger method (FP/15/91) and a method for the determination of folpet residues in oily crops (Nishioka *et al*, 1996) to determine whether they were robust enough to be successfully and reproducibly used by competent chemists without outside assistance and with no prior experience of the method.

Williams suggested minor modifications which improved reproducibility. Dilutions of stock solutions for GLC were prepared in hexane containing 2% di(ethyleneglycol)diethyl ether, which reduced folpet degradation during gas chromatography; which had varied between runs and with different crop extracts. Additional clean-up was needed to produce a clean extract from onions. Satisfactory recoveries and repeatability were achieved with the modified Schlesinger method for folpet residues in apples, cantaloupe, cranberries, cucumbers, grapes, lettuce, onions, strawberries and tomatoes. Folpet residues in avocados were successfully analysed by the Nishioka method with some extra clean-up.

Turner and Partridge (1996) analysed cereal grains and straw for folpet residues by an HPLC method, achieving an LOD of 0.05 mg/kg. Folpet residues were extracted with ethyl acetate which was washed with aqueous phosphoric acid. Further clean-up was effected by gel permeation chromatography. Residues were determined on a reversed phase column using an acetonitrile-water mobile phase.

Folpet is included in Multi-residue Method 1, Pesticides amenable to gas chromatography (The Netherlands, 1996). LODs for various matrices were 0.01-0.05 mg/kg.

Stability of pesticide residues in stored analytical samples

Information was made available to the Meeting on the freezer storage stability of folpet residues in apple juice, wet apple pomace, apples, cranberries, cucumbers, grape juice, lettuce, onions, potatoes, tomato paste, tomato purée, tomatoes , wheat grain and wheat straw. Storage stability data are shown in Table 11.

Table 11. Freezer storage stability of folpet in various substrates fortified at 1 mg/kg. Most raw commodities were stored whole, but cereals were chopped. Recoveries were calculated from the analytical results at day 0 and after storage, neither of which were corrected for analytical recoveries.

Sample	Storage temp	Folpet added, mg/kg	Duration, days	%, folpet remaining	Reference
Apple juice	-12 to -27°C	1.0	7 14 30	106 77 77	95-0059
Apple pomace, wet	-12 to -27°C	1.0	16 35	99 90	95-0059
Apple, whole	-12 to -27°C	1.0	14 30 149	105 98 111	95-0059
Cranberries	-12 to -27°C	1.0	14 29 144 176	81 90 109 83	AA950306
Cucumber	below -10°C	1.0	16 29	78 98	95-0065

Sample	Storage temp	Folpet added, mg/kg	Duration, days	%, folpet remaining	Reference
Grape juice	below -12°C	1.0	7 14 29 36	111 116 108 105	95-0100
Lettuce	-10 to -27°C	1.0	14 30 90	101 96 100	95-0066
Onions	-12 to -27°C	1.0	14 41	106 93	95-0070
Potato, whole	below -10°C	1.0	20 34 55	103 96 119	95-0101 AA960303
Tomato paste	below -10°C	1.0	14 30	89 99	95-0060
Tomato purée	below -10°C	1.0	14 31	91 89	95-0060
Tomatoes, whole	below -10°C	1.0	13 35 74 136	92 93 91 80	95-0060
Wheat grain, chopped and blended.	frozen -26°C	1.0	91 182 366	102 92 95	OA00382 R9156
Wheat straw, chopped and blended.	frozen -26°C	1.0	91 182 366	75 91 92	OA00382 R9156

Triplicate samples of raisins (hydrated) from the processing trials (95-0100) were analysed for folpet stored below -12°C for 21 days and then analysed again. Folpet residues had decreased by an average of 6%.

The temperature of storage of the wheat grain and straw was not stated.

Folpet was stable in freezer storage for the periods tested, but some periods did not exceed 30 days.

Definition of the residue

The Meeting agreed that the current residue definition is suitable for enforcing compliance with MRLs and for estimation of dietary intake.

Definition of the residue for compliance with MRLs and for estimation of dietary intake: folpet.

USE PATTERN

Folpet is a broad-spectrum, non-systemic fungicide used on food and other crops. The major uses are against diseases of grapes, pome and stone fruit and vegetables. Information was provided on registered uses around the world. Labels were provided for uses in many countries. Those not supported by a label are indicated by a footnote.

Table 12. Registered uses of folpet.

Crop	Country	Form	Application	PHI, days

			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Almonds	Spain	WP	foliar		0.13-0.15		10
Apples	Argentina	WP	foliar		0.12		15
Apples	Canada	WP	foliar		0.075-0.10		1
Apples	Chile	WP	foliar	1.5-2.0	0.09-0.11		3
Apples	France (north) 1/	SC	foliar	1.04	0.10-0.14	11	14
Apples	France (south) 1/	SC	foliar	0.98-1.2	0.081-0.12	9	14
Apples	Hungary	WP	foliar	1.5			10
Apples	Mexico	WP	foliar	1.0-1.3			
Apples	Portugal	WP	foliar		0.13		21
Apples	Spain	WP	foliar		0.13-0.15		10
Apples	Switzerland	WG	foliar		0.08		21
Avocado	Mexico	WP	foliar	1.0-1.3			
Barley, winter	France, north 1/	SC	foliar	1.8	0.58	2	36-56
Barley, winter	France, south 1/	SC	foliar	1.8	0.44	2	40-49
Blueberries	Canada	WP	foliar		0.10		1
Celery	Argentina	WP	foliar		0.13		7
Celery	Canada	WP	foliar		0.10		7
Celery	Costa Rica	WP	foliar	0.10-0.13	0.10-0.13		7
Celery	El Salvador	WP	foliar	0.10-0.13	0.10-0.13		7
Celery	Honduras	WP	foliar	0.10-0.13	0.10-0.13		7
Celery	Mexico	WP	foliar	1.0-2.0			no limit
Cherries	Argentina	WP	foliar		0.12		7
Cherries, sour	Canada	WP	foliar		0.10		1
Chickpeas	Spain	WP	foliar		0.13-0.15		10
Citrus fruits	Mexico	WP	foliar	1.0-1.5			
Cranberries	Canada	WP	foliar		0.50		30
Cucumbers	Argentina	WP	foliar		0.12		7
Cucumbers	Canada	WP	foliar		0.10-0.20		1
Cucumbers	Mexico	WP	foliar	1.3-1.8			no limit
Currants	Canada	WP	foliar		0.20		7
Egg plant	Spain	WP	foliar		0.13-0.15		10
Endive	Spain	WP	foliar		0.13-0.15		21
Garlic	Argentina	WP	foliar		0.12-0.13		7
Garlic	Chile	WP	foliar	1.5-2.0	0.10-0.13		7
Garlic	Mexico	WP	foliar	1.0-1.5			no limit
Gooseberries	Canada	WP	foliar		0.20		7
Grapes	Canada	WP	foliar		0.10		1
Grapes	Chile	WP	foliar	1.5-2.0	0.10-0.15		3
Grapes	France 2/	SC	foliar	1.0-1.5			21, 30
Grapes	France 2/	WG	foliar	1.0-1.5			21, 28
Grapes	France 2/	WP	foliar	1.0-1.8			28
Grapes	Mexico	WP	foliar	1.0			no limit
Grapes	Spain	WP	foliar		0.15-0.20		21
Grapes, table	Argentina	WP	foliar		0.10-0.13		7
Grapes, table	Italy	WP	foliar		0.16		10
Grapes, wine	Argentina	WP	foliar		0.10-0.13		20
Grapes, wine	Germany 1/	SC	foliar	0.45-1.2	0.075	8	[1]
Grapes, wine	Germany 1/	SC	foliar	0.6-1.6	0.1	6	[2]
Grapes, wine	Italy	WP	foliar		0.16		40
Green beans	Spain	WP	foliar		0.13-0.15		21
Leek	Spain	WP	foliar		0.13-0.15		10
Lettuce	Greece	SC	foliar		0.13-0.16		
Lettuce	Mexico	WP	foliar	1.3			no limit
Lettuce	Portugal	WP	foliar		0.10-0.13		14

[1] Up to stage 61 and stages 68-81.

[2] Up to stage 81.

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Lettuce	Spain	WP	foliar		0.13-0.15		21
Melons	Argentina	WP	foliar		0.12		7
Melons	Canada	WP	foliar		0.10-0.20		1
Melons	Costa Rica	WP	foliar	0.10-0.13	0.10-0.13		7
Melons	El Salvador	WP	foliar	0.10-0.13	0.10-0.13		7
Melons	Greece	SC	foliar		0.13-0.16		20
Melons	Honduras	WP	foliar	0.10-0.13	0.10-0.13		7
Melons	Mexico	WP	foliar	1.3-1.8			no limit
Olives	Spain	WP	foliar		0.13-0.15		10
Onions	Argentina	WP	foliar		0.12-0.13		7
Onions	Chile	WP	foliar	1.5-2.0	0.10-0.13		7
Onions	Costa Rica	WP	foliar	0.10-0.13	0.10-0.13		7
Onions	El Salvador	WP	foliar	0.10-0.13	0.10-0.13		7
Onions	Greece	SC	foliar		0.13-0.16		
Onions	Honduras	WP	foliar	0.10-0.13	0.10-0.13		7
Onions	Hungary	WP	foliar		0.10-0.13		5
Onions	Mexico	WP	foliar	1.3-1.5			no limit
Onions	Portugal	WP	foliar		0.10-0.13		7
Peach	Argentina	WP	foliar		0.12		7
Pears	Argentina	WP	foliar		0.12		15
Pears	Chile	WP	foliar	1.5-2.0	0.09-0.11		3
Peas	Spain	WP	foliar		0.13-0.15		10
Peppers	Argentina	WP	foliar		0.13		7
Potato	Argentina	WP	foliar		0.12-0.18		7
Potato	Chile	WP	foliar	1.0-1.7	0.10-0.15		7
Potato	Spain	WP	foliar		0.13-0.15		10
Pumpkins	Canada	WP	foliar		0.10-0.20		1
Squash	Canada	WP	foliar		0.10-0.20		1
Stone fruit	Spain	WP	foliar		0.13-0.15		10
Strawberries	Argentina	WP	foliar		0.13		7
Strawberries	Canada	WP	foliar		0.10		1
Strawberries	Chile	WP	foliar	1.5-2.0	0.10-0.15		7
Strawberries	Costa Rica	WP	foliar	0.10	0.10		7
Strawberries	El Salvador	WP	foliar	0.10	0.10		7
Strawberries	Honduras	WP	foliar	0.10	0.10		7
Strawberries	Mexico	WP	foliar	0.75-1.3			no limit
Strawberries	Netherlands	WP	field		0.13		4
Strawberries	Netherlands	WP	glasshouse		0.13		14
Strawberries	Spain	WP	foliar		0.13-0.15		21
Summer squash	Mexico	WP	foliar	1.3-1.8			no limit
Tomato	Argentina	WP	foliar		0.13-0.14		7
Tomato	Canada	WP	foliar		0.20		1
Tomato	Chile	WP	foliar	1.0-1.7	0.10-0.15		7
Tomato	Costa Rica	WP	foliar	0.13	0.13		7
Tomato	El Salvador	WP	foliar	0.13	0.13		7
Tomato	Honduras	WP	foliar	0.13	0.13		7
Tomato	Hungary	WP	foliar		0.10-0.13		14
Tomato	Mexico	WP	foliar	1.5-2.0			no limit
Tomato	Portugal	WP	foliar		0.13		7
Tomato	Spain	WP	foliar		0.13-0.15		10
Watermelon	Argentina	WP	foliar		0.12		7
Watermelon	Costa Rica	WP	foliar	0.10-0.13	0.10-0.13		7
Watermelon	El Salvador	WP	foliar	0.10-0.13	0.10-0.13		7
Watermelon	Honduras	WP	foliar	0.10-0.13	0.10-0.13		7
Watermelon	Mexico	WP	foliar	1.3-1.8			no limit
Wheat, winter	France, north 1/	SC	foliar	1.8	0.58	2	25-51

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Wheat, winter	France, south 1/	SC	foliar	1.8	0.44	2	19-49
Wheat, winter	Germany 1/	SC	foliar	0.8	0.25	2	35
Wheat, winter	UK 1/	WG	foliar	1.6	0.8	2	39-45

1/ No label available.
2/ In some formulations, folpet is mixed with another fungicide which may influence the PHI.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residues from supervised residue trials on fruit and vegetables are shown in Tables 13-23.

Table 13	*Apples.* Argentina, Canada, Chile, France, Germany, Hungary, Poland, Portugal, Spain, Switzerland, USA.
Table 14	*Grapes*. Argentina, Chile, France, Germany, Italy, Mexico, Russia.
Table 15	*Strawberry*. Italy, Mexico, The Netherlands.
Table 16	*Onion.* Chile, Germany, Greece, Hungary, Mexico, The Netherlands, Portugal, Spain.
Table 17	*Cucumber*. Canada, Mexico.
	Melons. Greece, Guatemala, Honduras, Mexico.
Table 18	*Tomato.* Chile, Hungary, Italy, Mexico, The Netherlands, Portugal, Spain, USA.
Table 19	*Head lettuce*. Greece, Hungary, Mexico, Portugal.
	Leaf lettuce. Greece, Mexico, Spain.
	Lamb's lettuce. Germany
Table 20	*Potato.* Italy, Mexico, Poland, Russia, South Africa.
Table 21	*Barley, wheat.* France, Germany, UK.
Table 22	*Cereal fodder.* France, Germany, UK.
Table 23	*Cereal forage.* France, Germany, UK.

Where residues were not detected, results are recorded as below the limit of determination (LOD), e.g. <0.05 mg/kg. Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure. Although trials included control plots, no control data are recorded in the tables except where residues in control samples exceeded the LOD. Residues are recorded uncorrected for recoveries where possible. Results were corrected for recovery in some trials on onions, potatoes, strawberries and tomatoes and the reports did not include uncorrected data. In some trials it was not clear whether or not the results were corrected.

Trials were mainly fully reported as well as on summary sheets except German trials on apples and lamb's lettuce, some French trials on cereals and apples, and potato trials in Poland.

Folpet was applied to apple trees in supervised trials in France, Hungary, Portugal, Spain and Switzerland by backpack airblast or lance sprayers. Plot sizes were in the range 86-240 m^2. In the label-rate trials 3 field samples were analysed from each of 2 treated plots. In Table 13 analyses of replicate field samples from one plot or from duplicate plots in the same trial are shown separately.

No field report was available for the apple trial in Poland so it was not evaluated.

Supervised apple trials took place at 4 sites in Canada, 2 in Argentina and 2 in Chile where folpet was applied with a motorised pump backpack sprayer or an airblast sprayer driven by a power take-off (Table 13). Plot sizes ranged from 190 to 784 m^2. Two field samples each of 2 kg were analysed from each plot.

In a series of trials on grapes in Argentina, Chile, Italy and Mexico folpet was applied by backpack sprayers with motorized pumps. Plot sizes ranged from 55 to 520 m^2. Duplicate field samples (2 kg) were taken from each treated plot (1 treated plot per trial). The trials were on table grapes (1 trial each in Argentina, Chile and Italy), wine grapes (1 each in Chile and Italy) and raisin grapes (Mexico). Residues in the grapes in the Mexican trial were much lower than in the others. The maximum daily temperature in the final weeks of this trial was high (41°C) and this may have had an influence.

Folpet was applied by airblast knapsack sprayers 8 or 9 times at 6-15 day intervals at 1.5 kg ai/ha to grapes in 4 supervised trials in France in 1995. Plot sizes were 378-792 m^2. Duplicate samples (3 kg) of grapes were harvested from each plot 0-21 days after the final application, and extracted within 3 days of receipt at the laboratory. The crude extracts were stored below -18°C. Wasser (1997) has shown that folpet residues in crude extracts of grapes were stable during refrigerator storage at 4°C for 1 month. Folpet residues in the control plot of trial EA950170 FR04 resulted from an unexpected application of folpet by the farmer approximately 2 months before harvest.

In 6 further grape trials in France in 1996 folpet was applied by atomiser sprayer 8 times with samples (1.1-3.6 kg) taken for analysis 3 and 4 weeks after the final application. Plot sizes were 49-93 m^2.

Folpet was applied by boom sprayer in the strawberry trials in Italy in 1995. Plot sizes in the two trials were 18.9 m^2 and 10 m^2. Field sample sizes were in the range 1-1.5 kg. In trial R-8989 rain (400 mm) fell between 7 and 14 days after the final application and may have decreased the residues. In trial R-8986 rain (total ~80 mm) occurred on 9 successive days immediately after the final application. The results for trial R-8986 are corrected for recovery, but recoveries were in the range 84-108%, so the adjustments are small. In the Italian trials in 1996 data are also corrected for recovery. Strawberries sampled on the day of the last application were very small (300 fruit in 1 kg) and the results may not represent a commercial situation.

Strawberries were produced in plastic tunnels in the trials in The Netherlands in 1996. Three field samples (1 kg each) were analysed from each plot; there were 2 plots in each trial at the label rate and 1 plot in trials at twice the rate.

Motorised backpack sprayers were used to apply folpet to strawberries growing in 480-1200 m^2 plots in supervised trials in Mexico. Two field samples (2 kg each) were taken from each plot for analysis. Procedural recoveries were 52-53% from strawberries from trial AA950310.01, but despite investigations no clear reason was discovered. The recorded results are not corrected for recovery.

In onion trials in Chile and Mexico folpet was applied to the foliage by backpack sprayer with a motorized pump or a CO_2 pressure source. Plot sizes were in the range 108-368 m^2. Onions (8-24 per field sample) were pulled from the ground and allowed to dry for one day in the field., then placed in a freezer after the upper foliage and the roots were trimmed off. In onion trials in Greece, Hungary, Portugal and Spain folpet was applied with back boom sprayers. Plot sizes were approximately 50 m^2, with duplicate treated plots in each trial at the label rate and single plots in each of two Hungarian trials at twice the label rate. One field sample (at least 2 kg, 12 or more onions) per plot was analysed. The soil was removed by hand and the whole plant was analysed.

A compressed air sprayer was used to apply folpet in the onion trials (plot size, 7.5 m of row) in The Netherlands in 1996. Field samples were 2 kg or 12 bulbs. Results were corrected for recovery in the German trial on onions but not in The Netherlands trials.

In cucumber trials in Mexico and Canada folpet was applied with a motorized backpack sprayer (Mexico) or a CO_2 pressurized backpack sprayer (Canada). Plot areas ranged from 90 to 280 m^2, each trial consisting of a treated plot and a control plot. Field samples from the treated plot were 2kg. Folpet was applied with a backpack boom sprayer to melons in trials in Greece. Two field samples, each of 12 melons about 15 cm diameter, were taken from each plot (90-180 $m^{2)}$. Trials at the label rate were with 2 treated plots and a control plot. Duplicate field samples from each trial were analysed; the residue reported in Table 17 is the mean with the individual analyses in brackets. whole melons were analysed.

Melons were treated with folpet by backpack sprayer in supervised trials in Guatemala, Honduras and Mexico. Plot sizes were in the range 120-540 m^2, with 1 treated plot and 1 control plot per trial. Each field sample consisted of 12 melons and duplicate field samples were analysed from each plot.

Plot sizes were 10 and 40 m^2 in the Italian tomato trials in 1995. Folpet was applied as a high-volume spray by knapsack or by compressed air sprayer. Field samples comprised 24 tomatoes. The plot size was 50-60 m^2 in the Italian tomato trials in 1996 where folpet was applied by gas pressured knapsack. Field samples were 2.5-4 kg (24-32 fruit).The 1995 and 1996 results were corrected for recovery.

Folpet was applied from a backpack boom sprayer in the tomato trials in Hungary, Spain and Portugal, except in one trial in Spain (MAK/375-07) where spray was applied with a lance to staked tomatoes. There were 2 treated plots in each trial at the label rate and 1 treated plot in the trials at twice the label rate. Plot size was 50 m^2. One field sample (2 kg or more) from each plot was analysed. Trials MAK/375-01 and MAK/375-03 were subject to overhead irrigation but the precise dates were not recorded. Residue levels could be reduced if irrigation occurred while spray deposits were fresh.

Tomatoes at 5 sites in Mexico and 1 site in Chile were treated with folpet using backpack sprayers with motorized pumps. Plot sizes were 117-224 m^2. Two field samples (2 kg each)were analysed from each treated plot (1 per trial).

Folpet was applied by motor sprayer to the tomatoes in The Netherlands greenhouse trials in 1995, the plot size was 72 m^2 and field samples were 2.5 kg. Samples were stored for 490 days before analysis in trial R9118.

Folpet was applied by backpack CO_2 boom sprayer to lettuce in trials in Greece, Portugal and Spain. In the two trials in Greece and the one in Spain the lettuce were irrigated by overhead sprinkler 1 or 2 days after the final application and in each of these trials residues were below the LOD, 0.05 mg/kg. Drip irrigation was used in the trial in Portugal and the residues were substantially higher. It is quite likely that the use of sprinkler irrigation was the cause of the low residues.

A backpack boom sprayer was used to apply folpet to head lettuce grown in plastic tunnels in Hungarian trials in 1997-97. Plot size was 50 m^2. The field sample from each plot constituted 12 lettuce.

In the Mexican trials on lettuce folpet was applied with a motorized backpack sprayer. Plot areas ranged from 50 to 120 m^2. Lettuce heads (12 per field sample) were cut and the outermost, trash leaves were removed in the field. Duplicate field samples from each trial were analysed.

Folpet was applied by boom sprayers and precision sprayers to plots of 54-62 m^2 in potato trials in Italy in 1995-96. Field samples were 24 tubers (2-4 kg). Results were corrected for

recoveries. In some trials sampled tubers were gently brushed to remove soil. In trials R8988 and R9094 no clear description of sample cleaning was provided.

Plot size was 200 m^2 in the Mexican trials on potatoes where folpet was applied with back pack motorized sprayers. On field sampling, the dirt was brushed off each potato using a paint brush and the potatoes were patted dry with a clean paper towel.

Field reports were not available for the potato trials in Poland and Russia. Folpet was applied by hand sprayer in Poland and tractor sprayer and knapsack in Russia. A TLC method was used for residue analysis in the Russian trials.

Folpet was applied with a CO_2 knapsack boom sprayer in the South African trials on potatoes in 1995. No field or analytical report was provided.

The Meeting received information on a series of wheat and barley trials in France and the UK from 1992 to 1996. Field reports were not included for the French trials nor for the UK wheat trials R8559-5 and R8559-6. In the UK trials on wheat in 1995 (trials R8580-1 and R8580-2) folpet was applied to plots of 48 and 144 m^2. Minimum sample sizes were 1 kg grain and 0.5 kg straw.

Table 13. Folpet residues in apples resulting from supervised trials in Argentina, Canada, Chile, France, Germany, Hungary, Poland, Portugal, Spain, Switzerland and the USA. Analyses on replicate field samples from one plot or from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Country, year (variety)	Application				PHI, days	Folpet residues, mg/kg	Ref
	Form	kg ai/ha	kg ai/hl	no.			
Argentina, 1996 (Cooper 8)	WP	3.6	0.12	3	10	1.1, 1.4	AA950314.07 95-0064
Argentina, 1996 (Red Delicious)	WP	3.6	0.12	3	10	2.6	AA950314.08 95-0064
Canada, 1996 (Cortland)	WP	0.81	0.10	8	7	0.36, 0.43	AA950314.02 95-0064
Canada, 1996 (McIntosh)	WP	0.81	0.10	8	7	1.1, 0.61	AA950314.03 95-0064
Canada, 1996 (McIntosh)	WP	0.81	0.10	8	7	0.65, 0.45	AA950314.04 95-0064
Canada, 1996 (Red Delicious)	WP	0.78	0.10	8	7	1.4 1.3	AA950314.01 95-0064
Chile, 1996 (Imperial Gala)	WP	2.0	0.11	3	7	1.6, 2.0	AA950314.05 95-0064
Chile, 1996 (Royal Gala)	WP	2.0	0.11	3	7	3.2, 3.7	AA950314.06 95-0064
France (nth), 1996 (Star Crimson)	SC	0.98	0.10	11	14	0.9, 0.6, 0.7 0.7, 0.8, 0.5	MAK/374-08 R-9162
France (nth), 1996 (Star Crimson)	SC	1.0	0.10	11	14	0.7, 1.4, 0.7 0.8, 0.8, 0.6	MAK/374-09 R-9162
France (sth), 1996 (Golden Delicious)	SC	1.2	0.10	9	14	1.8, 1.2, 1.8 1.1, 1.5, 1.0	MAK/374-06 R-9162
France (sth), 1996 (Golden Delicious)	SC	0.98	0.10	9	14	1.2, 1.4, 0.8 0.7, 0.7, 1.4	MAK/374-07 R-9162
Germany, 1985 (Gloster)	WP +SC	0.75	10×0.075 +0.15	10 11	24 3	0.81 0.85	BBA 85/Ob/12885
Germany, 1985 (Gloster)	WP +SC	0.75	10×0.075 +0.15	10 11	24 3	0.84 0.81	BBA 85/Ob/12885
Germany, 1985 (Gloster)	WP +SC	0.75	10×0.075 +0.3	10 11	24 3	0.54 0.83	BBA 85/Ob/12885

Country, year (variety)	Application				PHI, days	Folpet residues, mg/kg	Ref
	Form	kg ai/ha	kg ai/hl	no.			
Germany, 1985 (Gloster)	WP +SC	10×0.75 +0.5	10×0.075 +0.1	10 11	24 3	0.32 0.52	BBA 85/Ob/12885
Germany, 1985 (Gloster)	WP +SC	10×0.75 +0.5	10×0.075 +0.2	10 11	24 3	0.54 0.61	BBA 85/Ob/12885
Germany, 1985 (Gloster)	WP +SC	10×0.75 +0.5	10×0.075 +0.2	10 11	24 3	0.32 0.43	BBA 85/Ob/12885
Hungary, 1996 (Star King)	WP	1.6	0.10	8	10	5.4, 4.4, 5.1 6.5, 5.9, 8.0	MAK374-01 R-9162
Poland 1996 (Elstar)	WG	3.6		3	1 7 14 21	7.4 8.0 4.4 4.7 4.2 4.5 2.9 3.3	R9852
Portugal, 1996 (Jonagold Red)	WP	1.6	0.13	8	21	2.7, 2.8, 2.6 3.0, 3.2, 2.3	MAK/374-05 R-9162
Portugal, 1996 (Jonagold Red)	WP	3.1	0.26	8	21	5.5, 10.8, 9.9	MAK/374-05 R-9162
Spain, 1996 (Red Mornet)	WP	1.9	0.16	6	10	1.7, 2.0, 3.1 2.2, 2.3, 1.7	MAK/374-04 R-9162
Spain, 1996 (Red Mornet)	WP	3.7	0.31	6	10	6.9, 4.1, 3.0	MAK/374-04 R-9162
Switzerland, 1996 (Fiorina)	WG	2.0	0.10	4	21	2.2, 3.1, 2.8 2.7, 3.4, 3.3	MAK/374-03 R-9162
USA (NY), 1995 (Northern Spy)	WP	2.9	0.31	4	7	2.1 note[1] 1.2 fw 5.4 wp 0.072 j	SARS-95-50 95-0059

Table 14. Folpet, and phthalimide residues in grapes resulting from supervised trials in Argentina, Chile, France, Germany, Italy, Mexico and Russia. Analyses of replicate field samples from one plot are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref
	Form	kg ai/ha	kg ai/hl	no.		folpet	phthalimide	
Argentina, 1996 (Emperador)	WP	1.0	0.13	4	7	1.6, 1.5		R-9141g AA950313.07 95-0071
Chile, 1996 (Red Globe)	WP	2.0	0.15	3	14	1.8, 2.6		R-9141g AA950313.06 95-0071
Chile, 1996 (Red Globe)	WP	2.0	0.15	3	14	1.5, 3.0		R-9141g AA950313.08 95-0071

[1] fw: whole fruit washed. wp: wet pomace. j: juice.

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref
	Form	kg ai/ha	kg ai/hl	no.		folpet	phthalimide	
France (Beaune), 1992	WG	1.5		8	27	1.9, 0.73, 0.88, 0.93	0.21, 0.095, 0.062, 0.091	R-7194a
					52	0.58, 0.56, 0.46, 0.68	0.071, 0.057, 0.052, 0.071	
France (Bordeaux), 1992	WG	1.5		7	0	3.6, 2.5, 2.5, 2.9	0.20, 0.18, 0.18	R-7194
					21	0.47, 1.6, 0.95, 0.39	0.18, 0.33, 0.24, 0.13	
					60	0.52, 0.14, 0.23, 0.50	0.16, 0.091, 0.091, 0.17	
France (Orange), 1992	WG	1.5		12	0	1.1, 1.5, 3.8, 6.5 c 0.066	0.50, 0.31, 0.94, 1.4 c 0.070	R-7194a
					15	1.8, 4.3, 1.3, 2.0 c 0.098	0.94, 0.91, 0.52, 0.91 c 0.11	
					30	0.76, 1.1, 0.42, 0.22 c 0.057	0.48, 0.53, 0.31, 0.28 c 0.056	
France, 1994 (Ugni blanc)	SC	1.5	0.43	6	52	2.8 0.27 m <0.01 w <0.01 sp		R-8411 R 5011 9401-MAK 94-66-06-22
France, 1994 (Ugni blanc)	WG	1.5	0.43	6	52	2.9 0.73 m <0.01 w <0.01 sp		R-8411 R 5011 9401-MAK 94-66-06-22
France, 1995 (Carignan)	SC	1.6	0.50	7 8	8 0 7 14 21	3.9, 8.1 8.3, 9.0 10.6, 7.1 4.4, 6.0 2.2, 2.2 c 0.012		EA950170 R-9146 FR03
France, 1995 (Chardonnay)	SC	1.4	0.50	8	21	2.4, 2.2		EA950170 R-9146 FR02
France, 1995 (Merlot)	SC	1.5	0.47	8	21	3.1, 2.3		EA950170 R-9146 FR01
France, 1995 (Pinot Noir)	SC	1.5	0.60	8 9	10 0 7 14 21	3.7, 3.1 6.1, 7.2 4.8, 4.0 3.2, 2.5 2.8, 2.3 c 0.06, 0.07 c 0.10, 0.06		EA950170 R-9146 FR04
France N 1996 (Chardonnay)	WG	4×1.9 +1×2.0 +2×1.9 +1×2.0	0.57-0.76	8	21 28	5.8 4.8		R9098 R6149 BKA/628/96/RES
France N 1996 (Chardonnay)	SC	1.9	0.55-0.78	8	21 28	2.6 3.5		R9098 R6149 BKA/628/96/RES
France N 1996 (Chardonnay)	SC	6×1.5 +1×1.6 1×1.4	0.57-0.63	8	21 28	1.9 1.7		R9098 R6149 BKA/628/96/RES
France S 1996 (Cinsault R110)	WG	2×1.6 +1×2.0 +1×1.7 +1×2.1 +3×1.9	0.64-0.84	8	21 28	4.6 2.7		R9098 R6149 BKA/628/96/RES

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref
	Form	kg ai/ha	kg ai/hl	no.		folpet	phthalimide	
France S 1996 (Cinsault R110)	SC	2×1.7 +2×1.9 +1×1.7 +1×1.9 +1×1.8 +1×1.9	0.49-0.76	8	21 29	5.7 3.8		R9098 R6149 BKA/628/96/RES
France S 1996 (Cinsault R110)	SC	1.3 +1×1.5 +1×1.6 +1×1.5 +1×1.4 +1×1.6 +2×1.5	0.54-0.65	8	21 28	5.9 1.5		R9098 R6149 BKA/628/96/RES
Germany, 1993 (Müller-Thurgau)	WP	0.6+0.9 +1.5+1.8 +2×2.2 +2×2.6	2×0.17 +2×0.26 +2×0.30 +2×0.35	8	14 28 35 28 28	0.91 0.66 0.66 0.68 m <0.05 w	<0.1 <0.1 <0.1 0.27 m 0.29 w	R-7993 HVA 7/94 UHL08
Germany, 1993 (Müller-Thurgau)	WP	0.7+1.0 +1.7+2.0 +2×2.3 +2×2.6	2×0.17 +0.28 +0.33 +2×0.39 +2×0.44	8	7 14 27 35 27 27	1.4 1.5 1.5 1.5 0.58 m <0.05 w	<0.1 <0.1 0.1 <0.1 0.44 m 0.47 w	R-7993 HVA 7/94 UHL10
Germany, 1993 (Müller-Thurgau)	WP	0.6+0.9 +1.6+1.9 +2.2+2.3 +2.6+2.5	2×0.16 +0.27 +0.32 +0.37 +2×0.43	8	7 14 28 35 28 28	1.0 1.6 1.1 0.51 0.27 m <0.05 w	<0.1 <0.1 <0.1 <0.1 0.39 m 0.39 w	R-7993 HVA 7/94 UHL12
Germany, 1993 (Müller-Thurgau)	SC	0.38+0.54 +0.91+1.1 +2×1.3 +2×1.5	2×0.1 +0.13 +0.16 +2×0.18 +2×0.21	8	14 28 35 28 28	2.1 1.2 0.41 0.25 m <0.05 w	<0.1 <0.1 <0.1 0.26 m 0.31 w	R-7993 HVA 7/94 UHL14
Germany, 1993 (Müller-Thurgau)	SC	0.39+0.60 +1.0+1.2 +2×1.4 +2×1.6	2×0.1 +0.17 +0.20 +2×0.23 +2×0.27	8	7 14 28 35 28 28	0.77 1.1 0.42 0.40 0.27 m <0.05 w	<0.1 <0.1 <0.1 <0.1 0.37 m 0.35 w	R-7993 HVA 7/94 UHL16
Germany, 1993 (Portugieser)	WP	0.7+1.0 +1.7+2.0 +2.3+2.5 +2×2.7	2×0.17 +0.28 +0.33 +2×0.39 +2×0.44	8	7 14 28 35 28 28	3.5 1.9 2.0 2.0 <0.05 m <0.05 w	<0.1 <0.1 <0.1 <0.1 1.8 m 0.99 w	R-7993 HVA 7/94 UHL09
Germany, 1993 (Portugieser)	SC	0.39+0.60 +1.0+1.1 +2×1.4 +2×1.6	2×0.1 +0.17 +0.20 +2×0.23 +2×0.27	8	7 14 28 35 28 28	1.7 0.54 0.29 0.23 <0.05 m <0.05 w	<0.1 <0.1 <0.1 <0.1 0.44 m 0.33 w	R-7993 HVA 7/94 UHL15
Germany, 1993 (Reisling)	WP	0.63+0.89 +1.3+1.5 +1.7+2.0 +2×1.3	0.17	8	0 14 28 35 28 28	9.7 2.2 5.6 4.7 0.83 m <0.05 w	<0.1 <0.1 0.2 <0.1 0.72 m 0.76 w	R-7993 HVA 7/94 UHL07

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref
	Form	kg ai/ha	kg ai/hl	no.		folpet	phthalimide	
Germany, 1993 (Reisling)	WG	0.6+1.0 +1.6+1.9 +2×2.2 +2.5+2.6	0.16+0.17 +0.27 +0.32 +2×0.37 +2×0.43	8	0 14 28 35 28 28	2.9 1.3 1.3 1.4 <0.05 m <0.05 w	<0.1 <0.1 <0.1 0.12 0.51 m 0.34 w	R-7993 HVA 7/94 UHL11
Germany, 1993 (Reisling)	SC	0.6+0.8 +1.2+1.4 +1.5+1.8 +2×1.2	0.1	8	0 14 28 35 28 28	12 5.6 3.3 1.9 1.0 m <0.05 w	<0.1 <0.1 0.1 <0.1 0.92 m 0.83 w	R-7993 HVA 7/94 UHL13
Italy, 1996 (Italia)	WG	1.6	0.16	5	10	3.3, 2.9		R-9141g AA950313.03 95-0071
Italy, 1996 (Rondinella)	WG	1.6	0.16	5	41	1.7, 1.7		R-9141g AA950313.04 95-0071
Mexico, 1996 (Perleete)	WP	1.0	0.14	7	10	<0.05, <0.05)		R-9141g AA950313.05 95-0071
Russia 1995 (Rkaziteli)	WG	1.0	0.10	4	0 10 20 30 40	6.0 0.05 <0.02 <0.02 <0.02		R9572
Russia 1995 (Rkaziteli)	WP	1.0	0.10	4	0 10 20 30 40	3.5 <0.02 <0.02 <0.02 <0.02		R9572

c: control sample m: must. w: wine sp: spirit

Table 15. Folpet residues in strawberries resulting from supervised trials in Italy, Mexico and The Netherlands. Analyses of replicate field samples from one plot and from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, mg/kg folpet	Ref
	Form	kg ai/ha	kg ai/hl	no.			
Italy, 1995 (Addie)	WP	1.3+3×1.2	0.13	4	0 7 10 14	0.70 0.22 0.10 0.07	R-8986 DA-10/915 IT 219/95
Italy, 1995 (Belruby)	WP	0.84+0.92 +0.89	0.15	3	0 7 14 21	0.86 0.09 <0.01 <0.01	R-8989 95I005R 95046/I1-FFST
Italy, 1996 (Addie)	WP	0.73-0.76	0.13	2 3	17 0 7 14 21	0.07 0.66 0.14 0.04 0.04	R9093 96009/I1-FFST ERSA-DA-05/96
Italy, 1996 (Marmolada WB)	WP	0.75	0.13	2 3	7 0 7 14 21	0.29 0.52 0.19 0.12 0.09	R9383 6077PI1 96IT32 ERSA-DA-15/96

Country, year (variety)	Application				PHI, days	Residues, mg/kg folpet	Ref
	Form	kg ai/ha	kg ai/hl	no.			
Mexico, 1995 (Seascape)	WP	1.2	0.38+0.32 +2×0.33	4	2	2.0, 2.2	R-9141s 950310.03 95-0068
Mexico, 1995 (Sweet Charlie)	WP	3×1.3+1.2	2×0.50 +0.52+0.62	4	2	1.7, 1.8	R-9141s 950310.01 95-0068
Mexico, 1995 (Sweet Charlie)	WP	1.2	0.31+3×0.26	4	2	0.92, 1.6	R-9141s 950310.02 95-0068
Netherlands, 1996 (Elsanta)	WP	2.7	0.27	2 pt	14	1.8, 2.0, 2.6	R-9161 MAK/372-01
Netherlands, 1996 (Elsanta)	WG	1.3	0.13	2 pt	14	0.4, 1.6, 0.8 0.8, 1.2, 1.0	R-9161 MAK/372-01
Netherlands, 1996 (Elsanta)	WP	1.4+1.3	0.13	2 pt	14	1.0, 1.4, 1.2 1.0, 0.7, 1.0	R-9161 MAK/372-02
Netherlands, 1996 (Elsanta)	WP	2.7	0.27	2 pt	14	3.0, 3.6, 1.8	R-9161 MAK/372-02
Netherlands, 1996 (Elsanta)	WP	1.3+1.4	0.13	2 pt[1]	14	1.3, 0.7, 1.2 1.0, 1.1, 1.9	R-9161 MAK/372-01

Table 16. Folpet residues in bulb onions resulting from supervised trials in Chile, Hungary, Germany, Greece, Mexico, The Netherlands, Portugal and Spain. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels. Samples from European trials include roots and foliage.

Country, year (variety)	Application				PHI, days	Residues, mg/kg	Ref
	Form	kg ai/ha	kg ai/hl	no.		folpet	
Chile, 1996 (Grano de oro)	WP	2.0	0.13	3	7	0.36, 0.27	R-9140 AA950307.03 95-0070
Germany 1996 (Elody) [DJH1]	SC	1.0	0.25	3	0 7 14 21	5.2 4.8 1.4 1.2	R9496 96222/01-RFON
Greece, 1996 (Banko)	SC	0.62 +0.61+0.62	0.12	3	20	<0.05, <0.05	R-9163 MAK/377-07
Greece, 1996 (Moranda)	SC	2×0.61 +0.62	0.12	3	20	<0.05, <0.05	R-9163 MAK/377-06
Hungary, 1996 (Deutona)	WP	0.40 +0.66+0.65	0.13	3	14	<0.05, 0.07	R-9163 MAK/377-02
Hungary, 1996 (Deutona)	WP	0.75 +2×1.3	0.26	3	14	0.2	R-9163 MAK/377-02
Hungary, 1996 (Makoi Bronz)	WP	0.40 +0.67+0.65	0.13	3	14	<0.05, <0.05	R-9163 MAK/377-03
Hungary, 1996 (Makoi Bronz)	WP	0.39 +0.65+0.67	0.13	3	14	0.21, 0.09	R-9163 MAK/377-04
Hungary, 1996 (Piroschka)	WP	0.39 +2×0.65	0.13	3	14	0.05, <0.05	R-9163 MAK/377-01
Hungary, 1996 (Piroschka)	WP	0.75 +2×1.3	0.26	3	14	1.0	R-9163 MAK/377-01
Mexico, 1995 (Suprema)	WP	1.5	2×0.56 +0.36+0.51	4	7	0.41, 0.31	R-9141 AA950307.01 95-0070

[1] pt:, plastic tunnel

Country, year (variety)	Application				PHI, days	Residues, mg/kg	Ref
	Form	kg ai/ha	kg ai/hl	no.		folpet	
Mexico, 1995 (Suprema)	WP	1.5	3×0.37 +0.56	4	7	0.41, 0.32	R-9141 AA950307.02 95-0070
Netherlands 1996 (Hyfield)	SC	0.91-0.98	0.30-0.33	2 3	7 0 7 14 21	0.17 0.51 <0.02 0.03 <0.02	R9234 MAH 96145 96020/N1-RPO
Netherlands 1996 (Hysam)	SC	0.89	0.30	2 3	7 0 7 14 21	0.24 0.60 0.02 0.02 0.02	R9234 MAH 96145 96020/N1-RPO
Portugal, 1996 (Valenciana tardia)	WP	0.53 +0.54+0.54	0.13	3	7	5.0, 3.6	R-9163 MAK/377-08
Spain, 1996 (Dulce Babosa)	WP	0.62 +2×0.65	0.16	3	10	1.6, 2.5	R-9163 MAK/377-09

Table 17. Folpet residues in cucumbers and melons resulting from supervised trials in Canada, Greece, Guatemala, Honduras and Mexico. Analyses of replicate field samples from one plot are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

CUCURBITS, country, year (variety)	Application				PHI, days	Folpet residues, mg/kg	Ref
	Form	kg ai/ha	kg ai/hl	no.			
CUCUMBERS							
Canada, 1996 (Panther)	WP	1.0	0.10	8	7	<0.05, 0.073	AA950312.05 95-0065
Mexico, 1995 (Dasher)	WP	1.8	0.50	4	3	0.11, 0.075	AA950312.04 95-0065
Mexico, 1995 (Fancipack)	WP	1.7	0.76	4	3	0.18, 0.36	AA950312.03 95-0065
Mexico, 1995 (pickle)	WP	1.8	0.82+0.78 +0.83+0.67	4	3	0.70, 0.41	AA950312.01 95-0065
Mexico, 1996 (Fancipack)	WP	1.8	0.79	4	3	0.55, 0.56	AA950312.02 95-0065
MELONS							
Greece, 1996	SC	0.49	0.061	4	20	<0.05, <0.05	R-9159 MAK/373-03
Greece, 1996	SC	0.49	0.061	4	20	<0.05, <0.05	R-9159 MAK/373-04
Greece, 1996 (Galia)	SC	0.49	0.061	4	20	<0.05, <0.05	R-9159 MAK/373-02
Greece, 1996 (Macmidon)	SC	0.49	0.061	4	20	<0.05, <0.05	R-9159 MAK/373-01
Greece, 1996 (Macmidon)	SC	0.98	0.12	4	20	<0.05	R-9159 MAK/373-01
Greece, 1996 (Macmidon)	SC	0.97	0.12	4	20	<0.05	R-9159 MAK/373-02
Guatemala, 1996 (Cristobal)	WP	0.49	0.10	6	3	0.23, 0.21	R-9141m AA950308.06 95-0067
Honduras, 1996 (Hy-Mark)	WP	0.65	0.13	4	3	0.32, 0.17	R-9141m AA950308.04 95-0067

CUCURBITS, country, year (variety)	Application				PHI, days	Folpet residues, mg/kg	Ref
	Form	kg ai/ha	kg ai/hl	no.			
Honduras, 1996 (Hy-Mark)	WP	0.65	0.13	4	3	0.20, 0.41	R-9141m AA950308.05 95-0067
Mexico, 1996 (Cruiser F1)	WP	1.8	0.86+0.87 +0.85+0.84 +2×0.79	6	7	2.2, 0.94	R-9141m AA950308.01 95-0067
Mexico, 1996 (Cruiser)	WP	1.8+1.6 +1.9+1.8 +1.9+1.8	0.62+0.44 +0.55+0.54 +0.54+0.55	6	7	0.89, 0.72	R-9141m AA950308.02 95-0067
Mexico, 1996 (Hiline)	WP	1.8	0.63	6	7	0.30, 0.40	R-9141m AA950308.03 95-0067

Table 18. Folpet residues in tomatoes resulting from supervised trials in Chile, Hungary, Italy, Mexico, The Netherlands, Portugal, Spain and the USA. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, mg/kg folpet	Ref
	Form	kg ai/ha	kg ai/hl	no.			
Chile, 1996 (Conservo)	WP	1.7	1.5	7	7	1.4, 2.4	R-9141t AA950311.06 95-0069
Hungary, 1996 (Kecskemet 407)	WP	0.65	0.13	3	14	<0.05, <0.05	R-9158 MAK/375.01
Hungary, 1996 (Kecskemet 407)	WP	1.3	0.26	3	14	0.098	R-9158 MAK/375.01
Hungary, 1996 (Koral)	WP	1.3	0.26	3	14	0.06	R-9158 MAK/375.02
Hungary, 1996 (Koral)	WP	0.66+0.64 +0.65	0.13	3	14	<0.05, <0.05	R-9158 MAK/375.02
Hungary, 1996 (Prima)	WP	0.65	0.13	3	14	<0.05, <0.05	R-9158 MAK/375.04
Hungary, 1996 (Rio Fiego)	WP	2×0.65 +0.66	0.13	3	14	<0.05, <0.05	R-9158 MAK/375.03
Italy 1995 (Marmande)	WP	1.2	0.13	4	0 7 10 14	1.1 0.62 0.43 0.28	R9099 95046/I1-FFTO ERSA-DA-11/95
Italy 1995 (Rita)	WP	pg 1.2	0.13	4	0 7 10 14 21	1.5 0.38 0.40 0.42 0.50	R9320 95046/I1-FGTO ERSA-DA-01/96
Italy 1995 (Rita)	SC	pg 1.8	0.18	4	0 7 10 14 21	1.1 0.53 0.48 0.39 0.33	R9320 95046/I1-FGTO ERSA-DA-01/96
Italy 1996 (Monica)	WP	pg 1.3	0.13	3 4	8 0 3 7 10 14	0.58 0.57 0.64 0.75 0.59 0.77	R9086 96009/I1-FGTO ERSA-DA-19/96

Country, year (variety)	Application				PHI, days	Residues, mg/kg folpet	Ref
	Form	kg ai/ha	kg ai/hl	no.			
Italy 1996 (Monica)	SC	pg 1.4	0.14	3 4	8 0 3 7 10 14	0.58 0.56 0.65 0.83 0.72 0.79	R9086 96009/I1-FGTO ERSA-DA-19/96
Italy 1996 (Red Setter)	WP	1.3	0.13	3 4	9 0 7 10 14	1.0 1.3 0.83 0.62 0.80	R9095 96009/I1-FFTO ERSA-DA-08/96
Italy 1996 (San Marzano)	WP	1.3	0.13	3 4	8 0 7 10 14	0.57 0.94 0.96 0.70 0.42	R9095 96009/I1-FFTO ERSA-DA-14/96
Italy, 1995 (UC 82 VF)	WP	1.2	0.13	4	0 7 10 14	0.95 0.55 0.60 0.20	R-8987 IT 217/95 DA-12/95
Mexico, 1995 (Rio Grande)	WP	2.0	0.58+0.72 +0.67+0.66 +0.67	5	2	0.86, 1.0	R-9141t AA950311.01 95-0069
Mexico, 1995 (SM10)	WP	2.0	0.96+0.91 +0.80 +2×0.71	5	2	0.81, 1.6	R-9141t AA950311.04 95-0069
Mexico, 1995 (SM10)	WP	2.0	0.96+0.86 +0.77 +2×0.66	5	2	1.1, 1.8	R-9141t AA950311.05 95-0069
Mexico, 1996 (Rio Grande Mejorada)	WP	2.0	2×0.80 +0.76+0.75 +0.71	5	2	0.45, 0.33	R-9141t AA950311.02 95-0069
Mexico, 1996 (Rio Grande Mejorada)	WP	2.0	0.87+0.80 +2×0.75 +0.72	5	2	0.64, 1.3	R-9141t AA950311.03 95-0069
Netherlands 1995 (Trust)	SC	g 1.8	0.12	2 3	7 0 2 4 7	0.77 0.96 0.98 0.88 0.75	R9118 96020/N1-RPT F95-21-NL-05
Netherlands 1995 (Trust) [DJH2]	SC	g 1.8	0.12	2 3	7 0 2 4 7	0.68 0.79 0.52 0.66 0.55	R9118 96020/N1-RPT F95-21-NL-05
Portugal, 1996 (Melero)	WP	1.3	0.16	4	7	0.27, 0.34	R-9158 MAK/375.08
Portugal, 1996 (Petto 95)	WP	1.3	0.16	4	7	0.28, 0.58	R-9158 MAK/375.09
Spain, 1996 (Petto 95)	WP	1.6	0.26 +5×0.20	6	10	1.3, 0.36	R-9158 MAK/375.06
Spain, 1996 (Prieto)	WP	2×1.6 +2×2.2 +2×2.5	0.26 +5×0.16	6	10	0.99, 1.2	R-9158 MAK/375.07
USA, 1995 (Peel Mech)	WP	2.2	0.58	5	7	1.8 <0.05 purée <0.05 paste	R-9101 SARS-95-51 95-0060

pg: plastic greenhouse. g: glasshouse.

Table 19. Folpet residues in head and leaf lettuce resulting from supervised trials in Greece, Hungary, Mexico, Portugal and Spain and from lamb's lettuce from trials in Germany. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

LETTUCE, country, year (variety)	Application				PHI, days	Residues, mg/kg folpet	Ref
	Form	kg ai/ha	kg ai/hl	no.			
HEAD LETTUCE							
Greece, 1996 (Crispa)	SC	0.61	0.12	3	20	<0.05, <0.05	R-9160 MAK/378-07
Hungary, 1996 (Chagal)	WP	0.64 -0.66	0.13	pt 3	14	18 24	MAK/378-01 MAK378/970321
Hungary, 1996 (Chagal)	WP	1.3	0.26	pt 3	14	50	MAK/378-01 MAK378/970321
Hungary, 1996 (Mildred)	WP	0.65 -0.67	0.13	pt 3	14	29 21	MAK/378-02 MAK378/970321
Hungary, 1996 (Mildred)	WP	1.3	0.26	pt 3	14	61	MAK/378-02 MAK378/970321
Hungary, 1997 (Oktavo)	WP	0.65	0.13	pt 3	14	12 9.9	MAK/378-04 MAK378/970321
Hungary, 1997 (Vicky)	WP	0.63 -0.66	0.13	pt 3	14	39 25	MAK/378-03 MAK378/970321
Mexico, 1995 (Great Lakes 407P)	WP	1.3	0.36+0.42 +0.41 +2×0.44	5	7	1.6, 4.5	AA950309.03 95-0066
Mexico, 1996 (Climax)	WP	1.3	0.46+3×0.45 +0.40	5	7	3.2, 9.8	AA950309.02 95-0066
Mexico, 1996 (Top Gun)	WP	1.3	0.44+0.42 +2×0.41 +0.46	5	7	wl[1] (16, 15) xwl (0.22, 0.26)	AA950309.04 95-0066
Portugal, 1996 (Grand rapids)	WP	0.52	0.13	3	14	4.3, 2.4	R-9160 MAK/378-09
LEAF LETTUCE							
Greece, 1996 (Romana)	SC	0.63	0.12	4	20	<0.05, <0.05	R-9160 MAK/378-06
Mexico, 1996 (Parris Island)	WP	1.2	0.58+2×0.57 +0.56+0.60	5	7	19, 22	AA950309.01 95-0066
Spain, 1996 (Romana)	WP	0.78	0.16	4	21	<0.05, <0.05	R-9160 MAK/378-08
LAMB'S LETTUCE							
Germany, 1975 (Polar)	WP	0.68	0.096	3	10	55	BBA 15/75
Germany, 1975 (Hild's Vit-Neuheit)	WP	0.68	0.096	2	10	56	BBA 15/75
Germany, 1976 (Stuttgarter)	WP	0.68	0.15	4	15	54	BBA 15/75
Germany, 1976 (Stuttgarter)	WP	0.68	0.15	4	15	51	BBA 15/75
Germany, 1975 (Felma GS)	WP	0.68	0.11	4	11	10	BBA 15/75
Germany, 1975 (Dunkelgrüner Vollherziger)	WP	0.68	0.11	4	10	66	BBA 15/75
Germany, 1975 (Hollander)	WP	0.68	0.11	4	10	44	BBA 15/75
Germany, 1975 (Holländischer Breitblättriger)	WP	0.68	0.11	4	10	12, 20	BBA 14/75

[1] wl: with wrapper leaves. xwl: without wrapper leaves.

LETTUCE, country, year (variety)	Application				PHI, days	Residues, mg/kg folpet	Ref
	Form	kg ai/ha	kg ai/hl	no.			
Germany, 1975 (Hilmar)	WP	0.68	0.11	4	10	20	BBA 14/75
Germany, 1975 (Dunkelgrüner Vollherziger)	WP	0.68	0.11	4	10	22, 22	BBA 14/75
Germany, 1975 (Felma GS)	WP	0.68	0.11	4	10	211	BBA 14/75
Germany, 1975 (Dunkelgrüner Vollherziger)	WP	0.68	0.11	4	10	188	BBA 14/75
Germany, 1975 (Stuttgarter Markt)	WP	0.68	0.096	3	10	1.3 c 14	BBA 14/75
Germany, 1975 (Stuttgarter Markt)	WP	0.68	0.084	3	10	33 c 6.7	BBA 14/75
Germany, 1975 (Stuttgarter Markt)	WP	0.68	0.096	2	14	5.6	BBA 14/75
Germany, 1975 (Dunkelgroßer Vollherziger)	WP	0.68	0.11	3	15	2.4	BBA 14/75

c: control pt: plastic tunnels

Table 20. Folpet residues in potatoes resulting from supervised trials in Italy, Mexico, Poland, Russia and South Africa. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, mg/kg folpet	Ref
	Form	kg ai/ha	kg ai/hl	no.			
Italy 1995 (Liseta)	WP	1.3	0.13	4	0 7 10 14	<0.01 <0.01 0.08 <0.01	R8988 ERSA-DA-07/95
Italy 1996 (Agata)	WP	1.2	0.13	2 3	8 0 7 10 14	0.04 0.05 <0.01 <0.01 <0.01	R9094 ERSA-DA-06/96 96009/I1-FFPO
Italy 1996 (Arinta)	WP	1.3	0.13	4	0 7 10 14	0.03 <0.01 <0.01 <0.01	R9374 95046/I1-FFPO ERSA-DA-02/96
Italy 1996 (Draga)	WP	1.3	0.13	2 3	8 0 7 10 14	<0.01 <0.01 <0.01 <0.01 <0.01	R9261 ERSA-DA-16/96 6076AB1
Mexico (Mexico State) 1996 (Alpha)	WP	2.4	0.45-0.48	5	30	0.01 <0.01	R9012 AA960303 95-0101
Mexico (Mexico State) 1996 (Alpha)	WP	4.5-5.2	0.90-0.96	5	30	0.01 <0.01	R9012 AA960303 95-0101
Mexico (Nuevo Leon) 1996 (Alpha)	WP	2.3-2.5	0.59-0.61	5	30	<0.01 (2)	R9012 AA960303 95-0101
Mexico (Nuevo Leon) 1996 (Alpha)	WP	4.8	1.2	5	30	<0.01 (2)	R9012 AA960303 95-0101

Country, year (variety)	Application				PHI, days	Residues, mg/kg folpet	Ref
	Form	kg ai/ha	kg ai/hl	no.			
Poland 1996 (Frezja)	WG	1.6		3	15 21	<0.01 <0.01	R9711
Russia 1996 (Detskoselkski)	WP	1.5	0.5	3	0 4 8 10 12	<0.1 <0.1 <0.1 <0.1 <0.1	R9772
Russia 1996 (Rezerv)	WP	1.5	0.38	3	0 10 20 31 40	<0.04 <0.04 <0.04 <0.04 <0.04	R9790
Russia 1996 (Rezerv)	WG	1.5	0.38	3	0 10 20 31 40	<0.04 <0.04 <0.04 <0.04 <0.04	R9790
Russia 1996 (Volzhanin)	WP	1.5	0.38	3	0 4 8 10 12	<0.1 <0.1 <0.1 <0.1 <0.1	R9772
South Africa 1995 (Sandvelder)	SC	1.0	0.2	7	15 22 44	<0.05 (2) <0.05 (2) <0.05 (2)	R9057 ZA-16-D 1095
South Africa 1995 (Sandvelder)	SC	2.0	0.4	7	15 22 44	<0.05 (2) <0.05 (2) <0.05 (2)	R9057

Table 21. Folpet residues in cereal grains resulting from supervised trials in France, Germany and UK. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately.

CEREALS, country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref
	Form	kg ai/ha	kg ai/hl	no.		folpet	phthalimide	
BARLEY, WINTER								
France N 1992 (Alpha)	SC	1.8	0.58	2	53	0.087		R7150 RF2095
France N[1] 1992 (Reinette)	SC	1.8	0.58	2	52	0.19		R7150 RF2095
France N 1992 (Plaisant)	SC	1.8	0.58	2	47	0.75		R7150 RF2095
France N 1992 (Plaisant)	SC	1.8	0.58	2	47	0.63		R7150 RF2095
France N 1993 (Pastoral)	WG	1.8	0.59	2	56	0.021 0.024	<0.02 (2)	R7795[DJH3] RF4019
France S[2] 1993 (Plaisant)	WG	1.8	0.44	2	49	0.12 0.089	<0.02 (2)	R7795 R4019
France S 1993 (Volga)	WG	1.8	0.44	2	40	<0.02 (2)	<0.02 (2)	R7795 R4019
France N 1993 (Pastoral)	SC	1.8	0.58	2	56	0.23 <0.02	<0.02 (2)	R7795 R4019
France S 1993 (Plaisant)	SC	1.8	0.44	2	49	0.20 0.21	<0.02 (2)	R7795 R4019

[1] France N: France, north.

[2] France S: France, south.

CEREALS, country, year (variety)	Form	Application kg ai/ha	kg ai/hl	no.	PHI, days	Residues, mg/kg folpet	phthalimide	Ref
France S 1993	SC	1.8	0.44	2	40	<0.02 0.16	<0.02 (2)	R7795
(Volga)								R4019
France N 1996	SC	0.79	0.32	2	56	0.02 0.03		R9376
(Plaisant)		0.75	0.30					96025/F1-RFWC
France S 1996	SC	0.79	0.39	2	55	0.02 (2)		R9376
(Volga)		0.78	0.31					96025/F1-RFWC
WHEAT, WINTER								
France N 1992	SC	1.8	0.58	2	50	0.050		R7150
(Scipion)								RF2095
France N 1992	SC	1.8	0.58	2	51	<0.04		R7150
(Pepital)								RF2095
France N 1992	SC	1.8	0.58	2	51	<0.04		R7150
(Rossini)								RF2095
France N 1992	SC	1.8	0.58	1	37	0.050		R7150
(Genial)								RF2095
France N 1993	WG	1.8	0.59	2	33	0.20		R7795
(Scipion)					[DJH4]			R4019
France S 1993	WG	1.8	0.44	2	49	0.05		R7795
(Gala)								R4019
France N 1993	SC	1.8	0.58	2	33	1.1		R7795
(Scipion)								R4019
France S 1993	SC	1.8	0.44	2	49	0.03		R7795
(Gala)								R4019
France 1994	SC	0.84	0.24	1	58	<0.02 (3)		R8111
(Thésée)								RF4088-2
France 1994	SC	0.77	0.24	2	43	<0.02 (3)		R8111
(Thésée)		0.68						RF4088-2
France N 1995	SC	0.75	0.3	2	61	<0.02		R8676
								R5072
France S 1995	SC	0.75	0.25	2	44	<0.02		R8676
								R5072
France S 1995	SC	0.75	0.25	2	33	<0.02		R8676
								R5072
France N (Soisson)	SC	0.79	0.32	2	59	0.02 (2)		R9376
1996								96025/F1-RFWC
France S (Tremie)	SC	0.74	0.30	2	56	0.02 (2)		R9376
1996		0.79	0.32					96025/F1-RFWC
Germany 1995	SC	0.75	0.25	2	35	0.02		R8444
(Haven)								95176/01-RP
UK 1995 (Hunter)	WG	1.6	0.8	2	39	0.08		R8559-5
								OA00341/R52855
								OPS/00514/MAK
UK 1995 (variety?)	WG	1.6	0.8	2	39	0.04		R8559-6
					45	0.01		OA00344/R52855
								OPS/00514/MAK
UK 1995 (Spark,	WG	1.6	0.8	2	36	0.07		R8580-1
Torfrida, Turpin)								OA00346/R52862
								OPS/00519/MAK
UK 1995 (Riband)	WG	1.6	0.8	2	39	0.06		R8580-2
					45	0.11		OA00345/R52862
								OPS/00519/MAK

Table 22. Folpet residues in cereal fodder resulting from supervised trials in France, Germany and UK. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately.

CEREAL FODDER, country, year	Application	PHI, days	Residues, mg/kg	Ref

(variety)	Form	kg ai/ha	kg ai/hl	no.		folpet	
BARLEY STRAW							
France N 1992 (Alpha)	SC	1.8	0.58	2	53	0.62	R7150[DJH5] RF2095
France N[1] 1992 (Reinette)	SC	1.8	0.58	2	52	1.2	R7150 RF2095
France N 1992 (Plaisant)	SC	1.8	0.58	2	47	0.56	R7150 RF2095
France N 1992 (Plaisant)	SC	1.8	0.58	2	47	0.28	R7150 RF2095
France N 1993 (Pastoral)	WG	1.8	0.59	2	56	3.0 c0.19	R7795 R4019
France S[1] 1993 (Plaisant)	WG	1.8	0.44	2	49	13 c0.25	R7795 R4019
France S 1993 (Volga)	WG	1.8	0.44	2	40	4.3 c0.10	R7795 R4019
France N 1993 (Pastoral)	SC	1.8	0.58	2	56	0.90 c0.19	R7795 R4019
France S 1993 (Plaisant)	SC	1.8	0.44	2	49	1.6 c0.25	R7795 R4019
France S 1993 (Volga)	SC	1.8	0.44	2	40	9.8 c0.10	R7795 R4019
France N 1996 (Plaisant)	SC	0.79 0.75	0.32 0.30	2	56	3.5 4.5	R9376 96025/F1-RFWC
France S 1996 (Volga)	SC	0.79 0.78	0.39 0.31	2	55	2.4 2.9	R9376 96025/F1-RFWC
WHEAT STRAW							
France N 1992 (Scipion)	SC	1.8	0.58	2	50	1.3	R7150 RF2095
France N 1992 (Pepital)	SC	1.8	0.58	2	51	1.8	R7150 RF2095
France N 1992 (Rossini)	SC	1.8	0.58	2	51	1.5	R7150 RF2095
France N 1992 (Genial)	SC	1.8	0.58	1	37	0.90	R7150 RF2095
France N 1993 (Scipion)	WG	1.8	0.59	2	33	5.6 c0.16	R7795 R4019
France S 1993 (Gala)	WG	1.8	0.44	2	49	14	R7795 R4019
France N 1993 (Scipion)	SC	1.8	0.58	2	33	10 c0.16	R7795 R4019
France S 1993 (Gala)	SC	1.8	0.44	2	49	7.0	R7795 R4019
France 1994 (Thésée)	SC	0.84	0.24	1	58	1.2 1.3 1.1 c0.22	R8111 RF4088-2
France 1994 (Thésée)	SC	0.77 0.68	0.24	2	43	2.8 2.9 3.1 c0.16	R8111 RF4088-2
France N 1995	SC	0.75	0.3	2	61	3.1 c0.47	R8676 R5072
France S 1995	SC	0.75	0.25	2	44	3.5 c0.70	R8676 R5072
France S 1995	SC	0.75	0.25	2	33	1.1 c0.19	R8676 R5072
France N (Soisson) 1996	SC	0.79	0.32	2	59	2.1 3.2	R9376 96025/F1-RFWC
France S (Tremie) 1996	SC	0.74 0.79	0.30 0.32	2	56	4.3 3.9	R9376 96025/F1-RFWC
Germany 1995 (Haven)	SC	0.75	0.25	2	35	4.6	R8444 95176/01-RP
UK 1995 (Hunter)	WG	1.6	0.8	2	39	4.3	R8559-5 OA00341/R52855 OPS/00514/MAK

[1] France S: France, south.

CEREAL FODDER, country, year (variety)	Application Form	kg ai/ha	kg ai/hl	no.	PHI, days	Residues, mg/kg folpet	Ref
UK 1995	WG	1.6	0.8	2	39	0.90 c0.11	R8559-6
					45	5.4 c0.28	OA00344/R52855
							OPS/00514/MAK
UK 1995 (Spark, Torfrida, Turpin)	WG	1.6	0.8	2	36	16	R8580-1
							OA00346/R52862
							OPS/00519/MAK
UK 1995 (Riband)	WG	1.6	0.8	2	39	11	R8580-2
					45	5.8	OA00345/R52862
							OPS/00519/MAK

c: sample from control plot

Table 23. Folpet residues in cereal forage resulting from supervised trials in France, Germany and UK. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately.

CEREAL FORAGE, country, year (variety)	Application Form	kg ai/ha	kg ai/hl	no.	PHI, days	Residues, mg/kg folpet	Ref
BARLEY WHOLE PLANT							
France N 1993	WG	1.8	0.59	2	36	1.3	R7795
(Pastoral)					47	2.7 c0.35	R4019
France N 1993	SC	1.8	0.58	2	36	1.6	R7795
(Pastoral)					47	1.8 c0.35	R4019
WHEAT WHOLE PLANT							
France N 1993	WG	1.8	0.59	2	25	4.4	R7795
(Scipion)					33	4.4 c0.06	R4019
France S 1993	WG	1.8	0.44	2	19	32 c0.23	R7795
(Gala)					34	13	R4019
France N 1993	SC	1.8	0.58	2	25	6.7	R7795
(Scipion)					33	8.9 c0.06	R4019
France S 1993	SC	1.8	0.44	2	19	16 c0.23	R7795
(Gala)					34	8.0	R4019
France 1994	SC	0.84	0.24	1	1 hr	8.6 9.9 10 c0.18	R8111
(Thésée)					30	2.1 1.7 1.6 c0.21	RF4088-2
France 1994	SC	0.77	0.24	2	1 hour	11 11 13 c0.15	R8111
(Thésée)		0.68			30	1.3 1.2 3.0 c0.18	RF4088-2
Germany 1995	SC	0.75	0.25	1	27	1.1	R8444
(Haven)				22	3 hr	5.4	95176/01-RP
					10	2.1 e2.3	
					21	1.7 e1.9 c0.12	
UK 1995	WG	1.6	0.8	1	25	18	R8559-6
				2	1 hr	58	OA00344/R52855
					19	e2.3 stem 22	OPS/00514/MAK
UK 1995 (Riband)	WG	1.6	0.8	1	25	11	R8580-2
				2	1 hr	29	OA00345/R52862
					19	e0.28 stem 11	OPS/00519/MAK

c: control sample. e: ears.

Table 24. Interpretation table for folpet residues on apples, grapes, strawberries, onions, cucumbers, melons, tomatoes, lettuce and potatoes from trials in Tables 13-20 and from 1993 Evaluations. GAP and trial conditions are compared for treatments considered valid for estimation of maximum residue levels and STMRs.

Crop	Country	Use pattern kg ai/ha	kg ai/hl	No of appl	PHI days	Trial	folpet, mg/kg

Crop	Country	Use pattern				Trial	folpet,
		kg ai/ha	kg ai/hl	No of appl	PHI days		mg/kg
Apple	Argentina GAP		0.12		15		
Apple	Argentina trial	3.6	0.12	3	10	AA950314.07	1.4
Apple	Argentina trial	3.6	0.12	3	10	AA950314.08	2.6
Apple	Hungary GAP	1.5			10		
Apple	Hungary trial	1.6	0.10	8	10	MAK374-01	8.0
Apple	Portugal GAP		0.13		21		
Apple	[1]Portugal trial	1.3	0.13	10	21	FP/25/91	1.8
Apple	Portugal trial	1.6	0.13	8	21	MAK/374-05	3.2
Apple	Spain GAP		0.15		10		
Apple	Spain trial	1.9	0.16	6	10	MAK/374-04	3.1
Apple	Switzerland GAP		0.08		21		
Apple	Switzerland trial	2.0	0.10	4	21	MAK/374-03	3.4
Grapes	Argentina GAP		0.13		7		
Grapes	Argentina trial	1.0	0.13	4	7	AA950313.07	1.6
Grape	France GAP	1.5			21		
Grape	France trial	1.5		8	27	R7194	1.9
Grape	France trial	1.5		7	21	R7194	1.6
Grape	France trial	1.6	0.50	8	21	R-9146 FR03	2.2
Grape	France trial	1.4	0.50	8	21	R-9146 FR02	2.4
Grape	France trial	1.5	0.47	8	21	R-9146 FR01	3.1
Grape	France trial	1.5	0.60	9	21	R-9146 FR04	2.8
Grape	France trial	1.9-2.0	0.57-0.76	8	21	R9098	5.8
Grape	France trial	1.9	0.55-0.78	8	21 (28)[2]	R9098	3.5
Grape	France trial	1.4-1.6	0.57-0.63	8	21	R9098	1.9
Grape	France trial	1.6-2.0	0.64-0.84	8	21	R9098	4.6
Grape	France trial	1.7-1.9	0.49-0.76	8	21	R9098	5.7
Grape	France trial	1.3-1.6	0.54-0.65	8	21	R9098	5.9
Grapes	Italy GAP		0.16		10		
Grapes	Italy trial	1.6	0.16	5	10	AA950313.03	3.3
Strawberries	Spain GAP		0.15		21		
Strawberries	Italy trial	0.89	0.15	3	21	R-8989	<0.01
Strawberries	Italy trial	0.76	0.13	3	21	R9093	0.04
Strawberries	Italy trial	0.75	0.13	3	21	R9383	0.09
Strawberries	Mexico GAP	1.3			no limit		
Strawberries	Mexico trial	1.2	0.62	4	2	950310.01	1.8
Strawberries	Mexico trial	1.2	0.26	4	2	950310.02	1.6
Strawberries	Mexico trial	1.2	0.33	4	2	950310.03	2.2
Strawberries	Netherlands GAP		0.13	g	14		
Strawberries	Netherlands trial	1.4	0.13	2 pt	14	MAK/372.01	1.9
Strawberries	Netherlands trial	1.3	0.13	2 pt	14	MAK/372.01	1.6
Strawberries	Netherlands trial	1.3	0.13	2 pt	14	MAK/372.02	1.4
Onions	Chile GAP	2.0	0.13		7		
Onions	Chile trial	2.0	0.13	3	7	AA950307.03	0.36
Onions	Portugal GAP		0.13		7		
Onions	Portugal trial	0.54	0.13	3	7	MAK/377-08	5.0
Onions	Spain trial	0.65	0.16	3	10	MAK/377-09	2.5
Melons	Greece GAP		0.16		20		
Melons	Greece trial	0.98	0.12	4	20	MAK/373-01	<0.05
Melons	Greece trial	0.97	0.12	4	20	MAK/373-02	<0.05
Tomato	Chile GAP	1.7	0.15		7		
Tomato	Chile trial	1.7	1.5	7	7	R-9141t	2.4
Tomato	Hungary GAP		0.13		14		
Tomato	Hungary trial	0.65	0.13	3	14	MAK/375.01	<0.05
Tomato	Hungary trial	0.65	0.13	3	14	MAK/375.04	<0.05
Tomato	Hungary trial	0.65	0.13	3	14	MAK/375.02	<0.05
Tomato	Hungary trial	0.66	0.13	3	14	MAK/375.03	<0.05
Tomato	[1]Hungary trial	0.63	0.12	5	14	FP/26/91	<0.02
Tomato	Mexico GAP	2.0			no limit		
Tomato	Mexico trial	2.0	0.67	5	2	AA950311.01	1.0

[1] From 1993 JMPR

[2] The residue on day 28 (3.5 mg/kg) exceeded the residue on day 21 (2.6 mg/kg).

Crop	Country	Use pattern				Trial	folpet, mg/kg
		kg ai/ha	kg ai/hl	No of appl	PHI days		
Tomato	Mexico trial	2.0	0.71	5	2	AA950311.04	1.6
Tomato	Mexico trial	2.0	0.66	5	2	AA950311.05	1.8
Tomato	Mexico trial	2.0	0.71	5	2	AA950311.02	0.45
Tomato	Mexico trial	2.0	0.72	5	2	AA950311.03	1.3
Tomato	Portugal GAP		0.13		7		
Tomato	Portugal trial	1.3	0.16	4	7	MAK/375.08	0.34
Tomato	Portugal trial	1.3	0.16	4	7	MAK/375.09	0.58
Tomato	Spain GAP		0.15		10		
Tomato	Italy trial	1.2	0.13	4	10	R-8987	0.60
Tomato	Italy trial	1.3	0.13	4	10	ERSA-DA-14/96	0.70
Tomato	Italy trial	1.3	0.13	4	10 (14)[1]	ERSA-DA-08/96	0.80
Tomato	Italy trial	1.2	0.13	4	10	ERSA-DA-11/95	0.43
Tomato	Spain trial	1.6	0.20	6	10	MAK/375.06	1.3
Tomato	Spain trial	2.5	0.16	6	10	MAK/375.07	1.2
Lettuce	Portugal GAP		0.13		14		
Lettuce, Head	Portugal trial	0.52	0.13	3	14	MAK/378-09	4.3
Lettuce	Spain GAP		0.15		21		
Lettuce, Leaf	Spain trial	0.78	0.16	4	21	MAK/378-08	<0.05
Potato	Spain GAP		0.15		10		
Potato	Italy trial	1.3	0.13	4	10	R8988	0.08
Potato	Italy trial	1.2	0.13	3	10	R9094	<0.01
Potato	Italy trial	1.3	0.13	3	10	R9261	<0.01
Potato	Italy trial	1.3	0.13	4	10	R9374	<0.01

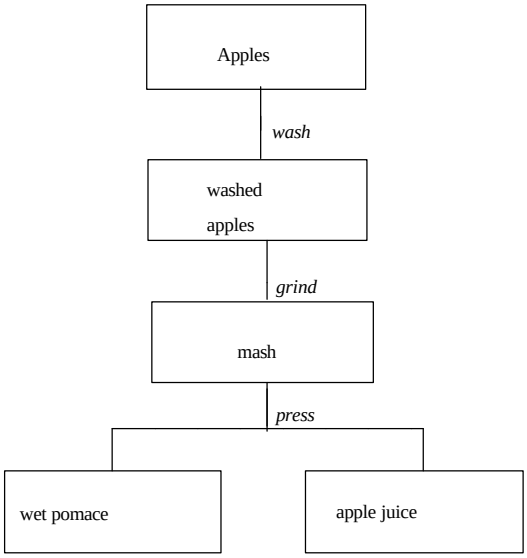
g: glasshouse use pt: plastic tunnel use

FATE OF RESIDUES IN STORAGE AND PROCESSING

The Meeting received information on the fate of folpet during the processing of apples, grapes and tomatoes.

[1] The residue on day 14 (0.80 mg/kg) exceeded the residue on day 10 (0.62 mg/kg).

Leppert (1996a) applied folpet four times at 2.9 kg ai/ha (spray 0.31 kg ai/hl) with airblast equipment to an apple orchard in a processing trial in the USA (NY). The treated plot was 357 m^2. Apples harvested 7 days after the final application (49 kg) were processed into wet pomace and juice. Residue levels on the unwashed and washed apples and processed commodities are shown in Table 13 (Hurley and Farthing 1996e, trial SARS-95-50).



Armstrong and Luke (1995) processed the apples to simulate commercial practice as closely as possible. Apples were washed, then ground in a hammer-mill to produce a wet mash. The wet mash was pressed in a hydraulic press to separate the juice and wet pomace. The results are shown in Table 25.

Table 25. Folpet residues in apples, pomace and juice after processing (Leppert 1996a, Armstrong and Luke 1995, Hurley and Farthing 1996e).

Commodity	Folpet, mg/kg	Processing factor
Apples, unwashed	2.1	
Apples, washed	1.2	0.60
Wet pomace	5.4	2.6
Apple juice	0.072	0.035

Singer (1997g) dipped 74 kg grapes (Thomson Seedless) in 7-10 kg portions for 30 seconds into a vat containing folpet spray mixture at 1.25 kg ai/hl, 5 times the maximum permitted concentration on grapes in Mexico. The grapes were then allowed to dry on polythene sheeting. Because folpet was shown in the metabolism studies to be a surface residue it was considered valid to treat grapes in this way instead of by field spraying. Abdelrahim (1996) processed the grapes into raisins and juice.

Bunches of the unwashed grapes were weighed and dried in the sun to unprocessed raisins. Grapes and stems were spread out on stainless steel screens on tables covered with black plastic and dried until the moisture level had dropped to 12-16%. Samples of the unprocessed raisins were then placed in the freezer. The remainder of the dried grapes were collected in plastic bags and kept in an incubator at 21°C until removed for destemming and sampling. After destemming, the dried grapes were returned to the incubator at 21°C and were subsequently rehydrated to 18-20% moisture to produce raisins.

Grapes were processed in a crusher/destemmer, which crushes the berries and separates the stems from the crushed berries and juice. Crushed berries and juice were treated with an enzyme and heated at 60°C for 2 hours to remove pectin and then separated by pressing into unclarified juice and pomace. The juice was heated at 88°C to inactivate the enzyme and filtered through diatomaceous earth, then placed in cold storage for 6 weeks to allow settling. Clear juice was then produced by filtration through diatomaceous earth, heated to canning temperature (94°C) and canned. Folpet residues in the grapes and processed commodities are shown in Table 26 (Farthing, 1996d).

Table 26. Folpet residues in grapes, juice and raisins produced from grapes dipped in a vat containing a 1.25 kg ai/hl folpet spray mixture (Singer 1997g, Abdelrahim 1996, Farthing, 1996d).

Commodity	Folpet, mg/kg	Processing factor
Grapes	19, 12, 15, 17, 14, 14	
Grape juice	<0.05 (3)	0 (<0.003)
Raisins (before rehydration)	58, 41, 46	3.2
Raisins (hydrated)	31, 28, 27	1.9

Folpet residues were not detected in the grape juice and were presumably lost in filtration or heating. Residues were concentrated during the drying process to produce raisins. The processing factors are included in Table 26.

In two trials in France, Wasser (1996a) treated grapes 6 times with folpet (SC and WG formulations) at 1.5 kg ai/ha and harvested the grapes 52 days after the final application. Residues were measured in the grapes and must, wine and spirits. The results are shown in Table 14 (trial R 5011). Some folpet residues appeared in the must, but none in the wine or spirits.

Folpet and phthalimide residues were measured in treated grapes and the must and wine produced from them in a series of trials in Germany. Treatment details are recorded in Table 14. Residue data for the processed commodities and the processing factors are shown in Table 27.

Table 27. Residue data and processing factors for folpet and phthalimide in grapes, must and wine after grapes were sprayed with folpet. Application details are provided in Table 14.

Commodity	Residues, mg/kg		Processing factor	Processing yield	Reference
	folpet	phthalimide	folpet	phthalimide	
Grapes	5.6	0.2			R-7993
Must	0.83	0.72	g→m 0.15	g→m 0.24	HVA 7/94
Wine	<0.05	0.76	g→w 0 (<0.009)	g→w 0.26	UHL07
Grapes	0.66	<0.1			R-7993
Must	0.68	0.27	g→m 0.97	g→m 0.83	HVA 7/94
Wine	<0.05	0.29	g→w 0 (<0.08)	g→w 0.89	UHL08
Grapes	2.0	<0.1			R-7993
Must	<0.05	1.8	g→m 0 (<0.03)	g→m 1.8	HVA 7/94
Wine	<0.05	0.99	g→w 0 (<0.03)	g→w 0.99	UHL09
Grapes	1.5	0.1			R-7993
Must	0.58	0.44	g→m 0.39	g→m 0.52	HVA 7/94
Wine	<0.05	0.47	g→w 0 (<0.03)	g→w 0.56	UHL10
Grapes	1.3	<0.1			R-7993
Must	<0.05	0.51	g→m 0 (<0.04)	g→m 0.79	HVA 7/94
Wine	<0.05	0.34	g→w 0 (<0.04)	g→w 0.53	UHL11
Grapes	1.1	<0.1			R-7993
Must	0.27	0.39	g→m 0.25	g→m 0.72	HVA 7/94
Wine	<0.05	0.39	g→w 0 (<0.05)	g→w 0.72	UHL12
Grapes	3.3	0.1			R-7993
Must	1.0	0.92	g→m 0.30	g→m 0.53	HVA 7/94
Wine	<0.05	0.83	g→w 0 (<0.02)	g→w 0.48	UHL13
Grapes	1.2	<0.1			R-7993
Must	0.25	0.26	g→m 0.21	g→m 0.44	HVA 7/94
Wine	<0.05	0.31	g→w 0 (<0.04)	g→w 0.52	UHL14
Grapes	0.29	<0.1			R-7993
Must	<0.05	0.44	g→m 0 (<0.17)	g→m 3.1	HVA 7/94
Wine	<0.05	0.33	g→w 0 (<0.17)	g→w 2.3	UHL15

Commodity	Residues, mg/kg		Processing factor	Processing yield	Reference
	folpet	phthalimide	folpet	phthalimide	
Grapes	0.42	<0.1			R-7993
Must	0.27	0.37	g→m 0.64	g→m 1.8	HVA 7/94
Wine	<0.05	0.35	g→w 0 (<0.12)	g→w 1.7	UHL16

The processing factors for folpet residues from grapes to must and wine were 0, 0, 0, 0.15, 0.21, 0.25, 0.30, 0.39, 0.64 and 0.97, mean 0.29. Folpet was not detected in the wine so the processing factor is 0.

Phthalimide residues in must or wine may arise from phthalimide or folpet in the grapes either by transfer of the phthalimide or by conversion of folpet to phthalimide during the process. A processing yield for phthalimide has been calculated using the following formula.

$$\text{Processing yield} = \frac{\text{phthalimide residues in must or wine}}{(\text{folpet residues in grapes x } 0.496) + (\text{phthalimide residues in grapes})}$$

The factor 0.496 is the ratio of the molecular weight of phthalimide (147.13) to that of folpet (296.55).

The processing yields for phthalimide from grapes to must were 0.24, 0.44, 0.52, 0.53, 0.72, 0.79, 0.83, 1.8, 1.8 and 3.1, mean 1.1.

The processing yields for phthalimide from grapes to wine were 0.26, 0.48, 0.52, 0.53, 0.56, 0.72, 0.89, 0.99, 1.7 and 2.3, mean 0.90. This value suggests that most of the folpet on the grapes is converted to phthalimide, which finds its way into wine during the vinification process.

Leppert (1996b) applied folpet five times at 2.2 kg ai/ha (spray 0.58 kg ai/hl) to tomato plants in a processing trial in California. The treated plot was 186 m^2. Fruit were harvested 7 days after the final application (152 kg) and processed into tomato purée and paste. Residue levels in the unwashed tomatoes and processed commodities are shown in Table 18 (trial SARS-95-51).

Tomatoes were initially soaked in 0.5% sodium hydroxide for 3 minutes and then rinsed with a high pressure spray rinse for 30 seconds. The tomatoes were crushed, rapidly heated and held for 15 seconds in a steam jacketed kettle and then separated into pulp and juice. Purée was produced from juice by evaporation and adjustment of salt and water levels, then heated and canned. Paste was produced similarly, but with a higher salt level.

Folpet residues were not detected (<0.05 mg/kg) in tomato purée or paste produced from tomatoes containing 1.8 mg/kg of folpet. It is quite likely that the initial vigorous cleaning of the tomatoes would remove or destroy most of the folpet residues. The calculated processing factor for the transfer of folpet from tomatoes to purée and paste is 0 (<0.028).

Residues in the edible portion of food commodities

A head lettuce trial in Mexico provided evidence that almost all of the folpet residue was on the wrapper leaves.

The processing factor for folpet residues from unwashed apples to apple juice was 0.035.

Folpet residues were not detected (<0.05 mg/kg) in grape juice produced from folpet-treated grapes containing 12-19 mg/kg. The processing factors for producing dry raisins and hydrated raisins were 3.2 and 1.9 respectively. Folpet residues were not detected (<0.01 mg/kg) in wine or spirits produced from treated grapes in France.

Folpet residues were not detected (<0.05 mg/kg) in wine produced from treated grapes in a series of trials in Germany. The mean processing yield for phthalimide from grapes to wine was 0.90, suggesting that most of the folpet on the grapes is converted to phthalimide which finds its way into wine during the vinification process.

Folpet residues were not detected (<0.05 mg/kg) in tomato purée or paste produced from tomatoes containing 1.8 mg/kg of folpet.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Cugier (1992) reported a 3-year survey for 1990-1992 of residues in grapes and wine in France. Of the 57 grape samples analysed for folpet, residues were detected (LOD 0.05 mg/kg) in 13 and none exceeded the MRL in France of 3 mg/kg. Folpet was not detected (LOD 0.02 mg/kg) in the 7 wines analysed.

Monitoring for folpet residues on food in commerce for the years 1994-1996 in The Netherlands was reported:

Commodity	Number of samples				MRL, mg/kg 1/
	Analysed	residues not detected <0.01 mg/kg	residues detected, but <MRL	residues >MRL	
Apricots	91	89	2	0	2
Grapes	765	763	2	0	3
Strawberries	2743	2736	6	1	3
Tomatoes	1247	1246	1	0	3
Aubergines	176	176	0	0	0.1*
Cucumbers	1089	1089	0	0	0.1*
Courgettes	259	257	0	0	0.1*
Lettuce	3843	3820	24	0	2
Iceberg lettuce	535	528	7	1	2
Spinach	532	530	0	2	0.1*

* MRL at LOD
1/ residue definition: sum of captan and folpet.

NATIONAL MAXIMUM RESIDUE LIMITS

The following MRLs for folpet have been established for apples, cucumbers, grapes, lettuce, melons, onions, strawberries and tomatoes.

Country	MRL, mg/kg							
	apple	cucumber	grape	lettuce	melon	onion	strawberry	tomato
Argentina	10	15	15		15	2	15	15
Austria	3	0.1	3	2	0.1	0.1	3	3
Belgium	3	0.1	3	2	0.1	0.1	3	3
Brazil	10	2	15	15	2	2	20	
Canada	25	15	25	25	15		25	25
Chile	25		25		15		25	25
Costa Rica	25	15	25	50	15	15	25	25
Croatia	2		2					
Czech Rep	2		2					
Ecuador	25	15	25	50	25	25	25	25
EEC[1]	3		3	2			3	3
France	3	0.1	3	2	0.1	0.1	3	3
Greece		3	3	2	3	3	3	3
Guatemala	25	15	25	50	15	15	25	25
Hungary	2	2	5t, 2w[2]	5	5	5	5	5
Israel	10	0.5						
Italy	3	0.1	3	2	0.1	0.1	0.1	3
Korea	5	5	5	2	2	2	5	2
Macedonia	2		2					
Mexico	25	15	25	50	15	15	25	25
Portugal	3		3	2	0.1	0.1	0.1	3
Romania	2		2					
Slovakia	2		2					
Sth Africa			15					
Spain	3	0.1	3	2	0.1	0.1	3	3
Sweden	3	0.1	3	2	0.1	0.1	3	3
Switzerland	3		15		3			
Uruguay	10	2	25	15	2	2	20	20
USA	25	15	25	50	25	25	25	25
Yugoslavia	2		2					

Germany and The Netherlands provided the following information on national MRLs (January 1998).

Country	MRL, mg/kg	Commodity
Germany[3]	3	pome fruit, small fruits and berries, tomatoes
	2	beans (fresh), leek, lettuce, peas (fresh), scarole, stonefruit, witloof,
	0.1	other foods of plant origin
Netherlands[3]	3	pome fruit, berries and other small fruit (other than wild), tomatoes
	2	stone fruit, endive, head lettuce, iceberg lettuce, cos-lettuce, witloof, leeks, legume vegetables
	0.1*	other fruit, other vegetables
	0*(0.1)	other food commodities

* at or about the LOD

[1] Directive 76/893/EEC

[2] t - table grapes. w - wine grapes.

[3] Residue definition: sum of captan and folpet.

APPRAISAL

Folpet was first evaluated in 1969 and has been reviewed several times since. It was listed by the 1997 CCPR (29th Session, ALINORM 97/24A, Appendix III) for periodic re-evaluation for residues by the 1998 JMPR. Residue aspects were reviewed in 1997, when it was agreed that the 1997 review would be included in the 1998 Periodic Review for completeness. The Meeting received information on metabolism, analytical methods, freezer storage stability, registered uses, data from supervised trials on fruit and vegetable crops and processing studies.

When a lactating goat was dosed orally with [*tricloromethyl*-^{14}C]folpet at 0.55 mg/kg bw (equivalent to 20 ppm in the feed) daily for 3 days, most of the dose was rapidly excreted in the faeces (42% of the dose) and in expired air (31%). ^{14}C levels in the milk were 0.23-0.38 mg/kg as folpet and accounted for 1% of the dose. The tissues contained ^{14}C at 0.8% of the dose with most in the liver and kidneys (0.34 and 0.26 mg/kg respectively, expressed as folpet).

When a lactating goat was dosed orally with [*benzene*-^{14}C]folpet at 0.34 mg/kg bw (equivalent to 14 ppm in the feed) daily for 6 days 93% of the ^{14}C was excreted in the urine and faeces. The ^{14}C in the tissues and milk constituted less than 0.1% of the dose. ^{14}C levels (expressed as folpet) in the milk, liver and kidneys were 0.004-0.006, 0.022 and 0.052 mg/kg respectively.

The metabolism studies showed that folpet is rapidly degraded in goats, initially by loss of the CCl_3 group. The carbon from the CCl_3 becomes incorporated into thiazolidine and natural products. The remainder of the molecule was metabolized to phthalimide and phthalamic acid.

When the roots of tomato plants were treated with [*carbonyl*-^{14}C]folpet the ^{14}C was rapidly absorbed into the plants (85% within 1 day). After 11 days 90% of the absorbed ^{14}C was in the tops. Folpet itself was a very minor part (<0.1-0.2%) of the residue within the plant. The main identified components were phthalimide, phthalamic acid and phthalic acid. Unidentified polar metabolites, possibly ring-hydroxylated phthalamic acid derivatives, accounted for 15-30% of the ^{14}C in the tops.

Levels of ^{14}C were lower in the roots than in the straw or grain of wheat treated with [*benzene*-^{14}C]folpet at a rate equivalent to 1.6 kg ai/ha and harvested 43 and 54 days after the second treatment. Folpet was the major component of the residue in or on the straw (4.7 mg/kg) and grain (9.3 mg/kg), with phthalic acid (4.3 mg/kg in straw and 6.4 mg/kg in grain) and phthalimide (1.5 mg/kg in straw and 3.1 mg/kg in grain) also prominent.

When Thomson Seedless grape vines were treated 3 times with [*benzene*-^{14}C]folpet at a rate equivalent to 1.5 kg ai/ha and the grapes harvested 25 days after the final treatment, surface rinsing removed 26% of the grape residue. Folpet itself constituted 27% of the residue in or on the grapes, and phthalic acid and phthalimide 5.8% and 11% respectively. An unidentified compound in the water-soluble fraction accounted for 41% of the residue. It was very polar and yielded phthalic acid on hydrolysis, so was likely to be a conjugate or conjugates of phthalic acid.

A small avocado tree was treated with 3 foliar applications equivalent to 3.4 kg ai/ha of [*benzene*-^{14}C]folpet and fruit were harvested at maturity 97 days after the final application. Very little residue was removed by rinsing the fruit, but most was extractable with ethyl acetate from the peel and pulp. The residues in or on the fruit were folpet 0.026 mg/kg, phthalimide 0.22 mg/kg and phthalic acid 4.5 mg/kg. Polar and other unidentified residues amounted to about 0.7 mg/kg. Folpet and phthalimide residues were mainly on the peel, but most of the phthalic acid was in the pulp.

No information was provided on the environmental fate of folpet in soil or water/sediment systems. Such studies are needed for a periodic review (page 13 of *FAO Manual on the Submission and Evaluation of Pesticide Residues Data for the Estimation of Maximum Residue Levels in Food*

and Feed). The Meeting was informed at a late stage that studies were available on aerobic and anaerobic degradation and photolysis in soil, field dissipation, adsorption, desorption and mobility in soil, leaching of aged residues and aqueous photolysis.

The Meeting agreed to withdraw its previous recommendations for MRLs and agreed that maximum residue levels estimated from the trials could not be recommended as suitable for establishing MRLs until these critical supporting studies had been evaluated.

The 1993 JMPR reviewed the Schlesinger analytical method for residues of folpet and phthalimide. The methods used in the supervised trials on apples, lettuce, melons, onions, strawberries and tomatoes were developed from the Schlesinger method. Folpet was determined in the cleaned up extract by GLC with an ECD. Methods were validated for all the above commodities and some others. The recovery of folpet from various fortified commodities was commonly 70-100%, but with some excursions outside this range. In a total of 340 recovery tests the mean and median were 87% and 86% respectively. The LOD was 0.05 mg/kg.

Care is needed that there is no opportunity for conversion of folpet to phthalimide during analysis because folpet is very susceptible to hydrolysis.

Cereal grains and straw in the UK trials were analysed by an HPLC method with an LOD of 0.05 mg/kg. Folpet residues were extracted with ethyl acetate and clean-up was effected by gel permeation chromatography. Separations were on a reversed-phase column with an acetonitrile-water mobile phase.

Folpet is included in an official multi-residue method of The Netherlands for pesticides amenable to gas chromatography. LODs for various matrices are 0.01-0.05 mg/kg.

Folpet residues were shown to be stable during frozen storage for the intervals tested in apple juice (30 days), wet apple pomace (35 days), apples (149 days), cranberries (176 days), cucumbers (29 days), grape juice (36 days), lettuce (90 days), onions (41 days), potatoes (55 days), tomato paste (30 days), tomato purée (31 days), tomatoes (136 days), chopped wheat grain (366 days) and chopped wheat straw (366 days).

The Meeting agreed that the current definition of the residue is suitable for enforcing compliance with MRLs and for estimation of dietary intake.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: *folpet*

Information was made available to the Meeting on registered uses of folpet and on supervised trials on apples, grapes, strawberries, onions, cucumbers, melons, tomatoes, lettuce, potatoes, barley, wheat, cereal fodder and cereal forage. Relevant data from the 1993 and 1994 monographs were also included where possible to support the evaluations.

Trials on apples were reported from Argentina, Canada, Chile, France, Hungary, Germany, Poland, Portugal, Spain, Switzerland and the USA. Six trials in Germany and one in Poland suggest that folpet residues on apples decrease quite slowly and that some latitude in the PHI can be accepted in evaluating the trials.

Folpet is registered in Argentina for use on apples with a spray concentration of 0.12 kg ai/hl and a PHI of 15 days. Residues in apples from 2 trials where the spray concentration accorded with GAP but the PHI was 10 days (sufficiently close for a persistent residue) were 1.4 and 2.6 mg/kg.

The Canadian trials were based on a PHI of 7 days, which was too remote from Canadian GAP (1 day) to be used. Trials in France, Germany and the USA were not evaluated because labels with relevant GAP were not available. No field report was available for the trial in Poland.

Two trials on apples in Chile where the trial conditions corresponded to the registered application rate (2.0 kg ai/ha), but the harvest was 7 days after the final application instead of the official 3 days, could not be evaluated because the difference in the PHI was too great .

In a Hungarian trial according to GAP (application at 1.6 kg ai/ha and a PHI of 10 days), the highest folpet residue on apples was 8.0 mg/kg. In a Swiss trial which complied with GAP (spray concentration of 0.10 kg ai/hl and a PHI of 21 days), the residue was 3.4 mg/kg, and in a Spanish trial complying with GAP (spray concentration of 0.16 kg ai/hl and a PHI of 10 days), the highest residue was 3.1 mg/kg.

Folpet may be sprayed at 0.13 kg ai/hl on apples in Portugal with the harvest 21 days after the final application. In a trial meeting these conditions the folpet residue on apples was 3.2 mg/kg. In a trial recorded in the 1993 Evaluations folpet was applied 10 times at a concentration of 0.13 kg ai/hl and the resulting residue 21 days after the final application was 1.8 mg/kg

In summary, the folpet residues in apples from trials according to GAP were Argentina 1.4 and 2.6 mg/kg, Chile 2.0 and 3.7 mg/kg, Hungary 8.0 mg/kg, Switzerland 3.4 mg/kg, Spain 3.1 mg/kg and Portugal 1.8 and 3.2 mg/kg. The residues in rank order (median underlined) in the 7 trials were 1.4, 1.8, 2.6, <u>3.1</u>, 3.2, 3.4 and 8.0 mg/kg.

The Meeting estimated a maximum residue level for folpet in apples of 10 mg/kg but could not recommend it as suitable for use as an MRL until the critical supporting studies on environmental fate have been evaluated.

The folpet residue in grapes was 1.6 mg/kg in a supervised trial that complied with GAP in Argentina (spray concentration 0.13 kg ai/hl and PHI 7 days).

Italian GAP permits application to table grapes at a spray concentration of 0.16 kg ai/hl with harvest 10 days after the final application. In an Italian trial under these conditions the folpet residue was 3.3 mg/kg. A second Italian trial could not be evaluated because the PHI of 41 days was too long.

Folpet may be used on grapes in France at 1.0-1.5 kg ai/ha (SC and WG formulations) or 1.0-1.8 kg ai/ha (WP formulations) with specified PHIs of 21 and 30 days for SC, 21 and 28 days for WG and 28 days for WP. Variations of rate and PHI may depend on other fungicides in the same formulation. Trials in France in 1992, 1994, 1995 and 1996 were accepted as complying with maximum GAP conditions where the application rate was within 30% of 1.5 kg ai/ha and the PHI was 16-28 days. The residues in grapes from 12 trials meeting these conditions in rank order (median underlined) were 1.6, 1.9, 1.9, 2.2, 2.4, <u>2.8</u>, <u>3.1</u>, 3.5, 4.6, 5.7, 5.8 and 5.9 mg/kg.

Trials in Chile could not be evaluated because the interval between final application and harvest was 14 days whereas GAP specifies 3 days. Trials in Germany and Russia could not be evaluated because relevant GAP and registered labels were not available.

In summary, the folpet residues in grapes from trials according to GAP were Argentina 1.6 mg/kg, Italy 3.3 mg/kg and France 1.6, 1.9, 1.9, 2.2, 2.4, 2.8, 3.1, 3.5, 4.6, 5.7, 5.8 and 5.9 mg/kg. The residues in rank order (median underlined) in the 14 trials were 1.6, 1.6, 1.9, 1.9, 2.2, 2.4, <u>2.8</u>, <u>3.1</u>, 3.3, 3.5, 4.6, 5.7, 5.8 and 5.9 mg/kg

The Meeting estimated a maximum residue level for folpet on grapes of 10 mg/kg but could not recommend it as suitable for use as an MRL until the critical supporting studies on environmental fate have been evaluated.

Folpet is registered for use on strawberries in Spain at a spray concentration of 0.15 kg ai/hl with a PHI of 21 days. The residues in three trials in Italy according to Spanish GAP were <0.01, 0.04 and 0.09 mg/kg. Data from a fourth Italian trial could not be used because the longest interval between the final application and harvest was 14 days.

Mexican GAP permits the application of folpet to strawberries at 1.3 kg ai/ha with no restriction on the PHI (the label statement is “interval between final application and harvest – no limit”). The residues in 3 Mexican trials complying with GAP (the PHI of 2 days is sufficiently close to the label statement, which implies a 0-day PHI) were 1.6, 1.8 and 2.2 mg/kg.

In three trials on strawberries in plastic tunnels in The Netherlands which complied with glasshouse GAP (spray concentration 0.13 kg ai/hl and 14 days PHI) the folpet residues were 1.4, 1.6 and 1.9 mg/kg.

In summary, the folpet residues in strawberries from trials according to GAP were Italy <0.01, 0.04 and 0.09 mg/kg, Mexico 1.6, 1.8 and 2.2 mg/kg and The Netherlands 1.4, 1.6 and 1.9 mg/kg. The Meeting agreed that the data from Italy appeared to be in a different population from the others and should not be considered for the estimation of an STMR. The folpet residues in strawberries in rank order (median underlined) in the 6 trials were 1.4, 1.6, <u>1.6</u>, <u>1.8</u>, 1.9 and 2.2 mg/kg.

The Meeting estimated a maximum residue level for folpet on strawberries of 5 mg/kg but could not recommend it as suitable for use as an MRL until the critical supporting studies on environmental fate have been evaluated.

The folpet residues in onions from a trial in Chile complying with GAP (2 kg ai/ha and 7 days PHI) was 0.36 mg/kg. Portuguese GAP for onions allows a spray concentration of 0.13 kg ai/hl and a 7 days PHI. Folpet residues in a Portuguese and a Spanish trial which complied with GAP were 5.0 and 2.5 mg/kg respectively. (The PHI in Spain was 10 days).

Trials in Greece could not be evaluated because the PHIs were 20 days whereas Greek GAP does not specify the PHI, suggesting that 0 days is permissible. Similarly, Hungarian data could not be used because the PHIs in the trials were 14 days, while Hungarian GAP specifies 5 days. Mexican trials also could not be evaluated because the label does not limit the PHI, implying 0 days, while the interval in the trials was 7 days. No relevant GAP was available for the evaluation of trials in The Netherlands and Germany.

The Meeting could not estimate a maximum residue level for folpet in onions because there were too few trials (3) according to GAP.

Folpet may be used on cucumbers in Mexico at 1.8 kg ai/ha with no limit for the PHI, implying that harvest on the day of the final application is permissible. In the 4 trials in Mexico the PHI was 3 days, which was too far from 0 days to be considered as maximum GAP for such a rapidly growing crop as cucumbers. The single Canadian trial could not be used because the trial conditions did not correspond to GAP.

The Meeting agreed to withdraw the recommendation of the 1994 JMPR for folpet on cucumbers (0.5 mg/kg).

In Greece folpet is registered for use on melons with a spray concentration of 0.16 kg ai/hl and a PHI of 20 days. Folpet residues were below the LOD (<0.05 mg/kg) in melons from 2 Greek trials complying with GAP (0.12 kg ai/hl and 20 days PHI).

GAP in Honduras permits a spray concentration of 0.13 kg ai/hl with harvest 7 days after the final application. Melons were harvested 3 days after the final application in one trial in Guatemala and 2 trials in Honduras but the data could not be used because the interval was too short to be considered to comply with GAP for Honduras.

Mexican GAP permits application at 1.8 kg ai/ha with harvest on the day of the final application (the label does not limit the PHI). The three trials in Mexico could not be evaluated because the interval between the final application and harvest was 7 days, which is not sufficiently close to maximum GAP.

The Meeting agreed to withdraw the 1997 recommendation for folpet in melons (3 mg/kg) because there were too few trials (2) according to GAP.

Data were available from supervised trials on tomatoes in Chile, Hungary, Italy, Mexico, The Netherlands, Portugal, Spain and the USA. Trials in the USA and The Netherlands, and trials in plastic greenhouses in Italy could not be evaluated because no relevant GAP was available.

The folpet residue in tomatoes from a trial in Chile complying with GAP (1.7 kg ai/ha and 7 days PHI) was 2.4 mg/kg. Mexican GAP permits application of folpet to tomatoes at 2.0 kg ai/ha and harvest without timing restriction. The residues in tomatoes in five Mexican trials complying with GAP (the PHI of 2 days is sufficiently close to the implied 0 days of GAP) were 0.45, 1.0, 1.3, 1.6 and 1.8 mg/kg.

In Hungary folpet is registered for use on tomatoes at a spray concentration of 0.13 kg ai/hl with harvest 14 days after the final application. In four Hungarian trials with conditions complying with GAP and in one recorded in the 1993 Evaluations complying with GAP, the residues were all below the LOD (<0.02 and <0.05 mg/kg (4)).

In two Portuguese trials (0.16 kg ai/hl and 7 days PHI) in compliance with Portuguese GAP (0.13 kg ai/hl and 7 days PHI) the residues were 0.34 and 0.58 mg/kg.

Folpet is registered for use on tomatoes in Spain at a spray concentration of 0.15 kg ai/hl with a 10 days PHI. The residues in two Spanish and four Italian trials substantially according to Spanish GAP were 1.2 and 1.3 mg/kg in Spain and 0.43, 0.60, 0.70 and 0.80 mg/kg in Italy.

In summary, the folpet residues in tomatoes from trials according to GAP were Chile 2.4 mg/kg, Mexico 0.45, 1.0, 1.3, 1.6 and 1.8 mg/kg, Hungary <0.02 and <0.05 4 mg/kg, Portugal 0.34 and 0.58 mg/kg, Spain 1.2 and 1.3 mg/kg and Italy 0.43, 0.60, 0.70 and 0.80 mg/kg. The residues in rank order in the 19 trials were <0.02, <0.05 (4), 0.34, 0.43, 0.45, 0.58, 0.6, 0.7, 0.80, 1.0, 1.2, 1.3, 1.3, 1.6, 1.8 and 2.4 mg/kg

The residues from the Hungarian trials appear to be in a different population from the others. The residues in the 14 trials in the other countries (median underlined) which were used to estimate an STMR for tomatoes were 0.34, 0.43, 0.45, 0.58, 0.6, 0.7, <u>0.80</u>, <u>1.0</u>, 1.2, 1.3, 1.3, 1.6, 1.8 and 2.4 mg/kg.

The Meeting estimated a maximum residue level for folpet on tomatoes of 3 mg/kg but could not recommend it as suitable for use as an MRL until the critical supporting studies on environmental fate have been evaluated.

Portuguese GAP for the use of folpet on lettuce allows a 0.13 kg ai/hl spray with a 14 days PHI. The residue in head lettuce from a trial in Portugal complying with GAP was 4.3 mg/kg. A trial in Spain on leaf lettuce complied with Spanish GAP (0.13-0.15 kg ai/hl and 21 days PHI). The residue was undetectable (<0.05 mg/kg).

Trials in Greece could not be evaluated because the interval between the final application and harvest was 20 days whereas Greek GAP does not specify a PHI, implying that 0 days is permitted. Lettuce were harvested 7 days after the final application in Mexican trials, but again the registered use specifies no limit for the PHI, so the trial conditions were not sufficiently close to GAP. Trials in Hungary and Germany could not be evaluated because no relevant GAP was available.

The Meeting agreed that there were too few results to estimate a maximum residue level or STMR for lettuce.

Supervised trials on potatoes were carried out in Italy, Mexico, Poland, Russia and South Africa. Translocation to the tubers from foliar applications would not be expected from a compound with such low solubility in water as folpet. Occasional residues could occur if a tuber is exposed above the soil surface to direct spray.

Four Italian trials (0.13 kg ai/hl, 10 days PHI) complied with Spanish GAP (spray concentration 0.15 kg ai/hl and PHI 10 days). The residues were 0.08 and <0.01 (3) mg/kg.

No relevant GAP was available to evaluate the other trials.

There were too few results to estimate a maximum residue level or STMR. The Meeting recommended the withdrawal of the current CXL for folpet on potatoes (0.02* mg/kg).

Documented studies of numerous folpet trials in France and the UK on barley and wheat, which included extensive data on forage and fodder, were reported but could not be evaluated because no information on GAP supported by registered labels was made available. Field reports for many of the trials were lacking.

The Meeting noted that feeding studies on farm animals had not been reported. These would be needed before MRLs could be established for cereal grains, fodder and forage.

Studies of the effects of processing on folpet residues in apples, grapes and tomatoes were reported.

Field-treated apples were processed to juice and wet pomace by procedures simulating commercial practice as closely as possible. The process included an initial washing step which removed about 40% of the residue. The calculated processing factors for the production of wet pomace and apple juice from unwashed apples were 2.6 and 0.035 respectively.

Grapes were treated post-harvest by dipping bunches for 30 seconds into a vat containing folpet (1.25 kg ai/hl). The grapes were allowed to dry and then processed into raisins and juice. Because folpet residues are on the surface the treatment was considered valid.

The treated grapes were dried in the sun until the moisture level had reached 12-16%. After destemming, the dried grapes were rehydrated to 18-20% moisture in an incubator at 21°C to produce raisins. Juice was produced from treated grapes by crushing, enzyme treatment, heating and filtering.

Folpet residues were not detectable (<0.05 mg/kg) in the grape juice. The calculated processing factor for grapes to juice is 0 (<0.003). Folpet residues in the dried raisins and hydrated raisins were higher than in the original grapes, with processing factors of 3.2 and 1.9 respectively.

The Meeting estimated a maximum residue level for folpet residues in dried grapes or raisins of 40 mg/kg after rounding up, from the processing factor (3.2) and the estimated maximum residue level in grapes (10 mg/kg).

In ten trials in Germany in 1993 residues of folpet were measured in must and wine produced from folpet-treated grapes. The processing factors for must ranged from 0 to 0.97 (mean 0.29). Folpet was not detected (<0.05 mg/kg) in any wine sample, so the processing factor was 0. The metabolite phthalimide was consistently present in the must and wine at levels typically 25-50% of the folpet levels in the grapes. The metabolism study on grapes had shown the formation of a water-soluble conjugate of phthalic acid in grapes which also has the potential to reach the wine.

A tomato crop was treated five times with folpet (2.2 kg ai/ha) and harvested seven days after the final application for processing. Tomatoes were treated in 0.5% sodium hydroxide and then vigorously washed before being processed to juice, purée and paste. Purée was produced from juice by evaporation and adjustment of salt and water levels before heating and canning. Paste was produced similarly, but with a higher salt level.

Folpet residues were not detected (<0.05 mg/kg) in tomato purée or paste produced from tomatoes containing 1.8 mg/kg of folpet. It is likely that the initial vigorous cleaning of the tomatoes and the sodium hydroxide treatment completely removed or destroyed the folpet. The estimated processing factor for the transfer of folpet from tomatoes to purée and paste is therefore 0.

RECOMMENDATIONS

The Meeting recommended the withdrawal of previous recommendations of the JMPR as shown below. Although the Meeting was able to estimate maximum residue levels for some commodities, they could not be recommended for use as MRLs because critical supporting studies on the environmental fate were not provided for the 1998 Meeting.

Definition of the residue (for compliance with MRLs and for the estimation of dietary intake): folpet.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	current	
FP 0226	Apple	W [1]	10	
VC 0424	Cucumber	W	0.5	
DF 0269	Dried grapes (currants, raisins and sultanas)	W [1]	40	
FB 0269	Grapes	W [1]	10	
VC 0046	Melons, except Watermelon	W	3	
VR 0589	Potato	W	0.02*	
FB 0275	Strawberry	W [1]	5	
VO 0448	Tomato	W [1]	3	

W: the previous recommendation is withdrawn.
[1] The previous recommendation is withdrawn because critical supporting studies on environmental fate have not been evaluated because they were not provided for the 1998 meeting.

* At or about the limit of determination

FURTHER WORK OR INFORMATION

Desirable

1. Expression of the residues found in forage and fodder on a dry-weight basis so that the results can be used in the estimation of maximum residue levels for animal commodities.

2. Studies on the environmental fate of folpet in soil and in water/sediment systems are needed before MRLs can be recommended for folpet (see page 13 of *Manual on the Submission and Evaluation of Pesticide Residues Data for the Estimation of Maximum Residue Levels in Food and Feed*).

DIETARY RISK ASSESSMENT

Recommendations for folpet MRLs have been withdrawn because critical supporting studies were not available for the periodic review. Consequently, no MRLs or STMRs are available for the estimation of dietary intake.

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R8559 Turner. and Partridge 1996
R8559-5 Byast 1995c
R8559-6 Byast 1995a
R8580 Daniel and Partridge 1996
R8580-1 Byast 1995d
R8580-2 Byast 1995b
R8676 Wasser 1996b
R-8987 De Paoli and Bruno 1995a
R-8988 Balluff 1995b
R-8989 Balluff 1995a
R-9008 Williams 1996
R9012 Farthing 1996e
R9012 Singer. 1997h
R9057 Viljoen 1996
R-9086 Balluff 1997a
R-9093 Balluff 1996f
R-9094 Balluff 1996d
R-9095 Balluff 1996a
R9098 Hautvoine 1997
R9098 Wasser 1997b
R-9099 Balluff 1996b
R-9101 Leppert 1996b
R9118 Mende 1996b
R9137 Corden 1997a
R9137 Corden 1997b
R-9141c Singer 1997d
R-9141g Singer 1997e
R-9141M Singer 1996a
R-9141s Singer 1996b
R-9141t Singer 1997c
R-9146F Grolleau 1996
R9156 Byast 1997b
R-9158 Wilson 1997d
R-9159 Wilson 1997e
R-9160 Wilson 1997b
R-9160 Wilson 1997g
R-9161 Wilson 1997a
R-9162 Wilson 1997c
R-9163 Wilson 1997f
R9234 Mende 1996a
R9261 Puy 1997a
R-9320 Balluff 1996c
R-9374 Balluff 1996e
R9376 Hautavoine 1996
R9376 Mende 1996c

R9383 Puy 1997b
R9496 Mende 1996d
R9572 Anon. 1995
R9711 Nowacka and Dabrowski 1996a.
R9772 Anon. 1996b
R9790 Anon. 1996a
R9852 Nowacka and Dabrowski 1996b.
Report95/MAK204/0049 Crowe 1995
ReportERSA-DA-12/95 De Paoli and Bruno 1995a
RF2095 Mellet 1993
RF4019 Mellet 1994
RF4088-2 Mellet 1995
SARS 95-50 Leppert 1996a
SARS 95-51 Leppert 1996b
SARS-95-50 Hurley and Farthing 1996e
SARS-95-51 Hurley and Farthing 1996d
SARS-95-NY-50P Armstrong and Luke 1995
StAA960307 Abdelrahim 1996
UHL07 Mader 1994a
UHL08 Lipps 1994a
UHL09 Ipach 1994a
UHL10 Ipach 1994b
UHL11 Ipach 1994c
UHL12 Ipach 1994d
UHL13 Mader 1994b
UHL14 Lipps 1994b
UHL15 Ipach 1994e
UHL16 Ipach 1994f

Page: 660

[DJH1] R9496. Onion. Field report is lacking. What is the nature of the sample? What is the sprayer? {Answer of July – still to follow up.]

Page: 663

[DJH2] AnalysisPage: 663

date is Aug 1996, so samples could have been stored up to 16 months before analysis.

Page: 666

[DJH3] Are the replicates analytical replicates or replicate field samples? The variance suggests replicate samples but there is no clear statement.

Page: 667

[DJH4] Trial R7795 R4019. It is difficult to relate the data in the study to the data in the summary. In the study the PHIs appear to be 45 and 49 days whereas in the summary we have 33 and 49 days.

Page: 668

[DJH5] There is no field report for R7150 - size of plots, type of sprayer?

Page: 688

[DJH6] This report is deficient in lacking a field report. There is no information on plot areas and sprayers used. It is difficult to relate the study report to the summary because the recorded PHIs are different for some wheat trials.

GLUFOSINATE-AMMONIUM (175)

EXPLANATION

Glufosinate-ammonium is a herbicide and desiccant. It was first evaluated for residues and toxicology by the 1991 JMPR and subsequently for residues in 1994.

Glufosinate-tolerant crops have now been developed with new use patterns necessitating revised MRLs. The manufacturer has provided many new reports for evaluation dealing with animal and plant metabolism, environmental fate in soil and water, methods of residue analysis, stability in stored analytical samples, supervised residue trials, animal transfer studies, fate of residues in processing and national residue limits.

The delegation of The Netherlands was requested by the 1996 CCPR to send their comments on the definition of the residue to the JMPR (ALINORM 97/24 para 73).

Information was provided to the Meeting by Germany, The Netherlands, Poland and the basic manufacturer.

METABOLISM AND ENVIRONMENTAL FATE

Information was made available on the metabolism and environmental fate of glufosinate in animals, crops, soils and water-sediment systems.

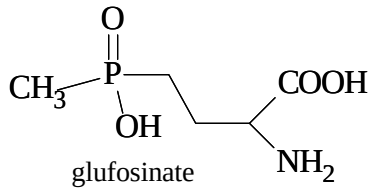
A variety of code numbers and abbreviations have been used for the metabolites and degradation products of glufosinate-ammonium. There are nine different code numbers for glufosinate itself, covering the salts and free acid, and the racemate and separate stereoisomers. Earlier publications used HOE numbers but they have recently been replaced by AEF, AEC or AE numbers. The names, structures and code numbers of glufosinate and its metabolites and degradation products are listed below.

In this evaluation “glufosinate” and the abbreviations NAG, MPP, etc. refer to the compounds without specifying their stereoisomerism or whether they are presents as salts or free acid. Where such extra information is important, e.g. because of molecular weight considerations, extra information will be given, e.g. “glufosinate, expressed as the free acid”.

Structures, names and code numbers of glufosinate, metabolites and degradation products

Glufosinate

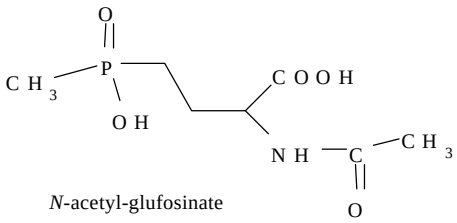
	racemate	L-isomer	R-isomer	MW
free acid	AE F035956	AE F057740	AE F090532	181.1
Ammonium salt	AE F039866	AE F058192	AE F093854	198.2
HCl salt	AE F035125	AE F057742	AE F057741	217.6



glufosinate

N-acetyl-glufosinate (NAG)

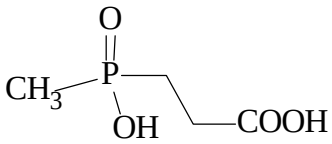
	racemate	L-isomer	R-isomer	MW
free acid	AE F085355	AE F099729	AE F124451	223.2
Disodium salt	AE F098412	AE F099730	AE F124450	267.2



N-acetyl-glufosinate

3-methylphosphinicopropionic acid (MPP)

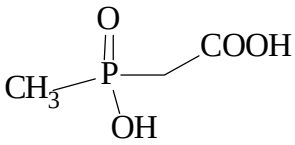
		MW
Free acid	AE F061517	152.1
Disodium salt	AE C527855	196.1



3-methyl-phosphinico-propionic acid

2-methylphosphinicoacetic acid (MPA)

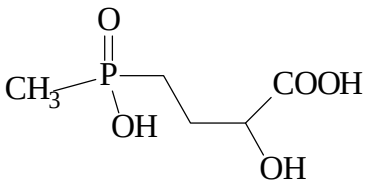
		MW
Free acid	AE F064619	138.1
Disodium salt	AE F159481	182.1



2-methyl-phosphinico-acetic acid

4-methylphosphinico-2-hydroxybutanoic acid (MHB)

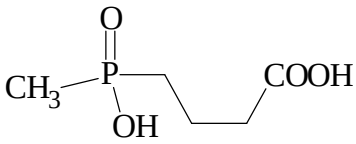
		MW
Free acid	AE F053705	182.1
Disodium salt	AE F042231	226.1



4-methyl-phosphinico-2-hydroxy-butanoic acid

4-methylphosphinicobutanoic acid (MPB)

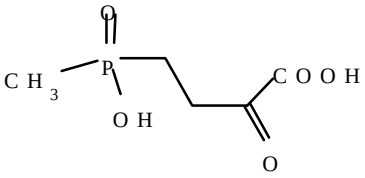
		MW
Free acid	AE F039046	166.1



4-methyl-phosphinico-butanoic acid

4-methylphosphinico-2-oxobutanoic acid

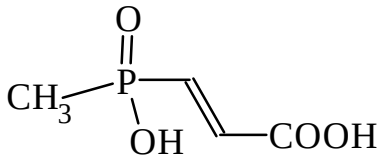
		MW
Free acid	AE F065594	180.1



4-methyl-phosphinico-2-oxo-butanoic acid

3-methylphosphinico-acrylic acid

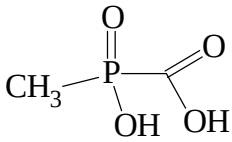
		MW
Free acid	AE 0015081	150.1



AE 0015081
3-methyl-phosphinico acrylic acid

Methylphosphinico-formic acid

		MW
Free acid	AE F130947	124.0



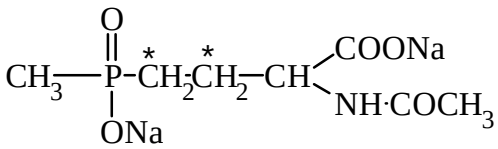
methylphosphinico-formic acid

Animal metabolism

Information on the metabolism of glufosinate-ammonium and NAG (*N*-acetyl-L-glufosinate) in laboratory rats, lactating goats and laying hens was reported. In summary, most of the administered dose of both compounds is rapidly excreted. NAG may be partially metabolized back to glufosinate.

Bremmer and Leist (1997) examined the possible conversion of NAG to glufosinate in rats. Up to 10% deacetylation occurred at a low dose of 3 mg/kg bw as shown by the occurrence of glufosinate in the faeces. The authors concluded however that most of the conversion was caused by bacteria in the colon and rectum although toxicity findings indicate partial bioavailability (Bremmer and Leist, 1998).

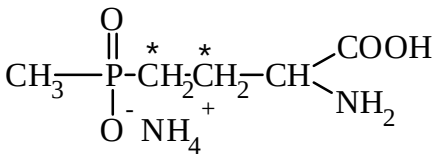
Kellner *et al*. (1993) showed that almost all the radiolabel was excreted in the faeces within 4 days when rats were dosed orally with single doses of [^{14}C]NAG disodium salt at 3 mg/kg body weight. The ^{14}C label was in positions 3 and 4.



Labelled AE F099730

Unchanged NAG was the main source of the radiolabel (85-89%) in faecal extracts from rats dosed orally with [^{14}C]NAG disodium salt at 1000 mg/kg body weight (Lauck-Birkel, 1995a). Small amounts (approx. 1%) of glufosinate were produced.

When [3,4-^{14}C]glufosinate-ammonium was administered in a single oral dose of 500 mg/kg bw to rats, 75% in males and 89% in females of the radiolabel was excreted in the faeces within 48 hours (Lauck-Birkel, 1995b) and 8-11% in the urine. Glufosinate was the principal labelled component in faecal extracts – 72% and 84% of the dose in males and females respectively.



Labelled glufosinate-ammonium

Lauck-Birkel (1996) identified the labelled compounds in urine and faeces from rats dosed orally with [3,4-^{14}C]glufosinate-ammonium at 2 mg/kg bw. The main compound in faecal extracts was glufosinate (77% of the dose); other identified components were NAG (7.5%), MHB (4.3%) and MPP (1.3%). The main components in the urine were glufosinate (4.3% of the dose) and MPP (0.8%).

Tissue, milk and excreta residues were measured in a lactating goat weighing 60 kg dosed orally twice daily for 4 consecutive days by capsule with [3,4-^{14}C]glufosinate at a rate equivalent to 101 ppm glufosinate-ammonium in the dry-weight diet and 3.0 mg/kg bw/day (Huang and Smith, 1995a). The feed intake was 1.8 kg/day. The animal was milked twice daily and slaughtered 15 hours after the final dose.

Most of the administered ^{14}C (69%) was excreted in the faeces with 2.9% in the urine and 11% in the GI tract with contents. Less than 0.1% and 0.02% of the dose was found in the tissues and milk respectively. The levels in the kidneys were higher than in other tissues (Table 1). Levels of ^{14}C reached a plateau in milk by day 2.

The parent compound was the main residue detected in the kidneys, liver and milk, with MPP forming a substantial part of the residue in the kidneys and liver (Table 2).

Table 1. Distribution of ^{14}C in the tissues and milk of a goat dosed twice daily for 4 days with [3,4-^{14}C]glufosinate (Huang and Smith, 1995a).

Sample	^{14}C as glufosinate-ammonium, mg/kg
Kidney	0.61
Liver	0.40
Muscle	0.007
Fat	0.004
Milk day 1, am and pm	0.003 0.009
Milk day 2, am and pm	0.016 0.020
Milk day 3, am and pm	0.022 0.020
Milk day 4, am and pm	0.020 0.014

Table 2. Compounds identified in the tissues and milk of a goat dosed twice daily for 4 days with [3,4-^{14}C]glufosinate (Huang and Smith, 1995a). Residue levels are expressed as glufosinate-ammonium equivalents.

Compound	Kidney		Liver		Milk	
	% of total ^{14}C	mg/kg	% of total ^{14}C	mg/kg	% of total ^{14}C	mg/kg
Glufosinate	49	0.30	53	0.21	49	0.010
NAG, L-isomer	4.2	0.026	not detected		2.2	<0.001
MPP	29	0.18	37	0.15	6.3	0.001
MPA	1.2	0.008	0.4	0.001	5.3	0.001

Tissue, milk and excreta residues were measured in a lactating goat weighing 36 kg dosed orally twice daily for 3 consecutive days by capsule with [3,4-^{14}C]*N*-acetyl-L-glufosinate disodium salt at a rate equivalent to 84 ppm in the dry-weight diet or 3.0 mg/kg bw/day (Huang and Smith, 1995b). The feed intake was 1.4 kg/day. The animal was milked twice daily and slaughtered 16 hours after the final dose.

Most of the administered ^{14}C was excreted in the faeces (68%) with 7.3% in the urine and 19% in the GI tract with contents. NAG and glufosinate accounted for 52% and 34% of the ^{14}C in the faeces respectively.

Only 0.2% of the administered dose was found in the tissues and blood, with <0.1% in the milk. Levels in the kidneys were higher than in other tissues (Table 3). Levels of ^{14}C reached a plateau in milk by day 2. Glufosinate was the main residue detected in the kidneys, liver and milk, with NAG (the administered material) and MPP forming a substantial part of the residue in the kidneys and liver (Table 4).

Table 3. Distribution of ^{14}C in the tissues and milk of a goat dosed twice daily for 3 consecutive days with [3,4-^{14}C]*N*-acetyl-L-glufosinate disodium salt (Huang and Smith, 1995b).

Tissue or milk	^{14}C as N-acetyl-L-glufosinate disodium salt, mg/kg
Kidneys	0.93
Liver	0.29
Muscle	0.007
Fat	<0.010
Milk day 1, am and pm	0.005 0.012
Milk day 2, am and pm	0.018 0.020
Milk day 3, am and pm	0.023 0.022

Table 4. Compounds identified in the tissues and milk of a goat dosed twice daily for 3 consecutive days with [3,4-^{14}C]*N*-acetyl-L-glufosinate disodium salt (Huang and Smith, 1995b). Residue levels are expressed as *N*-acetyl-L-glufosinate disodium salt equivalents.

Compound	Kidneys		Liver		Milk	
	% of total ^{14}C	mg/kg	% of total ^{14}C	mg/kg	% of total ^{14}C	mg/kg
Glufosinate	40	0.37	33	0.095	40	0.009
NAG, L-isomer	32	0.30	19	0.054	9.2	0.002
MPP	20	0.19	21	0.060	14	0.003
MPA	1.6	0.015	2.0	0.006	4.8	0.001

Tissue, eggs and excreta residues were measured in 6 laying hens weighing 1.27-1.67 kg dosed orally twice daily for 14 consecutive days by capsule with [3,4-^{14}C]glufosinate-ammonium at a

rate equivalent to 25 ppm glufosinate-ammonium in the diet (it was not clear whether the feeding level was expressed on a fresh-weight or dry-weight basis) or 2.0 mg/kg bw/day (Huang and Smith, 1995c). The feed intake was 120 g/bird/day. Eggs were collected twice daily and the birds were slaughtered 16 hours after the final dose .

92% of the administered dose was excreted with 1.3% remaining in the GI tract. Glufosinate-ammonium accounted for 81% of the ^{14}C in the faeces.

Less than 0.02% of the administered dose was present in the edible tissues. Levels of ^{14}C as glufosinate-ammonium in the liver, muscle and fat were 0.11, <0.004 and 0.003 mg/kg respectively. Those in the eggs are shown in Table 5. ^{14}C in egg whites reached a plateau by day 6, but in the last 3 days there was again a small increase. The levels in egg yolks increased very slowly throughout the 14 days.

MPP was the main residue identified in the liver with glufosinate-ammonium also a substantial component (Table 6). Glufosinate constituted most of the residue in eggs.

Table 5. ^{14}C in eggs from hens dosed orally twice daily for 14 consecutive days by capsule with [3,4-^{14}C]glufosinate- (Huang and Smith, 1995c).

Collection day	Mean ^{14}C, mg/kg as glufosinate-ammonium	
	Egg white	Egg yolk
1	<0.003	<0.003
2	0.004	<0.003
3	0.034	0.005
4	0.053	0.009
5	0.049	0.012
6	0.057	0.015
7	0.056	0.016
8	0.056	0.017
9	0.058	0.019
10	0.059	0.021
11	0.058	0.021
12	0.067	0.021
13	0.065	0.022
14	0.067	0.024

Table 6. Compounds identified in the tissues and eggs from hens dosed orally twice daily for 14 consecutive days with [3,4-^{14}C]glufosinate-ammonium (Huang and Smith, 1995c). Residues are expressed as glufosinate-ammonium equivalents.

Compound	Liver		Egg white (day 14)		Egg yolk (day 13)	
	% ^{14}C in liver	mg/kg	% ^{14}C in egg white	mg/kg	% ^{14}C in egg yolk	mg/kg
glufosinate	31	0.036	78	0.052	53	0.012
NAG, L-isomer	4.9	0.006	not detected		2.4	0.001
MPP	44	0.050	1.3	0.001	4.1	0.001
MPA	3.5	0.004	not detected		3.1	0.001

Tissue, eggs and excreta residues were measured in 6 laying hens weighing 1.27-1.60 kg dosed orally twice daily for 14 consecutive days by capsule with [3,4-^{14}C]*N*-acetyl-L-glufosinate disodium salt equivalent to 27 ppm *N*-acetyl-L-glufosinate disodium salt in the diet (it was not clear whether the feeding level was expressed on a fresh- or dry-weight basis) or 2.2 mg/kg bw/day (Huang and Smith, 1995d). The mean feed intake was 116 g/bird/day. Eggs were collected twice daily and the birds were slaughtered 15 hours after the final dose.

86% of the administered dose was excreted with 1.0% remaining in the GI tract. *N*-acetyl-L-glufosinate disodium salt accounted for 73% of the ^{14}C in the faeces with glufosinate and MPP accounting for 13% and 8.6% respectively.

Less than 0.1% of the administered dose was present in the edible tissues and blood. Levels of ^{14}C (as *N*-acetyl-L-glufosinate disodium salt) in the liver, muscle and fat were 0.076, 0.013 and 0.011 mg/kg respectively. Those in eggs are shown in Table 7. Levels in egg whites were slightly above the LOD throughout the study; those in egg yolks increased slowly but steadily throughout the 14 days.

NAG (the administered material) was the main residue identified in liver and egg yolk (Table 8). Glufosinate and MPP were also substantial components of the liver residue. Glufosinate was the main identified residue in egg whites, but the levels in eggs were quite low, making further identification difficult.

Table 7. ^{14}C in eggs from hens dosed orally twice daily for 14 consecutive days with [3,4-^{14}C]*N*-acetyl-L-glufosinate disodium salt (Huang and Smith, 1995d).

Collection day	Mean ^{14}C level, mg/kg as N-acetyl-L-glufosinate disodium salt	
	Egg white	Egg yolk
1	<0.009	<0.002
2	<0.009	<0.002
3	<0.009	0.012
4	0.010	0.020
5	0.010	0.027
6	0.011	0.035
7	<0.009	0.037
8	0.012	0.040
9	0.014	0.042
10	0.012	0.045
11	0.012	0.046
12	0.013	0.050
13	0.015	0.049
day 14 sac	0.014	0.052
necropsy	<0.009	0.056

Table 8. Compounds identified in the tissues and eggs from hens dosed orally twice daily for 14 consecutive days with [3,4-^{14}C]*N*-acetyl-L-glufosinate disodium salt (Huang and Smith, 1995d). Residues are expressed as *N*-acetyl-L-glufosinate disodium salt equivalents.

Compound	Liver		Egg white (day 13)		Egg yolk (necropsy)	
	% ^{14}C	mg/kg	% ^{14}C	mg/kg	% ^{14}C	mg/kg
Glufosinate	15	0.011	14	0.002	2.8	0.002
NAG, L-isomer	27	0.020	5.1	0.001	13	0.007
MPP	17	0.013	2.0	<0.001	2.2	0.001
MPA	not detected		1.1	<0.001	0.6	<0.001

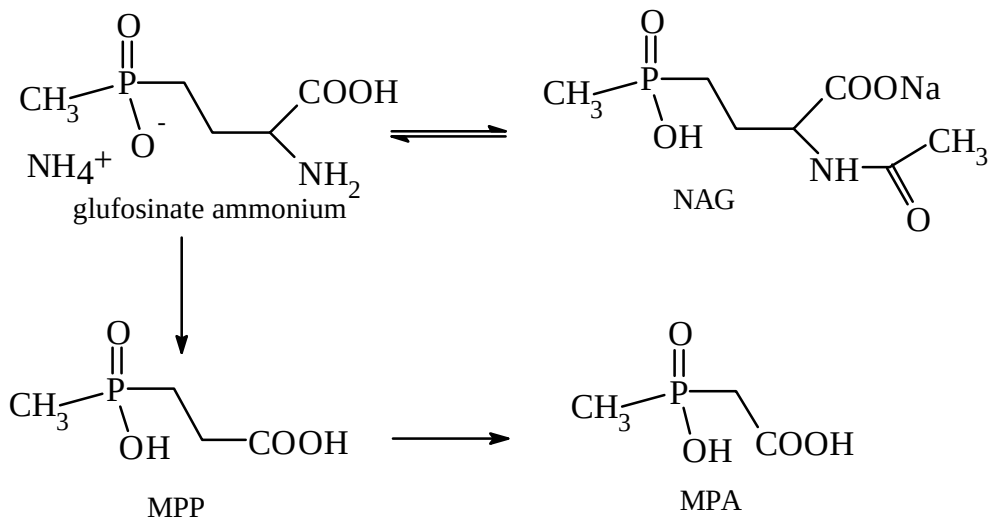
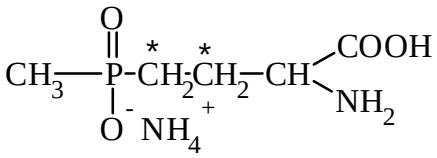


Figure 1. Proposed metabolic pathways of glufosinate and *N*-acetyl glufosinate in ruminants and poultry.

Plant metabolism

Information was reported on the metabolism of glufosinate-ammonium in genetically modified rape (canola), sugar beet, maize, soya and tomatoes. The studies examined the disposition of the residue throughout the plant and its composition. In some cases the metabolism of glufosinate-ammonium in genetically modified and unmodified crops was compared.

Stumpf *et al*. (1995b) placed cut rape plants, genetically modified and unmodified, in a nutrient solution containing 4.7 mg/l of [3,4-^{14}C]glufosinate-ammonium for 6 days. In the genetically modified plants the ^{14}C represented NAG (57%) and glufosinate-ammonium (36%). In the unmodified plants the ^{14}C was mainly due to unchanged glufosinate-ammonium (80%) with 16% MPP. The experiment demonstrated the rapid acetylation of glufosinate in genetically modified rape.



Labelled glufosinate-ammonium

Tshabalala (1993) treated canola plants (*var* 19-2XACS-N3) at the 3-5 leaf stage once with [3,4-^{14}C]glufosinate-ammonium at a rate equivalent to 0.75 kg ai/ha and collected samples for radio-analysis on days 1, 21 and 120. The results are shown in Table 9.

The levels in the top-growth and roots were much the same after 21 days, but at maturity were much higher in the roots than in other plant parts. The residues in the canola seed were investigated by two HPLC systems but the low residue levels made further identification difficult. Glufosinate and MPP were the main constituents with considerably lower levels of NAG.

Table 9. Levels of ^{14}C in canola plants treated once with [3,4-^{14}C]glufosinate-ammonium at 0.75 kg ai/ha (Tshabalala 1993).

Sample	Time since treatment	^{14}C as glufosinate-ammonium, mg/kg
whole plant	1 hour	145
topgrowth	21 days	5.3 3.2
roots	21 days	3.8 5.2
topgrowth	120 days	0.058 0.064 0.024 0.021
roots	120 days	0.22 0.13 0.15 0.19
hulls	120 days	0.12 0.26 0.11 0.076
seed	120 days	0.054 0.11 0.056 0.045

Thalacker (1994) applied [^{14}C]glufosinate-ammonium to glufosinate-tolerant canola and samples were taken after 1 hour and 21 days. After 1-hour 73% of the ^{14}C was in glufosinate and 18% in NAG, and after 21-days 60, 21 and 7% of the ^{14}C corresponded to NAG, glufosinate-ammonium and MPP respectively. Again, genetically modified rape seed (canola) produced NAG very rapidly from glufosinate-ammonium.

In another trial, genetically modified sugar beets were treated twice (22 days interval) with [3,4-^{14}C]glufosinate-ammonium at rates equivalent to 0.6 kg ai/ha (Allan, 1996). The leaves and beets (when formed) were harvested 0, 8 and 15 days after the first treatment and 0, 21 and 146 days after the second. The leaves were rinsed with water to separate surface residues from absorbed residues

The residues after the first treatment are shown in Table 10. The glufosinate isomer composition was unchanged in the surface residue, but in the absorbed residue L-glufosinate was metabolized to NAG (*N*-acetyl-L-glufosinate).

The composition of the residue after the second treatment is shown in Table 11. Identified residues accounted for 93-98% of the total ^{14}C in leaves + rinses and roots. After the first treatment NAG was the main identified residue except in the leaves on the day of treatment, but even after 146 days glufosinate accounted for 19% of the ^{14}C in the roots and 26% in the leaves. The reason is presumably that L-glufosinate is rapidly converted to NAG, but D-glufosinate remains unchanged.

Table 10. Identified residues in genetically modified sugar beets after a single treatment with [3,4-^{14}C]glufosinate-ammonium.

Time after treatment	Sample	Residue as % of total ^{14}C in the sample			
		Glufosinate	D-glufosinate	L-glufosinate	NAG
3 hours	rinse	41	20	21	
8 days	rinse	18	9	9	
15 days	rinse	14	7	7	
3 hours	leaves	45.1	24.6	20.5	9.0
8 days	leaves	35.6	28.4	5.5	39
15 days	leaves	29.3	25.2	3.3	49

Table 11. Identified residues in genetically modified sugar beets after 2 treatments with [3,4-^{14}C]glufosinate-ammonium (Allan, 1996).

Time after 2nd treatment, days	Sample	Glufosinate		MPP		NAG	
		% of ^{14}C in (rinse + leaves) or roots	mg/kg as glufosinate-ammonium	% of ^{14}C in (rinse + leaves) or roots	mg/kg as glufosinate-ammonium	% of ^{14}C in (rinse + leaves) or roots	mg/kg as glufosinate-ammonium
0	rinse	59	12	-	-	-	-
0	leaves	25	5.1	0.4	0.07	13	2.7
0	roots	31	0.62	2.2	0.04	64	1.3
21	rinse	14	1.7	-	-	-	-
21	leaves	28	3.4	1.1	0.13	55	6.8
21	roots	31	2.1	2.0	0.14	63	4.3
146	rinse	2.3	0.05	0.3	0.006	0.2	0.005
146	leaves	24	0.49	2.7	0.055	67	1.4
146	roots	19	0.18	6.0	0.055	68	0.63

In another trial transgenic maize plants were treated twice (40 cm and 60 cm growth stages) with [3,4-^{14}C]glufosinate-ammonium at rates equivalent to 0.50 kg ai/ha (Burnett, 1994). Plants were sampled on the days of treatment and at intervals until 102 days after the second treatment. The levels of ^{14}C as glufosinate-ammonium were 23 and 5.8 mg/kg 1 hour and 5 days after the first treatment respectively and 14.5 and 9.9 mg/kg 1 hour and 5 days after the second.

Glufosinate-ammonium was generally a minor component of the residue whereas the main component in the forage, silage and fodder was NAG and the main component in the grain, cobs and husks was MPP. 73-83% of the residue was identified except in the grain where the very low residue level made further identification difficult.

A sub-sample of the maize forage was analysed by a GLC enforcement analytical method (Czarnecki and Bertrand, 1994), in which samples are extracted with distilled water, and after clean-up which includes ion-exchange chromatography, the residues are derivatized with trimethyl orthoacetate for GLC analysis. The enforcement method and the radiolabel method were in reasonable agreement (Table 13).

Table 12. Identified residues in grain and animal feeding commodities from transgenic maize treated twice with [3,4-^{14}C]glufosinate-ammonium (Burnett, 1994). Forage and silage were sampled 28 and 55 days respectively after the second treatment and other commodities after 102 days.

Compound	Residue components as % of ^{14}C in the sample and as mg/kg glufosinate-ammonium											
	Forage		Silage		Fodder		Grain [1]		Cobs		Husks	
	^{14}C %	mg/kg	^{14}C %	mg/kg	^{14}C %	mg/kg	^{14}C %	mg/kg	^{14}C %	mg/kg	^{14}C %	mg/kg
Glufosinate	13	0.35	11	0.20	9.9	0.20	1.5	0.002	2.6	0.006	2.1	0.018
MPP	12	0.32	12	0.21	11	0.22	33	0.043	44	0.10	41	0.36
NAG	52	1.4	55	0.98	54	1.1	9.1	0.012	20	0.046	19	0.17
MPA	4.6	0.12	3.9	0.070	2.9	0.058	4.4	0.006	12	0.028	11	0.097
Identified	82	2.2	82	1.5	76	1.6	58	0.076	79	0.18	73	0.64
Total		2.6		1.8		2.0		0.13		0.25		0.87

[1] MPB accounted for 9.8% of the ^{14}C in the grain, equivalent to 0.013 mg/kg of glufosinate-ammonium.

Table 13. Comparison between analysis of maize forage from [3,4-^{14}C]glufosinate-ammonium-treated maize by an enforcement GLC method (Czarnecki and Bertrand, 1994) and the ^{14}C HPLC method (Burnett, 1994).

Analyte	Residue, mg/kg as glufosinate-ammonium		
	HPLC ^{14}C	GLC enforcement, not adjusted for recovery	Spike recovery, %, GLC enforcement
Glufosinate	0.366	0.256	113
MPP	0.304	0.185	69.5
NAG	1.43	1.42	105

In another trial transgenic soya bean plants were treated twice at third trifoliate leaf and full bloom growth stages with [3,4-^{14}C]glufosinate-ammonium at rates equivalent to 0.50 kg ai/ha (Rupprecht and Smith, 1994). Forage was sampled just before the second application and the mature crop was harvested 85 days after the second treatment.

NAG was the main residue in all the samples. The levels of MPP were greater than those of glufosinate in the pods and beans. 90-94% of the residue was identified in all the samples. The results are shown in Table 14. They were also reported by Rupprecht *et al*. (1996b).

The samples were extracted with distilled water or acetonitrile + water and analysed by the method of Czarnecki and Bertrand (1994). The GLC and HPLC radiolabel methods produced similar results (Table 15) at the higher levels but at low levels those from the enforcement method were lower.

Table 14. Identified residues in beans, pods, forage and straw from transgenic soya plants treated twice with [3,4-^{14}C]glufosinate-ammonium (Rupprecht and Smith, 1994).

Compound	Identified residue components as % of ^{14}C in the sample and as glufosinate-ammonium, mg/kg							
	Forage		Straw		Pods		Beans	
	^{14}C %	mg/kg	^{14}C %	mg/kg	^{14}C %	mg/kg	^{14}C %	mg/kg
Glufosinate	23	0.45	19	0.58	5.8	0.29	6.2	0.091
MPP	6.5	0.13	14	0.42	22	1.1	16	0.23
NAG	60	1.2	53	1.7	63	3.1	61	0.89
MPA	0.7	0.014	5.7	0.18	2.9	0.142	7.1	0.10
Identified	91	1.8	91	2.8	94	4.6	90	1.3
Total		1.9		3.2		4.7		1.4

Table 15. Comparison between analysis of samples from [3,4-^{14}C]glufosinate-ammonium-treated soya beans by an enforcement GLC method (Czarnecki and Bertrand, 1994) and the ^{14}C HPLC method (Rupprecht and Smith, 1994)

Sample			Residue, mg/kg as glufosinate-ammonium		
	Extract	Method	Glufosinate	NAG	MPP
Forage	water	^{14}C HPLC	0.364	0.962	0.101
Forage	water	GLC	0.321	1.04	0.053
Straw	water	^{14}C HPLC	0.542	1.58	0.404
Straw	water	GLC	0.348	1.89	0.202
Pods	water	^{14}C HPLC	0.250	2.88	1.02
Pods	water	GLC	0.238	3.23	0.781
Beans	water	^{14}C HPLC	0.073	0.687	0.187
Beans	water	GLC	0.034	0.605	0.129
Forage	acetonitrile + water	^{14}C HPLC	0.084	0.195	0.025
Forage	acetonitrile + water	GLC	0.046	0.156	0.022

Köcher and Becker (1991) applied [^{14}C]glufosinate-ammonium at the 7-leaf stage to the leaves of glufosinate-resistant and unmodified tomato plants. After intervals of 1 and four days foliar absorption of the ^{14}C was the same in both types of plant, but translocation of the ^{14}C from the treated leaves to shoots, other leaves and roots was approximately four times as high in the resistant plants.

Stumpf *et al.* (1995a) treated genetically modified tomato plants at the 7-8 leaf stage with [3,4-^{14}C]glufosinate-ammonium at a rate equivalent to 0.8 kg ai/ha. Samples of plants were taken on the day of treatment and subsequently at intervals up to maturity, 74 days after treatment. The composition of the surface residues (in the rinse) and absorbed residues is shown in Table 16.

The major part (83-97%) of the surface residue in the rinse was glufosinate itself, even after long intervals. Glufosinate was very rapidly converted to NAG once absorbed into the tomato leaves and eventually accounted for about half of the residue, which is in accord with the rapid conversion of L-glufosinate and the stability of both D-glufosinate and NAG. The composition of the residue in the stems followed a similar pattern except that NAG accumulated to almost 70% of the residue and glufosinate fell to about 30%.

There were no detectable residues on the tomato fruit surface, probably because the plants were sprayed before any fruit were formed. NAG accounted for about 90% of the residue in the fruit, with glufosinate itself at essentially negligible levels. MPP was a minor residue in the fruit. NAG is evidently sufficiently mobile to translocate to the fruit, but D-glufosinate is not.

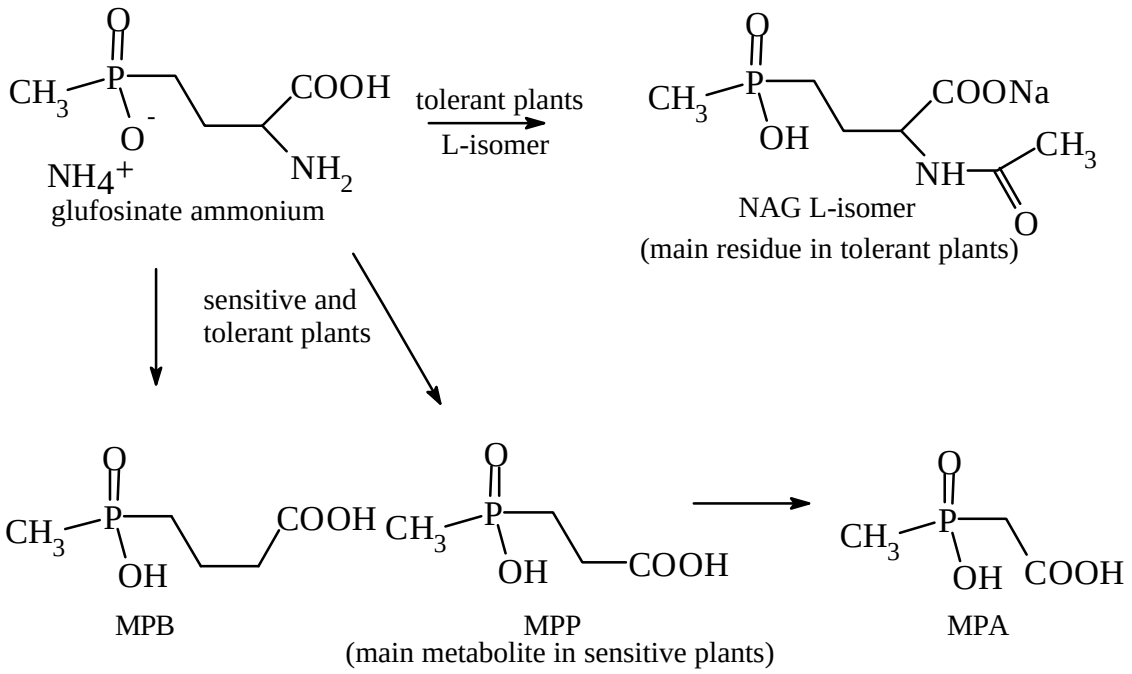
The composition of the glufosinate surface residue on the tomato leaves and stems on day 74 was shown to consist essentially of equal amounts of D- and L-glufosinate. The composition was quite different in the absorbed residue in the leaves (90% D- and 10% L-glufosinate) and in the stems (86% D- and 14% L-glufosinate), showing that within the tissue the L-isomer was more rapidly metabolized

In a separate experiment Stumpf *et al.* (1995a) placed genetically modified and normal tomato plants in solutions of labelled glufosinate for 2 days and examined the uptake and composition of the residue in the plants. The genetically modified plants took up much more glufosinate and converted about half of it to NAG. In the normal tomato plants about 4% was converted to MPP and the D- and L-glufosinate remained approximately equal.

Table 16. Residues in genetically modified tomato plants at the 7-8 leaf stage after treatment with [3,4-^{14}C]glufosinate-ammonium (Stumpf *et al.*, 1995a).

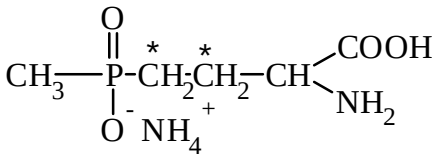
Sample		Days after treatment	% of ^{14}C, mg/kg as glufosinate-ammonium					
			glufosinate-ammonium		MPP		NAG	
			^{14}C %	mg/kg	^{14}C %	mg/kg	^{14}C %	mg/kg
leaves	Rinse	0 (2 h)	94		1.8		0.0	
leaves	Rinse	0 (4 h)	94		1.5		0.0	
leaves	Rinse	1	95		1.5		0.0	
leaves	Rinse	4	94		1.6		0.3	
leaves	Rinse	6	93		1.8		0.6	
leaves	Rinse	32	93		1.4		1.2	
leaves	Rinse	74	86		4.1		3.3	
leaves	Rinse	74	83		7.2		3.9	
leaves	After rinsing	0 (2 h)	69		0.0		27	
leaves	After rinsing	0 (4 h)	61		0.0		36	
leaves	After rinsing	1	64		0.0		33	
leaves	After rinsing	4	52		1.0		42	
leaves	After rinsing	6	53		2.4		41	
leaves	After rinsing	32	57		3.5		37	
leaves	After rinsing	74	44		5.6		51	
leaves	After rinsing	74	42	2.2	2.5	0.13	50	2.6
leaves	Not rinsed	12	30		1.6		65	
leaves	not rinsed	14	17		0.0		83	
leaves	not rinsed	27	0.0		0.0		100	
leaves	not rinsed	32	75		2.7		20	
leaves	not rinsed	74	51	4.4	2.5	0.22	42	3.6
stems	rinse	0 (2 h)	95		1.0		0.0	
stems	rinse	0 (4 h)	97		0.5		0.0	
stems	rinse	1	93		1.9		1.2	
stems	rinse	4	94		1.1		2.0	
stems	rinse	6	94		1.1		2.3	
stems	rinse	32	88		2.1		5.7	
stems	rinse	74	87		2.2		7.4	
stems	rinse	74	92		0.0		7.7	
stems	after rinsing	0 (2 h)	75		0.0		16	
stems	after rinsing	0 (4 h)	61		0.0		39	
stems	after rinsing	1	58		0.0		39	
stems	after rinsing	4	42		0.0		58	
stems	after rinsing	6	45		0.0		53	
stems	after rinsing	32	32		6.4		61	
stems	after rinsing	74	31		-		69	
stems	after rinsing	74	26	0.51	3.8	0.07	67	1.3
stems	not rinsed	12	8.6		0.0		91	
stems	not rinsed	14	7.2		0.0		93	
stems	not rinsed	27	0.0		0.0		100	
stems	not rinsed	32	47		3.6		49	
stems	not rinsed	74	37	0.95	2.6	0.07	57	1.5
fruit	rinse	74	0		0		0	
fruit	after rinsing	74	0.0	-	6.2	0.009	94	0.14
fruit	not rinsed	74	0.0	-	9.5	0.02	85	0.17
fruit, green	not rinsed	32	1.7		4.6		88	
fruit, red	not rinsed	60	0.0		0.0		100	
fruit, red	not rinsed	74	0.0		0.0		100	

Figure 2. Proposed metabolic pathways of glufosinate-ammonium in plants.



Environmental fate in soil

Aerobic degradation


Labelled glufosinate-ammonium

Allan (1995) studied the aerobic degradation of [3,4-^{14}C]glufosinate-ammonium in a sandy loam soil (pH 6.0, organic carbon 1.8%) both when applied directly to the soil at 2 mg/kg and when incorporated as a residue in bushbean leaves which, having been desiccated with labelled glufosinate-ammonium, contained ^{14}C equivalent to 76 mg/kg of glufosinate-ammonium. The bean leaves (1.66 g) were added to 50 g of soil giving a theoretical level of 2.5 mg/kg. The soil was adjusted to 40% of maximum water holding capacity and incubated at 20°C in the dark. The results are shown in Table 17.

Glufosinate disappeared very quickly with a half-life of 3-6 days (Table 18). The main product was MPP, reaching its peak after about 14 days. MPA was also an important product and in the absence of plant material became the main residue after long intervals. NAG was a very minor soil residue.

Table 17. Distribution of ^{14}Cfrom [3,4-^{14}C]glufosinate-ammonium incubated aerobically in a soil in the dark or incorporate-d into the soil as a plant-metabolized residue (Allan 1995).

Days incubated	Residues and evolved $^{14}CO_2$ expressed as % of applied ^{14}C.					
	Soil treatment			Plant incorporation		
	extractable	Unextractable	$^{14}CO_2$	extractable	Unextractable	$^{14}CO_2$
0	106	1.8	-	97	9.7	0
1	80	8.3	0.6	90	14	0.1
3	82	11	1.5	87	17	0.4
7	77	15	5.6	80	20	1.8
14	70	21	11	75	21	4.1
21	61	21	17	69	24	7.6
28	60	20	23	68	28	8.6
41	46	19	26	58	20	9.5
59	32	24	43	32	26	22
90	8.7	25	57	23	29	26
120	5.6	21	62	18	23	31

Table 18. Composition of residues resulting from aerobic incubation of [3,4-^{14}C]glufosinate-ammonium in a soil in the dark or incorporated into the soil as a plant-metabolized residue (Allan 1995).

Days incubated	% of applied ^{14}C							
	Soil treatment				Plant incorporation			
	glufosinate	MPP	NAG	MPA	glufosinate	MPP	NAG	MPA
0	104	-	-	-	75	14	3.2	-
1	77	11	2.3	-	70	18	-	-
3	56	19	2.4	2.1	47	30	4.8	2.2
7	32	31	2.2	6.4	15	52	-	7.3
14	18	37	0.7	11	2.9	62	-	6.3
21	7.8	33	0.4	15	0.6	56	-	9.2
28	3.3	34	-	19	-	61	-	6.9
41	0.9	22	0.3	20	-	55	-	0.3
59	0.5	13	-	17	-	30	-	-
90	0.1	1.4	-	6.8	-	23	-	-
120	0.5	1.6	-	1.6	-	17	-	-

Field dissipation

In a 1-year field dissipation study in California Belcher (1996a) applied glufosinate-ammonium three times to bare ground at rates of 1.7 kg ai/ha between rows in a level vineyard. The soil was a coarse sandy loam. Irrigation supplemented rainfall and followed the growers' standard practices. Soil samples were analysed for glufosinate, MPP and MPA, the main residues. The results are shown in Table 19.

Glufosinate dissipated rapidly, possibly owing to increasing soil moisture and temperature, with calculated half-lives of 15, 7.2 and 2.7 days after the first, second and third applications respectively.

The maximum MPP residues were 0.11, 0.16 and 0.14 mg/kg on days 30, 10 and 5 after the first, second and third applications respectively and the estimated half-lives were 38, 14 and 16 days from these times. The estimated half-lives for MPA were 25, 19 and 7 days for the successive

applications. MPA residues reached their highest levels of 0.06, 0.06 and 0.04 mg/kg on days 60, 10 and 5 after the first, second and third applications respectively.

No residues were detected below the 45-60 cm depth segment. Glufosinate was detected once at the analytical LOD (0.01 mg/kg) after the first application and at 0.02 mg/kg 5 and 10 days after the final application in the 45-60 cm samples. Glufosinate was detectable at low levels 5 and 10 days after application in the 30-45 cm samples, but not at other times. MPP occurred in the 30-45 cm segment on several occasions at 0.01-0.02 mg/kg. MPP was detected only once in the 45-60 cm depth segment, 10 days after the final application at 0.01 mg/kg. MPA was not detected in any sample from 30-45 cm or deeper.

Glufosinate and its soil degradation products have some mobility but their further degradation ensures that travel down the soil profile is limited.

Table 19. Residues of glufosinate and its degradation products at intervals after three applications of glufosinate-ammonium at 1.7 kg ai/ha to bare ground in a level California vineyard (Belcher, 1996a).

Interval after application days	Residues, mg/kg as glufosinate free acid, in soil					
	glufosinate		MPP		MPA	
	soil 0-15 cm	soil 15-30 cm	soil 0-15 cm	soil 15-30 cm	soil 0-15 cm	soil 15-30 cm
Application 1						
0	0.34	<0.01	0.01	<0.01	<0.01	<0.01
5	0.26	<0.01	0.04	<0.01	<0.01	<0.01
10	0.13	<0.01	0.06	<0.01	0.01 <0.01	<0.01
15	0.16	0.05 <0.01	0.07	<0.01	0.02	<0.01
28	0.1	<0.01	0.10	<0.01	0.03	<0.01
47	0.04	<0.01	0.10	<0.01	0.04	<0.01
65	0.02	<0.01	0.05	0.02	0.05	<0.01
93	<0.01	<0.01	0.02	0.02	0.04	<0.01
124	<0.01	<0.01	<0.01	<0.01	0.01	<0.01
Application 2						
0	0.47	<0.01	0.03	<0.01	0.02	<0.01
5	0.10	0.07	0.09	0.03	0.03	<0.01
10	0.02	0.08	0.08	0.04	0.05	0.01
15	0.02	0.03	0.06	0.03	0.05	0.01
30	<0.01	0.02 <0.01	0.03	0.02	0.02	0.01
45	<0.01	0.01	0.01	0.03	0.01 <0.01	0.01 <0.01
59	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
90	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
119	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Application 3						
0	0.41	<0.01	0.02	<0.01	<0.01	<0.01
5	0.03	0.04	0.06	0.04	0.03	0.01
10	0.01	0.01	0.04	0.02	0.02	0.02
15	0.01	<0.01	0.03	0.01	0.01	0.01
30	<0.01	<0.01	0.02	<0.01	<0.01	<0.01
45	<0.01	<0.01	0.02	<0.01	<0.01	<0.01
60	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
93	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Stumpf (1993a) incubated 3.6 mg/kg [3,4-^{14}C]*N*-acetyl-L-glufosinate disodium salt in a sandy loam soil (pH 5.8, organic carbon 1.1%) in the dark at 20°C under aerobic conditions for 62 days. The results are shown in Table 20.

N-acetyl-L-glufosinate was very rapidly degraded to L-glufosinate, which was then further degraded. The degree of mineralization (40%) and the level of bound residues (21%) in 62 days parallel the 43% mineralization of glufosinate-ammonium and 24% unextractable residues in 59 days reported by Allan (1995), and suggest that the degradation pathway for NAG is through glufosinate.

Table 20. Aerobic soil degradation of [3,4-^{14}C]*N*-acetyl-L-glufosinate disodium salt in soil (Stumpf, 1993c).

Day	Residues and evolved $^{14}CO_2$ expressed as % of applied ^{14}C and as NAG mg/kg										
	$^{14}CO_2$	NAG		L-glufosinate		MPP		MPA		bound residues	
	%	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
0.1	0	47	1.7	47	1.7	2.1	0.08	1.0	0.04	0.7	0.03
1	0.5	8.7	0.31	80	2.9	6.7	0.24	1.3	0.05	1.5	0.05
3	1.0	3.1	0.11	69	2.5	20	0.73	3.4	0.12	1.0	0.04
23	15	1.4	0.05	16	0.57	40	1.4	9.5	0.34	11	0.38
41	24	1.6	0.06	4.7	0.17	39	1.4	9.9	0.36	13	0.44
62	40	0	0	1.5	0.05	27	0.98	9.9	0.36	21	0.75

Stumpf *et al.* (1995c) incubated 0.5 mg/kg [2-^{14}C]2-methylphosphinicoacetic acid (MPA) in a sandy loam (pH 5.8, organic carbon 1.1%) and a loamy sand (pH 4.9, organic carbon 2.4%) in the dark at 20°C under aerobic conditions for 122 days and measured the rate of degradation and mineralization (Table 21). No important degradation products other than CO_2 were identified.

In the sandy loam bound residues accounted for 22% and 25% of the applied ^{14}C on days 28 and 122 respectively. Estimated decline and mineralization half-lives were 24 and 74 days respectively, but the curves were not simple first-order and the rates were slower at longer intervals. The rates in the loamy sand were much slower, with only 20% mineralization after 122 days and a decline half-life of 120-160 days. Bound residues again accounted for about 25% of the applied ^{14}C throughout the study.

Table 21. Aerobic soil degradation of [2-^{14}C]2-methylphosphinicoacetic acid (Stumpf *et al.* 1995c).

day	loamy sand			sandy loam		
	$^{14}CO_2$	MPA		$^{14}CO_2$	MPA	
	% of applied ^{14}C	% of applied ^{14}C	mg/kg	% of applied ^{14}C	% of applied ^{14}C	mg/kg
0		87	0.47		99	0.54
3	0.7	89	0.48	4.0	90	0.49
7	1.8	86	0.47	6.6	89	0.49
14	4.2	76	0.42	14.5	77	0.42
28	7.9	69	0.38	31	47	0.26
60	17	62	0.34	63	45	0.25
94	23	53	0.29	75	3.8	0.002
122	20	56	0.30	75	3.5	0.002

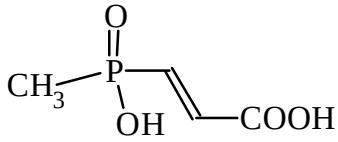
Stumpf *et al.* (1995d) incubated [3,4-^{14}C]glufosinate-ammonium at 1.9 mg/kg and [3-^{14}C]MPP at 0.9 mg/kg in the same sandy loam soil in the dark at 10°C under aerobic conditions for 120 days. The results are shown in Table 22 and 23.

The estimated half-life for glufosinate-ammonium disappearance was 24 days; the rate of mineralization was slow with an estimated half-life of 300 days or more. MPP and subsequently MPA were major components of the residue after the longer periods of incubation. NAG and

AE F065594 (4-methylphosphinico-2-oxobutanoic acid) and possibly AE F086486 (3-methylphosphinico-3-oxopropionic acid) were identified as minor products.

The estimated half-life for MPP disappearance and mineralization were 86 days and 220 days respectively. MPA was the only product of significance accounting for 40% of the extractable residue by day 120.

Stumpf and Zumdick (1998) further investigated the nature of the minor soil product previously identified as AE F086486 and, using LC-MS-MS, identified the compound as 3-methylphosphinicoacrylic acid (AE 0015081). The structure was confirmed by synthesis.



AE 0015081
3-methyl-phosphinico
acrylic acid

Table 22. Residues resulting from incubation of 1.9 mg/kg [3,4-^{14}C]glufosinate-ammonium in a sandy loam soil in the dark at 10°C under aerobic conditions for 120 days (Stumpf *et al.*, 1995d).

Incubation, days	Residues, % of applied ^{14}C					
	Extractable residue	Glufosinate	MPA	MPP	NAG/ AE F065594	AE F086486[1]
0	94	90	<0.5	1.6	1.8	<0.5
1	93	85	<0.5	5.3	2.5	<0.5
4	91	72	1.9	12	1.8	2.3
7	86	57	3.3	20	2.2	4.0
14	87	42	5.5	32	2.6	4.9
21	87	32	7.9	38	2.5	7.1
30	86	25	9.5	43	1.8	6.8
56	79	9.9	14	45	2.5	6.7
91	69	2.0	19	41	3.1	4.1
120	69	5.4	22	36	2.7	3.9

[1]Subsequently identified as AE 0015081 (Stumpf and Zumdick, 1998).

Table 23. Aerobic degradation of [3-^{14}C]3-methylphosphinicopropionic acid (MPP) incubated at 0.9 mg/kg in a sandy loam soil in the dark at 10°C for 120 days (Stumpf *et al.*, 1995d).

Incubation, days	Residues, % of applied ^{14}C			
	Extractable residue	CO_2	MPP`	MPA
0	97	0	97	<1.0
1	95	0.1	95	<1.0
4	96	0.6	94	1.8
7	90	1.1	87	3.1
14	91	3.0	79	11.4
21	89	5.4	80	9.0
30	90	6.1	76	13.5
56	74	18	49	25
91	68	21	46	22
120	62	32	37	25

Zumdick (1995a) incubated 2.1 mg/kg [3,4-^{14}C]L-*N*-acetyl-glufosinate in a sandy loam and a loamy sand under aerobic conditions for 120 days at 20°C in the dark (Table 24). In a second experiment glufosinate-tolerant tomato leaves containing residues equivalent to 1 mg glufosinate-

ammonium per kg soil were incorporated into the sandy loam and incubated under the same conditions (Table 25). Bound residues accounted for about 14-23% of the applied residue in each of the three incubations from days 28 to 120.

N-acetyl-glufosinate disappeared very quickly, with half-lives of only hours, producing initially L-glufosinate, which was then degraded further to MPP, MPA and CO_2. MPP became the major component of the residue after 1-3 days.

The tolerant-tomato residue comprised mainly glufosinate and *N*-acetyl-glufosinate. After 3 days incubation in the sandy loam soil most of the residue had been converted to MPP, which itself was degraded more slowly to MPA and ultimately to CO_2.

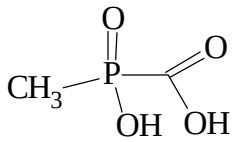
Table 24. Residues resulting from incubation of 2.1 mg/kg [3,4-^{14}C] L-*N*-acetyl-glufosinate in a sandy loam and a loamy sand under aerobic conditions for 120 days at 20°C in the dark (Zumdick 1995a).

Days	Residues, % of applied ^{14}C									
	loamy sand					sandy loam				
	NAG	CO_2	L-glufosinate	MPP	MPA	NAG	CO_2	L-glufosinate	MPP	MPA
0	70	-	20	8.4	0.4	61	-	30	4.7	0.0
0.25	14	0.3	58	13	1.2	29	0.2	58	8.1	0.7
1	15	1.1	23	35	4.7	9.2	0.9	49	22	2.2
2	6.2	3.6	23	38	5.9	4.3	2.3	41	29	3.4
3	5.1	2.8	16	42	7.4	3.1	4.9	24	37	5.9
7	4.1	11	6.3	36	9.6	1.8	1.1	38	34	8.1
14	2.8	21	5.2	27	7.6	1.0	10.5	2.6	39	19
28	1.3	39	2.2	5.2	0.8	0.4	23	1.0	28	18
62	0.5	49	1.3	1.9	0.0	0.2	56	1.0	2.1	1.2
90	0.5	52	1.1	0.7	0.0	0.4	67	1.0	0.7	0.3
120	0.3	72	0.4	0.1	0.0	0.2	66	0.4	0.5	0.1

Table 25. Residues resulting from incubation of [3,4-^{14}C]glufosinate metabolized in tolerant tomato leaves, incorporated at 1 mg glufosinate-ammonium equivalent per kg soil, in a sandy loam under aerobic conditions for 120 days at 20°C in the dark (Zumdick 1995a).

Days	Residues, % of applied ^{14}C				
	glufosinate	CO_2	NAG	MPP	MPA
0	46	-	33	4.1	0.3
0.25	47	0.0	27	4.3	0.4
1	44	0.0	30	8.9	0.6
2	27	0.1	20	27	4.1
3	5.4	0.2	2.9	52	16
7	1.4	5.3	0.4	47	25
14	0.7	5.8	0.0	40	18
28	0.6	16	0.0	31	0.6
62	0.7	48	0.0	6.7	1.2
90	0.2	49	0.0	0.8	0.0
120	0.3	43	0.0	2.4	0.0

Zumdick (1995b) incubated 1 mg/kg [3,4-^{14}C]L-*N*-acetyl-glufosinate in a sandy loam from Germany and a silt loam from Nebraska under aerobic conditions for 120 days at 20°C in the dark (Table 26). The results were consistent with other similar experiments, with the NAG rapidly forming glufosinate, which was in turn converted to MPP and MPA. An additional product (AE F130947, methylphosphinicoformic acid) was separated from the others by the HPLC systems used. Bound residues from days 14 to 90 constituted 14-22% of the applied ^{14}C.



AE F130947
methylphosphinico-formic acid

Table 26. Residues resulting from incubation of 1 mg/kg [3,4-^{14}C] L-*N*-acetyl-glufosinate in a sandy loam and a silt loam under aerobic conditions for 120 days at 20°C in the dark (Zumdick 1995b).

Days	Residues, % of applied ^{14}C											
	sandy loam						silt loam					
	NAG	CO_2	L-glufos	MPP	MPA	130947	NAG	CO_2	L-glufos	MPP	MPA	130947
0.1	91	-	9.7	0.8	0.1	<0.1	85	-	13	1.7	0.1	<0.1
0.25	16	0.2	66	7.3	0.6	0.4	26	0.3	36	11	0.3	0.3
1	7.5	0.8	48	21	1.8	2.0	11	1.7	46	23	3.2	2.8
3	4.7	7.0	26	35	5.2	4.2	3.5	6.3	26	25	11	5.9
7	3.2	16	10	32	9.1	6.3	2.4	15	11	18	21	10
14	1.9	29	4.3	20	12	7.3	0.7	36	2.6	2.8	18	8.7
21	1.2	41	6.1	12	8.8	5.3	0.3	44	2.8	1.9	15	4.5
30	0.7	48	4.2	5.8	5.3	3.9	0.3	59	1.5	0.4	4.4	1.3
59	1.3	64	1.5	1.5	0.2	0.3	<0.1	63	0.8	<0.1	<0.1	<0.1
90	0.3	68	0.6	0.3	<0.1	<0.1		65				
120		77						67				

Stumpf *et al.* (1989) subjected [3,4-^{14}C]glufosinate-ammonium in a thin layer of a microbiologically active sandy loam soil to UV irradiation (xenon arc with 290 nm cut-off filters) for 35 days in a 12 hours light-dark cycle at 25°C and identified the products. The calculated degradation half-life was 35 days, with 7.6% production of $^{14}CO_2$ in that time. Three degradation products were identified: MPP (6-21% of the applied ^{14}C), MPA (0-5%) and NAG (0-10%). Three other products were in too small amounts (0-3% and 4-9%) to be identified. Degradation was caused by microbiological processes and photolysis in the presence of humic acids.

In a rotational crop study Campbell and Bennett (1997) treated bare ground plots in North carolina, Missouri and California twice at 10-day intervals with glufosinate-ammonium at 0.39 and 0.54 kg ai/ha and planted winter wheat 75 and 90 days after the final treatment. No residues of glufosinate or MPP were detected (LOD 0.05 mg/kg) in forage, hay, grain or straw samples. No uptake of glufosinate or MPP should occur in winter wheat following a previous use of glufosinate-ammonium.

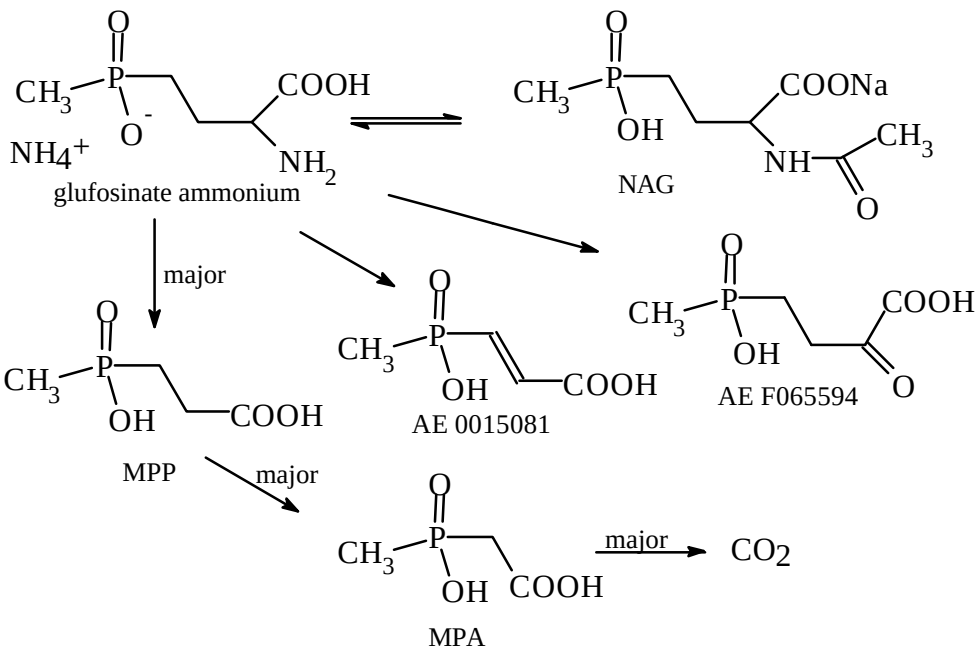
In a confined rotational crop study, Meyer *et al.* (1995) applied [3,4-^{14}C]glufosinate-ammonium to a bare sandy loam soil in a greenhouse in stainless steel tanks at 1.0 kg ai/ha and planted radishes, lettuce and wheat 28 and 119 days later. The intervals represented resowing after crop failure and immediate recropping. Residue levels are shown in Table 27. Product A was not identified, but was characterized as a relatively simple polar unconjugated compound that may be a degradation product taken up by roots. The products were similar in the root, leafy and small cereal grain crops. Levels were much lower after the longer sowing interval. Residues should be undetectable or very low in rotational crops.

Table 27. ^{14}C residues in rotational crops after application of [3,4-^{14}C]glufosinate-ammonium at 1.0 kg ai/ha to a bare sandy loam soil (Meyer *et al.*, 1995).

Commodity	Residues, mg/kg, as glufosinate free acid							
	28 days interval to sowing				119 days interval to sowing			
	total ^{14}C	MPP	MPA	Compound A	total ^{14}C	MPP	MPA	Compound A
Radish top	0.110	0.053	0.006	0.021	0.013[1]			
Radish root	0.090	0.047	0.008	0.024	0.009[1]			
Lettuce	0.079	0.020	0.006	0.013	0.013[1]			
Wheat forage	0.30	0.17	0.019	0.027	0.047[1]			
Wheat straw	0.78	0.35	0.073	0.19	0.14	0.029	0.008	0.035
Wheat grain	0.33	0.11	0.035	0.035	0.12	0.015	<0.001	0.016

[1]Residue too low for characterization.

Figure 3. Proposed aerobic soil degradation pathways of glufosinate-ammonium.



Environmental fate in water/sediment systems

Stumpf and Schink (1992) subjected [3,4-^{14}C]glufosinate-ammonium dissolved in surface water from a gravel pit to UV irradiation for 118 hours (equivalent to 33 days sunlight) at 25°C. Glufosinate suffered little degradation under these conditions, with 3-5% conversion to MPP and 0.2% mineralization. Photolytic degradation of glufosinate in surface waters is a minor degradation route.

Stumpf (1993b) incubated [3,4-^{14}C]glufosinate-ammonium at 0.1 mg/kg in aerobic systems consisting of 180 ml water and 20 g sediment at 20°C and 8°C for 361 days. The sediment was sandy with 0.4% organic carbon.

Glufosinate disappeared from the water/sediment system with half-lives of 3 and 20 days at 20°C and 8°C respectively. Mineralization occurred to the extent of only 25 and 20% at the two temperatures in the 361 days of the study. Within a few days at 20°C and after 29 days at 8°C MPP became the major component of the residue. Seven other products were observed, but five were very minor. Two others amounting to 5% and 20% of the applied dose at various times were not positively identified. At all times most of the total residue was in the aqueous phase.

In sterile (autoclaved) samples incubated for 29 and 120 days up to 50% of the residue was converted to NAG in some samples, but heat resistant bacteria may have been present.

Table 28. Residues resulting from incubation of [3,4-^{14}C]glufosinate-ammonium in a water/sediment system under aerobic conditions at 8°C and 20°C (Stumpf 1993e).

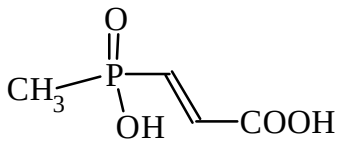
Days	Residues, % of applied ^{14}C									
	20°C					8°C				
	Glufosinate	CO_2	MPP	NAG	MPA	Glufosinate	CO_2	MPP	NAG	MPA
0	95	-	4.4	2.6	0.0	95	-	4.4	2.6	0.0
1	60	0.3	21	14	1.0	84	0.1	7.8	7.0	0.3
4	39	0.8	40	9.8	1.4	61	0.3	15	10.3	0.4
7	24	1.5	49	5.7	3.4	56	0.3	21	14	0.7
14	7.1	4.4	59	3.9	3.2	48	0.7	28	12	1.5
21	0.3	8.2	56	2.4	2.9	45	1.5	32	6.5	2.8
29	0.1	12	53	1.9	3.8	33	1.7	39	3.7	3.5
60	0.0	18	52	0.2	2.9	15	5.4	44	3.3	3.3
90	0.0	21	52	0.1	3.0	2.7	6.7	49	4.2	3.7
120	0.0	17	47	0.0	4.0	0.0	9.0	51	3.0	3.3
238	0.0	23	46	0.0	5.6	0.0	17	45	0.0	2.3
361	0.0	25	48	0.0	5.6	0.0	20	55	0.0	1.4

Stumpf (1994a) incubated [3,4-^{14}C]glufosinate-ammonium at 1 and 0.1 mg/kg in two aerobic systems consisting of 180 ml water and 20 g sediment at 20°C in the dark for 130 days (Tables 29 and 30).

The mineralization in130 days in the gravel pit sediment was 7% at the lower dose and 12% at the higher dose. The half-lives for the degradation of glufosinate itself were 11, 91 and 1.4 days for the loamy river water sediment at 1 mg/kg and the gravel-pit sediment at 1 mg/kg and 0.1 mg/kg respectively. MPP was the main product identified and it was quite persistent in both systems. In all cases most of the residue was in the water phase.

As in a previous experiment (Stumpf, 1993b) a number of minor products were detected but not identified. Two products, sometimes constituting 10-20% of the residue, were further investigated and identified as AE F086486 and possibly AE F130947 (methylphosphinicoformic acid).

In a subsequent study, Stumpf (1994b) used glufosinate labelled in different positions and a higher dose rate to produce sufficient material for positive identification as AE F130947, also identified as a soil degradation study (Zumdick, 1995b).



AE 0015081
3-methyl-phosphinico
acrylic acid

Stumpf and Zumdick (1998) corrected the identification of AE F086486 (3-methylphosphinico-3-oxopropionic acid) to AE 0015081 and confirmed AE F130947.

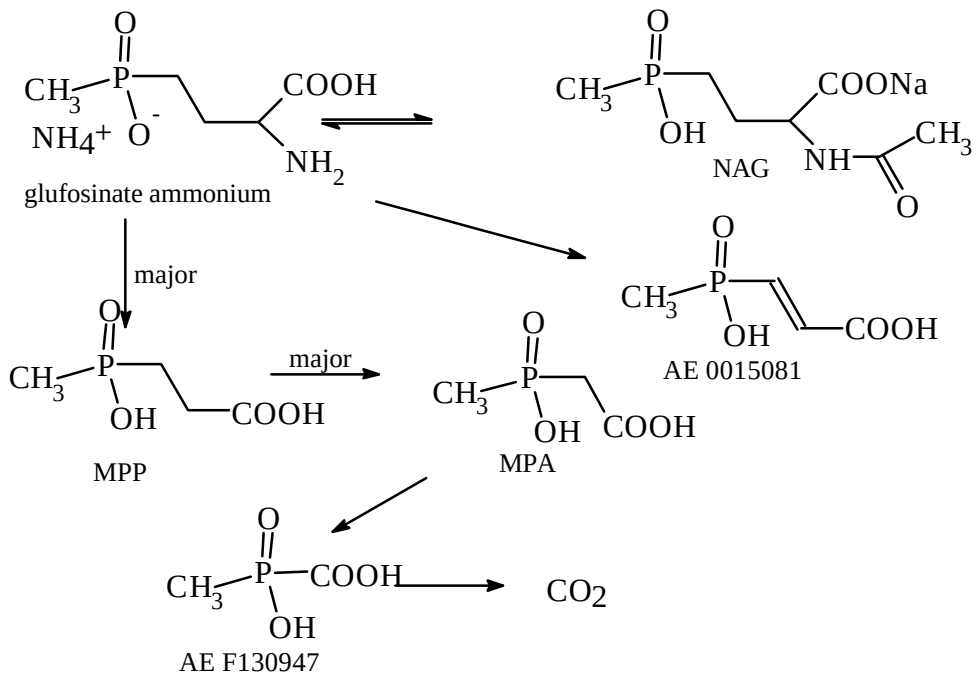
Table 29. Residues resulting from incubation of [3,4-^{14}C]glufosinate-ammonium in a gravel pit water/sediment system at 20°C in the dark for 130 days (Stumpf, 1994a).

Days	Residues, % of applied ^{14}C in whole system									
	gravel-pit sediment, 1 mg/kg					gravel-pit sediment, 0.1 mg/kg				
	Glufosinate	CO_2	MPP	NAG	MPA	Glufosinate	CO_2	MPP	NAG	MPA
0	91	-	2.0	0.7	0.0	89	-	2.9	1.7	0.0
1	86	0.0	6.8	2.0	0.4	59	0.0	23	9.9	0.9
3	74	0.0	15	4.0	0.7	21	0.2	55	7.5	3.5
7	69	0.2	19	4.1	2.4	3.8	1.0	79	1.8	4.7
14	60	0.5	25	3.7	4.1	0.1	2.8	80	0.3	5.7
21	57	0.8	27	2.5	6.2	0.0	4.4	78	0.0	4.6
30	46	1.9	28	3.3	10.0	0.0	6.8	76	0.0	4.1
50	39	2.9	31	4.3	12	0.0	8.6	76	0.0	4.2
77	36	4.3	30	2.9	14	0.0	10.6	74	0.0	4.4
91	37	5.0	30	1.4	14	0.0	12	70	0.0	5.1
130	33	7.1	30	2.1	16	0.0	12	67	0.0	6.8

Table 30. Residues resulting from incubation of [3,4-^{14}C]glufosinate-ammonium in a loamy river water sediment system at 20°C in the dark for 130 days (Stumpf, 1994a).

Days	Residues, % of applied ^{14}C				
	Glufosinate	CO_2	MPP	NAG	MPA
0	91	?	1.3	1.0	0.0
1	87	?	5.4	2.5	0.3
3	72	?	13	6.2	3.4
7	60		19	8.2	5.9
14	46		26	7.6	10.2
21	35		29	4.5	12
30	19		37	1.5	16
50	3.0		41	0.0	20
77	0.0		48	0.0	18
91	0.0		48	0.0	17
130	0.0		45	0.0	16

Figure 4. Proposed aerobic degradation pathways of glufosinate-ammonium in water/sediment systems



METHODS OF RESIDUE ANALYSIS

Analytical methods

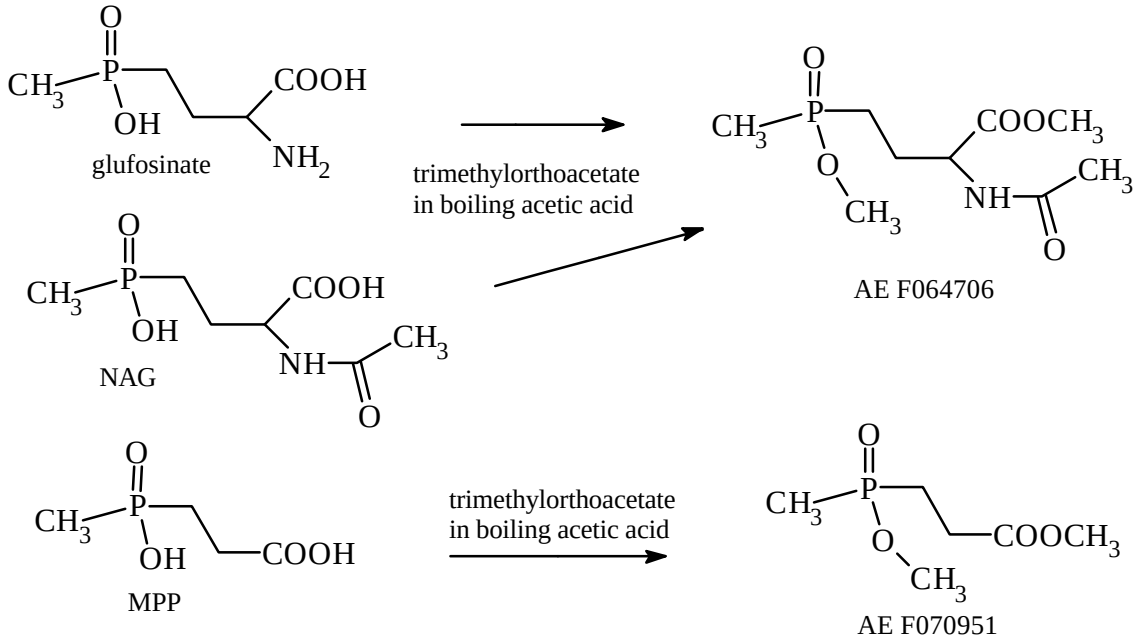
The main components of the residue in genetically modified tolerant crops are glufosinate, NAG (*N*-acetyl-L-glufosinate) and MPP (3-methyl-phosphinico-propionic acid). Analytical methods have been designed to measure the three components separately or, because glufosinate and NAG produce the same derivative in the analytical procedure, to measure glufosinate and NAG combined and MPP separately.

Holzwarth (1995) described the methods used for residue analysis of tolerant crops. Residues are extracted from the finely ground sample with water. The clear extract, after separation from solid material, is passed through an anion exchange resin and the residues are eluted with formic acid. After evaporation of the formic acid the residue is taken up in a 1:1 ethanol/water mixture which is then applied to a cation exchange column. NAG and MPP are eluted with ethanol/water and glufosinate with aqueous ammonia.

After evaporation to dryness the residues from both fractions are taken up in glacial acetic acid and methylated and acetylated with trimethyl orthoacetate in refluxing acetic acid. After solvent exchange and a final silica gel cartridge clean-up the residues are determined by GLC with flame photometric detection.

Variations on the extraction and initial clean-up are needed for samples such as maize oil. The lower limit of determination for crop samples is typically 0.05 mg/kg for each of the three analytes. For fats and milk a mixture of n-propanol and water is used for extraction instead of water.

Figure 5. Derivatization of glufosinate, NAG and MPP.



Czarnecki *et al.* (1989) used a method (HRAV-5A) similar in principle to that described above for the determination of glufosinate and MPP in apples, grapes, soya beans, maize and tree nuts. Czarnecki and Bertrand (1993) described a similar method (HRAV-24) for the determination of glufosinate, MPP and NAG in maize and its processed fractions. Sochor *et al.* (1991) measured residues of glufosinate, MPP and NAG in tomatoes, tobacco and potatoes by the same method and achieved practical LODs of 0.05-0.2 mg/kg.

Czarnecki (1995a) analysed animal commodities for glufosinate and MPP by a similar method but without the cation exchange column clean-up, achieving LODs of 0.02 mg/kg for milk, 0.05 mg/kg for eggs, meat and fat, and 0.1 mg/kg for kidneys and liver. Czarnecki (1995b) included NAG in the same method with the same LODs. NAG and glufosinate appear in the same GLC peak so the LOD is for either compound or the combined residue.

Czarnecki and Bertrand (1994) described a comprehensive procedure for the determination of glufosinate, MPP and NAG in many commodities. The method (AE-24) is essentially as described above with many variations on the extraction depending on the nature of the sample. Recoveries should lie within the range 70-120% at the practical LOD of 0.05 mg/kg for each compound, expressed as glufosinate free acid. The method was determined and used on maize grain, silage, forage, fodder, starch, grits, flour, meal and hulls, and soya bean seed, hay, hulls and meal. The same method was described by Czarnecki (1995c). Bertrand (1994) validated the method (Table 31). Most tests were at a fortification level of 0.05 mg/kg, but recoveries did not seem to depend on concentration. Median recoveries were 95%, 95% and 102% for glufosinate, MPP and NAG respectively.

Bertrand (1994) pointed out that part of the glufosinate added to glufosinate-tolerant plant material could be converted to NAG during recovery testing. When racemic glufosinate was added to transgenic soya bean seed at 0.5 mg/kg, 44-54% was recovered as glufosinate and 33-43% as NAG. When D-glufosinate was used, recoveries of glufosinate were 85-100%. In some transgenic materials it is necessary to use D-glufosinate, which is not subject to enzymic *N*-acetylation, to determine the analytical recovery of glufosinate. The method is not selective for either isomer.

Table 31. Recoveries of glufosinate, MPP and NAG from maize grain, forage, fodder, silage, flour, meal, hulls, starch, and crude oil, and soya bean seeds, hulls, meal, hay/fodder and crude oil (Bertrand, 1994).

Recovery range, %	Number of tests		
	Glufosinate	MPP	NAG
61-70		4	1
71-80	5	13	0
81-90	16	28	4
91-100	17	30	19
101-110	17	23	18
111-120	7	15	8
121-130		4	6
131-140		1	

Castro and Dacus (1994) validated analytical method AE-24 (suitable for enforcement) on commodities from transgenic maize and soya beans. D-glufosinate was used to determine recoveries from soya bean seed. An LOD of 0.05 mg/kg for each compound on each commodity was achieved (Table 32). The time needed to analyse a batch of six samples was about 18 working hours over 3 working days.

Table 32. Recoveries by analytical method AE-24 from transgenic maize and soya bean commodities (Castro and Dacus, 1994).

Commodity	Glufosinate		MPP		NAG	
	spiking levels, mg/kg	Recovery range, %	spiking levels, mg/kg	Recovery range, %	spiking levels, mg/kg	Recovery range, %
Maize grain	0.05 0.25	73-98% (n=4)	0.05 0.25	73-78% (n=4)	0.10 0.50	89-107% (n=4)
Maize forage	0.50 2.5	83-89% (n=4)	0.10 0.50	76-87% (n=4)	3.0 15	101-110% (n=4)
Corn oil, refined	0.05 0.25	57-96% (n=4)	0.05 0.25	70-82% (n=4)	0.05 0.25	113-149% (n=4)
Soya bean seed	0.05 0.25 (D-glufosinate)	65-89% (n=4)	0.10 0.50	80-91% (n=4)	0.20 1.0	85-109% (n=4)

Holzwarth (1996a) determined the suitability of analytical method AE-24 for residues in glufosinate-tolerant maize shoots. Recoveries of spiked analyte over the concentration range 0.05-5 mg/kg were glufosinate 60-99% (n=6), NAG 65-85% (n=6) and MPP 53-99% (n=12). Holzwarth (1996b) also validated method AE-24 for residues in maize grain from plants susceptible to glufosinate-ammonium. Recoveries over the concentration range 0.05-5 mg/kg were: glufosinate 81-95% (n=6), NAG 68-82% (n=6) and MPP 54-94% (n=11).

Snowdon and Taylor (1995b) validated method AE-24 for glufosinate-tolerant maize, achieving LODs of 0.05 mg/kg for each analyte. Recoveries are shown in Table 33.

Table 33. Recoveries by analytical method AE-24 from transgenic maize commodities (Snowdon and Taylor, 1995b).

Commodity	Glufosinate		MPP		NAG	
	spiking levels, mg/kg	Recovery range, %	spiking levels, mg/kg	Recovery range, %	spiking levels, mg/kg	Recovery range, %
Maize shoots	0.05 2.0 50	61-105 (n=7)	0.05 2.0 50	69-85 (n=14)	0.05 2.0 50	76-132 (n=7)
Cobs	0.05 0.50	64-104 (n=5)	0.05 0.50	66-89 (n=10)	0.05 0.50	80-113 (n=5)
Cob/spadix	0.05 0.50	95-131 (n=4)	0.05 0.50	74-105 (n=10)	0.05 0.50	97-122 (n=5)

Czarnecki (1995c) validated analytical method AE-24A for maize and its processed products. The method differs from AE-24 in omitting the cation-exchange column step before derivatization. Consequently, the compounds appear as a single peak and are reported as a combined residue. Recoveries were acceptable for maize grain, forage and fodder.

Niedzwiadek and Bertrand (1995b) validated analytical method AE-24A for residues in glufosinate-tolerant rape seed commodities (Table 34). The LOD was 0.05 mg/kg for each analyte in each sample.

Table 34. Recoveries by method AE-24A from transgenic rape seed commodities (Niedzwiadek and Bertrand 1995b).

Commodity	Glufosinate		MPP		NAG	
	spiking levels, mg/kg	Recovery range, %	spiking levels, mg/kg	Recovery range, %	spiking levels, mg/kg	Recovery range, %
Rape shoot	0.05 0.50 10	92-114 (n=15)	0.05 0.50 10	76-115 (n=30)	0.05 0.50 10	91-119 (n=15)
Rape pod	0.05 0.50 5.0	87-108 (n=15)	0.05 0.50 5.0	71-109 (n=30)	0.05 0.50 5.0	88-120 (n=15
Rape straw	0.05 0.50	95-116 (n=10)	0.05 0.50	71-108 (n=20)	0.05 0.50	101-134 (n=10)
Rape seed	0.05 0.50	76-109 (n=10)	0.05 0.50	82-117 (n=20)	0.05 0.50	99-118 (n=10)

Idstein *et al.* (1987b) extracted glufosinate and MPP from soya beans and derivatized the compounds with trimethyl orthoacetate. After clean-up on a silica gel cartridge, the residues were measured by GLC with a flame photometric detector. Idstein *et al.* (1987a extracted glufosinate and MPP from milk by dialysis and completed the analysis in the same way. Schuld (1988) extracted the residues from hens' eggs with water, washed the aqueous extract with dichloromethane and hexane to remove lipids and then followed a similar procedure.

Sochor *et al.* (1987a) extracted rape seed with water and removed oil with dichloromethane before proceeding with the Idstein method. Sochor *et al.* (1987b) extracted the residues from fats by an initial water/dichloromethane partition before following the remainder of the procedure. Sochor *et al.* (1988) extracted animal organs with water, precipitated high MW co-extractives with acetone and continued with the Idstein method, achieving practical LODs of 0.05-0.1 mg/kg.

The method used for glufosinate in The Netherlands relies on extraction of samples with water and clean-up by dialysis and ion-exchange. The residue is measured by GLC with an FPD after derivatization with trimethyl orthoacetate. Recoveries are 70-80% and the LOD 0.05 mg/kg.

Stability of pesticide residues in stored analytical samples

Information was made available on the frozen storage stability of glufosinate and its metabolites in genetically modified maize and processed commodities, soya bean and processed commodities, dairy

cow tissues and milk, eggs and chicken tissues, susceptible maize grain, and transgenic rape seed and sugar beet root.

Belcher (1995a) determined the stability of glufosinate and its metabolites in genetically modified maize commodities (hulls, grits, flour and refined maize oil) during frozen storage for 12 months (Table 35). The report did not state the storage conditions. Residues were generally stable for 12 months, but glufosinate decreased by 30% and NAG by 19% in refined maize oil.

Table 35. Recoveries of glufosinate, NAG and MPP from maize commodities spiked with 0.5 mg/kg and stored for periods up to 12 months under frozen conditions (Belcher 1995a). Results are means of duplicate samples, uncorrected for analytical recovery.

Storage, months	glufosinate ammonium, racemate				NAG, racemate, free acid				MPP, free acid			
	hulls	grits	flour	oil, refined	hulls	grits	flour	oil, refined	hulls	Grits	flour	oil, refined
0	88%	92%	94%	83%	80%	101%	87%	102%	82%	93%	73%	89%
3	81%	84%	71%	67%	91%	89%	82%	94%	92%	81%	86%	84%
6	76%	74%	83%	68%	90%	93%	93%	85%	87%	86%	85%	79%
12	87%	88%	103%	58%	81%	93%	108%	83%	77%	81%	75%	76%

Belcher (1996b) determined the stability of glufosinate and its metabolites in genetically modified maize grain, fodder and forage during frozen storage for 24 months (Table 36). Residues were generally stable. The report did not include the storage conditions.

Table 36. Recoveries of glufosinate, NAG and MPP from maize commodities spiked with 0.5 mg/kg and stored for periods up to 24 months under frozen conditions (Belcher 1996b). Results are means of duplicate samples, uncorrected for analytical recovery.

Storage, months	glufosinate ammonium, racemate			NAG, racemate, free acid			MPP, free acid		
	grain	fodder	forage	grain	fodder	forage	grain	fodder	forage
0	95%	87%	94%	99%	88%	96%	88%	91%	98%
3	89%	97%	91%	93%	89%	90%	86%	99%	97%
6	91%	91%	83%	109%	86%	100%	90%	91%	93%
12	83%	85%	76%	93%	95%	88%	94%	103%	105%
24	88%	79%	76%	101%	88%	78%	90%	89%	87%

Belcher (1995b) determined the stability of glufosinate and its metabolites in genetically modified soya bean meal, hulls and refined oil during frozen storage for 12 months (Table 37). In some samples of meal and hulls enzyme activity converted some of the added glufosinate to NAG. In these cases the sum of glufosinate and NAG was treated as the remaining residue and used for the calculation in Table 37. Residues were generally stable for the 12 months. The report did not specify the storage conditions.

Table 37. Recoveries of glufosinate, NAG and MPP from soya commodities spiked with 0.5 mg/kg and stored for periods up to 12 months under frozen conditions (Belcher 1995b). Results are means of duplicate samples, uncorrected for analytical recovery.

Storage, months	glufosinate ammonium, racemate			NAG, racemate, free acid			MPP, free acid		
	meal	hulls	oil, refined	meal	hulls	oil, refined	meal	hulls	oil, refined
0	68%	83%	79%	84%	91%	104%	113%	90%	87%
3	86%	86%	77%	92%	82%	86%	101%	96%	96%
6	93%	96%	78%	100%	104%	97%	90%	93%	82%
12	83%	94%	93%	78%	96%	103%	93%	95%	87%

Homogenized eggs, chicken tissue, milk and cow tissue samples were spiked with glufosinate-ammonium, NAG and MPP at 0.25 mg/kg and stored at -12°C to -27°C for 15 months (Crotts and McKinney, 1995, 1996; McKinney and Crotts, 1997). The results are shown in Table 38 and 39.All three compounds were stable for 15 months.

Table 38. Recoveries of glufosinate, NAG and MPP from homogenized eggs and chicken tissues spiked with 0.25 mg/kg and stored for periods up to 15 months under frozen conditions (Crotts and McKinney, 1995; McKinney and Crotts, 1997). Results are means of duplicate samples, uncorrected for analytical recovery.

Storage, months	Glufosinate ammonium, racemate			NAG, L-isomer, disodium			MPP, free acid		
	muscle	Liver	eggs	muscle	liver	eggs	muscle	liver	eggs
0	102%	106%	105%	103%	111%	102%	96%	88%	85%
1	104%	102%	109%	103%	102%	101%	89%	92%	82%
3	79%	81%	83%	76%	91%	81%	86%	87%	79%
15	102%	105%	100%	108%	108%	86%	90%	84%	87%

Table 39. Recoveries of glufosinate, NAG and MPP from milk and cow tissues spiked with 0.25 mg/kg and stored for periods up to 15 months under frozen conditions (Crotts and McKinney, 1996). Results are means of duplicate samples, uncorrected for analytical recovery.

Storage, months	glufosinate ammonium, racemate				NAG, L-isomer, disodium				MPP, free acid			
	kidneys	muscle	liver	whole milk	kidneys	muscle	liver	whole milk	kidneys	muscle	liver	whole milk
14	107			86	112			83	100			82
15		76	97			93	107			81	92	

Werner (1997a-d) spiked homogenized transgenic maize shoots, rape seed and sugar beet roots and susceptible maize grain with glufosinate-ammonium, NAG and MPP at 0.5 mg/kg (expressed as glufosinate free acid) and measured the stability of the residues stored deep-frozen (temperature not stated) for 24 months. Results are shown in Table. All three compounds were stable for 24 months.

Table 40. Recoveries of glufosinate, NAG and MPP from homogenized transgenic maize shoots, susceptible maize grain, transgenic rape seed and sugar beet root stored for periods up to 24 months under frozen conditions (Werner 1997a-d). Results are means of duplicate samples, uncorrected for analytical recovery.

Storage, months	glufosinate ammonium, racemate, % remaining				NAG, L-isomer, disodium, % remaining				MPP, free acid, % remaining			
	maize shoot	maize grain	rape-seed	sugar-beet	maize shoot	maize grain	rape-seed	sugar-beet	maize shoot	maize grain	rape-seed	sugar-beet
0	76	81	96	74	75	59	100	64	65	68	87	67
1		92		74		66		72		74		71
2	67		84		75		91		73		91	
3		80		67		83		67		61		63
4	75		85		60		97		51		90	
6				86	106[1]	68[1]	85[1]	79	108	78	71	80
12			103	94	100[1]	63[1]	88	96	96	73	81	77
15	87	100			68	58			57	84		
18	92	106	92	98	77	89	91	103	77	68	86	86
23			101				97				90	
23							104[1]				106	
24					91[1]	91[1]			86	88		
24	83	113		102	88	97		81	72	86		82

[1]Analyses by method AE-24A. % remaining is calculated as sum of glufosinate + NAG.

Definition of the residue

The current definition of the residue for glufosinate-ammonium is *Sum of glufosinate-ammonium and 3-[hydroxy(methyl)phosphinoyl]propionic acid, expressed as glufosinate (free acid).*

When glufosinate is used on glufosinate-tolerant crops a major part of the residue is *N*-acetyl-glufosinate (NAG). It should be included in the definition of the residue for enforcement because it is generally the main component of the residue and the same GLC derivative is produced in the analytical method from glufosinate and NAG, so unless the compounds are separated before derivatization they both appear in the GLC peak for their common derivative.

A suitable revised definition would be *Sum of glufosinate-ammonium, 3-[hydroxy(methyl)phosphinoyl]propionic acid and N-acetyl-glufosinate, expressed as glufosinate (free acid),* but this definition could not be adopted until *N*-acetyl-glufosinate had been toxicologically evaluated.

USE PATTERN

Glufosinate-ammonium is a non-selective herbicide registered for crop uses, including desiccation, and non-crop uses. It is used to control annual and perennial grasses and broad-leaved weeds in horticultural and agricultural crops. Glufosinate acts as an inhibitor of glutamine synthetase, which leads to poisoning of the plant by ammonia. For weed control in susceptible crops it must be used either before crop emergence or as a directed spray away from foliage.

Glufosinate resistance has been imparted to several agronomic crops by insertion of a gene that enables the plant to detoxify L-glufosinate (the active isomer) by acetylation to *N*-acetyl-L-glufosinate which is not herbicidal.

The use pattern is necessarily different for conventional crops and those with glufosinate tolerance.

Table 41. Registered uses of glufosinate-ammonium. Concentrations and rates are expressed in terms of the active ingredient glufosinate-ammonium.

Crop [1]	Country	Form	Application			Number	Growth stage [2]	PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl			
Almond	USA	120 g/l SL	directed	1.7	min spray vol 187 l/ha	max total 5.1 kg/ha/yr		14
Apple	Poland [4]	150 g/l SL		0.45-0.90	0.04-0.35	2		
Apricot	Poland [4]	200 g/l SL		0.60-1.2	0.06-0.60	2		
Asparagus	Germany [4]	200 g/l SL	spray	0.55	0.14-0.18	1		
Avocado	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Banana	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Banana	Malaysia	150 g/l SL	directed	0.3-0.5	0.11	4		14
Bean	Poland [4]	SL	spray HV	0.45-0.60	0.04-0.30	1	pre-emerg	
Blackberries	Netherlands	200 g/l 150 g/l	directed spray	0.75-1.0		2		-
Canola (tolerant)	Canada	150 g/l SL	foliar	0.30-0.50	min spray vol 110 l/ha	2	early bolting	[3]
Canola (tolerant)	Canada	150 g/l SL	foliar	0.60	min spray vol 110 l/ha	1	early bolting	[3]
Carambola (Starfruit)	Malaysia	150 g/l SL	directed	0.3-0.5	0.11	4		14
Carrot	Germany [4]	200 g/l SL	spray	0.55	0.14-0.18	1	pre-emerg	
Carrot	Poland [4]	SL	spray HV	0.45-0.60	0.04-0.30	1	pre-emerg	
Cashew nut	Malaysia	150 g/l SL	directed	0.3-0.5	0.11	4		14
Cherry	Poland [4]	150 g/l SL		0.45-0.90	0.04-0.35	2		
Currants	Germany [4]	200 g/l SL	spray with screening	0.92	0.15-0.31	1		14
Currants	Netherlands	200 g/l 150 g/l	directed spray	0.75-1.0		2		-
Durian	Malaysia	150 g/l SL	directed	0.3-0.5	0.11	4		14
Dwarf French beans	Germany [4]	200 g/l SL	spray between rows with screening	0.92	0.23-0.31	1		14
Dwarf French beans	Germany [4]	200 g/l SL	spraying	0.46	0.08-0.15	1	desiccation	14
Feijoa	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Field peas	Germany [4]	200 g/l SL	spraying	0.46	0.08-0.15	1	desiccation	14
Fruit trees	Netherlands	200 g/l 150 g/l	directed under trees	0.75-1.0		2		-
Gooseberries	Germany [4]	200 g/l SL	spray with screening	0.92	0.15-0.31	1		14
Gooseberries	Poland [4]	200 g/l SL		0.60-1.2	0.06-0.60	2		
Guava	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Guava	Malaysia	150 g/l SL	directed	0.3-0.5	0.11	4		14
Hazelnut	Italy	120 g/l SL	directed	0.5-1.6	0.08-0.78	max total 2.5 kg/ha/yr		-
Horse beans	Germany [4]	200 g/l SL	spraying	0.46	0.08-0.15	1	desiccation	14

Crop [1]	Country	Form	Application			Number	Growth stage [2]	PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl			
Jack fruit	Malaysia	150 g/l SL	directed	0.3-0.5	0.11	4		14
Kiwifruit	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Lamb's lettuce	Germany [4]	200 g/l SL	spray	0.55	0.14-0.18	1	pre-emerg	
Leek	Germany [4]	200 g/l SL	spray	0.55	0.14-0.18	1	pre-emerg	
Litchi	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Macadamia	USA	120 g/l SL	directed	1.7	min spray vol 187 l/ha	max total 5.1 kg/ha/yr		14
Maize	Germany [4]	200 g/l SL	spray	0.92	0.23-0.31	1	pre-sowing	
Maize	Germany [4]	200 g/l SL	spray, under leaf	0.92	0.23-0.31	1	stage 16-20	
Maize (tolerant)	Germany [5]	200 g/l SL	foliar	0.90	0.23-0.45	1	3-8 leaf	
Maize (tolerant)	Germany [5]	200 g/l SL	foliar	0.45	0.11-0.23	2[1]	8 leaf	
Maize (tolerant)	Canada	200 g/l SL	foliar	0.30-0.50	min spray vol 110 l/ha	2[2]	8-leaf	86 grain 20 (graze)
Maize (tolerant)	Portugal	200 g/l SL	foliar	0.40-0.80	rec spray vol 200-400 l/ha	2	2-4 leaf[3]	
Maize (tolerant)	USA	18.2%		0.20-0.36		2	60 cm	60 (corn forage) 70 (corn grain, fodder)
Maize (tolerant)	USA	200 g/l SL	foliar	0.23-0.41		2	60 cm	70 grain 70 maize fodder 60 maize forage
Mango	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Mango	Malaysia	150 g/l SL	directed	0.3-0.5	0.11	4		14
Onion	Germany [4]	200 g/l SL	spray	0.55	0.14-0.18	1	pre-emerg	
Onion	Poland [4]	SL	spray HV	0.45-0.60	0.04-0.30	1	pre-emerg	
Papaya	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Parsley	Poland [4]	SL	spray HV	0.45-0.60	0.04-0.30	1	pre-emerg	
Passion fruit	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Peach	Poland [4]	200 g/l SL		0.60-1.2	0.06-0.60	2		
Pear	Poland [4]	150 g/l SL		0.45-0.90	0.04-0.35	2		
Pecan	USA	120 g/l SL	directed	1.7	min spray vol 187 l/ha	max total 5.1 kg/ha/yr		14
Pineapple	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Plum	Poland [4]	200 g/l SL		0.60-1.2	0.06-0.60	2		
Potato	Germany [4]	200 g/l SL	spray	0.55	0.14-0.18	1	stage 8-9	
Potato	Germany [4]	200 g/l SL	spraying	0.46	0.08-0.15	1	desiccation	14
Potato	Netherlands	200 g/l 150 g/l	aerial parts, haulm kill	0.45-0.60		1		-
Potato	Netherlands	200 g/l 150 g/l	directed spray	0.45-1.0		1		-
Potato	Netherlands	200 g/l 150 g/l	pre-emergence	0.45-1.0		1		-

[1] Germany, split application on maize, 6 weeks interval.

[2] Maximum rate in the 2nd application is 0.40 kg ai/ha.

[3] For the second application, the maize should have no more than 8-10 leaves.

Crop [1]	Country	Form	Application			Number	Growth stage [2]	PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl			
Rambutan	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Rape seed	Poland [4]	SL	spray HV	0.38-0.50	0.04	0.25	desiccation	
Raspberries	Germany [4]	200 g/l SL	spray with screening	0.92	0.15-0.31	1		14
Raspberries	Netherlands	200 g/l 150 g/l	directed spray	0.75-1.0		2		-
Raspberries	Poland [4]	200 g/l SL		0.60-1.2	0.06-0.60	2		
Spinach	Netherlands	200 g/l 150 g/l	aerial parts, haulm kill	0.6-0.8		1		-
Soya beans (tolerant)	USA	200 g/l SL	foliar	0.23-0.41		2	bloom growth	70 seed forage[1]
Strawberries	Germany [4]	200 g/l SL	spray between rows with screening	0.73	0.18-0.24	1	stage 59	42
Strawberries	Germany [4]	200 g/l SL	spray with screening	0.73	0.12-0.24	1	after harvest	
Sugar beets	Germany [4]	200 g/l SL	spray	0.92	0.23-0.31	1	pre-sowing	
Sunflowers	Germany [4]	200 g/l SL	spraying	0.46	0.08-0.15	1	desiccation	14
Tree nuts	Australia	200 g/l SL	directed	0.2-1.0	spray vol 300-1000 l/ha			-
Walnut	Italy	120 g/l SL	directed	0.5-1.6	0.08-0.78	max total 2.5 kg/ha/yr		-
Walnut	USA	120 g/l SL	directed	1.7	min spray vol 187 l/ha	max total 5.1 kg/ha/yr		14
Winter rape	Germany [4]	200 g/l SL	spraying	0.46	0.08-0.15	1	desiccation	14

[1] tolerant: tolerant to glufosinate-ammonium
[2] growth stage at final application.
[3] Do not graze the treated crop or cut for hay; sufficient data are not available to support such use.
[4] Label not provided.
[5] Label not available. Registration document 4574-00 1 Sept 1998 provided.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residue data from glufosinate-ammonium supervised residue trials on fruit, tree nuts and field crops are summarized in Tables 42-61.

Table 42	*Tropical fruits -avocado, mango, guava, carambola, papaya*. Australia, Malaysia.
Table 43	*Tree nuts – pecan, walnut, almond, hazel nuts macadamia*. USA, Italy, Australia.
Table 44	*Maize.* France, Germany, Italy, Spain.
Table 45	*Maize*. USA, Argentina.
Table 46	*Maize.* Canada.
Table 47	*Soya beans*. USA.
Table 48	*Rape seed.* France, Germany, UK.
Table 49	*Canola.* Canada.
Table 50	*Canola.* Australia.
Table 51	*Sugar beet root.* France, Germany, UK.
Table 52	*Sugar beet root.* USA.

[1] Do not feed treated green immature growing soya bean plants to livestock.

Table 53	*Maize forage and fodder.* France, Germany, Italy, Netherlands, Spain.
Table 54	*Maize forage and fodder.* USA, Argentina.
Table 55	*Maize forage and fodder.* Canada.
Table 56	*Rape seed forage and fodder.* France, Germany, UK.
Table 57	*Canola forage and fodder.* Australia.
Table 58	*Soya bean forage and fodder.* USA.
Table 59	*Sugar beet tops and leaves.* France, Germany, UK.
Table 60	*Sugar beet tops.* USA.
Table 61	*Almond hulls.* USA.

Where residues were not detected they are recorded as below the limit of determination (LOD), e.g. <0.05 mg/kg. Residue levels of glufosinate and its metabolites are generally expressed as glufosinate free acid. Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure. Although all trials included control plots residues in control samples are recorded only when they exceeded the LOD. Residues are not corrected for recoveries. Recoveries were mainly in the range 70-120%.

Reports did not generally state whether residues in forage and fodder commodities were expressed on a fresh-weight or dry-weight basis.

Trials were fully reported as well as on summary sheets except the US trials on pecans and walnuts and the Italian trials on hazel-nuts. These trials were all reported on the detailed summary sheets used in Germany.

Glufosinate-ammonium is used as a directed spray for weed control in orchards, so that residues usually only occur in the crop through root uptake from the soil. Glufosinate-ammonium itself is not taken up, but the metabolite 3-methylphosphinicopropionic acid (MPP) can be taken up and translocated by the crop. This metabolite is not herbicidally active, so its residues may occur in the crop when glufosinate-ammonium is used as a directed spray.

In tropical fruit trials in Australia and Malaysia glufosinate-ammonium was applied to weeds around the trees as a directed spray. Plot sizes ranged from 1 tree to 1050 m^2. Intervals of 109 to 468 days of frozen sample storage elapsed before analysis. Residues are expressed on a pulp + peel basis for the avocados and mangoes in the Australian trials, but this does not influence the results which were mainly below the LOD.

Glufosinate-ammonium was used in tree nut trials in the USA with plot sizes ranging from 1 to 9 trees. The method of spraying was not clearly expressed, but was presumably a directed spray. Samples were held in frozen storage for intervals of 400 to 700 days before analysis. The method of application was also not stated for the hazel nut trials in Italy. Samples were held 240 days in frozen storage before analysis. Directed sprays were used in the macadamia trials in Australia. Samples from the year 1992 were analysed 28 days after harvest while those from 1995 were stored for almost a year.

In Canadian trials on resistant maize in 1993-95 glufosinate-ammonium was applied by ground rigs. Two different SL formulations were used, with applications at two rates and at different growth stages.

Glufosinate-ammonium was applied to resistant maize in an extensive set of trials in France from 1993 to 1996. Plot sprayers were used on plots of 11 to 79 m^2. Harvested samples were held in frozen storage for 520-670 days (1993), 310-340 days (1994), 160-230 days (1995) and 50-90 days (1996).

In a similar series of resistant maize trials in Germany from 1994 to 1996, plot sprayers were used on plots of 48-64 m^2. Frozen storage periods were 300-400 days (1994), 150 days (1995) and 30-70 days (1996).

Further European trials on resistant maize were conducted in 1994-96 in Italy, The Netherlands and Spain. Hand-carried plot sprayers were used in Italy and Spain on plots of 40-60 m^2. Information on the sprayers and plot sizes was not available for The Netherlands. Analytical samples were stored frozen for 330-340 days (1994) and 50-150 days (1995-96).

Glufosinate-ammonium was extensively tested on resistant maize in US trials in 1993-1995. In 1993 it was applied by portable and tractor-mounted plot sprayers to plots of 28-186 m^2. In 1995 ground rigs and plot sprayers were used on plots of 110-740 m^2. Harvested samples were held in frozen storage for 280-330 days (1993) and 190-280 days (1995) before analysis. Some of the higher rate treatments in trial ER-93-USA-01 (Virginia and South Dakota) suffered phytotoxicity so grain samples were limited or unavailable for analysis.

Resistant soya beans were determined with glufosinate-ammonium in trials in many States of the USA in 1994-1996. Plots of 70-95 m^2 were sprayed with CO_2 pressurised backpack or plot sprayers in 1994. In 1995 tractor-mounted ground rigs and backpack or bicycle sprayers were used on plots of 40-130 m^2 and in 1996 backpack or plot sprayers were used on 90-280 m^2 plots. Harvested samples were held in frozen storage before analysis for 200-280 days (1994), 100-300 days (1995) and 200-230 days (1996).

Glufosinate-ammonium was determined on resistant rape seed in a supervised residue trial programme in France in 1993, 1994 and 1996. Plot sprayers were used on plots of 18-72 m^2. Periods of frozen storage of samples before analysis were 570-640 days (1993), 380-550 days (1994) and 112 days (1996). In trials on resistant rape seed in Germany (1994 and 1996) and the UK (1993 and 1996) glufosinate-ammonium was applied by plot sprayers to plots of 48-100 m^2 in Germany and 20-80 m^2 in the UK. Frozen storage periods for samples were 1 year and 2 months (1994 and 1996 respectively) in Germany and 600 days and 2 months (1993 and 1995 respectively) in the UK.

Glufosinate-ammonium was applied with boom sprayers to plots of 30-42 m^2 of resistant canola in Australian trials in 1996. Harvested samples were stored for 170-240 days before analysis.

Resistant canola was treated with glufosinate-ammonium in a series of supervised residue trials in Canada in 1993 and 1994. CO_2 powered backpack, plot sprayers and tractor-mounted rigs were used on plots of 24-80 m^2. Samples were held for 170-280 days (1993) and 80 days (1994) in frozen storage before analysis. No field reports were available for trials in report A53770 (Bertrand, 1993). One canola trial (A57514, MacDonald, 1996d) was not evaluated because the data sheets were from a barley trial. It was not clear in some of the canola trials whether the residues were expressed as glufosinate free acid or as the metabolites,.

Glufosinate-ammonium was applied with plot sprayers to plots of 38-76 m^2 of resistant sugar beet in French trials in 1995 and 1996. Harvested samples were stored for 120-300 days under frozen conditions before analysis. In similar trials in the UK in 1996-97 glufosinate-ammonium was applied by plot sprayer or knapsack to 48-64 m^2 plots. Frozen samples were stored for 150-280 days before analysis.

In a US trial programme on resistant sugar beet in 1995 and 1996 glufosinate-ammonium was applied by ground rig, backpack or bicycle sprayer to plots of 17-300 m^2. Storage periods for frozen samples were 240-320 days (1995) and 130-170 days (1996).

Table 42. Glufosinate residues in tropical fruits resulting from supervised trials in Australia and Malaysia. In the Australian trials on avocados and mangoes residues are expressed on a pulp + peel basis. Residues in samples from replicate plots are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

FRUIT, country, year	Application				PHI, days	Residues, mg/kg, as glufosinate free acid		Ref
(variety)	Form	kg ai/ha	kg ai/hl	no.		glufosinate	MPP	
AVOCADO								
Australia (Qld) 1991 (Sharwil)	SL	1.0	0.4	1	7 12 21	<0.1 (2) <0.1 (2) <0.1 (2)	<0.1 (2) <0.1 (2) <0.1 (2)	A59027 QD 27/90
Australia (Qld) 1991 (Sharwil)	SL	2.0	0.8	1	7 12 21	<0.1 (2) <0.1 (2) <0.1 (2)	<0.1 (2) <0.1 (2) <0.1 (2)	A59027 QD 27/90
Australia (Qld) 1996 (Fuerte)	SL	0.6	0.33	2	0 14 24 28	<0.05 (2) <0.05 (2) <0.05 (2) <0.05 (2)	<0.05 (2) <0.05 (2) <0.05 (2) <0.05 (2)	A59026 AU QD 26
Australia (Qld) 1996 (Fuerte)	SL	1.2	0.67	2	0 14 24 28	<0.05 (2) <0.05 (2) <0.05 (2) <0.05 (2)	<0.05 (2) <0.05 (2) <0.05 (2) <0.05 (2)	A59026 AU QD 26
Australia (Qld) 1995 (Haas)	SL	0.6	0.35 0.30	2	0 14 24 31	<0.05 (2) <0.05 (2) <0.05 (2) <0.05 (2)	<0.05 (2) <0.05 (2) <0.05 (2) <0.05 (2)	A59025 AU QD 24
Australia (Qld) 1995 (Haas)	SL	1.2	0.69 0.60	2	0 14 24 31	0.06 <0.05 <0.05 (2) <0.05 (2) <0.05 (2)	<0.05 (2) <0.05 (2) <0.05 (2) <0.05 (2)	A59025 AU QD 24
MANGO								
Australia (Qld) 1991 (Kensington Pride)	SL	1.0	0.4	1	7 14 20	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	A59030 QD 21/90
Australia (Qld) 1991 (Kensington Pride)	SL	2.0	0.8	1	7 14 20	<0.1 <0.1 <0.1	<0.1 <0.1 <0.1	A59030 QD 21/90
Australia (Qld) 1994-5 (Fascell)	SL	0.6	0.21	2	0 14 21 28	<0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05	A59029 AU QD 12
Australia (Qld) 1994-5 (Fascell)	SL	1.2	0.41	2	0 14 21 28	<0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05	A59029 AU QD 12
Australia (Qld) 1995 (Kensington Pride)	SL	0.6	0.2	2	0 14 21 28	<0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05	A59028 AU QD 13-94
Australia (Qld) 1995 (Kensington Pride)	SL	1.2	0.4	2	0 14 21 28	<0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05	A59028 AU QD 13-94
GUAVA								
Malaysia (Perat) 1995 (“with seeds”)	SL	0.50	0.11	4	0 3 7 14 21	<0.05 <0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05 <0.05	A57294 ER95MYS8800201 02

FRUIT, country, year	Application				PHI, days	Residues, mg/kg, as glufosinate free acid		Ref
(variety)	Form	kg ai/ha	kg ai/hl	no.		glufosinate	MPP	
Malaysia (Perat) 1995 (“with seeds”)	SL	1.0	0.22	4	0 3 7 14 21	<0.05 <0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05 <0.05	A57294 ER95MYS8800201 03
Malaysia (Perat) 1995 (“seedless”)	SL	0.50	0.11	4	0 3 7 14 21	<0.05 <0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05 <0.05	A57294 ER95MYS8800202 02
Malaysia (Perat) 1995 (“seedless”)	SL	1.0	0.22	4	0 3 7 14 21	<0.05 <0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05 <0.05	A57294 ER95MYS8800202 03
CARAMBOLA								
Malaysia (Selangor) 1995 (Bio)	SL	0.50	0.11	3	0 3 7 14 21	<0.05 <0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05 <0.05	A57295 ER95MYS8800101 02
Malaysia (Selangor) 1995 (Bio)	SL	1.0	0.22	3	0 3 7 14 21	<0.05 <0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05 <0.05	A57295 ER95MYS8800101 03
Malaysia (Perat) 1995 (Bio)	SL	0.50	0.11	3	0 3 7 14 21	<0.05 <0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05 <0.05	A57295 ER95MYS8800102 02
Malaysia (Perat) 1995 (Bio)	SL	1.0	0.22	3	0 3 7 14 21	<0.05 <0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05 <0.05	A57295 ER95MYS8800102 03
PAPAYA								
Australia (Qld) 1996 (Rictor Gold)	SL	0.6	0.26	2	0 14 21 30	<0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05	A59285 AU QD 25
Australia (Qld) 1996 (Rictor Gold)	SL	1.2	0.52	2	0 14 21 30	<0.05 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05	A59285 AU QD 25

Table 43. Glufosinate residues in tree nuts resulting from supervised trials in Australia, Italy and the USA. Analyses on samples from replicate plots are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

NUT, country, year (variety)	Application				PHI, days	Residues, mg/kg, as glufosinate free acid		Ref
	Form	kg ai/ha	kg ai/hl	No.		glufosinate	MPP	
PECAN								
USA (GA) 1985 (Witchita)	SL	1.7		3	14	<0.05 (3)	<0.05 (3)	A48446 16-GA-85-011
USA (GA) 1985 (Witchita)	SL	3.4		3	14	<0.05 (3)	<0.05 (3)	A48446 16-GA-85-011
USA (LA) 1985 (Cape Fear)	SL	1.7		3	21	<0.05 (3)	<0.05 (3)	A48446 16-LA-85-002
USA (LA) 1985 (Cape Fear)	SL	3.4		3	21	<0.05 (3)	<0.05 (3)	A48446 16-LA-85-002
USA (NM) 1985 (Western Schley)	SL	1.7		3	14	<0.05 (3)	<0.05 (3)	A48446 07-NM-85-032
USA (NM) 1985 (Western Schley)	SL	3.4		3	14	<0.05 (3)	<0.05 (3)	A48446 07-NM-85-032
WALNUT								
USA (CA) 1984 (English)	SL	1.6 +1.2		2	14	<0.05 (3)	<0.05 (3)	A34230
USA (CA) 1984 (English)	SL	3.2 +2.4		2	14	<0.05 (3)	<0.05 (3)	A34231
USA (CA) 1984 (English)	SL	1.6 +2×1.2		3	14	<0.05 (3)	<0.05 (3)	A34232
USA (CA) 1984 (English)	SL	3.2 +2×2.4		3	14	<0.05 (3)	<0.05 (3)	A34233
USA (CA) 1985 (Serr)	SL	1.7		3	14	<0.05 (3)	<0.05 (3)	A35706
USA (CA) 1985 (Serr)	SL	4.5		3	14	<0.05 (3)	<0.05 (3)	A35707
USA (CA) 1985	SL	1.7		3	14	<0.05 (3)	<0.05 (3)	A35708
USA (CA) 1985	SL	3.4		3	14	<0.05 (3)	<0.05 (3)	A35709
USA (CA) 1985 (Serr)	SL	1.7		3	11	<0.05 (3)	<0.05 (3)	A35710
USA (CA) 1985 (Serr)	SL	3.4		3	11	<0.05 (3)	<0.05 (3)	A35711
USA (CA) 1985 (Serr)	SL	1.7		3	14	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-019
USA (CA) 1985 (Serr)	SL	3.4		3	14	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-019
USA (CA) 1985 (Serr)	SL	1.7		3	14	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-024
USA (CA) 1985 (Serr)	SL	3.4		3	14	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-024
USA (CA) 1985 (Serr)	SL	1.7		3	11	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-038

NUT, country, year (variety)	Application				PHI, days	Residues, mg/kg, as glufosinate free acid		Ref
	Form	kg ai/ha	kg ai/hl	No.		glufosinate	MPP	
USA (CA) 1985 (Serr)	SL	3.4		3	11	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-038
ALMOND								
USA (CA) 1985 (Carmel)	SL	1.7		3	15	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-018
USA (CA) 1985 (Carmel)	SL	3.4		3	15	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-018
USA (CA) 1985 (Special)	SL	1.7		3	15	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-018
USA (CA) 1985 (Special)	SL	3.4		3	15	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-018
USA (CA) 1985 (Non-Peril)	SL	1.7		3	14	<0.05 (3)	0.07 0.07 0.07	A48446 07-CA-85-028
USA (CA) 1985 (Non-Peril)	SL	3.4		3	14	<0.05 (3)	0.14 0.22 0.17	A48446 07-CA-85-028
USA (CA) 1985 (Non-Peril)	SL	1.7		3	14	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-037
USA (CA) 1985 (Non-Peril)	SL	3.4		3	14	<0.05 (3)	<0.05 (3)	A48446 07-CA-85-037
HAZEL-NUT								
Italy 1985 (Gentile Del Piemonte)	SL	1.5	0.38	2	19	<0.05	<0.05	A35935
Italy 1985 (Nocchione)	SL	1.5	0.38	2	19	<0.05	<0.05	A35936
Italy 1985 (Gentile Del Piemonte)	SL	1.5	0.38	2	19	<0.05	<0.05	A35937
Italy 1985 (Gentile Del Piemonte)	SL	1.5	0.38	2	19	<0.05	<0.05	A35938
Italy 1985 (Gentile Del Piemonte)	SL	1.5	0.38	2	19	<0.05	<0.05	A35938
MACADAMIA NUT								
Australia 1992 (var 434)	SL	1.0	0.8	4	1 7 14 21	<0.1 (2) <0.1 (2) <0.1 (2) <0.1 (2)	<0.1 (2) <0.1 (2) <0.1 (2) <0.1 (2)	A59031 QDI/92 92/1222
Australia 1992 (var 434)	SL	2.0	1.6	4	1 7 14 21	<0.1 (2) <0.1 (2) <0.1 (2) <0.1 (2)	<0.1 (2) <0.1 (2) <0.1 (2) <0.1 (2)	A59031 QDI/92 92/1222
Australia 1995 (var 344)	SL	1.2	0.63	2	0 16 27	<0.05 (2) <0.05 (2) <0.05 (2)	<0.05 (2) <0.05 (2) <0.05 (2)	A59032 QD20-94 95/3715
Australia 1995 (var 344)	SL	2.4	1.3	2	0 16 27	<0.05 (2) <0.05 (2) <0.05 (2)	<0.05 (2) <0.05 (2) <0.05 (2)	A59032 QD20-94 95/3715

Table 44. Glufosinate residues in maize resulting from supervised trials in France, Germany, Italy and Spain. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Country, Year, Variety	Application				PHI days	Residues as glufosinate free acid, mg/kg			Ref
	form	kg ai/ha	kg ai/hl	no[1]		glufosinate	MPP	NAG[2]	
France 1993 (LH163×LH164-×F2×T14)	SL	0.45	0.23	2 GS25	145	<0.05	<0.05		A54225 ER93ECN550 FRA000402
France 1993 (LH206×LH74-×F2×T14)	SL	0.45	0.23	2 GS24	145	<0.05	<0.05		A54225 ER93ECN550 FRA000502
France 1993 (MLC 2101/T14)	SL	0.45	0.23	2 GS24	128	<0.05	<0.05		A54225 ER93ECN550 FRA000102
France 1993 (MLC 2101/T14)	SL	0.45	0.23	2 GS24	147	<0.05	<0.05		A54225 ER93ECN550 FRA000202
France 1993 (MLC 2101/T14)	SL	0.45	0.23	2 GS24	145	<0.05	<0.05		A54225 ER93ECN550 FRA000302
France 1994 ((LH82(4)T25)sf (-2)xSH298	SL	0.45	0.23	2 GS25	123	<0.05	<0.05		A54229 ER94ECN550 FRA000202
France 1994 (F6×M1)	SL	0.45	0.23	2 GS25	119	<0.05	<0.05		A54226 ER93ECS550 FRA000102
France 1994 (LH824xT25)AF4x-B73)	SL	0.45	0.15	2 GS25	120	<0.05	<0.05		A54230 ER94ECS550 FRA000102
France 1994 (SH298(LH82(4)T25)sf(2))	SL	0.45	0.23	2 GS25	119	<0.05	<0.05		A54229 ER94ECN550 FRA000102
France 1995 (F2xLH82-T25)	SL	0.45	0.23	2 GS18	100	<0.05	<0.05		A56445 ER95ECN550 FRA000202
France 1995 (F2xLH82-T25)	SL	0.45	0.23	2 GS19	100	<0.05	<0.05		A56445 ER95ECN550 FRA000203
France 1995 (tolerant 039866)	SL	0.45	0.23	2 GS18	106	<0.05	<0.05		A56445 ER95ECN550 FRA000103
France 1995 (tolerant 039866)	SL	0.45	0.23	2 GS18	106	<0.05	<0.05		A56445 ER95ECN550 FRA000102
France 1995 (transgenic hybrid)	SL	0.53	0.27	2 GS18	116	<0.05	<0.05	<0.05	A54760 ER95ECS550 FRA000103
France 1995 (transgenic hybrid)	SL	0.53	0.27	2 GS18	116	<0.05	<0.05	<0.05	A54760 ER95ECS550 FRA000102
France 1995 (transgenic hybrid)	SL	0.45	0.23	2 GS19	119	<0.05	<0.05	<0.05	A54760 ER95ECS550 FRA000203
France 1995 (transgenic hybrid)	SL	0.45	0.23	2 GS19	119	<0.05	<0.05	<0.05	A54760 ER95ECS550 FRA000202
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS18	104	<0.05	<0.05		A58191 ER96ECN550 FRA000102
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS18	104	<0.05	<0.05		A58191 ER96ECN550 FRA000103

Country, Year, Variety	Application				PHI days	Residues as glufosinate free acid, mg/kg			Ref
	form	kg ai/ha	kg ai/hl	no[1]		glufosinate	MPP	NAG[2]	
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS18	104	<0.05	<0.05		A58191 ER96ECN550 FRA000104
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS18	105	<0.05	<0.05		A58191 ER96ECN550 FRA000302
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS18	105	<0.05	<0.05		A58191 ER96ECN550 FRA000303
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS18	105	<0.05	<0.05		A58191 ER96ECN550 FRA000304
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS18	110	<0.05	<0.05		A58191 ER96ECN550 FRA000402
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS18	110	<0.05	<0.05		A58191 ER96ECN550 FRA000403
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS18	110	<0.05	<0.05		A58191 ER96ECN550 FRA000404
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS18	129	<0.05	<0.05		A58190 ER96ECS550 FRA000302
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS18	129	<0.05	<0.05		A58190 ER96ECS550 FRA000303
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS18	129	<0.05	<0.05		A58190 ER96ECS550 FRA000304
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS19	103	<0.05	<0.05		A58191 ER96ECN550 FRA000202
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	103	<0.05	<0.05		A58191 ER96ECN550 FRA000203
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS19	103	<0.05	<0.05		A58191 ER96ECN550 FRA000204
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS19	130	<0.05	<0.05		A58190 ER96ECS550 FRA000102
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS19	130	<0.05	<0.05		A58190 ER96ECS550 FRA000103
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	130	<0.05	<0.05		A58190 ER96ECS550 FRA000104
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS19	140	<0.05	<0.05		A58190 ER96ECS550 FRA000202
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS19	140	<0.05	<0.05		A58190 ER96ECS550 FRA000203
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	140	<0.05	<0.05		A58190 ER96ECS550 FRA000204
Germany 1995 (LH82^4T25sf^4F2)	SL	0.45	0.15	2 GS18	99	<0.05 (2)	<0.05 (2)		A56445 ER95ECN550 DEU010202

Country, Year, Variety	Application				PHI days	Residues as glufosinate free acid, mg/kg			Ref
	form	kg ai/ha	kg ai/hl	no[1]		glufosinate	MPP	NAG[2]	
Germany 1995 (LH82^4T25sf^4SH-298)	SL	0.45	0.15	2 GS18	90	<0.05	<0.05		A56445 ER95ECN550 DEU050102
Germany 1995 (LH82^4T25sf^4xF2)	SL	0.45	0.15	2 GS18	113	<0.05 (2)	<0.05 (2)		A56445 ER95ECN550 DEU010102
Germany 1996 (F2 hybride - LH-82)	SL	0.60	0.20	2 GS18	126	<0.05	<0.05		A58191 ER96ECN550 DEU050102
Germany 1996 (F2 hybride - LH-82)	SL	0.80	0.27	2 GS18	126	<0.05	<0.05		A58191 ER96ECN550 DEU050103
Germany 1996 (F2 hybride - LH-82)	SL	0.45	0.15	2 GS18	126	<0.05	<0.05		A58191 ER96ECN550 DEU050104
Germany 1996 (Facet - transgen)	SL	0.60	0.20	2 GS18	125	<0.05	<0.05		A58191 ER96ECN550 DEU060102
Germany 1996 (Facet - transgen)	SL	0.80	0.27	2 GS18	125	<0.05	<0.05		A58191 ER96ECN550 DEU060103
Germany 1996 (Facet - transgen)	SL	0.45	0.15	2 GS18	125	<0.05	<0.05		A58191 ER96ECN550 DEU060104
Germany 1996 (Facet - transgen)	SL	0.60	0.20	2 GS18	122	<0.05	<0.05		A58191 ER96ECN550 DEU060202
Germany 1996 (Facet - transgen)	SL	0.80	0.27	2 GS18	122	<0.05	<0.05		A58191 ER96ECN550 DEU060203
Germany 1996 (Facet - transgen)	SL	0.45	0.15	2 GS18	122	<0.05	<0.05		A58191 ER96ECN550DEU 060204
Germany 1996 (LH82 T25 SF x F2)	SL	0.60	0.20	2 GS19	137	<0.05	<0.05		A58191 ER96ECN550 DEU010202
Germany 1996 (LH82 T25 SF x F2)	SL	0.80	0.27	2 GS19	137	<0.05	<0.05		A58191 ER96ECN550 DEU010203
Germany 1996 (LH82 T25 SF x F2)	SL	0.45	0.15	2 GS19	137	<0.05	<0.05		A58191 ER96ECN550 DEU010204
Germany 1996 (LH82 T25 SF x Fe)	SL	0.60	0.20	2 GS19	145	<0.05	<0.05		A58191 ER96ECN550 DEU010102
Germany 1996 (LH82 T25 SF x Fe)	SL	0.80	0.27	2 GS19	145	<0.05	<0.05		A58191 ER96ECN550 DEU010103
Germany 1996 (LH82 T25 SF x Fe)	SL	0.45	0.15	2 GS19	145	<0.05	<0.05		A58191 ER96ECN550 DEU010104
Italy 1994 ([B73(4)xT14]sfx - LM82)	SL	0.45	0.15	2 GS23	105	<0.05	<0.05		A54230 ER94ECS550 ITA000102
Italy 1995 (transgenic hybrid)	SL	0.45	0.15	2 GS18	108	<0.05	<0.05	<0.05	A54760 ER95ECS550 ITA000104
Italy 1995 (transgenic hybrid)	SL	0.45	0.15	2 GS18	104	<0.05	<0.05	<0.05	A54760 ER95ECS550 ITA000204

Country, Year, Variety	Application				PHI days	Residues as glufosinate free acid, mg/kg			Ref
	form	kg ai/ha	kg ai/hl	no[1]		glufosinate	MPP	NAG[2]	
Italy 1995 (transgenic hybrid)	SL	0.45	0.15	2 GS18	108	<0.05	<0.05	<0.05	A54760 ER95ECS550 ITA000103
Italy 1995 (transgenic hybrid)	SL	0.45	0.15	2 GS18	104	<0.05	<0.05	<0.05	A54760 ER95ECS550 ITA000203
Italy 1995 (transgenic hybrid)	SL	0.45	0.15	2 GS18	108	<0.05	<0.05	<0.05	A54760 ER95ECS550 ITA000102
Italy 1995 (transgenic hybrid)	SL	0.45	0.15	2 GS18	104	<0.05	<0.05	<0.05	A54760 ER95ECS550 ITA000202
Italy 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	100	<0.05	<0.05		A58190 ER96ECS550 ITA000105
Italy 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	124	<0.05	<0.05		A58190 ER96ECS550 ITA000205
Italy 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS18	100	<0.05	<0.05		A58190 ER96ECS550 ITA000103
Italy 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	100	<0.05	<0.05		A58190 ER96ECS550 ITA000104
Italy 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS18	124	<0.05	<0.05		A58190 ER96ECS550 ITA000203
Italy 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	124	<0.05	<0.05		A58190 ER96ECS550 ITA000204
Italy 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS19	104	<0.05	<0.05		A58190 ER96ECS550 ITA000305
Italy 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS19	104	<0.05	<0.05		A58190 ER96ECS550 ITA000303
Italy 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS19	104	<0.05	<0.05		A58190 ER96ECS550 ITA000304
Spain 1994 (LH119-6xT14/LH82)	SL	0.45	0.15	2 GS25	102	<0.05	<0.05		A54230 ER94ECS550 ESP000102
Spain 1995 (transgenic hybrid)	SL	0.45	0.15	2 GS18	95	<0.05	<0.05	<0.05	A54760 ER95ECS550 ESP000103
Spain 1995 (transgenic hybrid)	SL	0.45	0.15	2 GS18	95	<0.05	<0.05	<0.05	A54760 ER95ECS550 ESP000102
Spain 1996 (transgenic hybrid)	SL	0.45	0.15	2 GS18	95	<0.05	<0.05		A58190 ER96ECS550 ESP000102
Spain 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS18	95	<0.05	<0.05		A58190 ER96ECS550 ESP000103
Spain 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	95	<0.05	<0.05		A58190 ER96ECS550 ESP000104
Spain 1996 (transgenic hybrid)	SL	0.45	0.15	2 GS18	96	<0.05	<0.05		A58190 ER96ECS550 ESP000202

Country, Year, Variety	Application				PHI days	Residues as glufosinate free acid, mg/kg			Ref
	form	kg ai/ha	kg ai/hl	no[1]		glufosinate	MPP	NAG[2]	
Spain 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS18	96	<0.05	<0.05		A58190 ER96ECS550 ESP000203
Spain 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	96	<0.05	<0.05		A58190 ER96ECS550 ESP000204
Spain 1996 (transgenic hybrid)	SL	0.45	0.15	2 GS18	113	<0.05	<0.05		A58190 ER96ECS550 ESP000302
Spain 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS18	113	<0.05	<0.05		A58190 ER96ECS550 ESP000303
Spain 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	113	<0.05	<0.05		A58190 ER96ECS550 ESP000304

[1]. GS: growth stage at final treatment
GS18 8 leaves unfolded
GS19 9 or more leaves unfolded
GS23 5th leaf unfolded
GS24 6th leaf unfolded
GS25 7th leaf unfolded
[2] included in glufosinate-ammonium result.

Table 45. Glufosinate residues in transgenic maize resulting from supervised trials in the USA and Argentina. Analyses of replicate samples are reported individually. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Country, Year, Variety	Application				PHI	Residues, mg/kg, as glufosinate free acid[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate-ammonium	MPP	NAG	
USA (NE) 1993 (LH59 X LH51) (LH119)(4) X T14)	SL	1.8 +2.6	1.9 +2.8	2 (60 cm)	96	NQ	NQ	NQ	ER-93-USA-01-NE-02
USA (IA) 1993 (LH216) (LH119) (4) X (T14))	SL	1.5	1.6	1 (60 cm)	100	NQ	NQ	NQ	ER-93-USA-01-IA-02
USA (IA) 1993 (LH216) X (LH119) (4) × T14)	SL	0.36		1 (30 cm)	118	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-IA-01
USA (IA) 1993 (LH216) X (LH119) (4) × T14)	SL	0.50		1 (30 cm)	114	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-IA-01
USA (IA) 1993 (LH216) X (LH119) (4) × T14)	SL	0.50		1 (60 cm)	114	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-IA-01
USA (IL) 1993 (LH 59x LH51)(LH119) (4) X T14)	SL	0.36	0.39	1 (30 cm)	100	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-IL-01
USA (IL) 1993 (LH 59x LH51)(LH119) (4) X T14)	SL	0.50	0.54	1 (30 cm)	100	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-IL-01
USA (IL) 1993 (LH 59x LH51)(LH119) (4) X T14)	SL	0.50	0.54	1 (60 cm)	95	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-IL-01

Country, Year, Variety	Application				PHI	Residues, mg/kg, as glufosinate free acid[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate-ammonium	MPP	NAG	
USA (IL) 1993 (LH 59x LH51)(LH119) (4) X T14)	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	95	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-IL-01
USA (NE) 1993 (LH 59x LH51)(LH119) (4) X T14)	SL	0.36		1 (30 cm)	107	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-NE-01
USA (NE) 1993 (LH 59x LH51)(LH119) (4) X T14)	SL	0.50	0.48	1 (30 cm)	107	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-NE-01
USA (NE) 1993 (LH 59x LH51)(LH119) (4) X T14)	SL	0.50	0.48	1 (60 cm)	95	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-NE-01
USA (IN) 1993 [LH119(4) X T14] X LH216)	SL	0.36	0.39	1 (30 cm)	115	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-IN-01
USA (IN) 1993 [LH119(4) X T14] X LH216)	SL	0.50	0.54	1 (30 cm)	115	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-IN-01
USA (IN) 1993 [LH119(4) X T14] X LH216)	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	106	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-IN-01
USA (ND) 1993 (LH85 X LH160) (LH119)(4) X T14)	SL	0.36	0.39	1 (30 cm)	107	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-ND-01
USA (ND) 1993 (LH85 X LH160) (LH119)(4) X T14)	SL	0.50	0.54	1 (30 cm)	107	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-ND-01
USA (ND) 1993 (LH85 X LH160) (LH119)(4) X T14)	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	97	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-ND-01
USA (ND) 1993 (LH85 X LH160) (LH119)(4) X T14)	SL	0.36	0.39	1 (30 cm)	117	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-ND-01
USA (ND) 1993 (LH85 X LH160) (LH119)(4) X T14)	SL	0.50	0.54	1 (60 cm)	117	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-ND-01
USA (ND) 1993 (LH85 X LH160) (LH119)(4) X T14)	SL	0.36 +0.50	0.39 +0.54	2 (31 cm)	107	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-ND-01
USA (MO) 1993 (LH216) X (LH119(4) X (T14))	SL	0.36	0.39	1 (30 cm)	97	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-MO-01
USA (MO) 1993 (LH216) X (LH119(4) X (T14))	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	95	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-MO-01
USA (CA) 1993 (LH59 X LH51) (LH119)(4) X T14)	SL	0.36	0.39	1 (30 cm)	119	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-CA-01
USA (CA) 1993 (LH59 X LH51) (LH119)(4) X T14)	SL	0.36	0.39	1 (30 cm)	129	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-CA-01
USA (CA) 1993 (LH59 X LH51) (LH119)(4) X T14)	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	106	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-CA-01
USA (CA) 1993 (LH59 X LH51) (LH119)(4) X T14)	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	116	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-CA-01

Country, Year, Variety	Application				PHI	Residues, mg/kg, as glufosinate free acid[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate-ammonium	MPP	NAG	
USA (SD) 1993 (LH85 X LH160) (LH119)(4) X T14))	SL	0.36	0.71	1 (30 cm)	95	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-SD-01
USA (SD) 1993 (LH85 X LH160) (LH119)(4) X T14))	SL	0.50	0.99	1 (30 cm)	95	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-SD-01
USA (SD) 1993 (LH85 X LH160) (LH119)(4) X T14))	SL	0.36 +0.50	0.71 +0.99	2 (60 cm)	95[1]	NQ (3)	NQ (3)	0.07 (3)	ER-93-USA-01-SD-01
USA (VA) 1993 (LH216) (LH119)(4) X T14)	SL	0.36	0.71	1 (30 cm)	106[2]	NQ	NQ	NQ	ER-93-USA-01-VA-01
USA (VA) 1993 (LH216) (LH119)(4) X T14)	SL	0.50	0.99	1 (30 cm)	106[6]	NQ	NQ	NQ	ER-93-USA-01-VA-01
USA (VA) 1993 (LH216) (LH119)(4) X T14)	SL	0.36 +0.50	0.71 +0.99	2 (60 cm)	97[6]	NQ	NQ	0.07	ER-93-USA-01-VA-01
USA (MO) 1993 (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (12-15 cm)	123	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-MO-02
USA (MO) 1993 (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (25-30 cm)	118	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-MO-02
USA (MO) 1993 (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (40-45 cm)	111	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-MO-02
USA (MO) 1993 (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (55-66 cm)	101	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-MO-02
USA (MO) 1993 (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (80-90 cm)	97	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-MO-02
USA (CA) 1993 (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (12-15 cm)	127	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-CA-02
USA (CA) 1993 (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (25-30 cm)	120	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-CA-02
USA (CA) 1993 (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (40-45 cm)	114	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-CA-02
USA (CA) 1993 (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (55-66 cm)	96	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-CA-02
USA (CA) 1993 (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (80-90 cm)	96	NQ (3)	NQ (3)	NQ (3)	ER-93-USA-01-CA-02
USA (FL) 1994 (LH51 X LH210) (LH119(4) X T14)	SL	0.40 +0.50	0.43 +0.54	2 (2-14 leaves)	69	NQ	NQ	glu	BK-94R-01-FL-01
USA (IA) 1994 (LH59 X LH51) (LH119(4) X T14))	SL	0.41 +0.53	0.44 +0.57	2 (60 cm)	122	NQ	NQ	glu	BK-94R-01-IA-01

[1] This crop suffered some phytotoxicity and the yield of grain was limited.

[2] Each of the treatments in the Virginia trials suffered from phytotoxicity and unusual weather conditions, resulting in limited collection of samples. CLICK HERE for continue

Country, Year, Variety	Application				PHI	Residues, mg/kg, as glufosinate free acid[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate-ammonium	MPP	NAG	
USA (IL) 1994 (LH59 X LH51) (LH119(4) X T14))	SL	0.40 +0.50	0.43 +0.54	2 (60 cm)	118	NQ	NQ	glu	BK-94R-01-IL-01
USA (MN) 1994 (LH74) (LH82(3) X T14))	SL	0.38 +0.48	0.41 +0.52	2 (60 cm)	114	0.05	NQ	glu	BK-94R-01-MN-01
USA (MO) 1994 (LH59 X LH51) (LH119(4) X T14))	SL	0.40 +0.53	0.43 +0.57	2 (60 cm)	89	NQ	NQ	glu	BK-94R-01-MO-01
USA (NC) 1994 (LH51 X LH210) (LH119(4) X T14))	SL	0.38 +0.52	0.41 +0.56	2 (60 cm)	92	NQ	NQ	glu	BK-94R-01-NC-01
USA (NY) 1994 (LH74) (LH82(3) X T14))	SL	0.38 +0.53	0.41 +0.57	2 (60 cm)	88	0.07	NQ	glu	BK-94R-01-NY-01
USA (TX) 1994 (LH51 X LH210) (LH119(4) X T14))	SL	0.38 +0.46	0.41 +0.49	2 (60 cm)	97	NQ	NQ	glu	BK-94R-01-TX-01
USA (WA) 1994 (LH74) (LH82)3) X T14))	SL	0.40 +0.50	0.43 +0.54	2 (60 cm)	86	NQ	NQ	glu	BK-94R-01-WA-01
USA (WI) 1994 (LH85 X LH160) (LH119(4) X T14))	SL	0.38 +0.56	0.41 +0.60	2 (60 cm)	107	NQ	NQ	glu	BK-94R-01-WI-01
USA (FL) 1994 (LH51 X LH210) (LH119(4) X T14)	SL200	0.40 +0.50	0.43 +0.54	2 (2-14 leaves)	69	NQ	NQ	glu	BK-94R-01-FL-01
USA (IA) 1994 (LH59 X LH51) (LH119(4) X T14))	SL	0.41 +0.53	0.44 +0.55	2 (60 cm)	122	NQ	NQ	glu	BK-94R-01-IA-01
USA (IL) 1994 (LH59 X LH51) (LH119(4) X T14))	SL	0.40 +0.50	0.43 +0.54	2 (60 cm)	118	NQ	NQ	glu	BK-94R-01-IL-01
USA (MN) 1994 (LH74) (LH82(3) X T14))	SL	0.40 +0.51	0.43 +0.55	2 (60 cm)	114	0.07	NQ	glu	BK-94R-01-MN-01
USA (MO) 1994 (LH59 X LH51) (LH119(4) X T14))	SL	0.40 +0.56	0.43 +0.60	2 (60 cm)	89	0.05	NQ	glu	BK-94R-01-MO-01
USA (NC) 1994 (LH51 X LH210) (LH119(4) X T14))	SL	0.40 +0.46	0.43 +0.49	2 (60 cm)	92	NQ	NQ	glu	BK-94R-01-NC-01
USA (NY) 1994 (LH74) (LH82(3) X T14))	SL	0.40 +0.53	0.43 +0.57	2 (60 cm)	88	NQ	NQ	glu	BK-94R-01-NY-01
USA (TX) 1994 (LH51 X LH210) (LH119(4) X T14))	SL	0.40 +0.49	0.43 +0.53	2 (60 cm)	97	NQ	NQ	glu	BK-94R-01-TX-01
USA (WA) 1994 (LH74) (LH82)3) X T14))	SL	0.40 +0.50	0.43 +0.54	2 (60 cm)	86	NQ	NQ	glu	BK-94R-01-WA-01
USA (WI) 1994 (LH85 X LH160) (LH119(4) X T14))	SL	0.38 +0.50	0.41 +0.54	2 (60 cm)	107	NQ	NQ	glu	BK-94R-01-WI-01
USA (MO) 1994 (LH59 X LH51) (LH119(4) X T14))	SL	2.0 +2.6	2.1 +2.5	2 (60 cm)	89	0.26 3.1 agf	0.06 0.75 agf	glu	BK-94R-03-MO-01

Country, Year, Variety	Application				PHI	Residues, mg/kg, as glufosinate free acid[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate-ammonium	MPP	NAG	
USA (MN) 1995 (LH202) (LH82 (4) x T25))	SL	0.39 +0.49	0.41 +0.53	2 (7-8 leaf)	100	NQ	NQ	glu	BK95R01-GGH-01
USA (KS) 1995 (B73(5)xT25) (LH51))	SL	0.39 +0.50	0.41 +0.53	2 (56-66 cm)	95	NQ	NQ	glu	BK95R01-MDA-02
USA (MI) 1995 (LH119 (9) x T14) (LH168))	SL	0.39 +0.50	0.41 +0.54	2 (61-77 cm)	111	NQ	NQ	glu	BK95R01-JRS-02
USA (MO) 1995 (B73 (5) x T25) (LH51))	SL	0.39 +0.52	0.44 +0.60	2 (60 cm)	90	NQ	NQ	glu	BK95R01-JLB-01
USA (NE) 1995 (LH119 (9) x T14) (LH51))	SL	0.39 +0.52	0.41 +0.55	2 (60 cm)	89	NQ	NQ	glu	BK95R01-MDA-01
USA (OH) 1995 (LH119 (9) x T14) (LH51))	SL	0.39 +0.52	0.43 +0.52	2 (60 cm)	117	NQ	NQ	glu	BK95R01-JRS-01
USA (TX) 1995 (LH216) (B73 (5) x T25))	SL	0.40 +0.50	0.42 +0.53	2 (53-66 cm)	84	NQ	NQ	glu	BK95R01-GLS-01
Argentina 1995)	SL	1.4	0.88	1	70	NQ	NQ		A57415 ER95ARG001 010102
Argentina 1996)	SL	1.4	0.88	1 GS17-32)	104	NQ	NQ		A57414 ER96ARG001 010102

[1] Growth stage in the US trials is recorded as the height of the plant or, in some cases, as the number of leaves.
[2] NQ - residues <LOD (0.05 mg/kg glufosinate free acid equivalents)
glu: included in glufosinate-ammonium result. agf: aspirated grain fraction from milling of the grain

Table 46. Glufosinate residues in transgenic maize resulting from supervised trials in Ontario, Canada. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Year	Application				PHI	Residues, mg/kg			Ref
	form	kg ai/ha	kg ai/hl	no[1]	days	glufosinate	MPP	NAG	
1993	SL	0.75		1 GS16	152	<0.05	<0.05	<0.05	A55207 93-IGN-CON-1-2
1993	SL	1.5		1 GS16	152	<0.05	<0.05	<0.05	A55207 93-IGN-CON-1-3
1993	SL	0.75		1 GS16	154	<0.05	<0.05	<0.05	A55207 93-IGN-CON-2-2
1993	SL	1.5		1 GS16	154	<0.05	<0.05	<0.05	A55207 93-IGN-CON-2-3
1994	SL	0.5		1 GS17-19	150	<0.05	<0.05	<0.05	A55207 94-IGN-CON-1-2
1994	SL	1.0		1 GS17-19	150	<0.05	<0.05	<0.05	A55207 94-IGN-CON-1-3

Year	Application				PHI	Residues, mg/kg			Ref
	form	kg ai/ha	kg ai/hl	no [1]	days	glufosinate	MPP	NAG	
1994	SL	0.5		1 GS17-19	136	<0.05	<0.05	<0.05	A55207 94-IGN-C ON-2-2
1994	SL	1.0		1 GS17-19	136	<0.05	<0.05	<0.05	A55207 94-IGN-C ON-2-3
1994	SL	0.5		1 GS17-19	136	<0.05	<0.05	<0.05	A55207 94-IGN-C ON-3-2
1994	SL	1.0		1 GS17-19	136	<0.05	<0.05	<0.05	A55207 94-IGN-C ON-3-3
1995	SL	0.6		1 GS18-19	138	<0.05	<0.05	<0.05	A55207 95-IGN-C ON-1-2
1995	SL	0.6		2 GS33	131	<0.05	<0.05	<0.05	A55207 95-IGN-C ON-1-3
1995	SL	1.2		1 GS40	126	<0.05	<0.05	<0.05	A55207 95-IGN-C ON-1-4
1995	SL	0.6		1 GS18	137	<0.05	<0.05	<0.05	A55207 95-IGN-C ON-2-2
1995	SL	0.6		2 GS33	128	<0.05	<0.05	<0.05	A55207 95-IGN-C ON-2-3
1995	SL	1.2		1 GS40	122	<0.05	<0.05	0.08	A55207 95-IGN-C ON-2-4
1995	SL	0.6		1 GS18-19	114	<0.05	<0.05	<0.05	A55207 95-IGN-C ON-3-2
1995	SL	0.6		2 GS33	107	<0.05	<0.05	<0.05	A55207 95-IGN-C ON-3-3
1995	SL	1.2		1 GS40	100	<0.05	<0.05	0.07	A55207 95-IGN-C ON-3-4
1995	SL	0.6		1 GS18	125	<0.05	<0.05	<0.05	A55207 95-IGN-C ON-4-2
1995	SL	0.6		2 GS33	117	<0.05	<0.05	<0.05	A55207 95-IGN-C ON-4-3
1995	SL	1.2		1 GS40	111	<0.05	<0.05	0.09	A55207 95-IGN-C ON-4-4

[1]. GS: growth stage at final treatment

GS16	6 leaves unfolded
GS17	7 leaves unfolded
GS18	8 leaves unfolded
GS19	9 or more leaves unfolded
GS33	3 nodes detectable
GS40	booting

Table 47. Glufosinate residues in soya beans resulting from supervised trials in the USA. Analyses of replicate samples from the treated plots are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Country, Year (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG	
USA (IA) 1993 (W98-7)	SL	0.5	0.51	1 trifoliate	85	<0.05 (3)	<0.05 (3)	0.06 <0.05 (2)	ER-93-USA-02-IA-01
	SL	0.5	0.51	1 full pod	65	1.2 (3)	0.44 0.44 0.39	5.0 5.4 4.9	
	SL	0.5	0.51	2 full pod	65	0.76 0.91 0.79	0.30 0.30 0.27	3.4 3.8 3.6	
USA (IL) 1993 (W98-7)	SL	0.5	0.53	1 trifoliate	85	<0.05 (3)	0.07 0.06 0.06	0.33 0.36 0.32	ER-93-USA-02-IL-01
	SL	0.5	0.53	1 full pod	65	0.96 1.0 0.90	0.51 0.61 0.57	5.0 5.4 5.1	
	SL	0.5	0.53	2 full pod	65	0.95 0.95 0.93	0.62 0.68 0.65	5.1 5.5 5.4	
USA (MO) 1993 (W98-7)	SL	0.5	0.53	1 trifoliate	85	<0.05 (3)	0.08 0.09 0.08	0.19 0.21 0.22	ER-93-USA-02-MO-01
	SL	0.5	0.53	1 full pod	65	1.4 (3)	0.89 0.61 0.79	6.7 6.7 7.2	
	SL	0.5	0.53	2 full pod	65	1.2 1.0 1.1	0.74 0.73 0.70	5.9 5.8 5.9	
USA (IN) 1993 (W98-7)	SL	0.5	0.53	1 trifoliate	85	<0.05 (3)	0.08 <0.05 (2)	0.12 0.10 0.08	ER-93-USA-02-IN-01
	SL	0.5	0.53	1 full pod	65	1.7 1.8 1.9	0.49 0.53 0.55	7.1 7.1 7.5	
	SL	0.5	0.53	2 full pod	65	1.6 1.8 1.8	0.56 0.64 0.74	5.9 6.1 7.1	
USA (IN) 1993 (W98)	SL	0.5	0.53	1 trifoliate	85	<0.05 (3)	<0.05 (3)	<0.05 (3)	ER-93-USA-02-IN-02
	SL	0.5	0.53	1 full pod	65	0.93 0.91 0.94	0.37 0.33 0.35	3.8 3.9 4.0	
	SL	0.5	0.53	1 full pod	75	0.80 0.84 0.81	0.29 0.32 0.36	3.1 3.6 3.7	
	SL	0.5	0.53	2 full pod	65	0.92 0.87 0.88	0.38 0.31 0.35	3.9 3.6 4.0	
	SL	0.5	0.53	2 full pod	75	0.69 0.70 0.68	0.30 0.36 0.33	3.4 3.5 3.4	
USA (AR) 1993 (W62)	SL	0.5	1.1	1 trifoliate	85	<0.05 (3)	<0.05 (3)	0.07 0.09 0.08	ER-93-USA-02-AR-01
	SL	0.5	1.1	1 full pod	65	0.87 0.76 0.73	0.61 0.56 0.46	6.8 5.8 4.5	
	SL	0.5	1.1	2 full pod	65	0.89 0.88 0.81	0.58 0.49 0.58	7.6 6.6 7.0	
USA (MS) 1993 (W98)	SL	0.5	1.1	1 trifoliate	85	<0.05 (3)	<0.05 (3)	0.10 0.10 0.12	ER-93-USA-02-MS-01
	SL	0.5	1.1	1 full pod	65	0.47 0.52 0.48	0.44 0.41 0.27	5.3 4.9 4.7	
	SL	0.5	1.1	2 full pod	65	0.46 0.40 0.48	0.48 0.41 0.47	5.1 5.1 5.0	
USA (VA) 1993 (W62)	SL	0.5	1.1	1 trifoliate	103	<0.05	<0.05	0.11	ER-93-USA-02-VA-01
	SL	0.5	1.1	1 full pod	65	0.10	0.10	0.69	
	SL	0.5	1.1	2 full pod	85	0.08	0.15	0.93	
USA (AR) 1994 (W62)	SL	0.39 +0.50	0.41 +0.53	2 bloom	82	0.68 <u>0.83</u>	0.06 <u>0.06</u>	glu	BK-94R-02-AR-01

Country, Year (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG	
USA (FL) 1994 (W62)	SL	0.39 +0.50	0.42 +0.54	2 bloom	93	0.58 0.62	0.09 0.09	glu	BK-94R-02-FL-01
USA (IA) 1994 (W98)	SL	0.39 +0.50	0.42 +0.54	2 bloom	86	1.1 1.1	0.14 0.10	glu	BK-94R-02-IA-01
USA (IL) 1994 (transgenic group 3)	SL	0.39 +0.50	0.42 +0.54	2 bloom	69	0.65 0.52	0.07 0.06	glu	BK-94R-02-IL-01
USA (IN) 1994 (W98)	SL	0.39 +0.50	0.42 +0.54	2 bloom	77	1.3 0.89	0.34 0.15	glu	BK-94R-02-IN-01
USA (MO) 1994 (W98)	SL	0.39 +0.50	0.42 +0.54	2 bloom	77	0.67 0.41	0.18 0.17	glu	BK-94R-02-MO-01
USA (NC) 1994 (W62)	SL	0.39 +0.50	0.42 +0.54	2 bloom	102	0.32 0.43	<0.05 (2)	glu	BK-94R-02-NC-01
USA (OH) 1994 (W98)	SL	0.39 +0.50	0.42 +0.54	2 bloom	76	0.80 0.71	0.22 0.18	glu	BK-94R-02-OH-01
USA (PA) 1994 (W98)	SL	0.39 +0.50	0.42 +0.54	2 bloom	91	0.73 0.54	0.08 0.07	glu	BK-94R-02-PA-01
USA (VA) 1994 (W62)	SL	0.39 +0.50	0.42 +0.54	2 bloom	82	1.6 1.3	0.28 0.36	glu	BK-94R-02-VA-01
USA (NC) 1994 (transgenic Group 5 W62 A5403)	SL SL SL SL	0.4 0.4 +0.5 0.4 +0.5 0.4 +0.5	0.43 0.43 +0.54 0.43 +0.54 0.43 +0.54	1 3rd node 2 6th node 2 bloom 2 full pod	136 123 90 77	<0.05 (2) <0.05 (2) 0.79 0.71 1.1 1.1	<0.05 (2) <0.05 (2) 0.13 0.14 0.23 0.27	glu glu glu glu	Project: BK-94R-06 Trial#: NC-01
USA (IN) 1995 (MG III, W98 A3322 group 3)	SL	0.39 +0.50	0.39 +0.51	2 R2.5-R3	64	1.1 0.96	0.16 0.19	glu	BK-95R-04-DJL-01
USA (IN) 1995 (MG III, W98 A3322 group 3)	SL	0.39 +0.50	0.39 +0.51	2 R2	62	1.1 0.90	0.23 0.24	glu	BK-95R-04-DJL-02
USA (MO) 1995 (MG III W62 A5504 group 5)	SL	0.39 +0.50	0.41 +0.53	2 R1	71	0.62 0.83	0.11 0.13	glu	BK-95R-04-JLB-01
USA (OH) 1995 (MG III, W98 A3322 group 3)	SL	0.39 +0.50	0.40 +0.52	2 R2	86	0.32 0.18	0.07 0.06	glu	BK-95R-04-JRS-01
USA (MI) 1995 (MG III, W98 A3322 group 3)	SL	0.39 +0.50	0.41 +0.53	2 R2	81	0.37 0.33	0.15 0.10	glu	BK-95R-04-JRS-02
USA (IA) 1995 (MG III, W98 A3322 group 3)	SL	0.39 +0.50	0.41 +0.53	2 R2	60	0.58 0.68	0.10 0.10	glu	BK-95R-04-GGH-01
USA (WI) 1995 (MG III, W98 A3322 group 3)	SL	0.38 +0.49	0.42 +0.54	2 R2.5	82	0.65 0.93	0.10 0.18	glu	BK-95R-04-GGH-02
USA (IA) 1995 (MG III, W98 A3322 group 3)	SL	0.39 +0.50	0.42 +0.53	2 R2	84	0.32 0.28	<0.05 (2)	glu	BK-95R-04-GGH-04
USA (NE) 1995 (MG III, W98 A3322 group 3)	SL	0.39 +0.50	0.41 +0.53	2 R3	80	0.12 0.62	0.05 0.06	glu	BK-95R-04-MDA-01
USA (KS) 1995 (MG III, W98 A3322 group 3)	SL	0.39 +0.50	0.41 +0.52	2 R2	78	0.50 0.42	0.06 0.05	glu	BK-95R-04-MDA-02

Country, Year (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG	
USA (LO) 1995 (MG III, W62 A5504 group 5)	SL	0.40 +0.54	0.42 +0.56	2 R2	70	0.95 0.64	0.61 0.84	glu	BK-95R-04-TLS-01
USA (MS) 1995 (MG III, W62 A5504 group 5)	SL	0.39 +0.50	0.41 +0.53	2 R2	90	1.1 0.93	0.16 0.15	glu	BK-95R-04-TLS-02
USA (IA) 1993 (transgenic W98-7)	SL	2.5	2.7	1 trifoliate	95	<0.05	0.08	0.07	ER-93-USA-02-IA-02
USA (IN) 1994 (transgenic group 3 W98 A3322)	SL	2.0 +2.6	2.1 +2.7	2 bloom	77	3.4	1.1	glu	BK-94R-04-IN-01
USA (MO) 1994 (transgenic group 3 W98 A3322)	SL	2.0 +2.6	2.1 +2.7	2 bloom	77	1.5	1.8	glu	BK-94R-04-MO-01

[1]growth stage described or provided as "R" code
R1 beginning bloom
R2 full bloom
R3 beginning pod
glu: included in glufosinate-ammonium result.

Table 48. Glufosinate residues in rape seed resulting from supervised trials in France, Germany and the UK.

Country Year (variety)	Application				PHI	Residues, mg/kg, expressed as glufosinate free acid			Ref
	form	kg ai/ha	Kg ai/hl	No[1]	days	glufosinate	MPP	NAG[2]	
France 1994 (Falcon)	SL	0.60 +0.45	0.30 +0.23	2 GS35	111	0.06	<0.05		A54228 ER93ECN553 FRA000202
France 1994 (Falcon)	SL	0.60 +0.45	0.30 +0.23	2 GS35	111	<0.05	<0.05		A54228 ER93ECN553 FRA000302
France 1994 (Gs 401×90)	SL	0.60 +0.45	0.30 +0.23	2 GS33	121	0.07	<0.05		A54228 ER93ECN553 FRA000102
France 1995 (Falcon B)	SL	0.6	0.30	2 GS35	127	<0.05	<0.05		A56444 ER94ECN553 FRA000203
France 1995 (Falcon)	SL	0.67 +0.60	0.32 +0.30	2 GS39	133	<0.05	<0.05		A56444 ER94ECN553 FRA000103
France 1996 (GMO hybrid)	SL	0.60	0.30 +0.24	2 GS32	108	0.13	<0.05		A57955 ER96ECN553 FRA000103
France 1996 (GMO hybrid)	SL	0.60	0.30 +0.24	2 GS32	108	0.12	<0.05		A57955 ER96ECN553 FRA000102

Country	Application				PHI	Residues, mg/kg, expressed as glufosinate free acid			Ref
Year (variety)	form	kg ai/ha	Kg ai/hl	No[1]	days	glufosinate	MPP	NAG[2]	
Germany 1995 (Falcon G-S40/90)	SL	0.60	0.20	2 GS35	106	0.06	<0.05		A56444 ER94ECN553 DEU030103
Germany 1995 (Falcon)	SL	0.60	0.20	2 GS35	105	0.06	<0.05		A56444 ER94ECN553 DEU040103
Germany 1995 (Falcon)	SL	0.60	0.20	2 GS35	110	0.05	<0.05		A56444 ER94ECN553 DEU040203
Germany 1995 (Falcon)	SL	0.60	0.20	2 GS37	104	<0.05	<0.05		A56444 ER94ECN553 DEU050103
Germany 1996 (Falcon)	SL	0.60	0.20	2 GS32	94	<0.05	<0.05		A57955 ER96ECN553 DEU030102
Germany 1996 (Falcon)	SL	0.80	0.27	2 GS32	94	0.06	<0.05		A57955 ER96ECN553 DEU030103
Germany 1996 (Falcon)	SL	0.60	0.20	2 GS32	97	0.11	<0.05		A57955 ER96ECN553 DEU050102
Germany 1996 (Falcon)	SL	0.80	0.27	2 GS32	97	0.13	<0.05		A57955 ER96ECN553 DEU050103
Germany 1996 (Falcon)	SL	0.60	0.20	2 GS37	97	0.14	<0.05		A57955 ER96ECN553 DEU040102
Germany 1996 s(Falcon)	SL	0.80	0.27	2 GS37	97	0.12	<0.05		A57955 ER96ECN553 DEU040103
UK 1994	SL	0.60	0.30	1 GS21	275	<0.05	<0.05		A54227 ER93ECN552 GBR000102
UK 1994	SL	0.60	0.30	1 GS21	212	<0.05 (2)	<0.05 (2)		A54227 ER93ECN552 GBR000202
UK 1994	SL	0.60 +0.45	0.30 +0.23	2 GS35	91	<0.05	<0.05		A54228 ER93ECN553 GBR000202
UK 1994 (Falcon)	SL	0.60 +0.45	0.30 +0.23	2 GS35	116	<0.05	<0.05		A54228 ER93ECN553 GBR000102
UK 1996 (Falcon)	SL	0.60	0.30	2 GS32	100	0.07	<0.05		A57955 ER96ECN553 GBR000103
UK 1996 (Falcon)	SL	0.60	0.30	2 GS32	92	0.1 [3]	<0.05 [3]		A57955 ER96ECN553 GBR000203
UK 1996 (Falcon)	SL	0.60	0.30	2 GS32	100	0.15	<0.05		A57955 ER96ECN553 GBR000102
UK 1996 (Falcon)	SL	0.80	0.40	2 GS32	100	0.07	<0.05		A57955 ER96ECN553 GBR000104
UK 1996 (Falcon)	SL	0.60	0.30	2 GS32	92	0.1 [3]	<0.05 [3]		A57955 ER96ECN553 GBR000202
UK 1996 (Falcon)	SL	0.80	0.40	2 GS32	92	0.12 [3]	<0.05 [3]		A57955 ER96ECN553 GBR000204

[1]: GS growth stage

GS21	first side shoot detectable
GS32	2 visibly extended internodes
GS33	3 visibly extended internodes
GS35	5 visibly extended internodes
GS37	7 visibly extended internodes
GS80	beginning of ripening
GS83	30% of pods ripe

[2] included in glufosinate-ammonium result.

[3]: Grain samples were harvested at GS80-83 and stored in paper bags for even drying and prepared to laboratory samples 10 days later.

Table 49. Glufosinate residues in canola resulting from supervised trials in Canada. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Location, Year, (variety)	Application				PHI	Residues, mg/kg[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG	
Canada (AB) 1992 (transgenic HCN92)	SL	0.75		1	63	<0.05	<0.05	<0.05	XEN93-09-AB-018 A53770
Canada (AB) 1992 (transgenic HCN92)	SL	0.75		1	63	<0.05	<0.05	<0.05	XEN93-09-AB019 A53770
Canada (AB) 1992 (transgenic HCN92)	SL	0.75		1	65	<0.05	<0.05	<0.05	XEN93-09-AB020 A53770
Canada (SK) 1992 (transgenic HCN92)	SL	0.75		1	65	<0.05	<0.05	0.07	XEN93-09-SK024 A53770
Canada (SK) 1992 (transgenic HCN92)	SL	0.75		1	62	<0.05	<0.05	0.14	XEN93-09-SK026 A53770
Canada (MB) 1992 (transgenic HCN92)	SL	0.75		1	65	<0.05 (2)	<0.05 (2)	<0.05 (2)	XEN93-09-MB015 A53770
Canada (MB) 1992 (transgenic HCN92)	SL	0.75		1	59	<0.05	<0.05	<0.05	XEN93-09-MB016 A53770
Canada (MB) 1992	SL	0.75		1	65	<0.05	<0.05	<0.05	XEN93-09-MB022 A53770
Canada (MB) 1992	SL	0.75		1	65	<0.05	<0.05	0.08	XEN93-09-MB028 A53770
Canada (AB) 1993 (transgenic HCN92)	SL	0.83		1 GS 3-6 leaf	95	<0.05	<0.05	<0.05	XEN93-29-AB-TC-5 A56394
Canada (AB) 1993 (transgenic HCN92)	SL	1.5		1 GS 3-6 leaf	95	<0.05	<0.05	<0.05	XEN93-29-AB-TC-5 A56394
Canada (AB) 1993 (transgenic HCN92)	SL	0.75	0.68	1 GS 3-5 leaf	80	<0.05	<0.05	<0.05	XEN93-29-AB-TC-1 A56394
Canada (AB) 1993 (transgenic HCN92)	SL	1.5	1.36	1	80	<0.05	<0.05	<0.05	XEN93-29-AB-TC-1 A56394
Canada (AB) 1993 (transgenic HCN92)	SL	0.5	0.45	1	75	<0.05	<0.05	<0.05	XEN93-29-AB-TC-2 A56394

Location, Year, (variety)	Application				PHI	Residues, mg/kg[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG	
Canada (AB) 1993 (transgenic HCN92)	SL	0.75	0.68	1	75	<0.05	<0.05	<0.05	XEN93-29-AB-TC-2 A56394
Canada (AB) 1993 (transgenic)	SL	0.5	0.45	1 GS 4-5 leaf	75	<0.05	<0.05	<0.05	XEN93-29-AB-TC-3 A56394
Canada (AB) 1993 (transgenic)	SL	1.5		1 GS 4-5 leaf	75	<0.05	<0.05	<0.05	XEN93-29-AB-TC-3 A56394
Canada (AB) 1993 (transgenic HCN92)	SL	0.5	0.45	1 GS 3-5 leaf	83	<0.05	<0.05	<0.05	XEN93-29-AB-TC-4 A56394
Canada (AB) 1993 (transgenic HCN92)	SL	0.75	0.68	1 GS 3-5 leaf	83	<0.05	<0.05	<0.05	XEN93-29-AB-TC-4 A56394
Canada (MB) 1993 (transgenic HCN92)	SL	0.75	0.68	1 GS 4-6 leaf	69	0.12	<0.05	<0.05	XEN93-29-MB-TC-2 A56394
Canada (MB) 1993 (transgenic HCN92)	SL	0.5	0.45	1 GS 4-5 leaf	67	<0.05	<0.05	<0.05	XEN93-29-MB-TC-3 A56394
Canada (MB) 1993 (transgenic HCN92)	SL	0.75	0.68	1 GS 4-5 leaf	67	<0.05	<0.05	<0.05	XEN93-29-MB-TC-3 A56394
Canada (MB) 1993 (transgenic HCN92)	SL	0.5	0.45	1 GS 4-5 leaf	68	<0.05	<0.05	<0.05	XEN93-29-MB-TC-4 A56394
Canada (MB) 1993 (transgenic HCN92)	SL	0.75	0.68	1 GS 4-5 leaf	68	<0.05	<0.05	<0.05	XEN93-29-MB-TC-4 A56394
Canada (SK) 1993 (transgenic HCN92)	SL	1.0		1 GS 5 leaf	66	<0.05	<0.05	0.05	XEN93-29-SK-TC-1 A56394
Canada (SK) 1993 (transgenic HCN92)	SL	2.0		1 GS 5 leaf	66	<0.05	<0.05	0.10	XEN93-29-SK-TC-1 A56394
Canada (SK) 1993 (transgenic HCN92)	SL	0.5	0.45	1 GS 3-4 leaf	57	<0.05	<0.05	<0.05	XEN93-29-SK-TC-3 A56394
Canada (SK) 1993 (transgenic HCN92)	SL	0.75	0.68	1 GS 3-4 leaf	57	<0.05	<0.05	<0.05	XEN93-29-SK-TC-3 A56394
Canada (SK) 1993 (transgenic HCN92)	SL	0.5	0.45	1 GS 10 leaf	69	<0.05	<0.05	<0.05	XEN93-29-SK-TC-6 A56394
Canada (SK) 1993 (transgenic HCN92)	SL	0.75	0.68	1 GS 10 leaf	69	<0.05	<0.05	<0.05	XEN93-29-SK-TC-6 A56394
Canada (MT) 1994 (transgenic HCN92)	SL	0.4	0.36	1 GS 2 leaf	77	<0.05	<0.05	<0.05	A56392 Minto
Canada (MT) 1994 (transgenic HCN92)	SL	0.8	0.73	1 GS 2 leaf	77	<0.05	<0.05	<0.05	A56392 Minto
Canada (MT) 1994 (transgenic HCN92)	SL	1.2	1.1	1 GS 2 leaf	77	<0.05	<0.05	<0.05	A56392 Minto
Canada (MT) 1994 (transgenic HCN92)	SL	0.4	0.36	1 GS 5-6 leaf	70	<0.05	<0.05	<0.05	A56392 Minto

Location, Year, (variety)	Application				PHI	Residues, mg/kg[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG	
Canada (MT) 1994 (transgenic HCN92)	SL	0.8	0.73	1 GS 5-6 leaf	70	<0.05	<0.05	<0.05	A56392 Minto
Canada (MT) 1994 (transgenic HCN92)	SL	1.2	1.1	1 GS 5-6 leaf	70	<0.05	<0.05	0.06	A56392 Minto
Canada (SK) 1994 (transgenic HCN92)	SL	0.4	0.36	1 GS 2-3 leaf	73	<0.05	<0.05	<0.05	A56392 Indian Head
Canada (SK) 1994 (transgenic HCN92)	SL	0.8	0.73	1 GS 2-3 leaf	73	<0.05	<0.05	<0.05	A56392 Indian Head
Canada (SK) 1994 (transgenic HCN92)	SL	1.2	1.1	1 GS 2-3 leaf	73	<0.05	<0.05	<0.05	A56392 Indian Head
Canada (SK) 1994 (transgenic HCN92)	SL	0.4	0.36	1 GS 5-7 leaf	57	<0.05	<0.05	0.17	A56392 Indian Head
Canada (SK) 1994 (transgenic HCN92)	SL	0.8	0.73	1 GS 5-7 leaf	57	<0.05	<0.05	0.24	A56392 Indian Head
Canada (SK) 1994 (transgenic HCN92)	SL	1.2	1.1	1 GS 5-7 leaf	57	<0.05	<0.05	0.26	A56392 Indian Head
Canada (MT) 1994 (transgenic HCN92)	SL	0.4	0.36	1 GS 4-5 leaf	65	<0.05	<0.05	<0.05	A56392 Portage la Prairie
Canada (MT) 1994 (transgenic HCN92)	SL	0.8	0.73	1 GS 4-5 leaf	65	<0.05	<0.05	0.07	A56392 Portage la Prairie
Canada (MT) 1994 (transgenic HCN92)	SL	1.2	1.1	1 GS 4-5 leaf	65	<0.05	0.06	0.05	A56392 Portage la Prairie
Canada (AB) 1994 (transgenic HCN92)	SL	0.4	0.36	1 GS 2-4 leaf	77	<0.05	<0.05	<0.05	A56392 Vauxhall
Canada (AB) 1994 (transgenic HCN92)	SL	0.8	0.73	1 GS 2-4 leaf	77	<0.05	<0.05	<0.05	A56392 Vauxhall
Canada (AB) 1994 (transgenic HCN92)	SL	1.2	1.1	1 GS 2-4 leaf	77	<0.05	<0.05	<0.05	A56392 Vauxhall
Canada (AB) 1994 (transgenic HCN92)	SL	0.4	0.36	1 GS 4-6 leaf	67	<0.05	<0.05	0.08	A56392 Vauxhall
Canada (AB) 1994 (transgenic HCN92)	SL	0.8	0.73	1 GS 4-6 leaf	67	<0.05	<0.05	0.17	A56392 Vauxhall
Canada (AB) 1994 (transgenic HCN92)	SL	1.2	1.1	1 GS 4-6 leaf	67	0.05	<0.05	0.24	A56392 Vauxhall

[1]GS: growth stage expressed in terms of leaf development.
[2]The expression of residues is unclear. In reports A56392 and A56394 glufosinate residues may be expressed as free acid or ammonium salt. MPP and NAG may be expressed as themselves rather than as glufosinate free acid.

Table 50. Glufosinate residues in canola resulting from supervised trials in Australia.

Location, Year, (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP[2]	NAG[2]	
Australia (NSW) 1996 (glufosinate selective line)	SL	0.6	0.72	1 GS 3-5 leaf	86	<0.05 (2)			YH 96 AH AU NW 06
Australia (NSW) 1996 (glufosinate selective line)	SL	1.2	1.4	1 GS 3-5 leaf	86	<0.05 (2)			YH 96 AH AU NW 06
Australia (WA) 1996 (var ex Canada)	SL	0.6	0.83	1 GS 1-2 leaf	124	<0.05 (2)			YH 96 AH AU WA 09
Australia (WA) 1996 (var ex Canada)	SL	1.2	1.7	1 GS 1-2 leaf	124	<0.05 (2)			YH 96 AH AU WA 09
Australia (SA) 1996 (transgenic Canadian line)	SL	0.6	0.75	1 GS 4-6 leaf	95	<0.05 (2)			YH 96 AH AU SA 17
Australia (SA) 1996 (transgenic Canadian line)	SL	1.2	1.5	1 GS 4-6 leaf	95	<0.05 (2)			YH 96 AH AU SA 17
Australia (Vic) 1997 (Canadian tolerant)	SL	0.6	0.6	1 GS 2 leaf	105	<0.05 (2)			YH 96 AH AU VN 12
Australia (Vic) 1997 (Canadian tolerant)	SL	1.2	1.2	1 GS 2 leaf	105	<0.05 (2)			YH 96 AH AU VN 12

[1]GS: growth stage expressed in terms of leaf development.
[2]included in glufosinate-ammonium result.

Table 51. Glufosinate residues in tolerant sugar beet root resulting from foliar application in supervised trials in France, Germany and the UK.

Country year (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	no[1]	days	glufosinate	MPP	NAG	
France 1995 (transgenic hybrid)	SL	0.60	0.30	2 GS31	85	0.87	<0.05	[2]	A56446 ER95ECN555 FRA000102
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	96	0.05	<0.05	[2]	A57574 ER96ECN551 FRA000102
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	96 124	0.12 0.06	<0.05 <0.05	[2]	A57574 ER96ECN551 FRA000202
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	91	0.48	<0.05	[2]	A57574 ER96ECN551 FRA000302
Germany 1995 (Sä-Nr. 951 959 – 36)	SL	0.80	0.27	2 GS31	96 116	0.39 0.3	<0.05 0.05	[2] [2]	A57574 ER96ECN551 DEU010102
UK 1995 (transgenic hybrid)	SL	0.60	0.30	2 GS19	83	0.79	<0.05	[2]	A56446 ER95ECN555 GBR000102
UK 1995 (transgenic hybrid)	SL	0.60	0.60	2 GS31	94	0.32	<0.05	[2]	A56446 ER95ECN555 GBR000202

Country year (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	no[1]	days	glufosinate	MPP	NAG	
UK 1996 (Roberta)	SL	0.80	0.80	2 GS31	111	0.88 0.99	0.06 <0.05	[2]	A57574 ER96ECN551 GBR000102
UK 1996 (transgenic hybrid)	SL	0.80	0.80	2 GS19	105	0.52	<0.05	[2]	A57574 ER96ECN551 GBR000202

[1]: GS growth stage

GS14	4 leaves (2nd pair unfolded)
GS15	5 leaves unfolded
GS19	9 or more leaves unfolded
GS31	beginning of crop cover formation

[2] included in glufosinate-ammonium result.

Table 52. Glufosinate residues in tolerant sugar beet root resulting from foliar application in supervised trials in the USA.

Location, Year, (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG[2]	
USA (CA) 1995 (Liberty Link)	SL	0.21 +0.20 +0.20	0.21 +0.20 +0.20	3 8-leaf	139	<0.05 (2)	0.14 (2)		BK-95R-06 CA-016 (Regimen B)
USA (CA) 1995 (Liberty Link)	SL	0.43 +0.40 +0.40	0.43 +0.39 +0.40	3 6-leaf	139	<0.05 (2)	0.30 0.32		BK-95R-06 CA-016 (Regimen C)
USA (CA) 1995 (Liberty Link)	SL	0.61	0.59	1 6-leaf	139	<0.05 0.05	0.27 0.31		BK-95R-06 CA-016 (Regimen D)
USA (MN) 1995 (Liberty Link)	SL	0.19 +0.20 +0.20	0.21	3 8-leaf	95	<0.05 (2)	<0.05 (2)		BK-95R-06 KBT-01 (Regimen B)
USA (MN) 1995 (Liberty Link)	SL	0.40 +0.41 +0.41	0.43	3 8-leaf	95	0.09 (2)	<0.05 (2)		BK-95R-06 KBT-01 (Regimen C)
USA (MN) 1995 (Liberty Link)	SL	0.61 +0.62	0.64	2 8-leaf	95	0.12 0.10	<0.05 (2)		BK-95R-06 KBT-01 (Regimen D)
USA (ID) 1995 (Liberty Link)	SL	0.21 +0.20 +0.21	0.21	3 8-leaf	41	0.06 <0.05 <0.05)	<0.05 (3)		BK-95R-06 TWM-01 Regimen B)
USA (ID) 1995 (Liberty Link)	SL	0.41 +0.43 +0.40	0.42	3 8-leaf	41	0.16 0.15	<0.05 (2)		BK-95R-06 TWM-01 Regimen C)
USA (ID) 1995 (Liberty Link)	SL	0.63 +0.61	0.64	2 8-leaf	41	0.21	0.06		BK-95R-06 TWM-01 Regimen D)
USA (ND) 1995 (Liberty Link)	SL	0.21 +0.21 +0.22	0.21 +0.22 +0.21	3 11-12-leaf	103	0.08 0.06 0.08	<0.05 (3)		BK-95R-06 PGM-01 (Regimen B)
USA (ND) 1995 (Liberty Link)	SL	0.43 +0.43 +0.46	0.43	3 11-12-leaf	104	0.14 (2)	<0.05 (2)		BK-95R-06 PGM-01 (Regimen C)
USA (ND) 1995 (Liberty Link)	SL	0.86 +0.64	0.85 +0.63	2 11-12-leaf	104	0.15 0.12	<0.05 (2)		BK-95R-06 PGM-01 (Regimen D)
USA (MI) 1996 (Liberty Link)	SL	0.60	0.61 +0.63	2 8-leaf	109	0.12 0.13	0.05 0.06		BK-96R-01 R05-02 (Regimen B)

Location, Year, (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG[2]	
USA (MI) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.64 +0.40 +0.66	3 10-leaf	106	0.24 0.21	0.05 <0.05		BK-96R-01 R05-02 (Regimen C)
USA (OH) 1996 (Liberty Link)	SL	0.60	0.63 +0.67	2 8-leaf	83	0.27 0.12	<0.05 (2)		BK-96R-01 R05-03 (Regimen B)
USA (OH) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.61 +0.41 +0.66	3 10-leaf	77	0.56 0.78	<0.05 (2)		BK-96R-01 R05-03 (Regimen C)
USA (ND) 1996 (Liberty Link)	SL	0.60	0.63	2 7.5-8.5-leaf	67	0.17 0.16	<0.05 (2)		BK-96R-01 R05-04 (Regimen B)
USA (ND) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.63 +0.41 +0.63	3 9.5-11-leaf	62	0.54 0.70	<0.05 (2)		BK-96R-01 R05-04 (Regimen C)
USA (NE) 1996 (Liberty Link)	SL	0.60	0.63	2 8-leaf	115	<0.05 (2)	<0.05 (2)		BK-96R-01 R07-01 Regimen B)
USA (NE) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.61 +0.41 +0.66	3 10-leaf	108	0.07 0.05	<0.05 (2)		BK-96R-01 R07-01 Regimen C)
USA (ND) 1996 (Liberty Link)	SL	0.60	0.63	2 8-leaf	73	0.12 0.14	<0.05 (2)		BK-96R-01 R07-02 (Regimen B)
USA (ND) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.63 +0.41 +0.63	3 10-leaf	66	0.28 0.33	0.07 0.11		BK-96R-01 R07-02 (Regimen C)
USA (CO) 1996 (Liberty Link)	SL	0.60	0.59	2 8-leaf	80	<0.05 (2)	<0.05 (2)		BK-96R-01 R08-01 (Regimen B)
USA (CO) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.63 +0.40 +0.58	3 10-leaf	68	0.53 0.55	<0.05 (2)		BK-96R-01 R08-01 (Regimen C)
USA (CO) 1996 (Liberty Link)	SL	0.60	0.61 +0.59	2 8-leaf	86	0.11 (2)	<0.05 (2)		BK-96R-01 R09-01 (Regimen B)
USA (CO) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.64 +0.41 +0.61	3 10-leaf	81	0.27 0.30	<0.05 (2)		BK-96R-01 R09-01 (Regimen C)
USA (CA) 1996 (Liberty Link)	SL	0.60	0.65 +0.62	2 8-leaf	132	0.06 0.08	0.07 0.06		BK-96R-01 R10-01 (Regimen B)
USA (CA) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.61 +0.42 +0.63	3 10-leaf	122	0.37 0.36	0.06 0.07		BK-96R-01 R10-01 (Regimen C)
USA (ID) 1996 (Liberty Link)	SL	0.60	0.62	2 8-10-leaf	128	0.07 0.06	<0.05 (2)		BK-96R-01 R11-01 (Regimen B)
USA (ID) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.61 +0.41 +0.63	3 10-leaf	121	0.19 0.22	<0.05 (2)		BK-96R-01 R11-01 (Regimen C)
USA (CA) 1996 (Liberty Link)	SL	2.8 +3.0 +3.0	3.0 +3.2 +3.2	3 8-leaf	136	0.23	0.93		BK-96-R05

[1]: growth stage is described in terms of number of leaves.
[2] included in glufosinate-ammonium result.

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Table 53. Glufosinate residues in maize forage and fodder resulting from supervised trials in France, Germany, Italy, The Netherlands and Spain.

Country, Year, (variety)	Application				PHI	Residues, as glufosinate free acid, mg/kg[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Glufosinate	MPP	NAG	
France 1993 (LH163×LH164-×F2×T14)	SL	0.45	0.23	2 GS25	0 39 119 119	20 shoot 0.10 shoot <0.05 shoot <0.05 cob	0.17 shoot <0.05 shoot <0.05 shoot <0.05 cob	13 shoot 0.44 shoot 0.06 shoot glu	A54225 ER93ECN550 FRA000402
France 1993 (LH206×LH74-×F2×T14)	SL	0.45	0.23	2 GS24	0 43 119 119	6.2 shoot <0.05 shoot <0.05 shoot <0.05 cob	0.15 shoot <0.05 shoot <0.05 shoot <0.05 cob	8.6 shoot <0.05 shoot <0.05 shoot glu	A54225 ER93ECN550 FRA000502
France 1993 (MLC 2101/T14)	SL	0.45	0.23	2 GS24	0 48 84 84	27 shoot 1.2 shoot <0.05 shoot <0.05 cob	0.11 shoot <0.05 shoot <0.05 shoot <0.05 cob	19 shoot 0.76 shoot <0.05 shoot glu	A54225 ER93ECN550 FRA000102
France 1993 (MLC 2101/T14)	SL	0.45	0.23	2 GS24	0 51 92 92	24 shoot 0.24 shoot <0.05 shoot <0.05 cob	0.47 shoot 0.06 shoot 0.12 shoot 0.23 cob	7.0 shoot <0.05 shoot <0.05 shoot glu	A54225 ER93ECN550 FRA000202
France 1993 (MLC 2101/T14)	SL	0.45	0.23	2 GS24	0 39 106 106	26 shoot 0.09 shoot <0.05 shoot <0.05 cob	0.22 shoot <0.05 shoot <0.05 shoot <0.05 cob	17 shoot <0.05 shoot 0.05 shoot glu	A54225 ER93ECN550 FRA000302
France 1994 ((LH82(4)T25)sf (-2)xSH298	SL	0.45	0.23	2 GS25	0 35 90 90	24 shoot 0.1 shoot 0.07 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A54229 ER94ECN550 FRA000202
France 1994 (F6×M1)	SL	0.45	0.23	2 GS25	0 35 77 77	9.9 shoot <0.05 shoot <0.05 shoot <0.05 cob	0.13 shoot <0.05 shoot <0.05 shoot <0.05 cob	6.5 shoot 0.11 shoot <0.05 shoot glu	A54226 ER93ECS550 FRA000102
France 1994 (LH824xT25)AF4x-B73)	SL	0.45	0.15	2 GS25	0 67 67	43 shoot <0.05 shoot <0.05 cob	0.27 shoot <0.05 shoot <0.05 cob	glu glu glu	A54230 ER94ECS550 FRA000102
France 1994 (SH298(LH82(4)T25)sf(2))	SL	0.45	0.23	2 GS25	0 27 69 69	24 shoot 0.12 shoot 0.36 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A54229 ER94ECN550 FRA000102
France 1995 (F2xLH82-T25)	SL	0.45	0.23	2 GS18	0 44 72 72	25 shoot 0.51 shoot 0.47 shoot <0.05 cob	0.26 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A56445 ER95ECN550 FRA000202
France 1995 (F2xLH82-T25)	SL	0.45	0.23	2 GS19	0 44 72 72	25 shoot 0.83 shoot 0.82 shoot <0.05 cob	0.29 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A56445 ER95ECN550 FRA000203
France 1995 (tolerant 039866)	SL	0.45	0.23	2 GS18	0 55 73 73	20 shoot 0.12 shoot 0.12 shoot <0.05 cob	0.2 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A56445 ER95ECN550 FRA000103
France 1995 (tolerant 039866)	SL	0.45	0.23	2 GS18	0 55 73 73	15 shoot 0.1 shoot 0.1 shoot <0.05 cob	0.15 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A56445 ER95ECN550 FRA000102

Country, Year, (variety)	Application				PHI	Residues, as glufosinate free acid, mg/kg[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Glufosinate	MPP	NAG	
France 1995 (Transgenic hybrid)	SL	0.53	0.27	2 GS18	0 49 65 65	7.9 shoot 0.43 shoot 0.16 shoot <0.05 cob	0.08 shoot 0.06 shoot 0.06 shoot <0.05 cob	4.2 shoot 0.28 shoot 0.37 shoot <0.05 cob	A54760 ER95ECS550 FRA000103
France 1995 (Transgenic hybrid)	SL	0.53	0.27	2 GS18	0 49 65 65	8.3 shoot 0.14 shoot <0.05 shoot <0.05 cob	0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	4.2 shoot 0.54 shoot 0.21 shoot <0.05 cob	A54760 ER95ECS550 FRA000102
France 1995 (Transgenic hybrid)	SL	0.45	0.23	2 GS19	0 49 60 60	8.9 shoot <0.05 shoot 0.05 shoot <0.05 cob	0.13 shoot 0.05 shoot 0.07 shoot <0.05 cob	5.1 shoot 0.24 shoot 0.37 shoot <0.05 cob	A54760 ER95ECS550 FRA000203
France 1995 (Transgenic hybrid)	SL	0.45	0.23	2 GS19	0 49 60 60	14 shoot <0.05 shoot <0.05 shoot <0.05 cob	0.14 shoot <0.05 shoot <0.05 shoot <0.05 cob	6.5 shoot 0.13 shoot 0.14 shoot <0.05 cob	A54760 ER95ECS550 FRA000202
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS18	0 56 75 75	9.1 shoot 0.14 shoot 0.19 shoot <0.05 cob	0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000102
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS18	0 56 75 75	18 shoot 0.28 shoot 0.65 shoot <0.05 cob	0.08 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000103
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS18	0 56 75 75	16 shoot 0.4 shoot 0.31 shoot <0.05 cob	0.1 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000104
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS18	0 57 76 76	26 shoot 0.24 shoot 0.57 shoot <0.05 cob	0.09 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000302
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS18	0 57 76 76	24 shoot 0.48 shoot 0.54 shoot <0.05 cob	0.09 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000303
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS18	0 57 76 76	14 shoot 0.2 shoot 0.23 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000304
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS18	0 62 76 76	16 shoot 0.13 shoot 0.22 shoot <0.05 cob	0.07 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000402
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS18	0 62 76 76	25 shoot 0.2 shoot 0.27 shoot <0.05 cob	0.08 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000403
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS18	0 62 76 76	20 shoot <0.05 shoot 0.15 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000404
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS18	0 46 75 75	16 shoot 0.31 shoot 0.37 shoot <0.05 cob	0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 FRA000302
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS18	0 46 75 75	19 shoot 0.33 shoot 0.64 shoot <0.05 cob	0.06 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 FRA000303

Country, Year, (variety)	Application				PHI	Residues, as glufosinate free acid, mg/kg[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Glufosinate	MPP	NAG	
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS18	0 46 75 75	34 shoot 0.44 shoot 0.47 shoot <0.05 cob	0.09 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 FRA000304
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS19	0 56 76 76	18 shoot 0.27 shoot 0.75 shoot <0.05 cob	0.07 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000202
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	0 56 76 76	23 shoot 0.44 shoot 0.46 shoot <0.05 cob	0.08 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000203
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS19	0 56 76 76	22 shoot 0.17 shoot 0.38 shoot <0.05 cob	0.09 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 FRA000204
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS19	0 64 91 91	31 shoot <0.05 shoot <0.05 shoot <0.05 cob	0.14 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 FRA000102
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS19	0 64 91 91	36 shoot 0.06 shoot 0.08 shoot <0.05 cob	0.2 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 FRA000103
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	0 64 91 91	50 shoot 0.12 shoot 0.13 shoot <0.05 cob	0.24 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 FRA000104
France 1996 (transgenic hybrid)	SL	0.45	0.18	2 GS19	0 57 86 86	6.5 shoot 0.25 shoot 0.31 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 FRA000202
France 1996 (transgenic hybrid)	SL	0.60	0.24	2 GS19	0 57 86 86	8.9 shoot 0.27 shoot 0.3 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 FRA000203
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	0 57 86 86	7.2 shoot 0.11 shoot 0.2 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 FRA000204
Germany 1994	SL	0.45	0.15	2 GS24	0 37 55 55 76	23 shoot 0.74 shoot 0.67 shoot <0.05 cob <0.05 cob	0.65 shoot <0.05 shoot <0.05 shoot <0.05 cob <0.05 cob	glu glu glu glu glu	A54229 ER94ECN550 DEU040202
Germany 1994 (F2xLH82-4)T25sf(2)	SL	0.45	0.15	2 GS23	0 55 87 87	39 shoot <0.05 shoot <0.05 shoot <0.05 cob	0.53 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A54229 ER94ECN550 DEU050102
Germany 1994 (LH82(4)T25st2xS-H298)	SL	0.45	0.15	2 GS25	0 31 51 84 84	29 shoot 0.78 shoot 0.19 shoot 0.26 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu glu	A54229 ER94ECN550 DEU030102
Germany 1995 (LH82^4T25sf^4F2)	SL	0.45	0.15	2 GS18	0 38 78 78	30 shoot 1.5 shoot 0.79 shoot 0.09 cob	0.17 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A56445 ER95ECN550 DEU010202

Country, Year, (variety)	Application				PHI	Residues, as glufosinate free acid, mg/kg[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Glufosinate	MPP	NAG	
Germany 1995 (LH82^4T25sf^4SH -298)	SL	0.45	0.15	2 GS18	0 59 77 77	18 shoot <0.05 shoot 0.05 shoot <0.05 cob	0.1 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A56445 ER95ECN550 DEU050102
Germany 1995 (LH82^4T25sf^4xF 2)	SL	0.45	0.15	2 GS18	0 48 90 90	26 shoot 0.34 shoot 0.23 shoot <0.05 cob	0.08 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A56445 ER95ECN550 DEU010102
Germany 1996 (F2 hybride - LH-82)	SL	0.60	0.20	2 GS18	0 55 103 103	20 shoot 0.12 shoot 0.12 shoot <0.05 cob	0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU050102
Germany 1996 (F2 hybride - LH-82)	SL	0.80	0.27	2 GS18	0 55 103 103	39 shoot 0.16 shoot 0.28 shoot <0.05 cob	0.09 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU050103
Germany 1996 (F2 hybride - LH-82)	SL	0.45	0.15	2 GS18	0 55 103 103	23 shoot 0.14 shoot 0.15 shoot <0.05 cob	0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU050104
Germany 1996 (Facet - transgen)	SL	0.60	0.20	2 GS18	0 40 69 69	24 shoot 0.15 shoot 0.17 shoot <0.05 cob	0.07 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU060102
Germany 1996 (Facet - transgen)	SL	0.80	0.27	2 GS18	0 40 69 69	40 shoot 0.18 shoot 0.52 shoot <0.05 cob	0.1 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU060103
Germany 1996 (Facet - transgen)	SL	0.45	0.15	2 GS18	0 40 69 69	31 shoot 0.08 shoot 0.15 shoot <0.05 cob	0.08 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU060104
Germany 1996 (Facet - transgen)	SL	0.60	0.20	2 GS18	0 38 70 70	32 shoot 0.23 shoot 0.4 shoot <0.05 cob	0.1 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU060202
Germany 1996 (Facet - transgen)	SL	0.80	0.27	2 GS18	0 38 70 70	51 shoot 0.55 shoot 0.21 shoot <0.05 cob	0.16 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU060203
Germany 1996 (Facet - transgen)	SL	0.45	0.15	2 GS18	0 38 70 70	23 shoot 0.29 shoot 0.9 shoot <0.05 cob	0.08 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550D EU060204
Germany 1996 (LH82 T25 SF x F2)	SL	0.60	0.20	2 GS19	0 48 106 106	34 shoot 0.12 shoot 0.09 shoot <0.05 cob	0.17 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU010202
Germany 1996 (LH82 T25 SF x F2)	SL	0.80	0.27	2 GS19	0 48 106 106	45 shoot 0.16 shoot 0.13 shoot <0.05 cob	0.17 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU010203
Germany 1996 (LH82 T25 SF x F2)	SL	0.45	0.15	2 GS19	0 48 106 106	27 shoot 0.08 shoot 0.06 shoot <0.05 cob	0.12 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU010204
Germany 1996 (LH82 T25 SF x Fe)	SL	0.60	0.20	2 GS19	0 50 113 113	28 shoot 0.1 shoot 0.06 shoot <0.05 cob	0.13 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU010102

Country, Year, (variety)	Application				PHI	Residues, as glufosinate free acid, mg/kg[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Glufosinate	MPP	NAG	
Germany 1996 (LH82 T25 SF x Fe)	SL	0.80	0.27	2 GS19	0 50 113 113	27 shoot 0.21 shoot 0.15 shoot <0.05 cob	0.14 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU010103
Germany 1996 (LH82 T25 SF x Fe)	SL	0.45	0.15	2 GS19	0 50 113 113	21 shoot 0.07 shoot 0.05 shoot <0.05 cob	0.11 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58191 ER96ECN550 DEU010104
Italy 1994 ([B73(4)xT14]sfx - LM82)	SL	0.45	0.15	2 GS23	0 40 67 67	42 shoot 0.75 shoot 0.68 shoot <0.05 cob	0.17 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A54230 ER94ECS550 ITA000102
Italy 1995 (Transgenic hybrid)	SL	0.45	0.15	2 GS18	0 45 77 77	10 shoot <0.05 shoot <0.05 shoot <0.05 cob	0.08 shoot <0.05 shoot <0.05 shoot <0.05 cob	4.3 shoot 0.22 shoot 0.16 shoot <0.05 cob	A54760 ER95ECS550 ITA000104
Italy 1995 (Transgenic hybrid)	SL	0.45	0.15	2 GS18	0 48 78 78	16 shoot <0.05 shoot <0.05 shoot <0.05 cob	0.12 shoot <0.05 shoot <0.05 shoot <0.05 cob	4.8 shoot 0.14 shoot 0.1 shoot <0.05 cob	A54760 ER95ECS550 ITA000204
Italy 1995 (Transgenic hybrid)	SL	0.45	0.15	2 GS18	0 45 77 77	7.8 shoot <0.05 shoot 0.07 shoot <0.05 cob	0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	4.1 shoot 0.21 shoot 0.45 shoot <0.05 cob	A54760 ER95ECS550 ITA000103
Italy 1995 (Transgenic hybrid)	SL	0.45	0.15	2 GS18	0 48 78 78	19 shoot <0.05 shoot <0.05 shoot <0.05 cob	0.13 shoot <0.05 shoot <0.05 shoot <0.05 cob	5.2 shoot 0.08 shoot 0.15 shoot <0.05 cob	A54760 ER95ECS550 ITA000203
Italy 1995 (Transgenic hybrid)	SL	0.45	0.15	2 GS18	0 45 77 77	11 shoot <0.05 shoot <0.05 shoot <0.05 cob	0.11 shoot <0.05 shoot <0.05 shoot <0.05 cob	3.4 shoot 0.11 shoot 0.12 shoot <0.05 cob	A54760 ER95ECS550 ITA000102
Italy 1995 (Transgenic hybrid)	SL	0.45	0.15	2 GS18	0 48 78 78	15 shoot <0.05 shoot <0.05 shoot <0.05 cob	0.17 shoot <0.05 shoot <0.05 shoot <0.05 cob	3.7 shoot 0.06 shoot 0.12 shoot <0.05 cob	A54760 ER95ECS550 ITA000202
Italy 1996 (Transgenic hybrid)	SL	0.80	0.27	2 GS18	0 38 64 64	46 shoot 0.76 shoot 1.0 shoot <0.05 cob	0.12 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ITA000105
Italy 1996 (Transgenic hybrid)	SL	0.80	0.27	2 GS18	0 39 67 67	20 shoot 0.35 shoot 0.46 shoot <0.05 cob	0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ITA000205
Italy 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS18	0 38 64 64	25 shoot 0.3 shoot 0.57 shoot <0.05 cob	0.09 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ITA000103
Italy 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	0 38 64 64	37 shoot 0.47 shoot 1.1 shoot <0.05 cob	0.11 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ITA000104
Italy 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS18	0 39 67 67	15 shoot 0.21 shoot 0.3 shoot <0.05 cob	0.08 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ITA000203
Italy 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	0 39 67 67	22 shoot 0.36 shoot 0.71 shoot <0.05 cob	0.1 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ITA000204

Country, Year, (variety)	Application				PHI	Residues, as glufosinate free acid, mg/kg[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Glufosinate	MPP	NAG	
Italy 1996 (Transgenic hybrid)	SL	0.80	0.27	2 GS19	0 38 54 54	21 shoot 0.18 shoot 0.79 shoot <0.05 cob	0.05 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ITA000305
Italy 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS19	0 38 54 54	19 shoot 0.58 shoot 0.56 shoot <0.05 cob	0.09 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ITA000303
Italy 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS19	0 38 54 54	20 shoot 0.43 shoot 0.7 shoot <0.05 cob	0.09 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ITA000304
Netherlands 1995 (Hudson)	SL	0.9	0.45-0.23	1 (6 leaf)	71 71	0.41 shoot <0.05 cob	<0.05 shoot <0.05 cob	glu glu	6 HMA 52-509
Netherlands 1995 (Scarlet)	SL	0.9	0.45-0.23	1 (5 leaf)	85 85	0.81 shoot <0.05 cob	0.05 shoot <0.05 cob	glu glu	6 HMA 52-510
Netherlands 1995 (Scarlet)	SL	0.9	0.45-0.23	1 (9 leaf)	72 72	1.7 shoot 0.06 cob	0.24 shoot 0.07 cob	glu glu	6 HMA 52-264
Spain 1994 (LH119-6xT14/LH82)	SL	0.45	0.15	2 GS25	0 40 70 70	27 shoot 0.14 shoot 0.05 shoot <0.05 cob	0.28 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A54230 ER94ECS550 ESP000102
Spain 1995 (Transgenic hybrid)	SL	0.45	0.15	2 GS18	0 46 57 57	24 shoot <0.05 shoot 0.07 shoot <0.05 cob	0.46 shoot <0.05 shoot <0.05 shoot <0.05 cob	4.2 shoot 0.08 shoot 0.25 shoot <0.05 cob	A54760 ER95ECS550 ESP000103
Spain 1995 (Transgenic hybrid)	SL	0.45	0.15	2 GS18	0 46 57 57	25 shoot 0.05 shoot 0.08 shoot <0.05 cob	0.39 shoot <0.05 shoot <0.05 shoot <0.05 cob	2.9 shoot 0.15 shoot 0.21 shoot <0.05 cob	A54760 ER95ECS550 ESP000102
Spain 1996 (transgenic hybrid)	SL	0.45	0.15	2 GS18	0 36 54 54	14 shoot 0.25 shoot 0.28 shoot <0.05 cob	0.06 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ESP000102
Spain 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS18	0 36 54 54	22 shoot 0.62 shoot 0.31 shoot <0.05 cob	0.07 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ESP000103
Spain 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	0 36 54 54	19 shoot 0.9 shoot 0.54 shoot <0.05 cob	0.07 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ESP000104
Spain 1996 (transgenic hybrid)	SL	0.45	0.15	2 GS18	0 35 55 55	12 shoot 0.66 shoot 0.54 shoot <0.05 cob	0.06 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ESP000202
Spain 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS18	0 35 55 55	17 shoot 1.2 shoot 0.72 shoot <0.05 cob	0.06 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ESP000203
Spain 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	0 35 55 55	24 shoot 0.88 shoot 0.48 shoot <0.05 cob	0.08 shoot <0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ESP000204
Spain 1996 (transgenic hybrid)	SL	0.45	0.15	2 GS18	0 46 59 59	25 shoot 0.33 shoot 0.47 shoot <0.05 cob	0.18 shoot 0.08 shoot 0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ESP000302

Country, Year, (variety)	Application				PHI	Residues, as glufosinate free acid, mg/kg[2]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Glufosinate	MPP	NAG	
Spain 1996 (transgenic hybrid)	SL	0.60	0.20	2 GS18	0 46 59 59	36 shoot 0.66 shoot 0.59 shoot <0.05 cob	0.25 shoot 0.05 shoot <0.05 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ESP000303
Spain 1996 (transgenic hybrid)	SL	0.80	0.27	2 GS18	0 46 59 59	28 shoot 0.8 shoot 1.0 shoot <0.05 cob	0.23 shoot 0.05 shoot 0.07 shoot <0.05 cob	glu glu glu glu	A58190 ER96ECS550 ESP000304

[1]. GS: growth stage at final treatment
GS18 8 leaves unfolded
GS19 9 or more leaves unfolded
GS23 5th leaf unfolded
GS24 6th leaf unfolded
GS25 7th leaf unfolded
[2] shoot: stems + leaves.
glu: included in glufosinate-ammonium result.

Table 54. Glufosinate residues in maize forage and fodder resulting from supervised trials in the USA and Argentina. Analyses on replicate samples are reported individually. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Location, Year, (variety)	Application				PHI	Commodity[2]	Residues, mg/kg, as glufosinate free acid[3]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days		glufosinate-ammonium	MPP	NAG	
USA (IA) 1993 (transgenic (LH216) X (LH119) (4) × T14)	SL	0.36		1 (30 cm)	30 60 118	Forage silage fodder	0.05 0.08 0.09 NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.36 0.49 0.45 0.18 0.19 0.17 0.15 0.19 0.19	ER-93-USA-01-IA-01
USA (IA) 1993 (transgenic (LH216) X (LH119) (4) × T14)	SL	0.50		1 (30 cm)	30 60 118	forage silage fodder	0.07 0.08 0.18 NQ (3) NQ (2) 0.05	NQ (3) NQ (3) NQ (3)	0.36 0.49 0.45 0.14 0.12 0.16 0.20 (3)	ER-93-USA-01-IA-01
USA (IA) 1993 (transgenic (LH216) X (LH119) (4) × T14)	SL	0.50		1 (60 cm)	30 62 114	forage silage fodder	0.12 0.12 0.07 0.12 0.13 0.08 0.13 0.15 0.12	NQ (3) NQ (3) NQ 0.05 NQ	0.80 0.75 0.51 0.71 0.94 0.47 0.81 0.64 0.48	ER-93-USA-01-IA-01
USA (IL) 1993 (transgenic (LH 59x LH51)(LH119) (4) X T14)	SL	0.36	0.39	1 (30 cm)	30 60 100	forage silage fodder	NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.10 0.06 NQ NQ (3) NQ (3)	ER-93-USA-01-IL-01
USA (IL) 1993 (transgenic (LH 59x LH51)(LH119) (4) X T14)	SL	0.50	0.54	1 (30 cm)	30 60 100	forage silage fodder	NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.06 0.18 0.06 NQ (3) NQ (3)	ER-93-USA-01-IL-01
USA (IL) 1993 (transgenic (LH 59x LH51)(LH119) (4) X T14)	SL	0.50	0.54	1 (60 cm)	30 61 95	forage silage fodder	NQ 0.06 0.08 NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.19 0.48 0.47 0.20 0.17 0.17 0.21 0.16 0.25	ER-93-USA-01-IL-01
USA (IL) 1993 (transgenic (LH 59x LH51)(LH119) (4) X T14)	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	30 6195	forage silage fodder	0.13 0.14 0.13 0.07 0.09 0.07 NQ (3)	NQ (3) NQ (3) NQ (3)	0.64 0.76 0.51 0.47 0.69 0.51 0.13 0.12 0.15	ER-93-USA-01-IL-01
USA (NE) 1993 (transgenic (LH 59x LH51)(LH119) (4) X T14)	SL	0.36		1 (30 cm)	30 72 107	forage silage fodder	NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	ER-93-USA-01-NE-01
USA (NE) 1993 (transgenic (LH 59x LH51)(LH119) (4) X T14)	SL	0.50	0.48	1 (30 cm)	30 72 107	forage silage fodder	NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.09 0.05 0.14 NQ (3) NQ (3)	ER-93-USA-01-NE-01

Location, Year, (variety)	Application				PHI		Residues, mg/kg, as glufosinate free acid[3]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Commodity[2]	glufosinate-ammonium	MPP	NAG	
USA (NE) 1993 (transgenic (LH 59x LH51)(LH119) (4) X T14)	SL	0.50	0.48	1 (60 cm)	30 60 95	forage silage fodder	0.16 0.20 0.15 0.05 0.05 0.06 0.16 0.08 0.14	NQ (3) NQ (3) 0.11 0.09 0.09	1.4 1.3 1.2 0.36 0.48 0.46 0.68 0.58 0.57	ER-93-USA-01-NE-01
USA (IN) 1993 (transgenic [LH119(4) X T14] X LH216)	SL	0.36	0.39	1 (30 cm)	30 69 115	forage silage fodder	NQ 0.07 0.05 NQ (2) 0.06 0.11 NQ 0.05	NQ (3) NQ (3) 0.06 NQ (2)	0.34 0.46 0.40 0.18 0.18 0.30 0.25 0.12 0.12	ER-93-USA-01-IN-01
USA (IN) 1993 (transgenic [LH119(4) X T14] X LH216)	SL	0.50	0.54	1 (30 cm)	30 69 115	forage silage fodder	0.06 0.05 0.05 NQ 0.09 NQ 0.05 NQ 0.05	NQ (3) NQ (3) NQ (2) 0.06	0.42 0.40 0.46 0.22 0.14 0.20 0.13 0.11 0.15	ER-93-USA-01-IN-01
USA (IN) 1993 (transgenic [LH119(4) X T14] X LH216)	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	30 60 106	forage silage fodder	0.26 0.25 0.23 0.22 0.18 0.21 0.32 0.31 0.45	0.06 NQ (2) 0.09 NQ (2) 0.18 0.13 0.16	1.6 1.5 1.4 1.4 1.3 1.5 1.2 1.4 1.7	ER-93-USA-01-IN-01
USA (ND) 1993 (transgenic (LH85 X LH160) (LH119)(4) X T14)	SL	0.36	0.39	1 (30 cm)	30 80 107	forage silage fodder	NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.19 0.20 0.23 0.06 NQ NQ NQ (3)	ER-93-USA-01-ND-01
USA (ND) 1993 (transgenic (LH85 X LH160) (LH119)(4) X T14)	SL	0.50	0.54	1 (30 cm)	30 80 107	forage silage fodder	0.07 0.06 NQ NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.35 0.29 0.24 NQ 0.05 NQ NQ (3)	ER-93-USA-01-ND-01
USA (ND) 1993 (transgenic (LH85 X LH160) (LH119)(4) X T14)	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	30 72 97	forage silage fodder	NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.29 0.22 0.20 0.12 0.12 0.10 0.07 0.11 0.08	ER-93-USA-01-ND-01
USA (MO) 1993 (transgenic(LH216) X (LH119(4) X (T14))	SL	0.36	0.39	1 (30 cm)	30 64 97	forage silage fodder	0.07 NQ NQ NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.22 0.16 0.14 0.06 NQ NQ NQ (3)	ER-93-USA-01-MO-01
USA (MO) 1993 (transgenic(LH216) X (LH119(4) X (T14))	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	30 60 95	forage silage fodder	0.35 0.20 0.17 0.26 0.11 0.08 0.10 0.10 0.12	NQ (3) NQ (3) NQ (3)	0.96 1.1 0.96 1.5 0.89 0.70 0.46 0.52 0.60	ER-93-USA-01-MO-01
USA (CA) 1993 (transgenic (LH59 X LH51) (LH119)(4) X T14)	SL	0.36	0.39	1 (30 cm)	30 73 119	forage silage fodder	NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.13 0.11 0.08 NQ (3) NQ (3)	ER-93-USA-01-CA-01
USA (CA) 1993 (transgenic (LH59 X LH51) (LH119)(4) X T14)	SL	0.36 +0.50	0.39 +0.54	2 (60 cm)	30 71 106	forage silage fodder	0.12 0.13 NQ (3) 0.09 0.10 0.09	0.08 0.11 NQ (3) 0.13 0.10 0.10	0.52 0.54 0.10 0.26 0.16 0.55 0.60 0.59	ER-93-USA-01-CA-01
USA (SD) 1993 (transgenic (LH85 X LH160) (LH119)(4) X T14))	SL	0.36	0.71	1 (30 cm)	30 71 95	forage silage fodder	0.12 NQ NQ NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3)	0.14 0.15 0.13 NQ (3) 0.07 0.08 0.08	ER-93-USA-01-SD-01
USA (SD) 1993 (transgenic (LH85 X LH160) (LH119)(4) X T14))	SL	0.50	0.99	1 (30 cm)	30 71 95	forage silage fodder	0.05 0.07 0.06 NQ (3) NQ NQ 0.05	NQ (3) NQ (3) NQ (3)	0.21 0.44 0.25 0.09 0.09 0.10 0.20 0.14 0.22	ER-93-USA-01-SD-01
USA (SD) 1993 (transgenic (LH85 X LH160) (LH119)(4) X T14))	SL	0.36 +0.50	0.71 +0.99	2 (60 cm)	30 60 95	forage silage fodder	0.29 0.23 0.19 0.08 0.07 NQ 0.20 0.09 0.20	NQ (3) NQ (3) 0.06 NQ 0.07	0.89 1.4 1.2 0.09 0.09 0.10 1.7 0.79 1.6	ER-93-USA-01-SD-01
USA (VA) 1993 (transgenic (LH216) (LH119)(4) X T14)	SL	0.36	0.71	1 (30 cm)	33 60	forage silage	0.05 NQ 0.06 NQ (3)	NQ (3) NQ (3)	0.41 0.22 0.33 0.15 0.11 0.08	ER-93-USA-01-VA-01
USA (VA) 1993 (transgenic (LH216) (LH119)(4) X T14)	SL	0.50	0.99	1 (30 cm)	33 60 106	forage silage fodder	0.07 NQ NQ NQ NQ 0.06 NQ NQ	NQ (3) NQ (3) 0.11 0.07	0.46 0.29 0.35 0.30 0.12 0.24 0.10 0.07	ER-93-USA-01-VA-01
USA (VA) 1993 (transgenic (LH216) (LH119)(4) X T14)	SL	0.36 +0.50	0.71 +0.99	2 (60 cm)	30 61 97	forage silage fodder	0.31 0.36 0.44 0.49 0.64 0.44 0.27 0.33	NQ (3) 0.17 0.34 0.20 0.41 0.43	1.9 2.4 3.1 2.4 2.5 2.1 0.97 0.93	ER-93-USA-01-VA-01
USA (MN) 1993 ((LH85 X LH160) (LH119)(4) X T14)	SL	0.52	1.1	1 (76 cm)	30 66	forage silage	0.34 0.27 0.25 0.20 0.20 0.28	NQ (3) NQ (3)	1.5 1.5 1.2 1.3 0.99 1.4	ER-93-USA-01-MN-01

Location, Year, (variety)	Application				PHI		Residues, mg/kg, as glufosinate free acid[3]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Commodity[2]	glufosinate-ammonium	MPP	NAG	
USA (MO) 1993 (transgenic (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (12 cm)	20 30 40 60 123	forage forage forage silage fodder	NQ (3) NQ (3) NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3) NQ (3) NQ (3)	0.09 0.12 0.11 NQ (3) NQ (3) NQ (3) NQ (3)	ER-93-USA-01-MO-02
USA (MO) 1993 (transgenic (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (28 cm)	20 30 40 60 118	forage forage forage silage fodder	NQ (3) NQ (3) NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3) NQ (3) NQ (3)	0.19 0.14 0.06 0.06 0.19 NQ NQ (3) NQ (3) NQ (3)	ER-93-USA-01-MO-02
USA (MO) 1993 (transgenic (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (46 cm)	20 30 40 60 111	forage forage forage silage fodder	0.09 0.08 0.07 0.06 0.05 NQ NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3) NQ (3) NQ (3)	0.68 0.55 0.46 0.29 0.23 0.16 0.06 0.12 0.11 0.13 NQ NQ NQ (3)	ER-93-USA-01-MO-02
USA (MO) 1993 (transgenic (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (61 cm)	20 30 40 60 101	forage forage forage silage fodder	0.41 0.40 0.40 0.27 0.37 0.35 0.50 0.22 0.44 0.14 0.14 0.14 0.23 0.20 0.18	NQ (3) 0.05 NQ NQ NQ (3) 0.31 0.45 0.34 0.05 NQ NQ	2.7 3.3 1.9 1.6 2.0 2.0 2.5 1.2 2.2 1.0 0.63 0.74 0.91 0.71 0.79	ER-93-USA-01-MO-02
USA (MO) 1993 (transgenic (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (86 cm)	20 30 40 61 97	forage forage forage silage fodder	0.17 0.11 0.14 0.11 0.14 0.06 0.11 0.11 0.08 NQ 0.05 NQ 0.13 0.06 0.08	NQ (3) NQ (3) NQ (3) NQ (3) NQ (3)	0.77 0.67 0.82 0.74 0.90 0.52 0.73 0.87 0.57 0.31 0.45 0.34 0.31 0.27 0.30	ER-93-USA-01-MO-02
USA (CA) 1993 (transgenic (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (13-15 cm)	20 30 40 60 127	forage forage forage silage fodder	NQ (3) NQ (3) NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3) NQ (3) NQ (3)	NQ (3) NQ (3) NQ (3) NQ (3) NQ (3)	ER-93-USA-01-CA-02
USA (CA) 1993 (transgenic (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (25-33 cm)	20 30 40 60 120	forage forage forage silage fodder	0.25 0.20 0.24 0.06 NQ 0.05 NQ (3) NQ (3) NQ (3)	0.12 0.14 0.11 NQ 0.05 NQ NQ (3) NQ (3) NQ (3)	1.3 0.87 1.2 0.25 0.23 0.35 0.11 0.14 0.13 NQ (3) 0.07 NQ 0.06	ER-93-USA-01-CA-02
USA (CA) 1993 (transgenic (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (33-51 cm)	20 30 40 60 114	forage forage forage silage fodder	0.24 0.29 0.18 0.09 0.16 0.13 NQ 0.09 0.08 NQ (3) NQ (3)	0.08 0.08 0.06 NQ NQ 0.05 NQ (3) NQ (3) NQ NQ 0.07	1.2 1.4 1.3 0.48 0.62 0.61 0.31 0.43 0.34 0.09 0.06 0.08 0.17 0.08 0.14	ER-93-USA-01-CA-02
USA (CA) 1993 (transgenic (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 (41-81 cm)	20 30 40 60 96	forage forage forage silage fodder	0.46 0.42 0.51 0.44 0.31 0.33 0.16 0.16 0.18 NQ 0.09 0.17 0.25 0.26 0.09	0.11 0.10 0.09 0.11 0.10 0.08 0.07 0.07 0.08 0.06 NQ 0.07 0.13 0.10 0.09	1.8 1.6 1.4 1.5 1.4 1.6 0.77 0.65 0.86 0.21 0.30 0.55 1.4 0.88 0.60	ER-93-USA-01-CA-02
USA (CA) 1993 (transgenic (LH59 X LH51) (LH119)(4) X (T14))	SL	0.50	0.53	1 66-117 cm)	20 30 40 60 96	forage forage forage silage fodder	0.29 0.36 0.34 0.21 0.34 0.19 0.11 0.14 0.22 0.08 0.09 NQ 0.18 0.18 0.23	0.06 0.07 0.06 0.07 0.06 0.05 NQ (3) NQ (3) 0.07 0.06 0.07	0.88 0.96 0.95 0.84 0.89 0.54 0.60 0.49 0.67 0.33 0.59 0.20 2.4 1.5 1.5	ER-93-USA-01-CA-02
USA (FL) 1994 (transgenic (LH51 X LH210) (LH119(4) X T14)	SL	0.40 +0.50	0.43 +0.54	2 (2-14 leaves)	29 60 69	forage silage fodder	2.1 0.70 1.0	NQ NQ 0.21	glu glu glu	BK-94R-01-FL-01
USA (IA) 1994 (transgenic (LH59 X LH51) (LH119(4) X T14))	SL	0.41 +0.53	0.44 +0.57	2 (61 cm)	31 60 100 122	forage silage forage fodder	0.66 0.36 0.18 0.25	NQ NQ NQ NQ	glu glu glu glu	BK-94R-01-IA-01
USA (IL) 1994 (transgenic (LH59 X LH51) (LH119(4) X T14))	SL	0.40 +0.50	0.43 +0.54	2 (61 cm)	31 60 76 118	forage silage forage fodder	0.26 0.11 0.12 0.12	NQ NQ NQ NQ	glu glu glu glu	BK-94R-01-IL-01
USA (MN) 1994 (transgenic (LH74) (LH82(3) X T14))	SL	0.38 +0.48	0.41 +0.52	2 (61 cm)	31 60 93 114	forage silage forage fodder	1.1 1.1 0.91 0.99	NQ NQ NQ 0.14	glu glu glu glu	BK-94R-01-MN-01

Location, Year, (variety)	Application				PHI		Residues, mg/kg, as glufosinate free acid[3]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Commodity[2]	glufosinate-ammonium	MPP	NAG	
USA (MO) 1994 (transgenic (LH59 X LH51) (LH119(4) X T14))	SL	0.40 +0.53	0.43 +0.57	2 (61 cm)	30 60 69 89	forage silage forage fodder	1.6 1.2 0.70 1.5	NQ NQ 0.08 0.26	glu glu glu glu	BK-94R-01-MO-01
USA (NC) 1994 (transgenic (LH51 X LH210) (LH119(4) X T14))	SL	0.38 +0.52	0.41 +0.56	2 (61 cm)	30 58 69 92	forage silage forage fodder	0.21 0.10 0.09 0.07	NQ NQ NQ NQ	glu glu glu glu	BK-94R-01-NC-01
USA (NY) 1994 (transgenic (LH74) (LH82(3) X T14))	SL	0.38 +0.53	0.41 +0.57	2 (61 cm)	30 69 77 88	forage silage forage fodder	4.0 2.1 2.9 5.3	NQ NQ NQ 0.1	glu glu glu glu	BK-94R-01-NY-01
USA (TX) 1994 (transgenic (LH51 X LH210) (LH119(4) X T14))	SL	0.38 +0.46	0.41 +0.49	2 (61 cm)	30 60 74 97	forage silage forage fodder	0.44 0.32 0.27 0.26	NQ NQ NQ 0.07	glu glu glu glu	BK-94R-01-TX-01
USA (WA) 1994 (transgenic (LH74) (LH82)3) X T14))	SL	0.40 +0.50	0.43 +0.54	2 (61 cm)	30 60 76 86	forage silage forage fodder	0.77 0.24 0.47 0.56	0.09 NQ 0.07 0.12	glu glu glu glu	BK-94R-01-WA-01
USA (WI) 1994 (transgenic (LH85 X LH160) (LH119(4) X T14))	SL	0.38 +0.56	0.41 +0.60	2 (61 cm)	30 60 92 107	forage silage forage fodder	0.61 0.36 0.33 0.43	NQ NQ NQ NQ	glu glu glu glu	BK-94R-01-WI-01
USA (FL) 1994 (transgenic (LH51 X LH210) (LH119(4) X T14)	SL200	0.40 +0.50	0.43 +0.54	2 (2-14 leaves)	29 60 69	forage silage fodder	1.8 0.84 1.2	NQ NQ 0.29	glu glu glu	BK-94R-01-FL-01
USA (IA) 1994 (transgenic (LH59 X LH51) (LH119(4) X T14))	SL	0.41 +0.51	0.44 +0.55	2 (61 cm)	31 60 100 122	forage silage forage fodder	0.53 0.40 0.17 0.22	NQ NQ NQ NQ	glu glu glu glu	BK-94R-01-IA-01
USA (IL) 1994 (transgenic (LH59 X LH51) (LH119(4) X T14))	SL	0.40 +0.50	0.43 +0.54	2 (61 cm)	31 60 76 118	forage silage forage fodder	0.32 0.15 0.11 0.11	NQ NQ NQ NQ	glu glu glu glu	BK-94R-01-IL-01
USA (MN) 1994 (transgenic (LH74) (LH82(3) X T14))	SL	0.40 +0.51	0.43 +0.55	2 (61 cm)	31 60 93 114	forage silage forage fodder	2.4 1.7 1.4 2.6	NQ NQ NQ 0.23	glu glu glu glu	BK-94R-01-MN-01
USA (MO) 1994 (transgenic (LH59 X LH51) (LH119(4) X T14))	SL	0.40 +0.56	0.43 +0.60	2 (61 cm)	30 60 69 89	forage silage forage fodder	1.5 1.2 0.86 1.2	NQ NQ 0.08 0.22	glu glu glu glu	BK-94R-01-MO-01
USA (NC) 1994 (transgenic (LH51 X LH210) (LH119(4) X T14))	SL	0.40 +0.46	0.43 +0.49	2 (61 cm)	30 58 69 92	forage silage forage fodder	0.19 0.13 0.09 0.08	NQ NQ NQ NQ	glu glu glu glu	BK-94R-01-NC-01
USA (NY) 1994 (transgenic (LH74) (LH82(3) X T14))	SL	0.40 +0.53	0.43 +0.57	2 (61 cm)	30 60 77 88	forage silage forage fodder	1.2 0.74 0.35 1.5	NQ NQ NQ NQ	glu glu glu glu	BK-94R-01-NY-01
USA (TX) 1994 (transgenic (LH51 X LH210) (LH119(4) X T14))	SL	0.40 +0.49	0.43 +0.53	2 (61 cm)	30 60 74 97	forage silage forage fodder	0.52 0.30 0.31 0.25	NQ NQ NQ 0.07	glu glu glu glu	BK-94R-01-TX-01
USA (WA) 1994 (transgenic (LH74) (LH82)3) X T14))	SL	0.40 +0.50	0.43 +0.54	2 (61 cm)	30 60 76 86	forage silage forage fodder	0.70 0.24 0.37 0.43	0.09 0.10 0.11 0.15	glu glu glu glu	BK-94R-01-WA-01
USA (WI) 1994 (transgenic (LH85 X LH160) (LH119(4) X T14))	SL	0.38 +0.50	0.41 +0.54	2 (61 cm)	30 60 92 107	forage silage forage fodder	0.49 0.19 0.28 0.50	NQ NQ NQ NQ	glu glu glu glu	BK-94R-01-WI-01

Location, Year, (variety)	Application				PHI		Residues, mg/kg, as glufosinate free acid[3]			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Commodity[2]	glufosinate-ammonium	MPP	NAG	
USA (MN) 1995 (transgenic (LH202) (LH82 (4) x T25))	SL	0.39 +0.49	0.41 +0.53	2 (7-8 leaf)	30 60 100	forage forage fodder	2.4 1.5 1.2	0.06 0.08 0.10	glu glu glu	BK95R01-GGH-01
USA (KS) 1995 (transgenic (B73(5)xT25) (LH51))	SL	0.39 +0.50	0.41 +0.53	2 (56-66 cm)	32 62 77 95	forage forage forage fodder	1.3 0.97 1.1 1.2	NQ NQ 0.09 0.14	glu glu glu glu	BK95R01-MDA-02
USA (MI) 1995 (transgenic (LH119 (9) x T14) (LH168))	SL	0.39 +0.50	0.41 +0.54	2 (61-77 cm)	30 61 98 111	forage forage forage fodder	0.73 0.46 0.42 0.50	0.08 0.07 0.11 0.15	glu glu glu glu	BK95R01-JRS-02
USA (MO) 1995 (transgenic (B73 (5) x T25) (LH51))	SL	0.39 +0.52	0.44 +0.60	2 (61 cm)	10 20 29 40 60 81 90	forage forage forage forage forage forage fodder	4.1 1.5 1.0 0.82 0.49 0.17 0.51	0.07 0.05 NQ NQ 0.05 0.05 0.18	glu glu glu glu glu glu glu	BK95R01-JLB-01
USA (NE) 1995 (transgenic (LH119 (9) x T14) (LH51))	SL	0.39 +0.52	0.41 +0.55	2 (61 cm)	20 60 80 89	forage forage forage fodder	0.41 0.33 0.30 0.53	NQ NQ NQ NQ	glu glu glu glu	BK95R01-MDA-01
USA (OH) 1995 (transgenic (LH119 (9) x T14) (LH51))	SL	0.39 +0.52	0.43 +0.52	2 (61 cm)	31 60 88 117	forage forage forage fodder	1.9 1.6 0.63 1.1	NQ 0.07 0.17 0.22	glu glu glu glu	BK95R01-JRS-01
USA (TX) 1995 (transgenic (LH216) (B73 (5) x T25))	SL	0.40 +0.50	0.42 +0.53	2 (53-66 cm)	10 20 30 40 61 71 84	forage forage forage forage forage forage fodder	3.2 1.6 0.88 0.85 0.72 0.83 1.6	0.07 NQ NQ NQ NQ 0.07 0.14	glu glu glu glu glu glu glu	BK95R01-GLS-01
Argentina 1996 (transgenic)	SL	1.4	0.88	1 GS17-32)	1 34 54 54	shoot shoot shoot cob	54 0.50 1.9 0.08	0.34 NQ NQ NQ		A57414 ER96ARG001010102

[1]. growth stage at final treatment is given as the height of the plant.
[2] commodity descriptions:
forage immature whole plant
silage mature whole plant collected prior to the dent stage
fodder mature plant without ears, collected at grain harvest
[3] NQ - residues <LOD (0.05 mg/kg glufosinate free acid equivalents)
glu: included in glufosinate-ammonium result.

Table 55. Glufosinate residues in transgenic maize forage and fodder resulting from supervised trials in Ontario, Canada.

Year	Application				PHI	Residues, mg/kg,			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG	
1993	SL	0.75		1 GS16	106 152 152	<0.05 shoot <0.05 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 cob	A55207 93-IGN-C ON-1-2
1993	SL	1.5		1 GS16	106 152 152	<0.05 shoot <0.05 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 cob	A55207 93-IGN-C ON-1-3
1993	SL	0.75		1 GS16	107 154 154	<0.05 shoot <0.05 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 cob	A55207 93-IGN-C ON-2-2
1993	SL	1.5		1 GS16	107 154 154	<0.05 shoot <0.05 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 cob	<0.05 shoot <0.05 shoot <0.05 cob	A55207 93-IGN-C ON-2-3
1994	SL	0.5		1 GS17-19	99 137	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	A55207 94-IGN-C ON-1-2
1994	SL	1.0		1 GS17-19	99 137	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	A55207 94-IGN-C ON-1-3
1994	SL	0.5		1 GS17-19	93 114	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	0.34 shoot <0.05 cob	A55207 94-IGN-C ON-2-2
1994	SL	1.0		1 GS17-19	93 114	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	0.20 shoot <0.05 cob	A55207 94-IGN-C ON-2-3
1994	SL	0.5		1 GS17-19	93 114	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	0.32 shoot <0.05 cob	A55207 94-IGN-C ON-3-2
1994	SL	1.0		1 GS17-19	93 114	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	0.15 shoot <0.05 cob	A55207 94-IGN-C ON-3-3
1995	SL	0.6		1 GS18-19	68 104	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	A55207 95-IGN-C ON-1-2
1995	SL	0.6		2 GS33	61 97	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	0.28 shoot <0.05 cob	A55207 95-IGN-C ON-1-3
1995	SL	1.2		1 GS40	56 92	0.12 shoot <0.05 cob	<0.05 shoot <0.05 cob	0.86 shoot <0.05 cob	A55207 95-IGN-C ON-1-4
1995	SL	0.6		1 GS18	71 105	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	0.11 shoot <0.05 cob	A55207 95-IGN-C ON-2-2
1995	SL	0.6		2 GS33	62 96	0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	0.33 shoot <0.05 cob	A55207 95-IGN-C ON-2-3
1995	SL	1.2		1 GS40	56 90	0.50 shoot <0.05 cob	<0.05 shoot <0.05 cob	3.8 shoot <0.05 cob	A55207 95-IGN-C ON-2-4
1995	SL	0.6		1 GS18-19	56 103	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	A55207 95-IGN-C ON-3-2
1995	SL	0.6		2 GS33	64 96	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	A55207 95-IGN-C ON-3-3
1995	SL	1.2		1 GS40	57 89	0.43 shoot <0.05 cob	<0.05 shoot <0.05 cob	3.7 shoot 0.05 cob	A55207 95-IGN-C ON-3-4

Year	Application				PHI	Residues, mg/kg,			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG	
1995	SL	0.6		1 GS18	70 104	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	A55207 95-IGN-C ON-4-2
1995	SL	0.6		2 GS33	63 96	<0.05 shoot <0.05 cob	<0.05 shoot <0.05 cob	0.09 shoot <0.05 cob	A55207 95-IGN-C ON-4-3
1995	SL	1.2		1 GS40	57 90	0.40 shoot <0.05 cob	<0.05 shoot <0.05 cob	2.7 shoot 0.10 cob	A55207 95-IGN-C ON-4-4

[1] GS: growth stage at final treatment

GS16	6 leaves unfolded
GS17	7 leaves unfolded
GS18	8 leaves unfolded
GS19	9 or more leaves unfolded
GS33	3 nodes detectable
GS40	booting

Table 56. Glufosinate residues in rape seed forage and fodder resulting from supervised trials in France, Germany, and the UK.

Country Year (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	Kg ai/hl	No[1]	days	glufosinate	MPP	NAG[2]	
France 1994 (Falcon)	SL	0.60 +0.45	0.30 +0.23	1 at GS23 2 at GS35	0 116 0 10 73 73 111	65 shoot 0.06 shoot 20 shoot 7.0 shoot 0.89 shoot 0.06 pod 1.6 straw	0.49 shoot <0.05 shoot 0.16 shoot <0.05 shoot <0.05 shoot <0.05 pod <0.05 straw		A54228 ER93ECN553 FRA000202
France 1994 (Falcon)	SL	0.60 +0.45	0.30 +0.23	1 at GS23 2 at GS35	0 116 0 10 73 73 111	58 shoot 0.05 shoot 24 shoot 7.2 shoot 0.82 shoot 0.1 pod 1.3 straw	0.17 shoot 0.05 shoot 0.19 shoot <0.05 shoot <0.05 shoot <0.05 pod <0.05 straw		A54228 ER93ECN553 FRA000302
France 1994 (Gs 401×90)	SL	0.60 +0.45	0.30 +0.23	1 at GS21 2 at GS33	0 73 0 38 99 99 121	6.5 shoot 0.12 shoot 45 shoot 0.16 shoot 0.11 shoot 0.24 pod 0.69 straw	0.05 shoot <0.05 shoot 0.34 shoot <0.05 shoot <0.05 shoot <0.05 pod 0.13 straw		A54228 ER93ECN553 FRA000102
France 1995 (Falcon B)	SL	0.6	0.30	2 GS35	0 16 69 69 127	7.9 shoot 2.5 shoot 0.39 shoot 0.12 pod 0.75 straw	0.08 shoot <0.05 shoot <0.05 shoot <0.05 pod <0.05 straw		A56444 ER94ECN553 FRA000203
France 1995 (Falcon)	SL	0.67 +0.60	0.32 +0.30	2 GS39	0 28 78 78 133	19 shoot 2.5 shoot 1.0 shoot 0.15 pod 1.2 straw	0.07 shoot <0.05 shoot <0.05 shoot <0.05 pod 0.11 straw		A56444 ER94ECN553 FRA000103

Country Year (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	Kg ai/hl	No[1]	days	glufosinate	MPP	NAG[2]	
France 1996 (GMO hybrid)	SL	0.60	0.30 +0.24	2 GS32	0 17 58 58 108	25 shoot 6.0 shoot 1.8 shoot 0.57 pod 5.5 straw	0.3 shoot 0.08 shoot <0.05 shoot <0.05 pod 0.22 straw		A57955 ER96ECN553 FRA000103
France 1996 (GMO hybrid)	SL	0.60	0.30 +0.24	2 GS32	0 17 58 58 108	13 shoot 2.9 shoot 0.93 shoot 0.4 pod 3.5 straw	0.11 shoot <0.05 shoot <0.05 shoot <0.05 pod 0.15 straw		A57955 ER96ECN553 FRA000102
Germany 1995 (Falcon G-S40/90)	SL	0.60	0.20	2 GS35	0 7 53 53 106	14 shoot 9.3 shoot 1.6 shoot 0.32 pod 1.0 straw	0.28 shoot 0.05 shoot <0.05 shoot <0.05 pod 0.11 straw		A56444 ER94ECN553 DEU030103
Germany 1995 (Falcon)	SL	0.60	0.20	2 GS35	0 20 55 55 105	14 shoot 2.7 shoot 2.4 shoot 0.38 pod 2.7 straw	0.15 shoot <0.05 shoot <0.05 shoot <0.05 pod 0.18 straw		A56444 ER94ECN553 DEU040103
Germany 1995 (Falcon)	SL	0.60	0.20	2 GS35	0 12 47 47 110	12 shoot 4.0 shoot 1.6 shoot 0.52 pod 2.3 straw	0.14 shoot <0.05 shoot <0.05 shoot <0.05 pod 0.12 straw		A56444 ER94ECN553 DEU040203
Germany 1995 (Falcon)	SL	0.60	0.20	2 GS37	0 21 61 61 104	19 shoot 1.0 shoot 0.15 shoot 0.1 pod 0.17 straw	0.08 shoot <0.05 shoot <0.05 shoot <0.05 pod <0.05 straw		A56444 ER94ECN553 DEU050103
Germany 1996 (Falcon)	SL	0.60	0.20	2 GS32	0 6 51 51 94	21 shoot 4.5 shoot 1.1 shoot 0.23 pod 1.7 straw	0.32 shoot <0.05 shoot <0.05 shoot <0.05 pod 0.08 straw		A57955 ER96ECN553 DEU030102
Germany 1996 (Falcon)	SL	0.80	0.27	2 GS32	0 6 51 51 94	28 shoot 5.8 shoot 1.1 shoot 0.22 pod 4.3 straw	0.43 shoot 0.07 shoot <0.05 shoot <0.05 pod 0.19 straw		A57955 ER96ECN553 DEU030103
Germany 1996 (Falcon)	SL	0.60	0.20	2 GS32	0 12 54 54 97	20 shoot 4.5 shoot 0.43 shoot 0.13 pod 1.8 straw	0.19 shoot 0.08 shoot <0.05 shoot <0.05 pod 0.09 straw		A57955 ER96ECN553 DEU050102
Germany 1996 (Falcon)	SL	0.80	0.27	2 GS32	0 12 54 54 97	26 shoot 4.7 shoot 1.1 shoot 0.35 pod 2.3 straw	0.28 shoot 0.06 shoot <0.05 shoot <0.05 pod 0.08 straw		A57955 ER96ECN553 DEU050103
Germany 1996 (Falcon)	SL	0.60	0.20	2 GS37	0 7 47 47 97	16 shoot 5.2 shoot 1.1 shoot 0.19 pod 3.0 straw	0.2 shoot 0.07 shoot <0.05 shoot <0.05 pod 0.14 straw		A57955 ER96ECN553 DEU040102
Germany 1996 (Falcon)	SL	0.80	0.27	2 GS37	0 7 47 47 97	18 shoot 6.7 shoot 1.7 shoot 0.51 pod 3.2 straw	0.2 shoot 0.07 shoot <0.05 shoot <0.05 pod 0.17 straw		A57955 ER96ECN553 DEU040103

Country Year (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	Kg ai/hl	No[1]	days	glufosinate	MPP	NAG[2]	
UK 1994	SL	0.60	0.30	1 at GS21	0 159 184 224 224 275	37 shoot <0.05 shoot <0.05 shoot <0.05 shoot <0.05 pod <0.05 straw	0.49 shoot <0.05 shoot <0.05 shoot <0.05 shoot <0.05 pod <0.05 straw		A54227 ER93ECN552 GBR000102
UK 1994	SL	0.60	0.30	1 at GS21	0 132 192 192 212	57 46 shoot 0.11 shoot <0.05 shoot <0.05 (2) pod <0.05 straw	0.67 0.60 shoot <0.05 shoot <0.05 shoot <0.05 (2) pod <0.05 straw		A54227 ER93ECN552 GBR000202
UK 1994	SL	0.60 +0.45	0.30 +0.23	1 at GS21 2 at GS35	0 121 0 11 71 71 91	52 shoot <0.05 shoot 16 shoot 2.2 shoot 0.18 shoot 0.07 pod 0.5 straw	0.62 shoot <0.05 shoot 0.08 shoot <0.05 shoot <0.05 shoot <0.05 pod <0.05 straw		A54228 ER93ECN553 GBR000202
UK 1994 (Falcon)	SL	0.60 +0.45	0.30 +0.23	1 at GS21 2 at GS35	0 159 0 25 65 65 116	13 shoot 0.13 shoot 0.11 shoot 1.2 shoot 0.31 shoot 0.09 pod 0.47 straw	0.42 shoot <0.05 shoot <0.05 shoot <0.05 shoot <0.05 shoot <0.05 pod <0.05 straw		A54228 ER93ECN553 GBR000102
UK 1996 (Falcon)	SL	0.60	0.30	2 GS32	0 10 61 61 100	16 shoot 4.8 shoot 1.3 shoot 0.17 pod 1.3 straw	0.31 shoot 0.07 shoot <0.05 shoot <0.05 pod 0.06 straw		A57955 ER96ECN553 GBR000103
UK 1996 (Falcon)	SL	0.60	0.30	2 GS32	0 9 58 58 92	26 shoot 6.7 shoot 1.8 shoot 0.31 pod 3.7 straw [3]	0.17 shoot 0.11 shoot <0.05 shoot <0.05 pod 0.11 straw [3]		A57955 ER96ECN553 GBR000203
UK 1996 (Falcon)	SL	0.60	0.30	2 GS32	0 10 61 61 100	14 shoot 4.7 shoot 1.2 shoot 0.20 pod 1.5 straw	0.28 shoot 0.07 shoot <0.05 shoot <0.05 pod <0.05 straw		A57955 ER96ECN553 GBR000102
UK 1996 (Falcon)	SL	0.80	0.40	2 GS32	0 10 61 61 100	20 shoot 6.9 shoot 1.2 shoot 0.19 pod 1.4 straw	0.45 shoot 0.09 shoot <0.05 shoot <0.05 pod 0.05 straw		A57955 ER96ECN553 GBR000104
UK 1996 (Falcon)	SL	0.60	0.30	2 GS32	0 9 58 58 92	22 shoot 5.2 shoot 1.5 shoot 0.22 pod 3.3 straw [3]	0.08 shoot 0.09 shoot <0.05 shoot <0.05 pod 0.09 straw [3]		A57955 ER96ECN553 GBR000202
UK 1996 (Falcon)	SL	0.80	0.40	2 GS32	0 9 58 58 92	30 shoot 7.7 shoot 1.9 shoot 0.34 pod 4.5 straw [3]	0.09 shoot 0.1 shoot <0.05 shoot <0.05 pod 0.12 straw [3]		A57955 ER96ECN553 GBR000204

[1]: GS growth stage

GS21	first side shoot detectable
GS32	2 visibly extended internodes
GS33	3 visibly extended internodes
GS35	5 visibly extended internodes
GS37	7 visibly extended internodes
GS80	beginning of ripening
GS83	30% of pods ripe

[2] included in glufosinate-ammonium result.

[3]: Straw samples were harvested at GS80-83 and stored in paper bags for even drying and prepared to laboratory samples 10 days later.

Table 57. Glufosinate residues in canola forage and fodder resulting from supervised trials in Australia.

Location, Year (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP[2]	NAG[2]	
Australia (NSW) 1996 (glufosinate selective line)	SL	0.6	0.72	1 GS 3-5 leaf	86	<0.1 straw			YH 96 AH AU NW 06
Australia (NSW) 1996 (glufosinate selective line)	SL	1.2	1.4	1 GS 3-5 leaf	86	0.12 straw			YH 96 AH AU NW 06
Australia (WA) 1996 (var ex Canada)	SL	0.6	0.83	1 GS 1-2 leaf	29 56 124	1.0 2.4 forage dw <0.05 forage dw <0.1 (2) straw			YH 96 AH AU WA 09
Australia (WA) 1996 (var ex Canada)	SL	1.2	1.7	1 GS 1-2 leaf	29 56 124	2.5 2.3 forage dw <0.05 forage dw <0.1 (2) straw			YH 96 AH AU WA 09
Australia (SA) 1996 (transgenic Canadian line)	SL	0.6	0.75	1 GS 4-6 leaf	42 95	0.8 0.6 forage dw 0.13 0.12 straw			YH 96 AH AU SA 17
Australia (SA) 1996 (transgenic Canadian line)	SL	1.2	1.5	1 GS 4-6 leaf	42 95	2.0 1.6 forage dw 0.14 0.12 straw			YH 96 AH AU SA 17
Australia (Vic) 1997 (Canadian tolerant)	SL	0.6	0.6	1 GS 2 leaf	42 105	<0.05 (2) forage <0.1 (2) straw			YH 96 AH AU VN 12
Australia (Vic) 1997 (Canadian tolerant)	SL	1.2	1.2	1 GS 2 leaf	42 105	<0.05 (2) forage <0.1 (2) straw			YH 96 AH AU VN 12

[1]: GS growth stage expressed in terms of leaf development

[2] included in glufosinate-ammonium result.

Table 58. Glufosinate residues in soya bean forage and fodder resulting from supervised trials in the USA.

Location, Year, (variety)	Application				PHI		Residues, mg/kg, expressed as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days		glufosinate	MPP	NAG	
USA (IA) 1993 (W98-7)	SL	0.5	0.51	1 trifoliate	87	hay	0.22	0.25 0.23	0.72 0.56	ER-93-USA-02-IA-01
	SL	0.5	0.51	1 full pod	65	hay	2.8	1.3	6.7	
	SL	0.5	0.51	2 full pod	65	hay	2.1	1.1	5.1	
USA (IL) 1993 (W98-7)	SL	0.5	0.53	1 trifoliate	85	hay	0.15	0.32	0.88	ER-93-USA-02-IL-01
	SL	0.5	0.53	1 full pod	65	hay	1.3	1.3	5.8	
	SL	0.5	0.53	2 full pod	65	hay	1.8	2.2	8.1	
USA (MO) 1993 (W98-7)	SL	0.5	0.53	1 trifoliate	87	hay	0.09	0.22	0.32	ER-93-USA-02-MO-01
	SL	0.5	0.53	1 full pod	65	hay	1.8	1.4	6.9	
	SL	0.5	0.53	2 full pod	65	hay	2.0	1.6	7.4	
USA (IN) 1993 (W98-7)	SL	0.5	0.53	1 trifoliate	87	hay	0.16	0.41	0.47	ER-93-USA-02-IN-01
	SL	0.5	0.53	1 full pod	65	hay	2.5	2.5	5.6	
	SL	0.5	0.53	2 full pod	65	hay	3.2	3.0	7.3	
USA (IN) 1993 (W98)	SL	0.5	0.53	1 trifoliate	87	hay	0.06 0.05 0.06	0.16 0.17 0.18	0.15 0.14 0.16	ER-93-USA-02-IN-02
	SL	0.5	0.53	1 full pod	65	hay	1.5 1.6 2.7	1.3 1.2 1.6	4.6 3.9 7.1	
	SL	0.5	0.53	2 full pod	65	hay	2.3 3.6 1.9	1.9 2.5 1.8	6.8 9.7 5.8	
USA (AR) 1993 (W62)	SL	0.5	1.1	1 trifoliate	112	hay	<0.05	<0.05	0.12	ER-93-USA-02-AR-01
	SL	0.5	1.1	1 full pod	65	hay	1.1	0.93	5.0	
	SL	0.5	1.1	2 full pod	65	hay	1.4	1.2	6.3	
USA (MS) 1993 (W98)	SL	0.5	1.1	1 trifoliate	86	hay	0.10	0.08	0.29	ER-93-USA-02-MS-01
	SL	0.5	1.1	1 full pod	65	hay	0.58	0.58	4.7	
	SL	0.5	1.1	2 full pod	65	hay	0.80	0.63	4.6	
USA (VA) 1993 (W62)	SL	0.5	1.1	1 trifoliate	103	hay	0.43	0.31	1.3	ER-93-USA-02-VA-01
	SL	0.5	1.1	1 full pod	64	hay	0.31	0.24	1.2	
	SL	0.5	1.1	2 full pod	64	hay	0.31	0.33	1.5	
USA (NC) 1994 (transgenic Group 5 W62 A5403)	SL	0.4	0.43	1 3rd node	21 42 136	forage forage hay	0.20 <0.05 <0.05	<0.05 <0.05 <0.05	glu glu glu	Project: BK-94R-06 Trial#: NC-01
	SL	0.4 +0.5	0.43 +0.54	2 6th node	21 123	forage hay	0.36 0.33 <0.05 (2)	0.29 0.34 <0.05 0.09	glu glu	
	SL	0.4 +0.5	0.43 +0.54	2 bloom	21 90	forage hay	2.9 3.2 0.61 0.49	0.27 0.36 0.31 0.29	glu glu	

Location, Year, (variety)	Application				PHI		Residues, mg/kg, expressed as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days		glufosinate	MPP	NAG	
	SL	0.4 +0.5	0.43 +0.54	2 full pod	11 77	forage hay	2.6 (2) 1.2 1.0 0.86	0.31 0.32 0.65 0.58 0.51	glu glu	

[1] growth stage described
glu: included in glufosinate-ammonium result.

Table 59. Glufosinate residues in tolerant sugar beet tops and leaves resulting from foliar application in supervised trials in France, Germany and the UK.

Country, Year, (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	glufosinate	MPP	NAG[2]	
France 1995 (transgenic hybrid)	SL	0.60	0.30	2 GS31	0 12 16 23 85	10 plant 4.1 plant 4.1 plant 2.8 plant 1.1 leaves	0.1 plant <0.05 plant <0.05 plant <0.05 plant <0.05 leaves		A56446 ER95ECN555 FRA000102
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	0 13 20 55 96	31 plant 3.3 plant 1.6 plant 0.34 plant <0.05 leaves	0.18 plant <0.05 plant <0.05 plant <0.05 plant <0.05 leaves		A57574 ER96ECN551 FRA000102
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	0 13 20 54 96	26 plant 2.4 plant 1.8 plant 0.68 plant <0.05 leaves	0.11 plant <0.05 plant <0.05 plant <0.05 plant <0.05 leaves		A57574 ER96ECN551 FRA000202
France 1996 (transgenic hybrid)	SL	0.80	0.32	2 GS19	0 11 16 51 91	20 plant 4.0 plant 3.6 plant 1.6 plant 0.44 leaves	0.14 plant 0.07 plant <0.05 plant <0.05 plant <0.05 leaves		A57574 ER96ECN551 FRA000302
Germany 1995 (Sä-Nr. 951 959 - 36)	SL	0.80	0.27	2 GS31	0 23 39 58 96	24 plant 4.0 plant 1.9 plant 1.2 plant 0.53 leaves	0.09 plant <0.05 plant <0.05 plant 0.05 plant 0.06 leaves		A57574 ER96ECN551 DEU010102
UK 1995 (transgenic hybrid)	SL	0.60	0.30	2 GS19	0 4 12 27 83	9.3 plant 6.9 plant 4.7 plant 2.7 plant 1.3 leaves	<0.05 plant 0.05 plant <0.05 plant <0.05 plant <0.05 leaves		A56446 ER95ECN555 GBR000102
UK 1995 (transgenic hybrid)	SL	0.60	0.60	2 GS31	0 8 21 38 94	6.5 plant 1.9 plant 1.8 plant 1.1 plant 0.65 leaves	<0.05 plant <0.05 plant <0.05 plant <0.05 plant <0.05 leaves		A56446 ER95ECN555 GBR000202
UK 1996 (Roberta)	SL	0.80	0.80	2 GS31	0 14 43 71 111	11 plant 6.1 plant 2.4 plant 2.2 plant 1.4 leaves	0.08 plant 0.07 plant 0.06 plant 0.06 plant 0.07 leaves		A57574 ER96ECN551 GBR000102
UK 1996 (transgenic hybrid)	SL	0.80	0.80	2 GS19	0 14 40 64 105	12 plant 5.2 plant 2.0 plant 1.3 plant 0.83 leaves	0.15 plant 0.09 plant 0.05 plant 0.05 plant <0.05 leaves		A57574 ER96ECN551 GBR000202

[1]: GS growth stage

GS14	4 leaves (2nd pair unfolded)
GS15	5 leaves unfolded
GS19	9 or more leaves unfolded
GS31	beginning of crop cover formation

[2] included in glufosinate-ammonium result.

Table 60. Glufosinate residues in tolerant sugar beet tops resulting from foliar application in supervised trials in the USA.

Location, Year, (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Glufosinate	MPP	NAG[2]	
USA (CA) 1995 (Liberty Link)	SL	0.21 +0.20 +0.20	0.21 +0.20 +0.20	3 8-leaf	10 15 30 60 139	0.19 0.23 0.31 0.29 0.23 0.28 0.13 0.12 <0.05 (3)	<0.05 (2) 0.14 0.17 0.53 0.54 0.37 0.33 0.08 0.06 0.12		BK-95R-06 CA-016 (Regimen B)
USA (CA) 1995 (Liberty Link)	SL	0.43 +0.40 +0.40	0.43 +0.39 +0.40	3 6-leaf	10 15 30 60 139	0.39 0.46 1.04 1.1 1.2 0.63 0.76 0.39 0.32 <0.05 (2)	<0.05 (2) 0.51 0.37 0.48 1.2 1.1 0.88 0.78 0.21 0.25		BK-95R-06 CA-016 (Regimen C)
USA (CA) 1995 (Liberty Link)	SL	0.61	0.59	1 6-leaf	10 15 30 60 139	3.0 3.5 2.5 2.8 2.0 1.2 1.4 0.48 0.60 0.45 0.05 0.08 <0.05	0.25 0.22 0.58 0.44 0.42 1.2 1.3 0.82 0.70 0.81 0.29 0.22 0.21		BK-95R-06 CA-016 (Regimen D)
USA (MN) 1995 (Liberty Link)	SL	0.19 +0.20 +0.20	0.21	3 8-leaf	95	<0.05 (2)	<0.05 (2)		BK-95R-06 KBT-01 (Regimen B)
USA (MN) 1995 (Liberty Link)	SL	0.40 +0.41 +0.41	0.43	3 8-leaf	95	<0.05 (2)	<0.05 (2)		BK-95R-06 KBT-01 (Regimen C)
USA (MN) 1995 (Liberty Link)	SL	0.61 +0.62	0.64	2 8-leaf	95	0.10 0.09	<0.05 (2)		BK-95R-06 KBT-01 (Regimen D)
USA (ID) 1995 (Liberty Link)	SL	0.21 +0.20 +0.21	0.21	3 8-leaf	49	0.08 0.09	<0.05 (2)		BK-95R-06 TWM-01 Regimen B)
USA (ID) 1995 (Liberty Link)	SL	0.41 +0.43 +0.40	0.42	3 8-leaf	49	0.22 0.23	<0.05 (2)		BK-95R-06 TWM-01 Regimen C)
USA (ID) 1995 (Liberty Link)	SL	0.63 +0.61	0.64	2 8-leaf	49	0.31	0.05		BK-95R-06 TWM-01 Regimen D)
USA (ND) 1995 (Liberty Link)	SL	0.21 +0.21 +0.22	0.21 +0.22 +0.21	3 11-12-leaf	103	0.05 0.09 0.05	<0.05 (3)		BK-95R-06 PGM-01 (Regimen B)
USA (ND) 1995 (Liberty Link)	SL	0.43 +0.43 +0.46	0.43	3 11-12-leaf	104	0.11 0.07 0.11	<0.05 (3)		BK-95R-06 PGM-01 (Regimen C)
USA (ND) 1995 (Liberty Link)	SL	0.86 +0.64	0.85 +0.63	2 11-12-leaf	104	0.07 0.08	<0.05 (2)		BK-95R-06 PGM-01 (Regimen D)
USA (MI) 1996 (Liberty Link)	SL	0.60	0.61 +0.63	2 8-leaf	109	0.14 0.16	0.05 <0.05		BK-96R-01 R05-02 (Regimen B)
USA (MI) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.64 +0.40 +0.66	3 10-leaf	106	0.30 (2)	<0.05 (2)		BK-96R-01 R05-02 (Regimen C)

Location, Year, (variety)	Application				PHI	Residues, mg/kg, as glufosinate free acid			Ref
	form	kg ai/ha	kg ai/hl	No[1]	days	Glufosinate	MPP	NAG[2]	
USA (OH) 1996 (Liberty Link)	SL	0.60	0.63 +0.67	2 8-leaf	83	0.16 (2)	<0.05 (2)		BK-96R-01 R05-03 (Regimen B)
USA (OH) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.61 +0.41 +0.66	3 10-leaf	77	0.46 (2)	<0.05 (2)		BK-96R-01 R05-03 (Regimen C)
USA (ND) 1996 (Liberty Link)	SL	0.60	0.63	2 7.5-8.5-leaf	67	0.25 0.24	<0.05 (2)		BK-96R-01 R05-04 (Regimen B)
USA (ND) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.63 +0.41 +0.63	3 9.5-11-leaf	62	0.65 0.53	<0.05 (2)		BK-96R-01 R05-04 (Regimen C)
USA (NE) 1996 (Liberty Link)	SL	0.60	0.63	2 8-leaf	115	<0.05 (2)	<0.05 (2)		BK-96R-01 R07-01 Regimen B)
USA (NE) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.61 +0.41 +0.66	3 10-leaf	108	<0.05 (2)	<0.05 (2)		BK-96R-01 R07-01 Regimen C)
USA (ND) 1996 (Liberty Link)	SL	0.60	0.63	2 8-leaf	73	0.13 0.16	<0.05 (2)		BK-96R-01 R07-02 (Regimen B)
USA (ND) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.63 +0.41 +0.63	3 10-leaf	66	0.23 0.24	0.06 0.08		BK-96R-01 R07-02 (Regimen C)
USA (CO) 1996 (Liberty Link)	SL	0.60	0.59	2 8-leaf	80	<0.05 (2)	<0.05 (2)		BK-96R-01 R08-01 (Regimen B)
USA (CO) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.63 +0.40 +0.58	3 10-leaf	68	0.38 (2)	<0.05 (2)		BK-96R-01 R08-01 (Regimen C)
USA (CO) 1996 (Liberty Link)	SL	0.60	0.61 +0.59	2 8-leaf	86	0.06 (2)	<0.05 (2)		BK-96R-01 R09-01 (Regimen B)
USA (CO) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.64 +0.41 +0.61	3 10-leaf	81	0.22 0.24	<0.05 (2)		BK-96R-01 R09-01 (Regimen C)
USA (CA) 1996 (Liberty Link)	SL	0.60	0.65 +0.62	2 8-leaf	132	<0.05 0.07	<0.05 (2)		BK-96R-01 R10-01 (Regimen B)
USA (CA) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.61 +0.42 +0.63	3 10-leaf	122	0.19 0.26	0.06 0.08		BK-96R-01 R10-01 (Regimen C)
USA (ID) 1996 (Liberty Link)	SL	0.60	0.62	2 8-10-leaf	128	0.10 0.07	<0.05 (2)		BK-96R-01 R11-01 (Regimen B)
USA (ID) 1996 (Liberty Link)	SL	0.60 +0.39 +0.60	0.61 +0.41 +0.63	3 10-leaf	121	0.32 0.30	0.06 0.05		BK-96R-01 R11-01 (Regimen C)

[1] growth stage is described in terms of number of leaves.
[2] included in glufosinate-ammonium result.

Table 61. Glufosinate residues in almond hulls resulting from supervised trials in California, USA, 1985 Analyses of samples from replicate plots are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels. CLICK HERE

(Variety)	Application				PHI, days	Residues, mg/kg, as glufosinate free acid		Ref
	Form	kg ai/ha	kg ai/hl	no.		glufosinate	MPP	
(Carmel)	SL	1.7		3	15	<0.5 (3)	<0.5 (3)	A48446 07-CA-85-018
(Carmel)	SL	3.4		3	15	<0.5 (3)	<0.5 (3)	A48446 07-CA-85-018
(Special)	SL	1.7		3	15	<0.5 (3)	<0.5 (3)	A48446 07-CA-85-018
(Special)	SL	3.4		3	15	<0.5 (3)	<0.5 (3)	A48446 07-CA-85-018
(Non-Peril)	SL	1.7		3	14	<0.5 (3)	<0.5 (3)	A48446 07-CA-85-037
(Non-Peril)	SL	3.4		3	14	<0.5 (3)	<0.5 (3)	A48446 07-CA-85-037

Farm animal feeding studies

Studies on cows and laying hens were reported.

Groups of 3 lactating Holstein dairy cows (each weighing 430-610 kg) were dosed with glufosinate-ammonium + NAG (15+85) in gelatin capsules at total nominal levels equivalent to 9.1, 27 and 91 ppm glufosinate free acid in the diet for 28 consecutive days (Czarnecki and Brady, 1995b). Doses were administered after the morning milking in four separate capsules, one containing glufosinate-ammonium and three containing NAG. Milk was collected twice each day and pooled for analysis. On day 29 the animals from each group were slaughtered. The cows consumed a nominal 21 kg (average 16.8-25.4 kg) feed each per day.

The dosing mixture (glufosinate-ammonium 15 parts + NAG 85 parts) was chosen to represent the typical terminal residue composition in glufosinate-resistant crops that might be fed to animals.

Residues were not detected in milk from the lowest dosing level, detected in a few samples from the middle level, and consistently detected the highest dose group where a plateau was reached on day 3. Two milk samples from the same cow (on days 16 and 18) had unusually high residues, which corresponded with a period of low feed consumption (a constant dose representing a higher feed concentration) and low milk production. Residues in the tissues were below the LODs at the lower doses. At the highest dose they were detected in the kidneys and liver, but not in muscle or fat.

Table 62. Residues in the tissues of lactating dairy cows dosed with glufosinate-ammonium + NAG (15+85) in gelatin capsules at levels equivalent to 9.1, 27 and 91 ppm glufosinate free acid in the diet for 28 consecutive days (Czarnecki and Brady, 1995b).

Tissue	Residues, mg/kg, expressed as glufosinate free acid					
	9.1 ppm		27 ppm		91 ppm	
	glufosinate + NAG	MPP	glufosinate + NAG	MPP	Glufosinate + NAG	MPP
Muscle	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)
Fat, perirenal	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)
Liver	<0.1 (3)	<0.1 (3)	<0.1 (3)	<0.1 (3)	<0.1 (3)	0.28 0.29 0.25
Kidneys	<0.1 (3)	<0.1 (3)	<0.1 (3)	<0.1 (3)	0.10 0.14 0.15	<0.1 (2) 0.13

Table 63. Residues in the milk of lactating dairy cows dosed with glufosinate-ammonium + NAG (15+85) in gelatin capsules at levels equivalent to 9.1, 27 and 91 ppm glufosinate free acid in the diet for 28 consecutive days (Czarnecki and Brady, 1995b).

Day	Residues, mg/kg, expressed as glufosinate free acid					
	9.1 ppm		27 ppm		91 ppm	
	glufosinate + NAG	MPP	glufosinate + NAG	MPP	glufosinate + NAG	MPP
1	<0.02 (3)	<0.02 (3)	<0.02 (3)	<0.02 (3)	<0.02 (3)	<0.02 (3)
3	<0.02 (3)	<0.02 (3)	<0.02 (3)	<0.02 (3)	0.05 0.04 0.05	<0.02 (3)
5	<0.02 (3)	<0.02 (3)	<0.02 (3)	<0.02 (3)	0.05 0.04 0.03	<0.02 (3)
7	<0.02 (3)	<0.02 (3)	0.02 <0.02 (2)	<0.02 (3)	0.04 0.05 0.02	<0.02 (3)
9	<0.02 (3)	<0.02 (3)	<0.02 (3)	<0.02 (3)	0.03 0.03 0.03	<0.02 (3)
11	<0.02 (3)	<0.02 (3)	0.02 <0.02 (2)	<0.02 (3)	0.04 0.03 0.03	<0.02 (3)
14	<0.02 (3)	<0.02 (3)	<0.02 (3)	<0.02 (3)	0.03 0.03 0.03	<0.02 (3)
16	<0.02 (3)	<0.02 (3)	<0.02 (2) 0.02	<0.02 (3)	0.05 0.23 0.03	<0.02 0.03 <0.02
18	<0.02 (3)	<0.02 (3)	<0.02 (3)	<0.02 (3)	0.04 0.14 0.03	<0.02 0.03 <0.02
21	<0.02 (3)	<0.02 (3)	0.03 <0.02 (2)	<0.02 (3)	0.05 0.05 0.04	<0.02 (3)
23	<0.02 (3)	<0.02 (3)	0.02 <0.02 0.03	<0.02 (3)	0.064 0.03 0.02	<0.02 (3)
25	<0.02 (3)	<0.02 (3)	0.02 <0.02 (2)	<0.02 (3)	0.072 0.02 0.03	<0.02 (3)
28	<0.02 (3)	<0.02 (3)	0.02 <0.02 (2)	<0.02 (3)	0.05 0.04 0.03	<0.02 (3)

Groups of 20 white leghorn laying hens (each bird weighing 1.4-1.5 kg) were dosed with glufosinate-ammonium + NAG L-isomer, 15+85 in gelatin capsules at nominal levels equivalent to 0.36, 1.1 and 3.6 ppm glufosinate free acid in the diet for 28 days (Czarnecki and Brady, 1995a; Helsten, 1995; Crotts and McKinney, 1995). On day 29 twelve hens from each group were slaughtered. The remaining hens from each group were placed on a residue-free diet and killed on days 35 and 42. Eggs were collected daily.

The dosing levels were chosen on the assumption of feed consumption of 180 g/bird/day, but the birds consumed 133-160 g feed each per day. The actual dosing levels would be about 20% higher than intended.

No residues of glufosinate + NAG or MPP were found above the LOD in any of the tissues or eggs (Table 64).

Table 64. Residues in the tissues and eggs of hens dosed with glufosinate + NAG, (15+85) at levels equivalent to 0.36, 1.1 and 3.6 ppm in the feed for 28 days (Czarnecki and Brady, 1995a).

Commodity	Residues expressed as glufosinate free acid, mg/kg					
	0.36 ppm		1.1 ppm		3.6 ppm	
	glufosinate + NAG	MPP	glufosinate + NAG	MPP	glufosinate + NAG	MPP
Skin	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Muscle	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Liver	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fat	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Eggs[1]	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

[1]Eggs from days 1, 3, 5, 7, 9, 11, 14, 16, 18, 21, 23, 25 and 28 were analysed.

FATE OF RESIDUES IN STORAGE AND PROCESSING

The effects of commercial processing on residues in sugar beet, maize, soya bean seed and canola seed were reported.

Zietz and Simpson (1997) processed tolerant sugar beet roots (80-100 kg in each trial) from three glufosinate-ammonium residue trials in France, Germany and the UK (Hees and Werner, 1997d) and measured the residues in the processed fractions. The crops were each treated twice with glufosinate-ammonium at 0.80 kg ai/ha with the final treatment at GS19 (9 or more leaves unfolded) or GS31 (beginning of crop cover formation) and harvest 111-124 days later. The process (Figure 6) simulated a commercial operation.

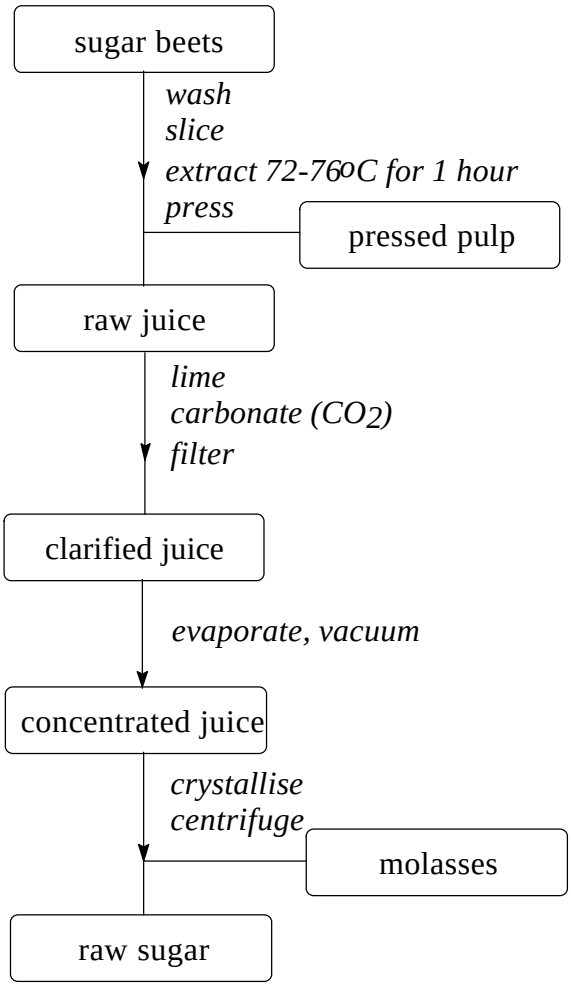


Figure 6. Sugar beet processing.

The results are shown in Table 65.

Residues generally tended to remain in the juice and ultimately to appear in the molasses. Residues were not detected (<0.05 mg/kg) in the raw sugar.

Processing factors were calculated only for the glufosinate + NAG residues because the MPP residues in the sugar beet were too low to be useful. Processing factors for raw sugar could not be determined because residues were not found in the sugar in any of the trials. The processing factors for molasses were 5.0, 11.5 and 3.8 (mean 6.8) showing that glufosinate residues in the roots become concentrated in the molasses after removal of water.

Table 65. Glufosinate residues in sugar beet roots and processing fractions arising from glufosinate-ammonium treatment of transgenic sugar beet in trials in Germany (DEU010102), France (FRA000202) and the UK (GBR000102) (Hees and Werner 1997d, Zietz and Simpson 1997).

Commodity	Residues, mg/kg as glufosinate free acid					
	DEU010102		FRA000202		GBR000102	
	glufosinate + NAG	MPP	glufosinate + NAG	MPP	glufosinate + NAG	MPP
Root	0.3	0.05	0.06	<0.05	0.99	<0.05
Pressed pulp	<0.05	<0.05	<0.05	<0.05	0.13	<0.05
Raw juice	0.25	<0.05	0.11	<0.05	0.77	0.05
Clarified juice	0.19	<0.05	0.09	<0.05	0.82	0.05
Concentrated juice	0.72	0.14	0.55	0.05	2.5	0.17

Commodity	Residues, mg/kg as glufosinate free acid					
	DEU010102		FRA000202		GBR000102	
	glufosinate + NAG	MPP	glufosinate + NAG	MPP	glufosinate + NAG	MPP
Raw sugar	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Molasses	1.5	0.23	0.69	0.06	3.8	<0.05

Brady and Bertrand (1997) treated transgenic sugar beet, variety T-4A, with glufosinate-ammonium three times at 3.0 kg ai/ha, about 5 times the label rate and harvested the crop 136 days after the final treatment at the eighth leaf stage. The laboratory processing of 141 kg sugar beet roots was designed to simulate a commercial process (Englar, 1997) and was similar to that in Figure 6. The results are shown in Table 66.

In this trial, in contrast to the Zietz and Simpson trial, MPP was the main component of the residue. The total residue was used to calculate processing factors of 0 (<0.08) for refined sugar, and 6.4 for molasses.

Table 66. Glufosinate residues in sugar beet root and processing fractions arising from glufosinate-ammonium treatment of transgenic sugar beet in trials in the USA at 3.0 kg ai/ha and harvest 136 days after the last of three treatments (Brady and Bertrand, 1997).

Commodity	Residues, mg/kg as glufosinate free acid	
	glufosinate + NAG	MPP
Root	0.27 0.24	1.0 0.96
Dried pulp	0.14 0.15	0.56 0.63
Refined sugar	<0.05 (2)	<0.05 (2)
Molasses	1.7 1.4	6.5 6.1

Czarnecki (1996) showed that the residues in grain dust were about 10 times as high as in the grain from glufosinate-ammonium-treated tolerant maize. The grain dust contained 0.62 mg/kg of MPP and 3.0 mg/kg glufosinate + NAG from grain containing MPP and glufosinate + NAG at 0.062 and 0.31 mg/kg respectively, all expressed as glufosinate free acid. Residue levels increased as particle size decreased, with levels in the <425 µm fraction 2.5-3 times those in the >2450 µm fraction.

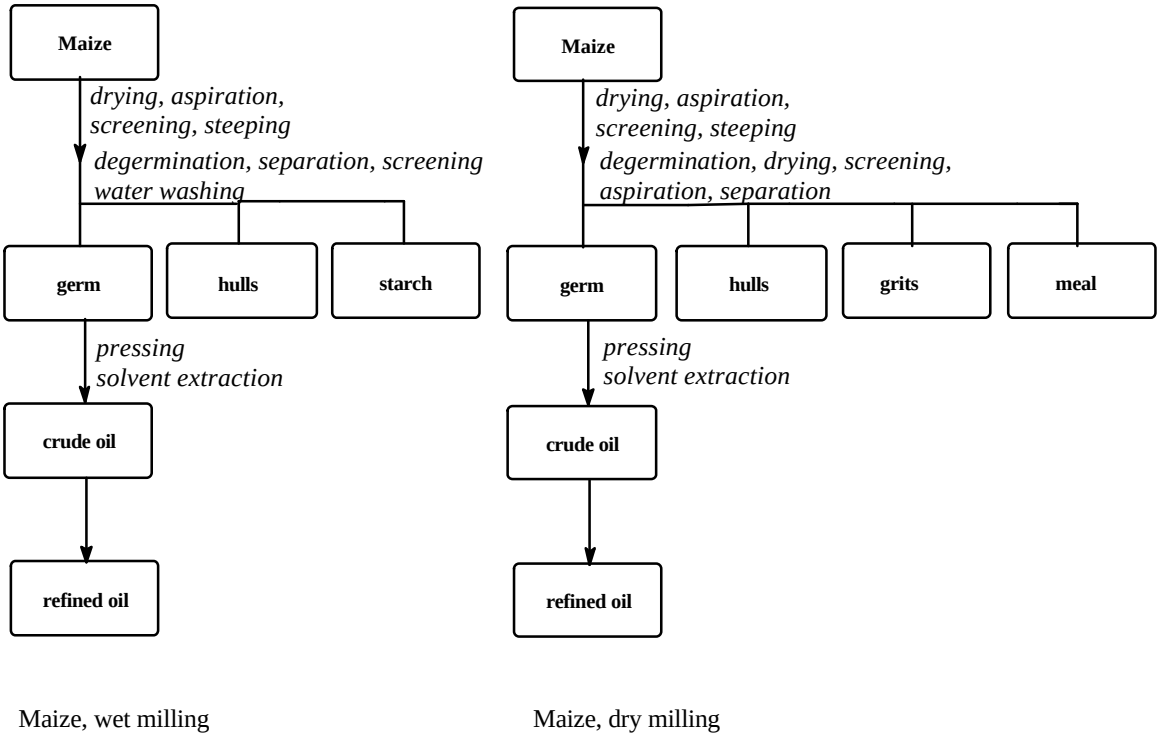
To provide samples for a processing study in the USA Brady *et al.* (1994) treated glufosinate-tolerant maize (60 cm stage) with glufosinate-ammonium at 0.50 kg ai/ha (3 times the proposed label rate) in a trial in Iowa. In a second trial in Nebraska glufosinate-ammonium was applied at 0.36 kg ai/ha to 30 cm maize with a second treatment at 0.50 kg ai/ha at the 60 cm growth stage. The maize was treated by wet and dry milling processes (Figure 7). The results are shown in Table 67.

The residues were all below the LOD (0.05 mg/kg) in the Iowa trial. NAG was present at the LOD in the meal, flour and grits and at 0.1 mg/kg in the hulls in the Nebraska trial. The best estimates for processing factors are corn meal, corn flour and grits 1, hulls 2.

Table 67. Residues in maize and processed fractions resulting from dry and wet milling of glufosinate-tolerant maize treated at excessive rates with glufosinate-ammonium (Brady *et al.* 1994).

Commodity	Iowa trial			Nebraska trial		
	Residues, mg/kg as glufosinate					
	Glufosinate	MPP	NAG	Glufosinate	MPP	NAG
Maize	<0.05	<0.05	<0.05	<0.05	<0.05	0.054
Corn meal (dry milled)	<0.05	<0.05	<0.05	<0.05	<0.05	0.051
Corn flour (dry milled)	<0.05	<0.05	<0.05	<0.05	<0.05	0.053
Corn hulls (dry milled)	<0.05	<0.05	<0.05	<0.05	<0.05	0.10
Corn grits (dry milled)	<0.05	<0.05	<0.05	<0.05	<0.05	0.05
Corn crude oil (dry milled)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Corn refined oil (dry milled)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Corn hulls (wet milled)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Corn starch (wet milled)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Corn crude oil (wet milled)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Corn refined oil (wet milled)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

Figure 7. Wet and dry milling of maize (Brady *et al.*, 1994).



Trial	soya bean seeds		grain dust	
	glufosinate + NAG	MPP	glufosinate + NAG	MPP
IN-01	3.4 mg/kg	1.1 mg/kg	31mg/kg	8.7 mg/kg
MO-01	1.5 mg/kg	1.8 mg/kg	4.3mg/kg	4.7 mg/kg

Brady (1995e) processed seed from transgenic soya bean crops treated at excessive rates with glufosinate-ammonium and measured the residues, expressed as glufosinate free acid, in the aspirated grain fractions (grain dust). In the two trials 32 kg of soya bean seed produced 78 and 228 g of grain dust. Residues in the grain dust were 8.6 and 2.8 times the levels in the grain in the two trials.

Czarnecki *et al.* (1994a) treated a transgenic soya bean crop in the USA (Iowa) with glufosinate-ammonium at 2.6 kg ai/ha (5 times the normal rate) at the six-trifoliate growth stage and harvested the soya beans for processing 96 days later. After processing 31 kg of the soya beans (Figure 8) the hulls contained the highest residues with lower levels in the meal. Residues of

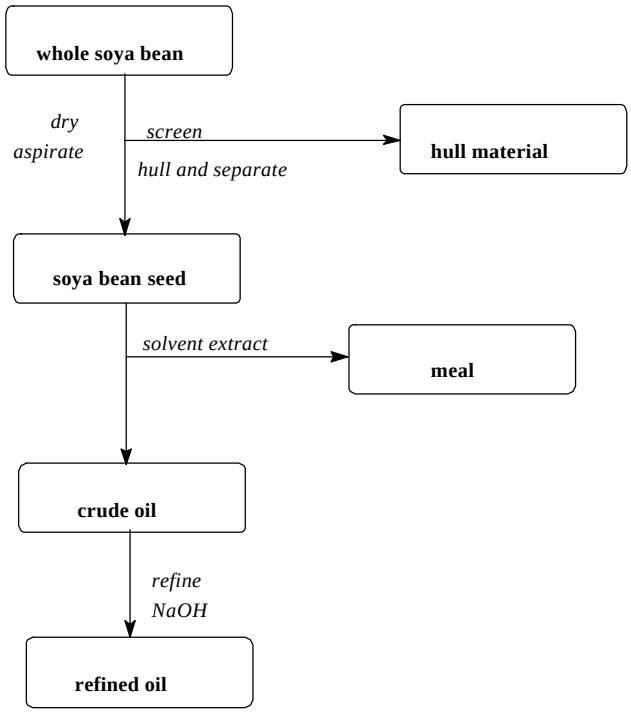


Figure 8. Simulated commercial processing of soya beans

glufosinate, NAG and MPP were not detected (<0.05 mg/kg) in the refined or crude oil. The results are shown in Table 68.

The calculated processing factors for residues in the meal and crude or refined oil are 1.3 and 0 (<0.3) respectively.

Table 68. Residues of glufosinate, NAG and MPP in seeds and processed commodities from glufosinate-treated transgenic soya beans (Czarnecki *et al.*, 1994a).

Commodity	Residues as glufosinate free acid, mg/kg		
	glufosinate	NAG	MPP
Seeds	<0.05	0.07	0.08
Hulls	0.07	0.27	0.30
Meal	<0.05	0.08	0.12
Refined oil	<0.05	<0.05	<0.05
Crude oil	<0.05	<0.05	<0.05

MacDonald (1996a) treated a transgenic canola crop in Canada (Saskatchewan) with single applications of glufosinate-ammonium at 0.75, 1.5 and 3.8 kg ai/ha (up to 4 times the normal rate) at the 4-6 leaf growth stage and harvested the seed (3.5-5 kg) for processing 70 days later.

Processing was on a small scale but was intended to simulate commercial practice. The canola seed was dried and cleaned and, after conditioning, crude oil was produced first by pressing and then by hexane extraction of the cake. The cake was toasted. The crude oil was refined, bleached and deodorised. The results are shown in Table 69.

Glufosinate itself was not detected in the seed or any processed fraction. The main residue was NAG. No residues were detected in the oils. The residues of NAG remain with the meal and

change little during toasting. The calculated processing factor for untoasted meal is 3.1 (2.7, 3.1, 3.7) and for toasted meal 3.7 (3.1, 3.3, 4.8).

Table 69. Residues in seed and processed fractions from transgenic canola treated with glufosinate at three rates and harvested 70 days later in Canada (MacDonald 1996a).

Commodity	Residues, mg/kg as glufosinate free acid								
	0.75 kh ai/ha			1.5 kg ai/ha			3.8 kg ai/ha		
	glufosinate	MPP	NAG	Glufosinate	MPP	NAG	glufosinate	MPP	NAG
Seed	<0.05	<0.05	0.063	<0.05	<0.05	0.060	<0.05	<0.05	0.21
Meal, untoasted	<0.05	<0.05	0.17	<0.05	<0.05	0.22	<0.05	0.11	0.64
Meal, toasted	<0.05	<0.05	0.21	<0.05	0.05	0.29	<0.05	0.11	0.64
Oil, crude	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Oil, refined	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Oil, bleached	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Oil, deodorized	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Soapstock	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.083

Residues in the edible portion of food commodities

The only information was the from processing studies on soya bean, canola and sugar beet.

The processing factors for the residues in soya bean meal and crude or refined oil were 1.3 and 0 (<0.3) respectively. Residues were not detected (<0.05 mg/kg) in the crude or refined oil.

The processing factor for residues in untoasted canola meal was 3.1 and for toasted meal 3.7. Residues were not detected (<0.05 mg/kg) in the crude, refined, bleached or deodorized oil.

The processing factors for raw sugar and molasses in one trial were 0 (<0.35) and 6.8 respectively. In another trial the processing factors for refined sugar and molasses were 0 (<0.08) and 6.4 respectively. No residues were detected (<0.05 mg/kg) in the raw or refined sugar.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was informed of the following national MRLs.

Country	MRL, mg/kg	Commodity
Argentina 1/	0.05	corn grain, corn forage, corn fodder
	2/	top fruits, stone fruits, citrus, grapes
Australia 3/	15	mixed pasture (legume/grasses)
	5	edible offal (mammalian)
	0.2	assorted tropical and sub-tropical fruits – inedible peel
	0.1	berries and other small fruits, citrus fruits, meat (mammalian), tree nuts, pome fruits
	0.05	milks, stone fruits
Austria 4/	0.1	all crops
Belgium 5/	2	potatoes

Country	MRL, mg/kg	Commodity
	0.05	all other crops
Brazil 6/	0.05	lettuce, cotton, banana, citrus, potatoes, coffee, apple, maize, peach, Savoy-cabbage, soya beans, wheat, grape, bean
Canada 7/	6	lentils
	3	rape seed (canola)
	1	liver and kidneys of cattle, goats, hogs, poultry and sheep
	0.5	dry white beans
	0.4	potatoes
	0.2	corn
Colombia	8/	cotton, banana, soya bean, papaya, citrus, grape, strawberry, passion-flower, African palm, potatoes, coffee
Denmark		9/
Finland		9/
France 10/	0.5	citrus, small berries, bananas, cherries, stone fruits, pome fruits, hazel nuts, tree nuts, olives, carrots, chicory, cabbage, spinach, beans, lettuce, lamb's lettuce, sweet maize, onions, potatoes
Germany 11/	3	pulses, sunflower seeds with hulls
	1	potatoes, rape seed
	0.5	currants, kiwifruit
	0.2	bananas, citrus
	0.1	other food of plant origin
Greece		9/
Ireland		9/
Italy	0.1	citrus, small berries and small fruits, stone fruits, pome fruits, tree nuts, hazel nuts, kiwis, onion, cabbage, lettuce, beans, carrots, kohlrabi, radish, asparagus, potatoes, soya beans
Japan	0.5	potato, rice, tea
	0.3	mandarin, other citrus, large fruits, small fruits, oil seeds, nuts
	0.2	wheat, other cereals, vegetables, beans (immature + pods), leafy vegetables, rhizomes, bulb vegetables, mushrooms
	0.1	soya bean
Luxemburg 5/	0.2	potatoes
	0.05	fruits and vegetables
Netherlands 12/	0.5	potatoes
	0.05	fruit, vegetables
	0-0.05 13/	other food commodities
Norway		9/
Poland	3	legume vegetables
	0.2	fruits, vegetables (except legume vegetables)
Portugal 14/	3	barley
	1	wheat
	0.5	potatoes
	0.1	citrus, berries, brassicae
	0.1 15/	tea, hop
	0.05 15/	pome fruits, stone fruits, other fruits, roots and tubercles, bulbs, fruits and vegetables, hard shelled fruits, leaf vegetables and fresh spice plants, fresh leguminosae, stalks, fungi, leguminosae (dried) grains, oil seeds, other cereals
Spain 16/	0.05	fruits, vegetables, potatoes, cereals
	0.01 17/	legumes, oily seeds, tea and other infusions, dried hops, spices, tobacco, sugar beet, sugarcane, forages and hays, dried products (raisins, plums, etc)
South Africa 18/	2	soya beans
	0.2	canola, maize
Sweden		9/
Switzerland	0.5	potatoes
	0.05	fruits and vegetables
UK 19/	5.0	barley
	3.0	peas

Country	MRL, mg/kg	Commodity
	1.0	potatoes, wheat, linseed, field beans
	0.5	rape seed
USA	25	aspirated grain fractions (grain dust) 20/
	6	corn stover 20/
	5	soya bean hulls 20/
	4	corn forage 20/
	2	soya beans 20/
	0.5	almond hulls 21/
	0.3	banana (0.2 in pulp) 22/
	0.2	corn grain 20/
	0.1	meat by-products such as kidneys and liver of cattle, goats, hogs, horses, poultry and sheep 21/
	0.1	tree nuts 21/
	0.05 21/	apples, cattle fat, cattle meat, eggs, goats fat, goats meat, grapes, hogs fat, hogs meat, horses fat, horses meat, poultry fat, poultry meat, sheep fat, sheep meat
	0.02	milk 21/

1/ Definition of the residue: glufosinate-ammonium, expressed as glufosinate free acid
2/ For these crops Argentina follows MRLs established in Brazil or Germany.
3/ Definition of the residue: sum of glufosinate-ammonium and 3-[hydroxy(methyl)phosphinoyl]propionic acid, calculated as glufosinate (free acid).
4/ Definition of the residue: DL-homoalanin-4-yl-(methyl)phosphinic acid: in total calculated as glufosinate
5/ Definition of the residue: DL-homoalanin-4-yl-(methyl)phosphinic acid and 3-methylphosphinicopropionic acid calculated as glufosinate free acid.
6/ Definition of the residue: glufosinate-ammonium, expressed as glufosinate free acid
7/ Definition of the residue: 4-(hydroxy-(methyl)-phosphinoyl)-DL-homoalaninate ammonium salt, including the metabolite 3-methyl-phosphinicopropionic acid.
8/ Definition of the residue: the authorities accept the MRLs established by Codex and EPA
9/ No MRLs have been established by Denmark, Finland, Greece, Ireland, Norway or Sweden. Codex MRLs or those established in other EU countries are accepted
10/ Definition of the residue: 4-(hydroxy(methyl)phosphinoyl)-D,L-homoalanine
11/ Definition of the residue: DL-homoalanin-4-yl-(methyl)phosphinic acid and 3-methylphosphinicopropionic acid calculated as glufosinate
12/ Definition of the residue: glufosinate-ammonium, expressed as glufosinate.
13/ Range of 0 - 0.05 mg/kg because the LOD is 0.05 mg/kg
14/ Definition of the residue: glufosinate-ammonium and its metabolites 2-acetamido-4-methylphosphinico-butanoic acid and 3-methylphosphinicopropionic acid, expressed as glufosinate
15/ At the limit of determination
16/ Definition of the residue: glufosinate and its ammonium salt, expressed as glufosinate;
17/ 0.01 mg/kg is based on an earlier lower limit of quantification but will be adjusted to 0.05 mg/kg in near future for harmonisation purposes
18/ Definition of the residue: Glufosinate-ammonium and its metabolites 2-acetamido-4-methylphosphinico-butanoic acid and 3-methylphosphinicopropionic acid, expressed a glufosinate free acid equivalents. MRLs are temporary until 1999 and will be re-evaluated in the light of JMPR evaluation and Codex Alimentarius standards.
19/ Definition of the residue: DL-homoalanin-4-yl-(methyl)phosphinic acid and 3-methylphosphinicopropionic acid calculated as glufosinate free acid.
20/ Definition of the residue: glufosinate-ammonium and its metabolites 2-acetamido-4-methylphosphinico-butanoic acid and 3-methylphosphinicopropionic acid. Time-limited tolerance expiring 13 July 1999.
21/ Definition of the residue: glufosinate and its metabolite 3-methylphosphinico-propionic acid. Time-limited tolerance expiring 13 July 1999.
22/ Definition of the residue: combined residues of glufosinate ammonium and 3-methylphosphinicopropionic acid expressed as glufosinate equivalents. Time-limited tolerance expiring 18 Jan 2000.

APPRAISAL

Glufosinate-ammonium was first evaluated for residues and toxicology by the 1991 JMPR and subsequently for residues in 1994. Glufosinate-tolerant crops have now been developed with new GAP and different residue patterns, requiring new MRLs.

The Meeting received information on metabolism and environmental fate, registered uses and supervised residue trials on tropical fruits, tree nuts and various genetically-modified field crops. Feeding and processing studies were also reported.

Studies on the metabolism of glufosinate-ammonium in genetically modified rape seed (canola), sugar beet, maize, soya beans and tomatoes showed that the tolerant crops rapidly converted the active glufosinate isomer (L-glufosinate) to *N*-acetyl-glufosinate (NAG). The main components of the residue in tolerant plants are the L-isomer of NAG and D-isomer of glufosinate.

The Meeting received information on animal metabolism studies on rats, lactating goats and laying hens.

When rats were dosed orally with L-[3,4-^{14}C]NAG some de-acetylation to glufosinate occurred and some glufosinate was bioavailable, but unchanged NAG was the main component (85-89%) of the TRR in the faecal extracts. Almost all of the administered ^{14}C was excreted in the faeces within 4 days.

When rats were dosed orally with [3,4-^{14}C]glufosinate-ammonium, 75-89% of the ^{14}C was excreted in the faeces and 8-11% in the urine within 48 hours. The main components in the faecal extracts were glufosinate (77% of administered ^{14}C), NAG (7.5%), 4-methylphosphinico-2-hydroxybutanoic acid or MHB (4.3%) and 3-methylphosphinicopropionic acid or MPP (1.3%). The main components in the urine were glufosinate (4.3%) and MPP (0.8%).

Very small amounts of the administered ^{14}C were found in the tissues (<0.1%) and milk (<0.02%) of a lactating goat dosed orally for 4 days with [3,4-^{14}C]glufosinate. Levels of ^{14}C reached a plateau in the milk by day 2. Levels of ^{14}C were higher in the kidneys and liver than in other tissues. Glufosinate and MPP constituted about 50% and 30% respectively of the residue in both kidneys and liver. Glufosinate accounted for 50% of the ^{14}C in the milk. When a lactating goat was dosed orally with L-[3,4-^{14}C]NAG the disposition of ^{14}C in the tissues and milk was similar to that after dosing with glufosinate. Glufosinate was the main residue in the kidneys, liver and milk with NAG and MPP forming a substantial part of the residue in the kidneys and liver.

Less than 0.02% of the administered ^{14}C was present in the edible tissues when laying hens were dosed orally for 14 days with [3,4-^{14}C]glufosinate-ammonium. MPP and glufosinate were the main residues identified in the liver and eggs respectively. After dosing orally for 14 days with L-[3,4-^{14}C]NAG less than 0.1% of the administered dose was present in the edible tissues and blood. NAG was the main residue identified in liver and egg yolks while glufosinate was the main residue in egg whites.

The Meeting received information on metabolism studies in rape seed, canola, sugar beet, maize, soya beans and tomatoes.

Genetically modified rape plants rapidly acetylated glufosinate. Cut rape plants were placed in a nutrient solution containing [3,4-^{14}C]glufosinate-ammonium for 6 days, by which time 57% of the ^{14}C in the plants was associated with NAG and 36% with glufosinate.

In glufosinate-tolerant canola plant tissues sampled 1 hour after treatment with [^{14}C]glufosinate, 73% and 18% of the ^{14}C was present as glufosinate and NAG respectively,

demonstrating very rapid acetylation of glufosinate. After 21 days 60%, 21% and 7% of the ^{14}C corresponded to NAG, glufosinate and MPP respectively.

When glufosinate-tolerant sugar beet plants were sprayed with [3,4-^{14}C]glufosinate-ammonium the racemic isomer composition in the surface residue was unchanged, but in the absorbed residue L-glufosinate was metabolised to L-NAG.

Glufosinate was generally a minor component of the residue in treated tolerant maize. NAG was the main residue in the forage, silage and fodder, while MPP was the major component in grain, cobs and husks. The GLC enforcement analytical method for glufosinate, MPP and NAG was in reasonable agreement with a radiolabel method for the residues in the forage.

NAG was the main residue in the forage, straw, pods and beans of treated tolerant soya bean plants. MPP levels exceeded glufosinate levels in the pods and beans. The GLC enforcement method and an HPLC radiolabel method were in reasonable agreement in analyses of forage, straw, pods and beans at the higher residue levels, but at low levels the result from the enforcement method was less than from the ^{14}C measurement.

The translocation of [^{14}C]glufosinate-ammonium from treated leaves to shoots, other leaves and roots was approximately 4 times as fast in glufosinate-resistant tomato plants as in susceptible tomatoes. Most of the surface residue was glufosinate itself, but this was very rapidly converted to NAG once absorbed into the leaves. NAG constituted essentially all the residue in the ripe fruit harvested 60 or 74 days after the plants were treated.

The Meeting received information on the degradation and dissipation of glufosinate-ammonium in soil, residues in rotational crops and fate in water-sediment systems.

Glufosinate disappeared with a half-life of about 3-6 days during aerobic incubation with a sandy loam soil. MPP, the major product, reached its maximum after about 14 days incubation. MPA, 2-methylphosphinicoacetic acid, became the main residue after long intervals. Glufosinate suffered 62% and 31% mineralization during 120 days incubation with and without incorporation of plant material into the soil respectively.

In a dissipation study glufosinate-ammonium, applied 3 times to bare ground, dissipated quickly with calculated half-lives of 15, 7.2 and 2.7 days, the increased rates probably being related to increased soil moisture and temperature. The estimated half-lives for MPP after its residues peaked were 38, 14 and 16 days, and for MPA 25, 19 and 7 days. No residues were detected below a 45-60 cm depth section, but glufosinate and MPP reached a depth of 30-45 cm on several occasions during the study. Glufosinate and its degradation products have some mobility in soil but their rapid dissipation ensures that travel down the soil profile is limited.

When L-[3,4-^{14}C]NAG was incubated in a sandy loam soil it was very rapidly converted to L-glufosinate, which was then itself broken down and mineralized. The comparable rate of mineralization and production of unextractable residues suggests that the degradation pathway for NAG is through glufosinate. Further experiments showed that the half-life of NAG was only hours.

No important degradation products other than CO_2 were identified when [2-^{14}C]MPA was incubated in a sandy loam under aerobic conditions. Estimated decline and mineralization half-lives were 24 and 74 days respectively. Degradation in a loamy sand was much slower. When MPP was incubated under aerobic conditions in a sandy loam, MPA was the only significant product after 120 days.

After 3 days incubation of a sandy loam soil with tolerant tomato leaves containing residues, mainly of glufosinate and NAG, most of the residue had been converted to MPP, which itself was degraded more slowly to MPA and ultimately to CO_2.

Residues of degradation products of glufosinate should be undetectable or at very low levels in rotational crops. When radishes, lettuce and wheat were sown in a confined rotational crop study 28 days after glufosinate treatment of bare ground (to simulate re-sowing a failed crop) residues of MPP and MPA were present at low levels in the crops, demonstrating possible uptake of these compounds. The pattern of residues was similar in the three crops. When sowing was 119 days after treatment (to simulate a following crop) residues were not detectable in lettuce or radishes but MPP and MPA were detected by ^{14}C methods at very low levels in the wheat grain and straw.

The photolytic breakdown of glufosinate in natural waters was very slow.

MPP became the major component of the residue within a few days when [3,4-^{14}C]glufosinate-ammonium was incubated in a water-sediment system at 20°C. Glufosinate itself disappeared with a half-life of 3 days, but only 25% mineralization occurred during the 361 days of the study. In other experiments the rates of degradation were shown to be affected by the source of the water and the residue level of glufosinate (with faster disappearance at lower levels). In all cases most of the residue was in the water phase.

Methods of residue analysis

The main components of the residue in genetically modified tolerant crops are glufosinate, NAG and MPP. Analytical methods have been designed to measure the three components separately or, because glufosinate and NAG produce the same derivative in the analytical procedure, to measure glufosinate and NAG combined and MPP separately. Residues are extracted from the finely ground sample with water, and the extract is cleaned up on an anion exchange resin column. After solvent exchange, NAG and MPP are separated from glufosinate on a cation exchange column. The residues are taken up in glacial acetic acid and methylated, and glufosinate acetylated, with trimethyl orthoacetate in refluxing acetic acid. After solvent exchange and final clean-up on a silica gel cartridge the derivatized residues are determined by GLC with flame-photometric detection.

Modifications of the extraction and initial clean-up are needed for samples such as maize oil, fats and milk. A variation of the method dispenses with the cation exchange separation and determines glufosinate and NAG as a combined GLC peak because both compounds produce the same analytical derivative. The LOD for crop samples is typically 0.05 mg/kg for each analyte. Analytical recoveries have been extensively tested and found satisfactory on many substrates.

Analysts should be aware that transgenic glufosinate-tolerant soya beans plants can convert L-glufosinate to NAG very rapidly, giving apparently low analytical recoveries in spiked samples.

Glufosinate, NAG and MPP were shown to be stable during frozen storage for intervals of 12, 15 or 24 months in the following substrates: genetically modified maize and soya beans and their processed commodities, cow and chicken tissues, milk, eggs, susceptible maize grain, and transgenic rape seed and sugar beet roots. The 1994 JMPR reported that residues of glufosinate and MPP (described as Hoe 061517) in apples, oranges, kiwifruit, maize, soya beans and almonds were stable during frozen storage.

Some samples from the supervised trials were stored for 2 years, but the storage stability studies have demonstrated that the residues were still stable.

Definition of the residue

The current definition includes glufosinate and MPP and is based on the residues occurring in conventional crops. When glufosinate is used on glufosinate-tolerant crops NAG is produced. It should be included in the residue definition for enforcement because NAG is generally the main component of the residue and because the same derivative is produced in the analytical method from glufosinate itself and NAG, and in the simplified method both appear in the GLC peak from their common derivative. The revised residue definition is also suitable for commodities from conventional crops because if NAG is absent it will not contribute to the analytical result and if present at low levels it is necessarily included in the analytical result.

A suitable revised residue definition would be *Sum of glufosinate-ammonium, 3-(hydroxy(methyl)phosphinoyl)propionic acid and N-acetyl-glufosinate expressed as glufosinate (free acid)*, but the Meeting could not consider the adoption of this definition until the toxicological evaluation of NAG had been completed.

The residue reported in the supervised trials consists of three components, but is often reported with the glufosinate and NAG residue combined. The metabolism studies show that residues of the main component constitute 65-75% of the combined residue when all three components are at measurable levels. It follows that if all three components are below the LOD a reasonable assumption is that the combined residue is also below or close to the LOD. When one component is above and the others are below the LOD, the combined residue is assumed to be equal to the residue of the main component.

The method of calculating the total residue for various situations is illustrated by the following example.

Glufosinate	MPP	NAG	Total
<0.05	<0.05	<0.05	<0.05
<0.05	<0.05	0.06	0.06
0.05	<0.05	0.09	0.14

Information was made available on uses of glufosinate around fruit trees and nut trees. Limited information was provided on GAP for use of glufosinate on transgenic crops.

Glufosinate-ammonium is registered for use in Australia as a directed spray for weed control around avocados, bananas, feijoa, guava, kiwifruit, litchis, mangoes, papaya, passion fruit, pineapples and rambutans at 0.20-1.0 kg ai/ha. Malaysia has similar registered uses for glufosinate-ammonium as a directed herbicide spray around bananas, carambola, durians, guava, jack fruit and mangoes at 0.3-0.5 kg ai/ha. Residues in the fruit would generally not be expected from this type of use. Glufosinate itself is not taken up by roots but MPP, the main degradation product in soil, can be absorbed by the roots and translocated through the crop.

Supervised trials

Supervised trials were reported on tropical fruits, nut trees, maize, soya beans, rape, canola and sugar beet.

Residues were not detected in avocados in 3 Australian trials where glufosinate was used at 1.0, 1.2 and 2.0 kg ai/ha. In one trial at 1.2 kg ai/ha, glufosinate was detected at 0.06 mg/kg (presumably direct contamination during application) in 1 sample on day 0, but in no other samples. Residues were not detected in the fruit from 3 Australian trials on mangoes where the application rates were 1.0, 1.2 and 2.0 kg ai/ha or 1 trial on papayas at 1.2 kg ai/ha.

Residues were not detected in the fruit from Malaysian trials on carambola and guavas (2 trials at 0.5 kg ai/ha and 2 at 1 kg ai/ha on each fruit).

The Meeting agreed to consider these fruits together as “tropical fruits with inedible peel” but noted that a CXL of 0.2 mg/kg had already been established for banana, which would have to be excluded from the group. The residues in rank order from the 16 trials were <0.05, <0.05, <0.05, <0.05, <0.05, <0.05, <0.05, <0.05, <0.05, <0.05, <0.05, 0.06, <0.1, <0.1, <0.1 and <0.1 mg/kg.

In view of the type of use and generally unquantifiable residues at 3-5 sampling intervals in all of the trials the Meeting estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.05 mg/kg for glufosinate in Assorted tropical and sub-tropical fruits – inedible peel (except banana).

The US registered use for glufosinate around almond, pecan and walnut trees permits a directed application at 1.7 kg ai/ha, with no more than 5.1 kg ai/ha total per year, and a 14-day PHI. MPP residues were 0.07 mg/kg in almonds from a US trial at the label rate and up to 0.22 mg/kg in a trial at twice the label rate. MPP is the main degradation product in soil, so its presence demonstrates the possibility of root uptake rather than contamination of foliage by spray. Residues were not detected in almonds from 3 other trials at the label rate or 3 trials at the double rate. The trials were in California in 1985.

Residues were not detected (<0.05 mg/kg) in nuts from 3 trials on pecans (USA, 1985) with glufosinate applied at 1.7 kg ai/ha and 3 at twice that rate. In 2 trials nuts were harvested 21 days after application rather than 14 days, but the use pattern is sufficiently close to GAP. Residues were not detected (<0.05 mg/kg) in nuts from 6 walnut trials at 1.7 kg ai/ha, 5 trials 3.4 kg/ha or 3 at other rates higher than GAP in the USA in 1985.

The Australian registration for glufosinate-ammonium permits 0.2-1.0 kg ai/ha as a directed spray around nut trees. Residues were not detected (<0.1, <0.05 mg/kg) in macadamia nuts in Australian trials from 1992 and 1995 at the label rate (2 trials) and double rate (2 trials).

Italian registration permits a directed application of 0.5-1.6 kg ai/ha (maximum 2.5 kg ai/ha per year) for weed control around hazelnuts. Residues were not detected (<0.05 mg/kg) in nuts from 5 hazelnut trials in Italy in 1985 according to GAP.

The Meeting considered the 4 almond, 6 pecan, 14 walnut, 4 macadamia and 5 hazelnut trials as a group. The residues in the 33 trials were <0.05 (30), 0.07 and <0.1 (2) mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg and an STMR level of 0.05 mg/kg for glufosinate in tree nuts.

Glufosinate-ammonium is registered in Canada for use on transgenic maize at 0.30-0.50 kg ai/ha with final application at the 8-10 leaf stage. In Canadian trials in 1994-5 no residues (<0.05 mg/kg) were detected in 7 trials at 0.5 or 0.6 kg ai/ha or 3 trials at 1.0 kg/ha applied at growth stage GS 17-19 (7-9 leaves), or in 4 trials at 0.6 kg ai/ha at a later growth stage (GS 33, 3 nodes detectable).

Glufosinate-ammonium is registered in Portugal for use on transgenic maize at 0.40-0.80 kg ai/ha with the final application when the plant has no more than 8-10 leaves. In 7 Italian trials and 3 Spanish trials in 1996 according to Portuguese GAP no residues (<0.05 mg/kg) were detected in the harvested maize.

The German registration for glufosinate-ammonium on tolerant maize allows a single application of 0.9 kg ai/ha during the 3-8 leaf growth stage or 2 applications 6 weeks apart at 0.45 kg ai/ha with the final application at the 8-leaf stage. Residues were below the LOD (0.05 mg/kg) in 13 trials in Germany where the trial conditions (2 applications of 0.45-0.60 kg ai/ha, the second at GS 18

or GS 19, i.e. 8 or 9 leaves) were considered to comply with the registered use, 22 trials in France in accord with German GAP, and in 5 trials in Germany and 7 in France where glufosinate-ammonium was used at excessive rates (2 applications of 0.80 kg ai/ha).

Glufosinate-ammonium is registered for use in the USA on tolerant maize with 2 applications at 0.23-0.41 kg ai/ha, the second at a plant height of 60 cm with harvest 70 days later. Supervised trials on maize in the USA at rates of 0.40-0.50 kg ai/ha (1 or 2 applications) at the nominated growth stage were accepted as equivalent to the maximum GAP. The PHI (70 days) was considered secondary to the growth stage in deciding the timing of the applications. In many cases the grain was harvested 90-120 days after the final treatment. The residues (glufosinate + NAG + MPP expressed as glufosinate) in the 35 trials according to GAP were <0.05 (29), 0.05 (2) and 0.07 (4) mg/kg.

In summary, the residues of glufosinate + NAG + MPP expressed as glufosinate in tolerant maize were Canada <0.05 (14) mg/kg, Italy <0.05 (7) mg/kg, Spain <0.05 (3) mg/kg, Germany <0.05 (18) mg/kg, France <0.05 (29) mg/kg, the USA <0.05 (29), 0.05 (2) and 0.07 (4) mg/kg. The residues in rank order were <0.05 (100), 0.05 (2) and 0.07 (4) mg/kg.

The Meeting estimated a maximum residue level of 0.1 mg/kg for glufosinate in maize and noted that this was equivalent to the existing CXL. The major residue in the glufosinate-tolerant crop is NAG, which is not included in the current residue definition. NAG was included in the reported residues where the derivatization GLC procedure without an ion-exchange separation step was used, and was below the LOD when determined separately.

Glufosinate is registered for use on transgenic glufosinate-tolerant canola in Canada with 1 application at 0.60 kg ai/ha or 2 applications of 0.30-0.50 kg ai/ha, the final application at the early bolting growth stage. The label carries the instruction not to graze the treated crop or cut for hay. The Meeting was informed that the 10 leaves stage is very close to bolting. Only two supervised trials in Canada met the condition of final treatment at the 10-leaf stage, each with 1 application of 0.5 or 0.75 kg ai/ha. Residues were not detected (<0.05 mg/kg) in either of the trials, but 2 trials were insufficient to support a recommendation.

Glufosinate-ammonium is registered for use in the USA on tolerant soya beans with 2 applications at 0.23-0.41 kg ai/ha, the second application at bloom with harvest 70 days later. Supervised trials on soya beans in the USA with 2 applications of 0.40-0.50 kg ai/ha at the nominated growth stage were accepted as equivalent to the maximum GAP. The PHI (70 days) was considered as secondary to the growth stage in deciding the timing of the applications. In the trials the grain was harvested 62-102 days after the final treatment. The residues of glufosinate + NAG + MPP expressed as glufosinate in the 20 trials according to GAP in rank order (median underlined) were 0.32, 0.39, 0.43, 0.52, 0.56, 0.71, 0.72, 0.78, 0.81, 0.85, 0.89, 0.92, 0.96, 1.02, 1.24, 1.26, 1.33, 1.56, 1.64 and 1.88 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg for soya beans but could not recommend it as suitable for use as an MRL until the toxicological evaluation of NAG had been completed.

Residues in almond hulls from 3 trials on almonds at the label rate and 3 at twice that rate (see above) were all <0.5 mg/kg. Unfortunately, residues in the hulls were not determined in the 2 trials where MPP was detected in the almonds. However, the Meeting estimated a maximum residue level of 0.5 mg/kg for almond hulls, which is recommended for use as an MRL.

The registered use of glufosinate-ammonium on tolerant maize in the USA (see above) specifies pre-harvest intervals of 60 and 70 days for maize forage and fodder respectively. The supervised trials on maize in the USA described above, which complied with GAP, showed residues

of glufosinate + NAG + MPP expressed as glufosinate in the forage or silage harvested 60-92 days after treatment (the residue is reasonably persistent) in rank order, median underlined, of 0.09, 0.12, 0.12, 0.13, 0.17, 0.2, 0.26, 0.28, 0.3, 0.32, 0.33, 0.33, 0.36, 0.4, 0.48, 0.53, 0.53, 0.54, 0.54, 0.68, 0.74, 0.78, 0.78, 0.79, 0.9, 1.07, 1.1, 1.19, 1.2, 1.45, 1.67, 1.7, 1.71, 1.76, 2.9 and 3.48 mg/kg.

The residues of glufosinate + NAG + MPP expressed as glufosinate in maize fodder harvested 84-122 days after treatment were 0.07, 0.08, 0.11, 0.12, 0.15, 0.22, 0.25, 0.25, 0.32, 0.33, 0.43, 0.5, 0.53, 0.58, 0.65, 0.68, 0.69, 0.72, 0.8, 0.94, 0.95, 1.13, 1.19, 1.32, 1.42, 1.5, 1.69, 1.74, 1.76, 1.78, 1.96, 2.31, 2.65, 2.83 and 5.4 mg/kg.

The Meeting estimated maximum residue levels of 5 mg/kg in maize forage and 10 mg/kg in maize fodder but could not recommend them as suitable for use as MRLs until the toxicological evaluation of NAG had been completed.

Feeding studies on lactating dairy cows and laying hens were reported.

Lactating dairy cows were dosed with glufosinate-ammonium + NAG (15 + 85% to simulate the typical terminal residue) at rates equivalent to 9, 27 and 91 ppm glufosinate free acid equivalents in the diet for 28 days. Residues were not detected in the milk at the 9 ppm feeding level, but reached a plateau on day 3 at the 91 ppm level. Residues (glufosinate, NAG and MPP) in the tissues were below the LODs at the lower feeding levels; at 91 ppm they were detected in the kidneys and liver, but not in muscle or fat. MPP was the major residue in the liver.

Laying hens were dosed with glufosinate-ammonium + NAG (15 + 85) at levels equivalent to 0.36, 1.1 and 3.6 ppm glufosinate free acid equivalents in the diet for 28 days. Residues (glufosinate, NAG and MPP) were not detected in the tissues or eggs.

Studies on the fate of residues during the commercial food processing of sugar beet, maize, soya beans and canola were reported.

When tolerant sugar beet were treated with glufosinate-ammonium and processed, residues of glufosinate, NAG and MPP tended to remain in the juice and ultimately appear in the molasses. Residues were not detected (<0.05 mg/kg) in the raw sugar. The processing factors for glufosinate + NAG for raw sugar in 3 trials were nominally 0 (<0.17), 0 (<0.83) and 0 (<0.05) on the basis of the residues in the roots. The mean processing factor for molasses was 6.8, showing that glufosinate residues are concentrated in the molasses on evaporation of the water. In another study on sugar beet with fivefold application rates MPP was the main residue component and again no residues were detected in the raw sugar. The calculated processing factors were 0 (<0.08) for refined sugar and 6.4 for molasses.

In 2 processing trials (wet and dry milling) of glufosinate-tolerant maize treated with excessive rates of glufosinate-ammonium, only NAG was quantifiable in the grain from only one trial. In this trial no residues (<0.05 mg/kg) were detected in crude or refined oil from either process or in the starch and hulls from the wet milling process. The estimated processing factors were meal 1, grits 1, and hulls 2, all from dry milling.

Residues of glufosinate, NAG and MPP were not detected (<0.05 mg/kg) in refined or crude oil in a processing study with a transgenic soya bean crop treated with glufosinate-ammonium at a fivefold rate. The calculated factors for processing seed to meal and seed to crude or refined oil are 1.3 and 0 (<0.3) respectively.

Glufosinate itself was not detected in the seed or any processed fraction of a transgenic canola crop treated at a fourfold rate with glufosinate-ammonium. The main residue was NAG. The

calculated processing factor for untoasted meal was 3.1 and for toasted meal 3.7. No residues (<0.05 mg/kg) were detected in the oils.

Information was made available to the Meeting on national MRLs. Governments have adopted a variety of residue definitions.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and for the estimation dietary intake: sum of glufosinate-ammonium and 3-[hydroxy(methyl)phosphinoyl]propionic acid calculated as glufosinate (free acid)

Commodity		Recommended MRL, mg/kg		STMR
CCN	Name	New	Previous	
FI 0030	Assorted tropical and sub-tropical fruits - inedible peel[1]	0.05*	-	0.05
FI 0341	Kiwifruit	W[2]	0.05*	
TN 0085	Tree nuts	0.1	-	0.05
AM 0660	Almond hulls	0.5	-	

[1]Except Banana
[2]Replaced by recommendation for group MRL
*At or about the limit of determination.

DIETARY RISK ASSESSMENT

Estimated STMRs for glufosinate-ammonium on tropical fruit and tree nuts have been added to the previous list of MRLs (21) for other commodities. The estimated dietary intakes of glufosinate-ammonium expressed as glufosinate for the 5 GEMS/Food regional diets were in the range of 3 to 10% of the ADI. The Meeting concluded that the intake of residues of glufosinate-ammonium resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

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A35708 Asshauer and Krebs 1987c
A35709 Asshauer and Krebs 1987d
A35710 Asshauer and Krebs 1987e
A35711 Asshauer and Krebs 1987f
A35794 Idstein, Pleines and Junker 1987b
A35935 Dorn and Krebs 1987a
A35936 Dorn and Krebs 1987b
A35937 Dorn and Krebs 1987c
A35938 Dorn and Krebs 1987d
A35939 Dorn and Krebs 1987e
A35957 Idstein, Pleines and Junker 1987a
A36196 Idstein and Klapper 1987
A38447 Sochor, Mainzer and Junker 1987b
A39229 Schuld 1988
A39283 Idstein and Klapper 1988
A39949 Sochor, Mainzer and Junker 1988
A40790 Czarnecki, Sochor, Kwiatkoski and Barry 1989
A41452 Stumpf, Schink and Schmidt 1989
A43485 Sochor and Schuld 1990
A44130 Sochor, Klapper and Junker 1987a
A46786 Sochor, Uhl and Junker 1991
A48381 Stumpf and Schink 1992
A48446 Horton and Kuhner 1988
A49978 Kellner Stumpf and Braun 1993
A50427 Stumpf 1993a
A51529 Tshabalala A. 1993
A51762 Stumpf 1993b
A52270 Czarnecki and Bertrand 1993
A53136 Stumpf 1994a
A53137 Stumpf 1994b
A53141 Thalacker 1994
A53473 Stumpf, Schmidt, Schink, Kuenzler and Dambach 1995a
A53474 Stumpf, Schink and Schmidt 1995b
A53536 Burnett 1994
A53606 Czarnecki, Rickard and Bertrand 1994a
A53607 Rupprecht and Smith 1994
A53607 Rupprecht, Dacus, Daniel, Singer, Stumpf and Smith 1996b
A53623 Bertrand 1994
A53624 Czarnecki, Rickard and Bertrand 1994b
A53624. Rickard 1994
A53690 Brady, Belcher, and Bertrand 1994
A53691 Czarnecki, Belcher, Norby and Bertrand 1994
A53696 Castro and Dacus 1994
A53770 Bertrand 1993
A53974 Czarnecki 1995b
A54051 Czarnecki and Bertrand 1994
A54108 Brady 1995c
A54155 Huang and Smith 1995b
A54155 Krautter 1995a
A54156 Brady 1995d
A54157 Huang and Smith 1995d
A54157 Krautter 1995b
A54158 Huang and Smith 1995a
A54159 Ampofo 1995
A54159 Huang and Smith 1995c
A54160 Brady 1995a
A54160 Czarnecki 1995d
A54161 Czarnecki 1995a
A54225 Kalter and Holzwarth 1995a
A54226 Kalter and Holzwarth 1995b
A54227 Kalter and Holzwarth 1995e
A54227 Niedzwiadek and Bertrand 1995a
A54228 Kalter and Holzwarth 1995f
A54229 Kalter and Holzwarth 1995c
A54229 Snowdon and Taylor 1995a
A54230 Kalter and Holzwarth 1995d
A54249 Holzwarth 1995
A54272 Meyer, Tull and Rupprecht 1995
A54283 Brady 1995e
A54284 Brady 1995b
A54333 Lauck-Birkel 1995a
A54334 Lauck-Birkel 1995b
A54336 Lauck-Birkel 1996
A54356 Zumdick 1995a
A54485 Crotts and McKinney 1995
A54485 Czarnecki and Brady 1995a
A54485 Helsten 1995
A54503 Czarnecki and Brady 1995b
A54528 Zumdick 1995b
A54760 Hees and Holzwarth 1996
A54760 Niedzwiadek and Bertrand 1996
A55062 Stumpf, Schink and Schmidt 1995c
A55104 Stumpf, Schink, and Schmidt 1995d
A55207 Bertrand 1996
A55211 Snowdon and Taylor 1995b
A55259 Niedzwiadek and Bertrand 1995b
A55305 Belcher 1995b
A55306 Belcher 1995a
A55393 Allan 1995
A55780 Brady 1996
A55793 Czarnecki 1996
A55807 Belcher 1996b
A55809 Rupprecht, Dacus, Daniel, Singer, Stumpf and Smith 1996b
A55823 Belcher 1996a
A55839 Brady 1997b
A55843 Crotts and McKinney 1996
A56386 MacDonald 1996a
A56392 MacDonald 1996b
A56394 MacDonald 1996c
A56405 Holzwarth 1996a
A56406 Holzwarth 1996b
A56444 Hees, Holzwarth and Werner 1996c
A56445 Hees, Holzwarth and Werner 1996b
A56446 Hees, Holzwarth and Werner 1996a
A56615 Holzwarth 1996c
A56812 Köcher and Becker 1991
A56922 Czarnecki 1995c
A57294 Sochor and SonderH. 1996b
A57295 Sochor and SonderH. 1996a
A57414 Sochor and SonderH. 1996c
A57415 Sochor and Sonder 1996d
A57514 MacDonald 1996d
A57574 Hees, and Werner 1997d
A57701 McKinney and Crotts 1997
A57723 Brady and Bertrand 1997
A57723 Englar 1997
A57728 Brady 1997a
A57730 Greenhalgh and Bertrand 1997
A57840 Campbell and Bennett 1997
A57955 Hees and Werner 1997c
A58109 Allan 1996
A58190 Hees and Werner 1997a
A58191 Hees and Werner 1997b
A58659 Bremmer and Leist 1997
A58845 Werner 1997a
A59025 Biffin 1995a
A59025 Mai 1996b
A59026 Biffin 1996a

A59026 Mai 1996c
A59027 Dunmall, T. 1991a
A59027 Shields 1991a
A59028 Biffin 1995d
A59028 Mai 1996e
A59029 Biffin 1995b
A59029 Mai 1996f
A59030 Dunmall, T. 1991b
A59030 Shields 1991b
A59031 Dunmall, T. 1992
A59032 Biffin 1995c
A59116 Werner 1997c
A59282 Clarke 1997
A59282 Shields and Mai 1997a
A59283 Anderson 1997
A59283 Shields and Mai 1997b
A59284 Cross 1997
A59284 Shields and Mai 1997d
A59285 Biffin 1996b
A59285 Mai 1996d
A59311 Hulme and Rouch 1997
A59311 Shields and Mai 1997c
A59403 Werner 1997b
A59404 Werner 1997d
A59802 Holzwarth 1997a
A59803 Holzwarth 1997b
A59805 Holzwarth 1997c
A600/U012B Meyer, Tull and Rupprecht 1995
A67420 Bremmer and Leist 1998
ACI96-35 MacDonald 1996d
AE-24 Czarnecki and Bertrand 1994
AL019/89-1 Sochor, Uhl and Junker 1991
AL2/87 Idstein, Pleines and Junker 1987a
AL32/88-0 Schuld 1988
AL35/88-0 Sochor, Mainzer and Junker 1988
AL37/87 Sochor, Klapper and Junker 1987a
AL40/87 Sochor, Mainzer and Junker 1987b
AL9/87 Idstein, Pleines and Junker 1987b
AL9/89-0 Czarnecki, Sochor, Kwiatkoski and Barry 1989
AU NW 06 Hulme and Rouch 1997
AU NW 06 Shields and Mai 1997c
AU SA 17/97 Shields and Mai 1997b
AU VN 12 Cross 1997
AU VN 12 Shields and Mai 1997d
AU WA 09 Shields and Mai 1997a
AUQD1/92 Dunmall, T. 1992
AUQD12/94 Biffin 1995b
AUQD13/94 Biffin 1995d
AUQD20/94 Biffin 1995c
AUQD21/90 Dunmall, T. 1991b
AUQD24/94 Biffin 1995a
AUQD25 Biffin 1996b
AUQD26/96 Biffin 1996a
AUQD27/90 Dunmall, T. 1991a
AUWA09 Clarke 1997
BK/01/95 Czarnecki 1995a
BK/03/95 Czarnecki 1995b
BK/05/95 Czarnecki 1995c
BK-94R-01 Brady 1995a
BK-94R-01 Czarnecki 1995d
BK-94R-02 Brady 1995d
BK-94R-03 Brady 1995b
BK-94R-03 Czarnecki 1996
BK-94R-04 Brady 1995e
BK-94R-05 Castro and Dacus 1994
BK-94R-06 Brady 1995c
BK-94R-08 Crotts and McKinney 1995
BK-94R-08 EN-CAS Czarnecki and Brady 1995a
BK-94R-08 Helsten 1995
BK-94R-08 McKinney and Crotts 1997
BK-94R-09 Crotts and McKinney 1996
BK-94R-09 Czarnecki and Brady 1995b
BK95R009 Campbell and Bennett 1997
BK95R01 Brady 1997a
BK-95R-04 Brady 1996
BK-95R-06 Brady 1997b
BK-96R-01 Greenhalgh and Bertrand 1997
BK-96R-05 Brady and Bertrand 1997
BK-96R-05 Englar 1997
C000151 Stumpf and Zumdick 1998
CB093/88 Stumpf, Schink, and Schmidt 1995d
CB88/093 Stumpf, Schink, and Schmidt 1995d
CB89/121 Stumpf, Schink and Schmidt 1989
CB90/109 Stumpf 1994a
CB90/109 Stumpf 1994b
CB91/061 Stumpf, Schink and Schmidt 1995c
CB91/089 Stumpf and Schink 1992
CB91/091 Stumpf 1993b
CB93/016 Zumdick 1995a
CB93/027 Allan 1995
CB94/008 Zumdick 1995b
CM90/042 Stumpf, Schink and Schmidt 1995b
CM90/042 Stumpf, Schink and Schmidt 1995b
CM90/043 Stumpf, Schmidt, Schink, Kuenzler and Dambach 1995a
CM93/070 Lauck-Birkel 1995a
CM93/071 Lauck-Birkel 1995b
CM95/013 Lauck-Birkel 1996
CM95/035 Allan 1996
CR 099/87 Sochor and Schuld 1990
CR037/86 Idstein and Klapper 1987
CR037/86 Idstein and Klapper 1988
CR94/006 Holzwarth 1996b
CR94/009 Werner 1997a
CR94/010 Werner 1997c
CR94/014 Werner 1997b
CR94/016 Holzwarth 1996a
CR95/023 Werner 1997d
CR96/003 Holzwarth 1996c
EN-CAS 94-0053 Helsten 1995
ER 96 ECN 551 Zietz and Simpson 1997
ER-93—01 Belcher 1996b
ER-93—02 Belcher 1995b
ER93ECN550 Kalter and Holzwarth 1995a
ER93ECN552 Kalter and Holzwarth 1995e
ER93ECN552 Niedzwiadek and Bertrand 1995a
ER93ECN553 Kalter and Holzwarth 1995f
ER93ECS550 Kalter and Holzwarth 1995b
ER-93-USA-01 Czarnecki, Belcher, Norby and Bertrand 1994
ER-93-USA-01 Brady, Belcher, and Bertrand 1994
ER-93-USA-02 Czarnecki, Rickard and Bertrand 1994a
ER-93-USA-02 Czarnecki, Rickard and Bertrand 1994b
ER-93-USA-02-AR-01 Rickard 1994
ER-93-USA-02-IA-01 Rickard 1994
ER-93-USA-02-IL-01 Rickard 1994
ER-93-USA-02-IN-01 Rickard 1994
ER-93-USA-02-IN-02 Rickard 1994
ER-93-USA-02-MO-01 Rickard 1994
ER-93-USA-02-MS-01 Rickard 1994
ER-93-USA-02-VA-01 Rickard 1994
ER94ECN550 Kalter and Holzwarth 1995c

ER94ECN550 Snowdon and Taylor 1995a
ER94ECN553 Hees, Holzwarth and Werner 1996c
ER94ECS550 Kalter and Holzwarth 1995d
ER95ARG001010102 Sochor and Sonder 1996d
ER95ECN550 Hees, Holzwarth and Werner 1996b
ER95ECN555 Hees, Holzwarth and Werner 1996a
ER95ECS550 Hees and Holzwarth 1996
ER95ECS550 Niedzwiadek and Bertrand 1996
ER95MYS880/BBA Sochor and SonderH. 1996a
ER95MYS880/BBA Sochor and SonderH. 1996b
ER96ARG001010102 Sochor and SonderH. 1996c
ER96ECN550 Hees and Werner 1997b
ER96ECN551 Hees, and Werner 1997d
ER96ECN553 Hees and Werner 1997c
ER96ECS550 Hees and Werner 1997a
HRAV-5A Czarnecki and Bertrand 1993
HRAV-5A Czarnecki, Sochor, Kwiatkoski and Barry 1989
HRAV93-0006 Czarnecki, Belcher, Norby and Bertrand 1994
HRAV93-0006 Brady, Belcher, and Bertrand 1994
HRAV93-0007 Czarnecki, Rickard and Bertrand 1994a
HRAV93-0007 Czarnecki, Rickard and Bertrand 1994b
HWI 6187-155 Ampofo 1995
HWI6408-100 Thalacker 1994
HWI6408-100 Tshabalala A. 1993
IF 96/24716-00 Zietz and Simpson 1997
ITA85H00601 Dorn and Krebs 1987a
ITA85H00602 Dorn and Krebs 1987b
ITA85H00603 Dorn and Krebs 1987c
ITA85H00604 Dorn and Krebs 1987d
ITA85H00605 Dorn and Krebs 1987e
Kö/ru5/1991 Köcher and Becker 1991
OE93/033 Stumpf 1993a
OE95/036 Holzwarth 1995
OE97/062 Holzwarth 1997c
OE97/066 Holzwarth 1997a
OE97/087 Holzwarth 1997b
PSR98/024 Stumpf and Zumdick 1998
PTRL 1613 Krautter 1995a
PTRL 1637 Krautter 1995b
QD1/92 Dunmall, T. 1992
QD12-94 Mai 1996f
QD13-94 Mai 1996e
QD20-94 Mai 1996a
QD21/90 Dunmall, T. 1991b
QD21/90 Shields 1991b
QD24-95 Mai 1996b
QD25-94 Mai 1996d
QD26-94 Mai 1996c
QD27/90 Dunmall, T. 1991a
QD27/91 Shields 1991a
QDI/92 Shields 1992
R141/U012 Brady 1997b
R142/U012C Greenhalgh and Bertrand 1997
RESID/95/29 Snowdon and Taylor 1995a
RESID/95/31 Snowdon and Taylor 1995b
TOX97/014 Bremmer and Leist 1997
TOX98/027 Bremmer and Leist 1998
U012A/A524 Huang and Smith 1995b
U012A/A524 Krautter 1995a
U012A/A524R Huang and Smith 1995a
U012A/A525 Huang and Smith 1995d
U012A/A525 Krautter 1995b
U012A/A525R Ampofo 1995
U012A/A525R Huang and Smith 1995c
U012B/R143 Brady 1996
VV-99730 Stumpf 1993a
XEN93-09 Bertrand 1993
XEN93-19A Bertrand 1994
XEN93-32 Belcher 1996b
XEN94-13 Belcher 1995a
XEN94-14 Belcher 1995b
XEN94-32 Bertrand 1996
XEN95-07 Niedzwiadek and Bertrand 1995b
XEN95-07A Niedzwiadek and Bertrand 1995a
XEN95-14A Niedzwiadek and Bertrand 1996
YH94AA Biffin 1995a
YH94AA Biffin 1995b
YH94AA Biffin 1995c
YH94AA Biffin 1995d
YH94AA Biffin 1996a

HEXYTHIAZOX (176)

EXPLANATION

Hexythiazox was evaluated by the JMPR in 1991 and 1994. The 28th Session of the CCPR (ALINORM 97/24, 1996, para 75) was informed that data for hexythiazox on hops would become available for a future evaluation and hexythiazox was scheduled for a residue evaluation in 1998.

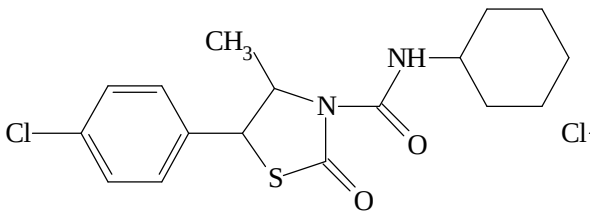
Information on methods of analysis, registered uses, supervised residue trials on hops, processing studies on hops and national MRLs was made available by two basic manufacturers. New information on the use pattern and national MRLs was provided by The Netherlands, Poland and Germany. Summary sheets for hexythiazox residue trials on apples and black currants were provided by Poland; the trials have already been evaluated by the 1994 JMPR.

METHODS OF RESIDUE ANALYSIS

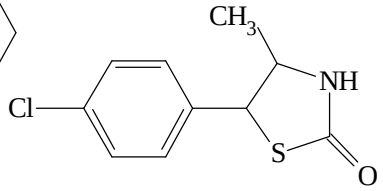
Tilting (1994) described analytical method 343 used for residue analysis in the German supervised trials and processing trials on hops. The method was tested and validated for a range of substrates including soil, beer, brewing wastes, yeast, apple, strawberry, green hops and dry hops.

Residues were extracted from solid substrates with methanol. Beer was mixed with calcium hydroxide and acetone before filtration through Celite. The sample extract was diluted with sodium chloride solution and the residues were extracted into hexane and dichloromethane. Column clean-up was effected on a Florisil-charcoal column. The residue from the evaporated eluate was taken up in hexane + acetone (9+1) for GLC with an NPD where the injection port temperature was 300°C. Hexythiazox and metabolites containing the 5-(4-chlorophenyl)-4-methylthiazolidin-2-one moiety are converted to PT 1-3 in the injector.

Comparison with PT 1-3 standards showed that on injection into the hot injector port the mean conversion of hexythiazox to PT 1-3 was 99% (CV 6.6%).



Hexythiazox



Reference substance PT 1-3

Recoveries from spiked samples established that the method was acceptable with the following LODs: beer, brewing wastes and fruit 0.05 mg/kg, green hops 0.1 mg/kg, and dried hops 0.5 mg/kg.

The 1991 JMPR reported that hexythiazox is the main residue in crops and its metabolites are present in negligible amounts. The residues determined by this “total residue” method may therefore be accepted as equivalent to residues of hexythiazox, the current definition of the residue.

Tilting (1995) validated method 343/1 (method 343 with an added GPC clean-up) for dried hops (LOD 0.5 mg/kg). Hexythiazox metabolites PT 1-3, PT 1-8 (the 4-hydroxycyclohexyl) and PT 1-9 (4-oxocyclohexyl metabolite) were determined by the method with satisfactory recoveries at 2

mg/kg on dry hops. The structures of the metabolites are shown in Figure 1 of the 1991 JMPR Residue Evaluations (page 462).

Williams (1996), in examining the specificity of the hexythiazox method, tested the GLC behaviour in method 343/1 of 26 pesticides registered in the USA for use on hops and found that only one, triforine, had potential interference. As triforine is removed by the Florisil-charcoal column it would not interfere.

Fomenko (1997) tested the behaviour of the hexythiazox metabolites PT 1-2 (5-(4-chlorophenyl)-4-methyl-2-oxothiazolidine-3-carboxamide), PT 1-4 (3-hydroxycyclohexyl metabolite) and PT 1-8 through the US FDA multi-residue methods. The compounds were eluted through DB-1, DB-17 and DB-225 columns with a good response on an ECD, but not on other detectors. The compounds were not recoverable from the Florisil column clean-up required before GLC analysis with an ECD, so the metabolites cannot be determined by the current FDA multi-residue methods.

Mckinney and Tomkinson (1995) described the analytical method (ENC-8/98) used in the US hexythiazox trials on hops. Hops samples were extracted with methanol-water and an aliquot of the extract was evaporated before the addition of dilute hydrochloric acid and sodium chloride followed by partition of the residues into dichloromethane. The residue was hydrolysed in 0.1M NaOH at 60°C for 30 minutes. After further partitioning, the residue was further cleaned up on a small C-18 column and a Celite activated charcoal column for determination by HPLC. An LOD of 0.1 mg/kg was achieved for dry hops. The mean and range of recoveries in 10 tests on hops were 76% and 62-87% respectively.

The hops from the Japanese trials were analysed by method RD-8808 (Soeda *et al*, 1988). Hops were extracted with a methanol-water mixture and the filtered extract was diluted with water and sodium chloride before extraction with hexane. The hexane layer was washed with a mixture of sodium chloride and sodium hydroxide mixture and the residues were extracted from the hexane into acetonitrile. Clean-up was effected on a C-18 Sep-pak and a Florisil column. Residues were then determined by HPLC on a reversed phase system with UV detection at 225 nm. An LOD of 0.2 mg/kg was achieved.

Stability of pesticide residues in stored analytical samples

The stability of hexythiazox residues in hops was tested by analysis of a sample stored for 3 days (15.0, 13.1 mg/kg) and 40 days (15.6, 11.4 mg/kg) at -30°C (Nippon Soda, 1994). The test provides some evidence of storage stability for 30-40 days.

The 1991 residue evaluation provides information on the stability of hexythiazox residues in various samples during frozen storage up to 6 months. No information was available on the stability of hexythiazox in hops during storage for 15 months.

Tilting (1998) tested the stability of hexythiazox residues in hops stored at –20°C and beer refrigerated at 4°C for 2 years. Residues were stable for the duration of the study in hops, but decreased by approximately half in beer (Table 1).

Table 1. Storage stability of hexythiazox in hops and beer (Tilting, 1998). Duplicate samples were analysed at each time and results are expressed as mg hexythiazox per kg sample.

Days	Green hops	Dried hops	Days	Spent hops	Beer

Days	Green hops		Dried hops		Days	Spent hops		Beer	
0	4.5	4.3	5.5	5.0	0	3.6	3.1	0.27	0.28
13	4.1	3.8	4.0	4.1	14	4.4	5.0	0.45	0.48
31	3.9	4.1	5.4	8.1 ✐	30	4.4	4.2	0.37	0.37
74	4.5	4.6	4.3	3.9	71	3.8	3.1	0.37	0.33
119-120	3.3	3.2	3.8	3.2	134	3.7	4.1	0.52	0.49
178	4.0	3.9	3.2	3.0	180	3.8	3.7	0.34	0.36
361	3.6	3.5	3.6	3.6	365	3.3	<0.05 ✐	0.27	0.24
538	7.2 ✐	5.5	<0.05 ✐	<0.05 ✐	538	4.5	4.9	0.43	0.32
741	4.9	4.7	4.3	5.0	755	5.2	5.6	0.19	0.21
					799			0.15	0.22

✐ aberrant result.

USE PATTERN

Hexythiazox is an acaricide used on fruit, vegetables and hops. The Meeting was provided with additional information on registered uses (Table 2).

Table 2. Registered uses of hexythiazox.

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Apples	Netherlands	WP	foliar spray	0.060	0.004	2	28
Apples	USA	WP	foliar spray	0.21		1	GS 3/
Aubergines	Netherlands	WP	foliar spray	0.025-0.075	0.005	1 g	3
Beans	Netherlands	WP	foliar spray	0.004-0.016	0.002	1	3
Blackberries	Netherlands	WP	foliar spray	0.050-0.060	0.005	1	-
Cherries	Netherlands	WP	foliar spray	0.060	0.004	2	28
Courgette	Netherlands	WP	foliar spray	0.025-0.075	0.005	1 g	3
Courgette	Netherlands	WP	foliar spray	0.020-0.040	0.005	1	3
Cucumber	Germany 5/	WP	foliar spray	0.03-0.06		2	3
Cucumber	Netherlands	WP	foliar spray	0.025-0.075	0.005	1 g	3
Cucumber	Poland	EC	high vol	0.01-0.06	0.003	g	3
Cucumber	Poland	EC WP	high vol	0.1-0.2	0.01		3
Currants	Poland	EC	high vol	0.04	0.004-0.005		14
Currants red black	Netherlands	WP	foliar spray	0.050-0.060	0.005	1	14
Eggplant	Poland	EC	high vol	0.01-0.06	0.003	g	3
Eggplant	Poland	EC WP	high vol	0.1-0.2	0.01		3
Filbert	Poland	EC WP	high vol	0.04-0.075	0.004-0.015		30
Fruit trees	Poland	EC WP	high vol	0.04-0.075	0.004-0.015		30
Gherkins	Netherlands	WP	foliar spray	0.020-0.040	0.005	1	3
Gherkins	Netherlands	WP	foliar spray	0.025-0.075	0.005	1 g	3
Gooseberries	Netherlands	WP	foliar spray	0.050-0.060	0.005	1	14
Grapes	Germany 5/	WP	foliar spray		0.004	1	28
Hops	Germany 5/	WP	foliar spray	1/	0.003	2	28
Hops	Germany 5/	WP	foliar mist LV	2/	0.0045	2	28
Hops	Japan 5/	WP	spray	0.20-0.30	0.0033-0.005	2	7
Hops	USA 6/	WP	foliar spray	0.21-0.28		1	GS 4/
Melons	Netherlands	WP	foliar spray	0.025-0.075	0.005	1 g	3
Okra	Netherlands	WP	foliar spray	0.025-0.075	0.005	1 g	3
Pears	Netherlands	WP	foliar spray	0.060	0.004	2	28
Pears	USA	WP	foliar spray	0.21-0.42		1	28
Peppers	Poland	EC	high vol	0.01-0.06	0.003	g	3
Peppers	Poland	EC WP	high vol	0.1-0.2	0.01		3
Peppers, chilli	Netherlands	WP	foliar spray	0.025-0.075	0.005	1 g	3
Peppers, sweet	Netherlands	WP	foliar spray	0.025-0.075	0.005	1 g	3

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Plums	Germany 5/	WP	foliar spray		0.004	1	28
Plums	Netherlands	WP	foliar spray	0.060	0.004	2	28
Pome fruits	Germany 5/	WP	foliar spray		0.004	1	28
Raspberries	Netherlands	WP	foliar spray	0.050-0.060	0.005	1	14
Strawberry	Germany 5/	WP	foliar spray		0.004	1	28
Strawberry	Netherlands	WP	foliar spray	0.025-0.050	0.005	1	3
Strawberry	Netherlands	WP	foliar spray	0.030-0.060	0.005	1 g	3
Strawberry	Poland	EC	high vol	0.04	0.004-0.005		14
Tomato	Netherlands	WP	foliar spray	0.025-0.075	0.005	1 g	3
Tomato	Poland	EC	high vol	0.01-0.06	0.003	g	3
Tomato	Poland	EC WP	high vol	0.1-0.2	0.01		3
Winter squash	Netherlands	WP	foliar spray	0.025-0.075	0.005	1 g	3

g: glasshouse use
1/ spray volume 1000-5000 l/ha. Max application rate 0.15 kg ai/ha.
2/ spray volume 700-3300 l/ha. Max application rate 0.15 kg ai/ha.
3/ growth stage - pink bud
4/ growth stage - before burr (cone formation)
5/ label provided
6/ proposed GAP

RESIDUES RESULTING FROM SUPERVISED TRIALS

Supervised residue trials on hops were carried out in Germany, Japan and the USA. The results are shown in Table 3.

Where residues were not detected, results are recorded in the tables as below the limit of determination (LOD), e.g. <0.1 mg/kg. Residue data, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure. Although all trials included control plots, no control results are recorded in the tables because residues in control samples did not exceed the LOD. Residues are recorded uncorrected for recovery. Recovery values were mainly in the range of 60-110%.

Hexythiazox was applied by mistblower to plots of approximately 390 m^2 in the hops trials in Germany in 1992. Samples of 0.5-1 kg were stored for about 470 days (1992 trials) and 180 days (1993 trials) before analysis. A mistblower was also used in the trials in 1993 where plot sizes were 27-36 m^2 . In trials D07/84/93, D07/83/93 and D07/82/93 light rainfall occurred within 45 minutes to 6½ hours after application, which may have reduced residue levels.

Hexythiazox was applied to hops in 50-146 m^2 plots by mist backpack or handgun sprayer in the US trials. Hop cones in the US trials were collected at normal maturity and were dried for 3.5 to 16 hours at 32-65°C, which is normal commercial practice. Samples (1.5 - 3 kg) were stored for 260 days before analysis.

In the Japanese trials the hop flowers were dried by hot air drier just after harvest at 50°C for 1 hour and then at 60°C for 7 hours.

Table 3. Hexythiazox residues in hops resulting from supervised trials in Germany, Japan and the USA. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Country, Year (Variety)	Application				PHI, days	Commodity	Hexythiazox, mg/kg	Ref
	Form	kg ai/ha	kg ai/hl	no.				
Germany 1992 (Perle)	WP	0.16	0.0045	1	0	hop catkins	2.8	D07/85/92
					21	hop catkins	0.95	
					28	hop catkins	0.48	
					35	hop catkins	0.14	
					28	kiln-dried hops	0.93	D07/85/92
					28	beer	<0.05	
					28	spent hops	0.15	
					28	spent hops (dry weight)	0.65	
Germany 1992 (Perle)	WP	0.16	0.0045	1	0	hop catkins	3.3	D07/86/92
					21	hop catkins	1.6	
					28	hop catkins	0.96	
					35	hop catkins	0.35	
					28	kiln-dried hops	1.5	D07/86/92
					28	beer	<0.05	
					28	spent hops	0.18	
					28	spent hops (dry weight)	0.61	
Germany 1992 (Perle)	WP	0.16	0.0045	1	0	hop catkins	3.6	D07/87/92
					21	hop catkins	0.93	
					28	hop catkins	0.53	
					35	hop catkins	0.47	
					28	kiln-dried hops	1.3	D07/87/92
					28	beer	<0.05	
					28	spent hops	0.18	
					28	spent hops (dry weight)	0.53	
Germany 1992 (Perle)	WP	0.16	0.0045	1	0	hop catkins	3.1	D07/88/92
					21	hop catkins	1.1	
					28	hop catkins	0.23	
					35	hop catkins	0.34	
					28	kiln-dried hops	0.88	D07/88/92
					28	beer	<0.05	
					28	spent hops	0.11	
					28	spent hops (dry weight)	0.32	
Germany 1993 (Perle)	WP	0.22	0.0045	1	0	leaves and hop catkins	5.2	D07/82/93
					21	hop catkins	0.11	
					27	hop catkins	0.18	
					35	hop catkins	<0.1	
					27	kiln-dried hops	0.79	
Germany 1993 (Perle)	WP	0.17	0.0045	1	0	leaves and hop catkins	5.8	D07/83/93
					21	hop catkins	<0.1	
					27	hop catkins	0.12	
					35	hop catkins	0.12	
					27	kiln-dried hops	0.71	
Germany 1993 (Northern Brewer)	WP	0.19	0.0045	1	0	leaves and hop catkins	5.5	D07/84/93
					21	hop catkins	<0.1	
					27	hop catkins	0.1	
					35	hop catkins	0.13	
					27	kiln-dried hops	0.64	
Germany 1993 (Northern Brewer)	WP	0.16	0.0045	1	0	leaves and hop catkins	6.4	D07/85/93
					20	hop catkins	0.27	
					27	hop catkins	0.29	
					34	hop catkins	0.13	
					27	kiln-dried hops	0.79	

Country, Year (Variety)	Application				PHI, days	Commodity	Hexythiazox, mg/kg	Ref
	Form	kg ai/ha	kg ai/hl	no.				
Germany 1993 (Magnum)	WP	0.18	0.0045	1	0	leaves and hop catkins	5.8	D07/86/93
					20	hop catkins	0.23	
					27	hop catkins	0.13	
					34	hop catkins	<0.1	
					27	kiln-dried hops	0.61	
Japan (Iwate) 1985 (Shinshyu-wase)	WP	0.35	0.005	2	7	dry hops	14	#94/10371
					14	dry hops	14	
					21	dry hops	5.4	
Japan (Yamagata) 1985 (Kirin 2-gou)	WP	0.25	0.005	2	7	dry hops	16	#94/10371
					14	dry hops	6.6	
					21	dry hops	12	
USA (ID) 1995 (Galena)	WP	0.29	0.030	1 1/	59	dry hops	0.1 <0.1	AA950601
USA (ID) 1995 (Galena)	WP	0.29	0.030	1 2/	45	dry hops	0.34 0.36	AA950601
USA (OR) 1995 (Nugget)	WP	0.29	0.037	1 3/	59	dry hops	0.21 0.20	AA950601
USA (OR) 1995 (Nugget)	WP	0.27	0.037	1 4/	44	dry hops	1.3 0.99	AA950601
USA (WA) 1995 (Galena)	WP	0.25	0.018	1 5/	60	dry hops	1.2 1.9	AA950601
USA (WA) 1995 (Galena)	WP	0.28	0.020	1 5/	45	dry hops	3.5 3.9	AA950601

1/ growth stage: pre-bloom to bloom. Note: hops growth stages are to the wire, lateral shoots, flower formation, burrs and cones.
2/ growth stage: bloom
3/ growth stage: early bloom
4/ growth stage: early burr
5/ growth stage: burr.

FATE OF RESIDUES IN STORAGE AND PROCESSING

The Meeting received information on the fate of hexythiazox residues during the drying of hops and brewing of beer.

Beck and Tilting (1994a) described the standardised procedures for drying hops and brewing beer. The green hops are dried at approximately 65ºC for 7 hours with good air circulation, during which time the moisture content of green hops is reduced from approximately 80% to about 10% (equivalent to a concentration factor of 3.3). The beer production process is shown in Figure 1. The residue data for the dried hops, beer and spent hops are included in the supervised trial results in Table 3.

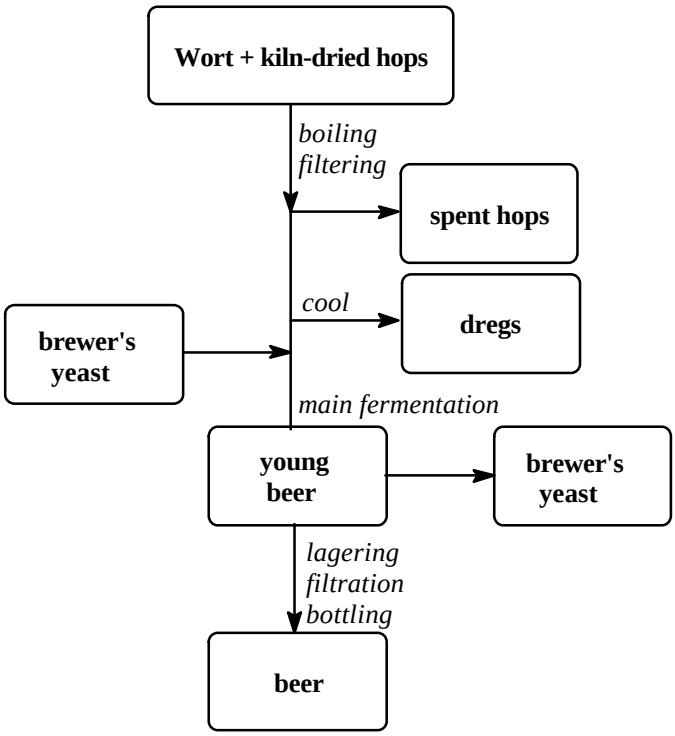


Figure 1. Beer production from wort and kiln-dried hops (Beck and Tilting, 1994a).

Table 4. Residue data and processing factors for hexythiazox in hops. Trial details are shown in Table 3.

	Hexythiazox residues, mg/kg				Processing factors		
Trial	green hops	dry hops	beer	spent hops (dry)	green hops → dry hops	dry hops → beer	dry hops → spent hops
D07/85/92	0.48	0.93	<0.05	0.65	1.9	0 (<0.054)	0.70
D07/86/92	0.96	1.5	<0.05	0.61	1.6	0 (<0.033)	0.41
D07/87/92	0.53	1.3	<0.05	0.53	2.5	0 (<0.038)	0.41
D07/88/92	0.23	0.88	<0.05	0.32	3.8	0 (<0.057)	0.36
D07/82/93	0.181	0.792			4.4		
D07/83/93	0.123	0.708			5.8		
D07/84/93	0.103	0.637			6.2		
D07/85/93	0.288	0.792			2.8		
D07/86/93	0.126	0.614			4.9		
				mean	3.7	0 (<0.046)	0.47
				median	3.8	0 (<0.046)	0.41

The mean processing factor for dry hops is 3.7 (range 1.6-6.2), which is quite close to the value calculated on the assumption of a moisture decrease from 80% to 10% and no loss of hexythiazox. Hexythiazox residues were not detected in beer in the four processing trials, which suggests that very little if any hexythiazox reaches the beer. Approximately half of the hexythiazox on the dry hops before brewing remains on the dry spent hops.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was informed of the following national MRLs for hexythiazox.

Country	MRL, mg/kg	Commodity
Belgium	0.05	apple, pear
France	0.5	beans, pome fruits, wine grapes
	0.2	citrus, maize, other vegetables, peach, plum, other vegetables
Germany	3	hops
	0.5	grapes
	0.2	pome fruits, stone fruits
	0.05	other foods of vegetable origin
Italy	1	apple, kiwifruit, peach
	0.5	cucumber, eggplant, pear, strawberry, sweet pepper
	0.05	soybean
Japan	35	tea
	30	hops
	2	fruit, other vegetables
	0.5	bean, pea, potato
	0.2	sugar beet
Netherlands	0.2	beans (legume vegetables), bilberries, blueberries, cranberries, currants (red, black and white), elderberries, gooseberries, grapes, raspberries
	0.1	fruiting vegetables (aubergines, courgettes, cucumbers, gherkins, melons, okra, peppers, pumpkins, tomatoes, watermelons), strawberries
	0.05	pome fruit
	0.02*	other small fruit
	0* (0.02)	other food commodities
New Zealand	0.5	peach
	0.2	mandarin
Poland	0.5	fruits, vegetables
Spain	1	citrus
	0.5	other fruit, sweet pepper
	0.1	cucurbits
	0.05	other food and feedstuffs of plant origin
Switzerland	0.5	fruit
Taiwan	2	citrus (peel), lemon (peel), grapefruit (peel), orange (peel)
	1	guava, kaki plum, strawberry, table grapes, wax apple, wine grapes
	0.5	apple, citrus (without peel), grapefruit (without peel), lemon (without peel), loquat, orange (without peel), peach, pear, plum
USA	0.3	pear
	0.02	apple

APPRAISAL

Hexythiazox was first evaluated in 1991 and again in 1994. It was scheduled for evaluation by the 1998 JMPR because the 28th Session of the CCPR (1996) was informed that data on hops would be made available (ALINORM 97/24, para 75). The Meeting received information on methods of analysis, registered uses, supervised residue trials and processing studies on hops.

The analytical method used in the supervised trials and processing studies in Germany relies on solvent partition and column chromatography for clean-up. In the GLC determination the residue is injected into a hot injector (300°C) where hexythiazox and its metabolites are converted to 5-(4-chlorophenyl)-4-methylthiazolidin-2-one (PT 1-3) which becomes the analyte. The LODs were 0.05 mg/kg in beer and brewing wastes, 0.1 mg/kg in green hops, and 0.5 mg/kg in dry hops.

The 1991 JMPR reported that hexythiazox is the main residue in crops and its metabolites are present in negligible amounts. The residues determined by this “total residue” method may therefore be accepted as equivalent to residues of hexythiazox, the current definition of the residue.

The method was shown to be free of interference from 26 pesticides registered for use on hops in the USA.

Hexythiazox was hydrolysed with alkali to convert it to PT 1-3 in the analytical method used in the US trials on hops. An LOD of 0.1 mg/kg was achieved for dry hops.

A similar extraction and clean-up was used in the Japanese trials but there was no hydrolysis step and the hexythiazox was determined by HPLC as the parent compound. An LOD of 0.2 mg/kg was achieved.

Hexythiazox residues on green and dry hops were stable during a two-year study of freezer storage stability, but the residues in beer declined by approximately half during refrigerator storage at 4°C for two years.

Hexythiazox is not registered for use on hops in the USA so the US trials could not be evaluated.

GAP for hops in Japan permits 2 applications at 0.0033-0.005 kg ai/hl or 0.2-0.3 kg ai/ha with harvest 7 days after the final application. In two Japanese trials in 1985 where the trial conditions were close to GAP the residues in dry hops were 14 and 16 mg/kg 7 days after the second application.

Hexythiazox is registered for use on hops in Germany where it may be applied at spray concentrations of 0.003-0.0045 kg ai/hl with an application rate not exceeding 0.15 kg ai/ha. Two applications are permitted and a 28 days PHI is specified. Hexythiazox was applied to hops in 9 trials in Germany in 1992 and 1993 following the conditions of German GAP. Only one application was made instead of the possible 2, but the average half-life of the hexythiazox residues in the 1992 trials was 10 days, which suggests that an earlier application would contribute no more than 20% of the final residue and probably much less because the first application would be at an earlier growth stage. The residues in dry hops from the 9 German trials according to GAP in rank order (median underlined) were 0.61, 0.64, 0.71, 0.79, <u>0.79</u>, 0.88, 0.93, 1.3 and 1.5 mg/kg.

The residues in the Japanese trials (14 and 16 mg/kg) could not be combined with those in the German trials because they appeared to be from separate populations. The Meeting considered that 2 trials were insufficient to support an MRL, so the estimated maximum residue level was based on the highest data population with sufficient support, in this case the 9 German trials.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR of 0.88-1.5 mg/kg for hexythiazox in dry hops.

In 4 trials where beer was brewed from dry hops containing hexythiazox residues of 0.88-1.5 mg/kg, no residues (<0.05 mg/kg) were detected in the beer. The level of hexythiazox residues in dry spent hops was approximately half that in the initial dry hops. From 57% to 86% of the hexythiazox residues in the dry hops was accounted for in the spent hops and dregs from the process. Calculation showed that if all the remaining hexythiazox was in the beer, i.e. no losses occurred during boiling and fermentation, the level in the beer would be less than 0.0009 mg/l. The Meeting concluded that the STMR for hexythiazox residues in beer should be 0 mg/kg.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue level for hops is recommended for use as an MRL.

Definition of the residue for compliance with MRLs and for the estimation dietary intake: hexythiazox.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
DH 1100	Hops, dry	2	-	0.79
	Beer			0

DIETARY RISK ASSESSMENT

A maximum residue level for hexythiazox in hops has been recommended for use as an MRL. A processing study has resulted in an estimated STMR level of 0 mg/kg for hexythiazox residues in beer. All the other in values used for the intake estimation are previously established CXLs.

Estimated daily intakes for hexythiazox for the 5 GEMS/Food regional diets are in the range of 0 to 5% of the ADI. The Meeting concluded that the intake of residues of hexythiazox resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

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KRESOXIM-METHYL

[FIGURES 1-13 are reproduced at the end of this monograph]

IDENTITY

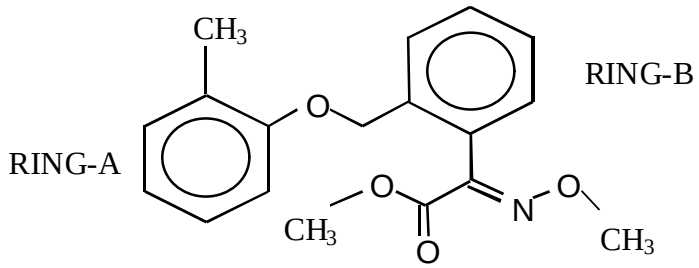
ISO common name: kresoxim-methyl (ISO-proposed).

Chemical name
IUPAC: methyl (*E*)-methoxyimino-[α-(*o*-tolyloxy)-*o*-tolyl]acetate
methyl (*E*)-2-methoxyimino-[2-(*o*-tolyloxymethyl)phenyl]acetate
CA: (*E*)-α-(methoxyimino)-2-[(2-ethylphenoxy)methyl]benzeneacetate

CAS registry no: 143390-89-0

Synonyms: LAB 242 009
BAS 490 F

Structural formula:



Molecular formula: $C_{18}H_{19}NO_4$

Molecular weight: 313.36

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

Physical State: white crystalline solid

Odour: mildly aromatic

Melting point: 101.6-102.5 (99.7% purity).

Boiling point: No boiling or sublimation of kresoxim-methyl up to 310 °C decomposition temperature using OECD method 113.

Relative Density: 1.258 at 20 °C using EEC method A 3.1.4.3

Solubility in water:	kresoxim-methyl (99.4%) 2.00 ± 0.08 mg/l at 20 °C (using EEC method A6) free acid 91 mg/l at 20 °C
Solubility in organic solvents (99.7%, 20°C)	1.7 g/kg in n-heptane 111 g/kg in toluene 939 g/kg in dichloromethane 14.9 g/kg in methanol 217 g/kg in acetone 123 g/kg in ethyl acetate
Vapour pressure:	kresoxim-methyl: 2.3 x 10^{-6} Pa at 20 °C (extrapolated). (*z*)-isomer (490M1): <1 x 10^{-5} Pa
Octanol/water partition coefficient:	kresoxim-methyl (99.4%): log K_{ow} = 3.40 at 25°C free acid: log K_{OW} = 0.15 (pH 7; 20 °C).
Dissociation constant:	kresoxim-methyl: pKa >2 and <12; titration for acidic range by OECD method 112. Dissociation in alkali claimed not to be possible because of structure. free acid: pKa = 4.2 (20 °C).
Surface tension (99.7%)	72.3 mN/m at 20°C. 0.5% (saturated) solution (EEC method A5)

Satisfactory IR, NMR and Mass Spectra of kresoxim-methyl (99.7%) were submitted.

(Binninger, 1995; BASF, 1994; Moult, 1996; Redecker, 1990, 1991; Gückel, 1992a,b; Türk 1994a,b,c; Kröhl, 1994 and Loeffler, 1992).

Technical material

Purity:	91% w/w minimum
Appearance:	light-brown powder
Physical state:	solid

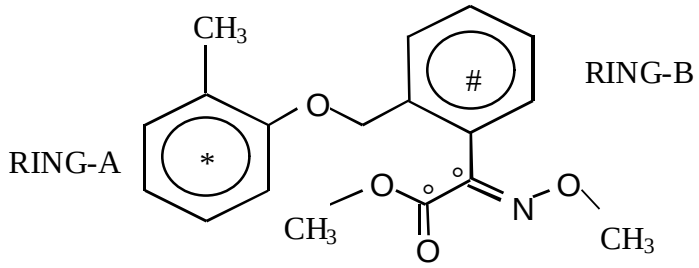
Formulations

Kresoxim-methyl is a broad spectrum fungicide structurally related to Strobilurin A, a natural product of the wood-decaying fungus *Strobilurus tenacellus*. It is a member of a new class of biologically active compounds - the strobilurins. It is formulated as an SC, WG or SE.

METABOLISM AND ENVIRONMENTAL FATE

Radiolabelled test materials

Kresoxim-methyl was labelled in one of three positions shown below.



Key to radiolabel positions:

* [*phenoxy*-U-^{14}C]kresoxim-methyl
\# [*phenyl*-^{14}C]kresoxim-methyl
° [^{13}C]kresoxim-methyl

A single page summary of the metabolism of kresoxim-methyl in animals and plants was submitted (Ammermann *et al.*, 1992) but was not used in the evaluation.

Animal metabolism

Rats. In a series of experiments on male and female Wistar rats (Kohl, 1994) the test substance was administered either orally or intravenously according to the dosing regime detailed in Table 1. Rats from groups A to D were used to determine metabolite patterns in faeces and urine, and those from dosing groups DY (phenyl-labelled) and DX (phenoxy-labelled) were used for the isolation and identification of urinary and faecal metabolites. HPLC was used to resolve the metabolites which were then identified by comparison with HPLC standards, mass spectrometry and NMR.

Table 1. Dose groups used in the metabolism studies on rats each containing 3-10 animals of each sex.

Group	Dose regime
A	Single i.v. dose 5 mg/kg bw (phenyl label). Urine and faeces analysed.
B	Single oral dose 50 mg/kg bw (phenyl label). Urine and faeces analysed.
C	Oral doses 50 mg/kg bw/day (14 daily doses no label, one dose phenyl label). Urine and faeces analysed.
D	Single oral dose 500 mg/kg bw (phenyl label). Urine and faeces analysed.
DX	Single oral dose 500 mg/kg bw (phenyl label, with 30% ^{13}C label on side chain). Urine and faeces analysed.
DY	Single oral dose 500 mg/kg bw (phenoxy label). Urine and faeces analysed.

All major and most minor metabolites were isolated, with a total of 33 metabolites (including conjugates) identified. Code numbers and chemical structures are given in Figure 13, following the section on plant metabolism.

Up to 75% of the oral dose in groups B-D was excreted unchanged in the faeces. No unchanged parent compound was detected 3.5-4 hours after oral dosing in plasma, liver or kidneys, and none was identified in the bile or urine, indicating that kresoxim-methyl is rapidly and completely metabolized after absorption from the G.I. tract.

The metabolite composition in plasma indicates that the ester cleavage, which leads to the free acid 490M1, is the fastest and most important biotransformation step which is assumed to occur

as a first-pass reaction. Accordingly, after intravenous dosing a considerable quantity of unchanged parent compound (16% of the dose) was found in the urine of female rats.

Most of the initially formed 490M1 is further metabolized, mainly by hydroxylation of the aromatic phenoxy ring and the aryl-CH_3 group. Thus, after oral administration, the metabolites 490M2 "alcohol acid", 490M9 "phenol-acid" and their glucuronides were generally the predominant final products in the excreta and in the plasma, liver and kidneys. In female rats these subsequent reactions seem to be less pronounced, since females generally excreted higher proportions of 490M1.

Mainly in males, the cleavage of the benzyl ether bridge contributes to a certain extent to the biotransformation. Fragments containing the phenyl ring were mainly recovered in the form of metabolites 490M6, 490M20, and 490M16. At the highest dose level and in the 14-day study 490M16 became relatively more important in the urine of males than females.

The phenoxy ring is further oxidized to monohydroxybenzyl alcohol, dihydroxybenzyl alcohol and salicylic acid, but these metabolites were found only as the sulfate conjugates (490M41, 490M42, 490M43 and 490M22) in the urine, together with the glucuronide of *o*-cresol, 490M37.

Glucuronated conjugates were detected in notable quantities in the bile, 490M26, 490M33, 490M25, 490M39, 490M29 being found in the largest quantity in the bile of both sexes.

The metabolite patterns in the excreta of groups B and C were qualitatively and quantitatively similar, so it would appear there was no induction of metabolic pathways by pre-dosing with kresoxim-methyl.

On the basis of these observations it is concluded that the phase I biotransformation of kresoxim-methyl is characterized by six metabolic reactions as shown in Figure 1: Cleavage of (1) the ester, (2) the oxime ether and (3) the benzyl ether bonds; (4) hydroxylation of the phenoxy ring *para* to the existing oxygen substituent, (5) oxidation of the aryl-methyl group to the benzyl alcohol and (6) its subsequent oxidation to the corresponding carboxylic acid. The (*E*)-(*Z*)-isomerization of the oxime ether group of the parent molecule is assumed to be a non-enzymatic reaction catalysed by light and/or acids. The combination of these reactions and the conjugation of the hydroxy compounds to form glucuronides or sulfates leads to the observed large number of metabolites.

Goats. In a study in 1991, either [^{13}C]- or [*phenyl*-^{14}C]kresoxim-methyl (radiochemical purity >98% and 94.6-97.6% respectively) was given orally by catheter to two goats (species not reported). Goat A was dosed with ^{14}C-labelled material at 7.1 ppm in the feed for 5 consecutive days. Goat B was dosed with a mixture of ^{13}C and ^{14}C-labelled material corresponding to an average of 450 ppm in the feed. During the dosing period blood, milk, urine and faeces were collected. Goats A and B were slaughtered 23 and 4 hours after the last dose respectively and liver, kidney, muscle, fat, bile and gastrointestinal tract were removed. Milk production appeared not to change significantly throughout the study. The total radioactivity was determined by LSC after combustion. The urine and milk samples were stored for 2 months and tissue samples for 1 month before analysis.

The distribution of radioactivity is shown in Table 2. Milk contained in total 0.031% (goat A) and 0.027% (goat B) of the total radioactivity administered. Goat A excreted 69.5% of the dose in the urine and 18.1% in the faeces, and goat B excreted 59.3% in the urine and 24.5% in the faeces. After slaughter the highest residue (mg/kg parent equivalent) was found in the kidneys and bile. In the low-dose goat A the residues in the milk, muscle and fat were below 0.01 mg/kg. The liver contained 0.038 mg/kg and kidneys 0.142 mg/kg.

Table 2. The distribution of radioactivity in goats dosed with [*phenyl*-^{14}C]kresoxim-methyl.

Sample	Goat A, 7.1 ppm feed		Goat B, 454 ppm feed	
	mg/kg as parent	% of TRR	mg/kg as parent	% of TRR
Milk, individual samples	0.001-0.003	0.001-0.005	0.068-0.316	0-0.004
Milk, total	0.025	0.031	2.74	0.027
Liver	0.04	0.06	6.81	0.07
Kidneys	0.15	0.03	14.04	0.02
Fat	0.001	0.01	0.33	<0.005
Muscle	0.001	0.01	0.22	0.01
Bile	0.49	0.03	146	0.03
Stomach lining	0.06	0.17	11.98	0.25
Stomach contents	0.18	1.09	95	8.90
Intestine lining	0.11	0.23	4.64	0.08
Intestine contents	1.13	3.10	48	1.56
Stomach/intestine cleaning water	0.03	0.09	6.84	0.44
Urine in bladder	2.15	0.91	482	0.26
Urine excreted Total (% of dose)	2.5-5.5	10.3-16.9 69.51	222-713	2.1-11.4 59.31
Faeces excreted Total (% of dose)	0.9-4.9	0.7-5.3 18.08	108-312	0.7-5.7 24.52
Blood	0.01	0.03	1.89	0.05
'Vomited' material (cud)[1]	0.03	<0.005	1.0	0.10
Tray water	0.0	<0.005	0.02	<0.005
Cage cleaning	0.11	1.08	17.63	1.47
TOTAL		94.48		97.10

[1]The report states that this material was collected from the mouth and oesophagus and is considered to be from regurgitation during normal digestion.

The identification of the radioactive compounds in various extracts from the high-dose goat is shown in Table 3. The radioactivity was measured by combustion and LSC. Urine samples were analysed directly by CI-MS, with preparative HPLC in some cases. Faeces samples were extracted with methanol followed by water. Pooled daily milk samples were extracted with methanol, centrifuged and filtered. Methanol was evaporated from the supernatant to leave the aqueous phase. Water and acetone were added and any precipitate was filtered and washed with acetone. The residues were redissolved in acetonitrile /water /formic acid and analysed by HPLC. All other samples were extracted with methanol followed by water, centrifuged and subjected to solvent partition (dichloromethane, hexane/acetonitrile and ethyl acetate separately or in combination). The extracts were further purified by silica and/or preparative HPLC where necessary. The residual precipitates were either incubated with pronase and extracted with HCl (liver) or ammonia (muscle and liver) and further purified by ion exchange or size exclusion chromatography, or were solubilized with Biolute S or toluene. Extracts were analysed by HPLC with a scintillator detector. Identification of compounds in extracts of milk and edible tissues was achieved by chromatographic comparison with extracts of urine.

The extraction of radioactivity by methanol and water ranged from 63% of the TRR in liver to 98% in kidney. The main metabolites were 490M1 (14% of the TRR in liver, 26% in muscle, present in milk), 490M2 (11% in liver, 34% in kidney), and 490M9 (10% in muscle, 63% in milk, present in fat). Minor metabolites identified were 490M6 in fat, liver and kidney, 490M18 in all tissues and 490M19 in muscle and liver. Other radioactive peaks characterized by HPLC accounted for 18% of the TRR in liver, 7% in kidney, 3% in fat, 16% in milk and 3% in muscle.

The three major metabolites were formed by cleavage of the methyl ester bond to yield the free acid 490M1, followed by side-chain hydroxylation to 490M2 and aromatic ring hydroxylation to 490M9. Minor metabolites were generated by cleavage of the oxime ether bond to 490M18, conjugation with glycine to 490M19, a combination of ring hydroxylation and oxime ether cleavage to 490M56, and by cleavage of the phenyl ether bond to 490M6. Ring hydroxylation without ester cleavage resulted in 490M15 which was found in the faeces only (Giese, 1992; Mayer, 1994).

Table 3. Compounds identified in goat tissues, milk and excreta after dosing with [*phenyl*-^{14}C]kresoxim-methyl at a level of 450 ppm in the feed. Levels expressed as mg/kg parent compound.

Sample	Extract	490-M6 mg/kg	490-M2 mg/kg	490-M9 mg/kg	490-M18 mg/kg	490-M19 mg/kg	490-M1 mg/kg	Polar mg/kg	Other extracted mg/kg	Total residual mg/kg
Urine[1]		2.1	31.7	27.7	2.1	0.3	31.5			
Faeces	methanol[2]	3.4	10.8	27.8	1.8	0.8	10.2	4.2	5.4	6.2
Milk	acetone		0.04	0.12			0.003		0.03	0.007
Muscle	EtAc[3]								0.02	
	DCM[4]								0.14	
	Hexane[5]							0.01	0.009	0.06
	ACN[3]		0.03	0.017	0.017	0.015	0.05			
	Residual			0.006			0.005		0.048	
Fat	ACN	0.03	0.08				0.08			0.06
	Hexane		0.006	0.001	0.002		0.004		0.012	
	Residual							0.033	0.04	
Liver	DCM		0.51	1.86			0.84	0.12		2.82
	EtAc		0.03	0.05	0.12					
	water	0.03	0.02	0.03	0.005	0.003	0.01	0.23		
	Residual	0.22	0.13	0.007	0.094	0.02	0.09	1.51		0.75
Kidney	methanol	0.44	4.56	4.04			2.92		0.59	0.28
	DCM								10.05	
	EtAc								1.27	
	water	0.04	0.05				0.03	0.20	0.22	
	Residual		0.007		0.03		0.02	0.19		0.034

[1]Also contained 0.2 mg/kg 490M56
[2]Also contained 12.1 mg/kg 490M15 and 1.3 mg/kg parent
[3]ethyl acetate
[4]dichloromethane
[5]acetonitrile
[6]Also contained 0.024 mg/kg parent

The metabolic pathways of kresoxim-methyl in goats are shown at the end of this monograph in Figure 2.

Hens. In a study carried out in 1992, [*phenyl*-^{14}C]kresoxim-methyl (radiochemical purity >99%) was fed to 5 hens (ISA strain) in six daily doses equivalent to 10 ppm in the feed and to 10 hens at 180 ppm in the feed. The hens were dosed in the morning before feeding but after collecting eggs and excreta. About 3 and 23 h after the final dose for the high- and low-dose groups respectively, samples were taken and stored up to 1 month before analysis. Sub-samples were combusted and analysed by LSC.

From the low dose 88.2% of the total administered radioactivity was recovered, 82.6% of which was excreted, and from the high dose 87% was recovered with 71.55% excreted. About 23 h after the final dose of 10 ppm total radioactive residues of 0.009, 0.065 and 0.082 mg/kg kresoxim-methyl equivalents were found in the skin, kidneys and liver respectively. The radioactivity in the eggs was 0.012 and 0.215 mg/kg and did not appear to reach a plateau during the study. The distribution of radioactivity is shown in Table 4.

Table 4. The distribution of radioactivity in hens dosed with [*phenyl*-^{14}C]kresoxim-methyl.

Sample	Time, h	^{14}C from 10 ppm dose		^{14}C from 180 ppm dose	
		mg/kg as kresoxim-methyl	%dose	mg/kg as kresoxim-methyl	% dose
Eggs	0-24	Nd	nd	0.100	0.02
	24-48	0.009	0.03	0.086	<0.01
	48-72	0.007	0.02	0.131	0.02
	72-96	0.009	0.02	0.164	0.02
	96-120	0.011	0.03	0.215	0.04
	120-123	-	-	-	-
	120-143	0.012	0.04	-	-
Eggs pooled[1]		0.009		0.155	
Skin	At slaughter	0.01	<0.01	0.68	<0.01
Kidney		0.06	0.01	6.36	0.04
Liver		0.08	0.02	6.98	0.14
Fat		<0.005	-	0.76	<0.01
Muscle		0.002	-	0.20	<0.01
GI tract			0.59		10.77
Balance					
Tissues			0.6		10.9
Excreta			82.6		71.5
Excreta pooled[1]		5.48		115.16	
Cage washings			4.9		5.2

[1] Used for characterization

Samples were extracted with methanol and water. Bound radioactivity was released by pronase treatment. The radioactivity was characterized by liquid/liquid partition and analysed by HPLC. The compounds in the excreta, eggs and edible tissues were isolated and identified as far as possible.

Methanol extracted 57-59% of the TRR in the skin and liver derived from the low dose, and a further 6%-9% was extracted by water. After 180 mg/kg dose, methanol extracted >75% of the TRR in the tissues and eggs from the high dose and a further 2-6% was extracted from the tissues by water. Pronase liberated 60-90% of the unextracted radioactivity from the eggs of the high-dose group and 21% from the tissues. Samples from the high-dose group were used for characterization and identification.

The main metabolites identified in the liver were the isomeric glucuronides 490M63 and 490M67 (9.2% of the TRR), 490M28 (13.7%) and 490M9 (20.1%). The main metabolites in muscle were the sulfates 490M51 and 490M66 (20.0% of the TRR) and 490M60 plus 490M20 (8.6%), in skin the parent (10.7% of the TRR) and 490M58 (10.4%), in fat the parent (41.2% of the TRR) and the non-polar 490M15 (16.6%) and 490M48 (7.7%), and in eggs the sulfates 490M51 and 490M66 (15.7% of the TRR), the glucuronide 490M31 (9.7%), 490M48 (11.4%) and the unchanged parent (8.3%). The results are shown in Table 5, and the metabolic pathways in poultry proposed by the manufacturer in Figure 3 (Burke, 1994; Grosshans, 1994c).

Table 5. Metabolites detected in hens dosed with [*phenyl*-^{14}C]kresoxim-methyl at a level equivalent to 180 ppm in the feed in six daily doses.

Sample	490-M1	490-M5	490-M6	490-M9	490-M8/11	490-M14	490-M15	490-M16	490-M20/60	490-M24	490-M25/26	490-M28	490-M31	490-M33	490-M46	490-M47	490-M48	490-M50/52
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Liver		0.30		1.35		0.18	0.18	0.16				0.92		0.20		0.21		
Muscle		0.006			0.002		0.004		0.015		0.004	0.003			0.007	0.003	0.003	0.008
Skin		0.02	0.015	0.03			0.03			0.01					0.04	0.01	0.04	
Fat							0.12			0.01					0.03		0.06	0.02
Eggs	0.005										0.004		0.012	0.005 (+M39)		0.003	0.014	0.006

Sample	490-M51/66	490-M55/65	490-M56	490-M57	490-M58	490-M59	490-M63/67	490-M64	Parent	Characterized (pronase incubated)	Characterized (polar)	Characterized (solvent)	Total Residual
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Liver					0.08	0.05	0.62			1.08	0.23	1.09	0.23
Muscle	0.03			0.003	0.01	0.004			0.005	0.03	0.01	0.019	0.007
Skin	0.03	0.0017		0.01	0.08	0.06			0.08	0.03	0.06	0.12	0.04
Fat	0.01		0.02		0.01	0.006			0.31	0.03	0.02	0.04	0.01
Eggs	0.02						0.003	0.004	0.01	0.03			0.008

Plant metabolism

Apples. In German studies carried out in 1991-93, [*phenyl*-^{14}C]kresoxim-methyl (radiochemical purity 96-98%), formulated as BAS 490 00F, was applied to 5 year old apple trees (variety Mutsu) in three different treatment patterns as follows (Hofmann, 1992a-c; Grosshans, 1994a).

(1) "Leaf application": 6 spray applications of 400 g ai/ha, PHI 14 days. The manufacturer stated that apples were present at the later leaf applications and were not protected from the spray.

(2) "Early application": 2 applications of 400 g ai/ha at the beginning of the vegetation period, PHI 149 days.

(3) "Fruit treatment": 2 applications of 800 g ai/ha to apples only, PHI 14 days.

Samples were stored frozen at -18°C for 1 month before analysis. Peel and pulp were extracted separately with methanol. The extractable radioactivity was characterized by solvent partition, TLC and HPLC. The compounds were isolated by HPLC and their structures elucidated by MS and/or chromatographic comparison with reference compounds. Acceptable chromatograms and spectra were submitted. To characterize the unextracted radioactivity, the unextractable radioactive residue was treated with dilute aqueous ammonia and lignin and cellulose fractions were separated. Individual residues in the peel and pulp were recalculated on a whole-apple basis. Extraction and characterization schemes are shown in Figures 4 and 5.

The calculated total radioactive residues in the whole apples (Table 6) were 0.36 mg/kg as kresoxim-methyl from the leaf application, 0.04 mg/kg from the early application and 0.84 mg/kg from the fruit treatment. The radioactivity remained mainly on the peel (89% to 98% of the TRR) with very low translocation to the pulp. Of the calculated TRR in the whole fruits, 94% to 98% could be extracted with methanol (Table 7). After liquid/liquid partition, the extractable radioactivity was predominantly found in the ethyl acetate phase (80% to 94% of the TRR). The unextractable ^{14}C in the peel after leaf application amounted to 4.5% of the TRR and an additional 2.2% could be released with aqueous ammonia. Part of the unextractable radioactivity was associated with lignin (3.1% of the TRR).

Table 6. The distribution of radioactivity in apples treated with phenyl-labelled [^{14}C]kresoxim-methyl. Measured and calculated TRR, parent equivalents.

Application	Application rate, kg ai/ha	PHI, days	Sample	Measured TRR[1], mg/kg	Calculated TRR[2], mg/kg
Leaf	6 x 0.4	14	fruit pulp	0.06	
			core	0.05	
			peel	1.39	2.16
			leaves	18.52	
			branches	1.73	
			total pulp (flesh + core)		0.03
			whole apple		0.36
Early	2 x 0.4	149	fruit pulp	0.01	
			core	0.04	
			peel	0.05	0.29
			leaves	1.03	
			branches	0.41	
			total pulp (flesh + core)		0.005
			whole apple		0.04
Fruit treatment	2 x 0.8	14	fruit pulp	0.02	
			core	0.02	
			peel	5.68	6.30
			leaves	0.23	
			total pulp (flesh + core)		0.02
			whole apple		0.84

[1]Total measured by combustion [2]Sum of extractable and unextractable radioactivity

Table 7. Fractionation of ^{14}C in whole apples after treatment with phenyl-labelled [^{14}C]kresoxim-methyl.

Fraction	Leaf application		Early application		Fruit treatment	
	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.359	100.0	0.041	100.0	0.837	100.0
MeOH extract	0.341	94.9	0.038	94.3	0.822	98.2
Unextractable residue	0.018	5.1	0.002	5.7	0.015	1.8
MeOH extract						
Ethyl acetate phase	0.317	88.1	0.033	80.0	0.784	93.6
Aqueous phase	0.025	6.9	0.005	12.8	0.027	3.2

The extracts from all three trials showed similar patterns of compounds (Table 8) and contained predominantly unchanged kresoxim-methyl (74-93% of the TRR). In extracts of the leaf application apples kresoxim-methyl (78.3% of the TRR), its isomer 490M0 (3.3%), the acid 490M1 (3.0%) and conjugates of 490M2 (1.8%) and 490M9 (2.1%) were all identified by MS.

Overall about 94% of the extractable residues from the leaf application (88.4% of the TRR) could be identified. The remaining extractable radioactivity, which was spread over several peaks, was too little for identification (0.0015 to 0.0045 mg/kg) and was characterized by chromatographic properties.

Table 8. Characterization of extractable residues in apples, calculated on a whole-apple basis.

Fraction	Metabolite identity	Leaf application		Early application		Fruit treatment	
		mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR
Al	{	0.0045	1.2	0.0011	2.7		
A2	{only	0.0015	0.4	0.0002	0.5	0.0002	<0.1
A3	{character-	-	-	-	-	0.0001	<0.1
A4	{ized as	-	-	-	-	0.0003	<0.1
A5	{polar	0.0044	1.2	0.0016	4.0	0.0008	0.1
A6	{	0.0026	0.7	0.0011	2.6	-	-
A7	conjugates	0.0188	5.2	0.0025	6.1	0.0088	1.1
A7 after enzyme treatment:							
Uncleaved A7	conjugates	0.0014	0.4				
Aglycone A7/1	490-M2	0.0065	1.8				
Aglycone A7/2	490-M9	0.0076	2.1				
Aglycone A7/3	isomer of 490-M9	0.0033	0.9				
A8	490-Ml	0.0106	3:0	0.0008	1.9	0.0118	1.4
A9*	mw 313	0.0057	1.6	0.0006	1.4	0.0032	0.4
A10	Parent	0.2810	78.3	0.0301	74.0	0.7788	93.0
All	(*Z*)-isomer	0.0117	3.3	0.0005	1.2	0.0182	2.2

* the manufacturer stated that A9 was also found in the wheat metabolism study "but the position of the OH-group group is unclear."

Wheat. In German studies carried out in 1990-91, [*phenyl*-^{14}C]kresoxim-methyl (radiochemical purity 97-99.7%, formulated as BAS 490 00F), was applied twice to wheat (variety Star) at growth stages 29 and 52, at either 0.25 or 1.25 kg ai/ha. Samples were stored at -20°C for 1-4 months before analysis. Milled samples were combusted and analysed by LSC to determine the total radioactive residue (TRR).

Extraction and characterization schemes are shown in Figures 7-9. The samples were first extracted with methanol and subsequently with dilute aqueous ammonia. The extractable radioactivity was characterized by solvent partition, solid-phase extraction, TLC and HPLC. The compounds were isolated by HPLC and their structures elucidated by MS and/or chromatographic comparison with reference compounds. The unextractable radioactive residue was treated with enzymes, acids and bases, and fractionations of lignins, cellulose, protein, and starch was followed by further subdivision of the starch fraction.

The distribution of the total radioactive residues is shown in Table 9. After treatment at 0.25 kg/ha 30-99% of the TRR in the separate parts of the plants could be extracted with methanol, with the lowest proportion extracted from mature grain (Table 10). The subsequent extraction with dilute aqueous ammonia released an additional 31% of the TRR from the grain and 16% from the straw. Most of radioactivity in the ammonia extracts was recovered by chromatography on phenyl SPE cartridges. After partition between ethyl acetate and water most of the radioactivity extracted with methanol was found in the ethyl acetate phase (85-99% of the TRR). The unextractable activity was equivalent to 0.27 mg/kg in the straw (2.9% of the TRR) and 0.025 mg/kg in the grain (38.8%).

Table 9. The distribution of radioactivity in wheat treated with phenyl-labelled [^{14}C]kresoxim-methyl. Measured and calculated TRR, parent equivalents.

Application rate, kg ai/ha	PHI, days after 2nd treatment (days after 1st treatment)	Sample	Measured TRR[1], mg/kg	Calculated TRR[2], mg/kg
0.25	-56 (0)	plant	8.06	12.01
	-1 (55)	plant	2.10	1.31
0.25	0 (56)	plant	7.72	5.26
	64 (120)	grain	0.06	0.06
		glumes	1.87	2.67
		straw	12.92	9.21
		roots	1.14	
1.25	-56 (0)	plant	53.00	75.48
	-1 (55)	plant	6.07	11.84
1.25	0 (56)	plant	53.78	29.69
	63 (119)	grain	0.28	0.26
		glumes	10.82	18.43
		straw	44.8	61.39
		roots	3.17	

[1]Total measured by combustion
[2]Sum of extractable and unextractable radioactivity (MeOH)

Table 10. Extraction of radioactivity from wheat with methanol and ammonia (cf. Figure 6).

Sample	PHI days after 2nd treatment	Primary extraction		Partition of MeOH extract				Secondary extraction				SPE separation of ammonia extract			
		Methanol extract (E1)		Ethyl acetate extract (EE)		Aqueous phase (EW)		Ammonia extract (E2)		Unextractable residue (R2)		Application eluate (EA)		Methanol eluate (EM)	
		mg/kg	% of TRR	mg/kg	% of E1	mg/kg	% of E1	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR
0.25 kg/ha															
Forage	-56	11.96	99.6	9.64	98.8	0.11	1.2	0.02	0.2	0.03	0.3	0.001	<0.1	0.02	0.2
Forage	-1	1.22	93.2	0.81	88.7	0.10	11.3	0.06	4.8	0.05	3.7	0.002	0.1	0.05	4.2
Forage	0	5.13	97.5	3.70	85.9	0.61	14.1	0.09	1.7	0.06	1.2	0.001	<0.1	0.08	1.5
Glumes	64	1.44	54.1	1.09	86.6	0.17	13.4	0.95	35.6	0.27	10.1	0.075	2.8	0.88	33.1
Straw	64	7.55	82.0	6.73	92.3	0.56	7.7	1.49	16.1	0.27	2.9	0.049	0.5	1.43	15.6
Grain	64	0.02	30.4	0.02	85.1	0.003	14.9	0.02	31.1	0.02	38.8	0.005	7.8	0.014	21.7
1.25 kg/ha															
Forage	-56	75.26	99.7	66.83	99.8	0.14	0.2	0.10	0.1	0.10	0.1	0.002	<0.1	0.09	0.1
Forage	-1	11.40	96.3	9.86	96.4	0.37	3.5	0.30	2.5	0.19	1.6	0.007	0.1	0.29	2.4
Forage	0	29.24	98.5	24.09	98.2	0.43	1.8	0.32	1.1	0.17	0.6	0.007	<0.1	0.30	1.0
Glumes	63	13.77	74.7	10.74	92.6	0.85	7.4	3.36	18.3	1.03	5.6	0.170	0.9	3.11	16.9
Straw	63	53.70	87.5	57.75	96.3	2.23	3.7	6.23	10.1	1.44	2.3	0.203	0.3	6.00	9.7
Grain	63	0.13	48.1	0.12	91.6	0.011	8.4	0.07	26.7	0.07	28.3	0.020	7.6	0.04	16.4

Table 11. Characterization of extractable residues in wheat treated with 0.25 kg/ha phenyl-labelled [^{14}C]kresoxim-methyl.

Frac-tion	Identity	Forage, day of 1st treatment		Forage, 55 days after 1st treatment		Forage, day of 2nd treatment		Straw, 64 days after 2nd treatment		Grain, 64 days after 2nd treatment	
		mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR
1		-		-		-		0.017	0.2	-	
2		-		-				0.011	0.1	0.001	1.5
3		-		-				0.027	0.3	0.0036	5.6
4		-		-				0.101	1.1	0.0025	3.9
5		-		0.015	1.1			0.026	0.3	0.0009	1.4
6		-		-		0.007	0.1	0.134	1.5	0.0027	4.2
7	conj[1]	-		-		0.007	0.1	0.148	1.6	-	
8	conj[1]	-		0.107	8.2	0.072	1.4	0.451	4.9	0.0020	3.1
9	conj[1]	-		0.029	2.2	0.019	0.4	0.875	9.5	0.0008	1.2
10	conj[1]	-		0.033	2.5	-		0.174	1.9	0.0002	0.3
11		-		-		-		-		0.0007	1.1
12		-		0.016	1.2	-		0.096	1.0	0.0015	2.3
13		-		-				-			
14		-		-				0.052	0.6	-	
15		-		-				0.045	0.5	-	
16		-		-				0.014	0.1	0.0021	3.3
17		-		-				0.011	0.1	-	
18		-		-				0.022	0.2	-	
19		-		-				0.033	0.4	-	
20	490M1	0.247	2.1	0.039	3.0	0.063	1.2	0.126	1.4	-	
21	490M17	-		0.037	2.8	0.031	0.6	0.329	3.6	0.0005	0.8
22		-		-				0.011	0.1	-	
23	Parent	11.506	95.8	0.980	74.8	4.889	92.8	5.923	64.3	0.0111	17.2
24		0.120	1.0	0.005	0.4	0.031	0.6	-		-	
25	490M0	0.108	0.9	0.016	1.2	0.087	1.7	0.359	3.9	0.0002	0.3
26		-		-		-		-		0.0010	1.5
27								-		0.0006	1.0
Total			99.8		97.4		98.9		97.6		48.7

[1]Conjugates include 490M2 and 490M9 (see text for levels)

The extracts of corresponding samples from the two treatment groups showed qualitatively similar patterns of compounds (see also Table 12). After treatment at 0.25 kg/ha the main radioactive residue was the unchanged parent at levels of 5.9 mg/kg in mature straw and 0.98 mg/kg in forage 1 day before the second treatment. The following compounds were also identified in the straw and -1 day forage: the (*Z*)-isomer 490M0, the acid 490M1, and conjugates of 490M2 and 490M9. The mature grain contained 0.011 mg/kg (17.2% of the TRR) of the parent and a variety of metabolites constituting 0.3-5.6% of the TRR. Enzymatic cleavage of the conjugate fractions 7-10 yielded the following respective levels of the acids 490M2 and 490M9 from the lower rate: 0.03 and 0.103 mg/kg in 55-day forage, 0.39 and 1.04 mg/kg in mature straw from the 0.25 kg/ha treatment; 0.019 and 0.003 mg/kg in mature grain from the 1.25 kg/ha treatment. Samples from the higher rate treatment contained higher relative and absolute amounts of the parent compound (Table 12).

Table 12. Characterization of extractable residues in wheat treated with 1.25 kg/ha phenyl-labelled [^{14}C]kresoxim-methyl.

Frac-tion	Identity	Forage, day of 1st treatment		Forage, 55 days after 1st treatment		Forage, day of 2nd treatment		Straw, 64 days after 2nd treatment		Grain, 64 days after 2nd treatment	
		mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR
1		-		-		-		-		-	
2		-		-		-		-		-	
3		-		-		-		-		0.0115	4.3
4		-		-		-		0.107	0.2	0.0076	2.9
5		-		0.011	0.1	-		0.186	0.3	-	
6		-		0.025	0.2	-		0.210	0.3	0.0023	0.9
7	conj	-		0.033	0.3	0.033	0.1	0.360	0.6	0.0010	0.4
8	conj	-		0.419	3.5	0.232	0.8	2.083	3.4	-	
9	conj	-		0.081	0.7	0.072	0.2	2.053	3.3	0.0218	8.3
10	conj	-		-		-		0.215	0.3	-	
11		-		-		-		-		-	
12		-		-		-		-		0.0032	1.2
13		-		-		-		-		0.0009	0.4
14		-		-		-		-		-	
15		-		-		-		-		-	
16		0.009	<0.1	-		-		-		-	
17		-		-		-		-		-	
18		0.005	<0.1	-		-		-		-	
19		-		-		-		-		-	
20	490M1	0.528	0.7	0.389	3.3	0.369	1.3	0.743	1.2	0.0009	0.4
21	490M17	-		0.308	2.6	0.263	0.9	2.202	3.6	0.0031	1.2
22		-		-		-		-		-	
23	Parent	73.30	97.1	10.22	86.4	27.92	94.0	50.73	82.6	0.1034	39.5
24		0.828	1.1	-		0.292	1.0	-		-	
25	490M0	0.677	0.9	0.194	1.6	0.351	1.2	0.805	1.3	-	
26		-		-		-		-		-	
W27		-		-		-		-		-	
Total			99.8		98.7		99.5		97.1		59.5

Fractionation of the unextractable radioactivity from the 0.25 kg/ha treatment (R2 residue, Table 13) in straw indicated that 2.1% of the TRR was associated with lignin and only 0.2% was incorporated into cellulose. In the grain 31.7% of the TRR was associated with or incorporated into starch, of which 9.4% of the TRR could be converted into $^{14}CO_2$ by fermentation of the glucose with yeast. The metabolic incorporation of ^{14}C in the glucose was thought to be caused by mineralization of the parent or its metabolites in soil and assimilation of the $^{14}CO_2$ by the plants at late growth stages. Lignin contained 7.9% of the TRR, protein 6.3% and cellulose 1.6%.

Table 13. Fractionation of unextractable ^{14}C in wheat treated with 0.25 kg/ha phenyl-labelled [^{14}C]kresoxim-methyl. See Figures 6-8 for details of fractionation schemes.

Fraction		Straw		Grain	
		mg/kg	% of TRR	mg/kg	% of TRR
Total radioactive residue El + Rl		9.52	100.0	0.07	100.0
MeOH extract	El	7.69	80.8	0.02	26.8
Residue	R1	1.83	19.2	0.05	73.2
Ammonia extract	E2	1.62	17.0	0.02	33.8
Residue	R2	0.32	3.3		
HCl extract of R2	E3	0.02	0.2		
EDTA extract of residue R3	E4	0.01	0.1		

Fraction		Straw		Grain	
		mg/kg	% of TRR	mg/kg	% of TRR
Enzyme extract of R4	E5	0.07	0.8	0.004	5.6
1M HC1-hydrolysis of R5	E6	0.03	0.3		
6M HCl hydrolysis of R5	E7	0.01	0.1		
NaOH hydrolysis of R7	E8	0.09	1.0		
Total dietary fibre extract of R5	E9	0.03	0.3	0.02	25.4
Lignin, cellulose, protein and starch fractionation					
TRR		9.213.	100.0	0.06	100.0
MeOH extract	El	7.551	82.0	0.02	31.7
Extraction residue	R1	1.662	18.0	0.04	68.3
Ammonia extract	E2	1.486	16.1	0.02	31.7
Extraction residue	R2	0.269	2.9	0.02	39.7
Lignin	R11/15	0.198	2.1	0.005	7.9
Cellulose	R12/16	0.020	0.2	0.001	1.6
Protein	E2B			0.004	6.3
Starch	E13B			0.02	31.7
Fermentation of glucose from starch					
Starch fraction				0.02	32.2
Ethylene glycol				0.0003	0.5
14[$C0_2$] traps				0.006	9.4
Yeast supernatant				0.003	4.6
Yeast				0.003	5.2

Table 14. Characterization of unextractable residues in wheat treated with 1.25 kg/ha phenyl-labelled [^{14}C]kresoxim-methyl.

Fraction		Straw		Grain	
		mg/kg	% of TRR	mg/kg	% of TRR
Lignin, cellulose, protein and starch fractionation					
TRR		61.39	100.0	0.30	100.0
MeOH extract	El	53.70	87.5	0.15	50.0
Residue	R1	7.69	12.5	0.15	50.0
Ammonia extract of R1	E2	6.23	10.1	0.07	23.5
Residue	R2	1.44	2.3	0.07	24.8
Lignin	R11/15	0.95	1.6	0.01	4.4
Cellulose	R12/16	0.07	0.1	0.05	18.5
Protein	E2B			0.008	2.7
Starch	E13B			0.002	0.7

Overall, >95% of the extractable residue could be identified or characterized in the forage and straw, and about 50% in the grain from the 0.25 kg/ha treatment. An additional 47.5% of TRR in grains was incorporated into or associated with natural products. The remaining extractable radioactivity, which was split into many peaks was too low for identification and was characterized only by chromatographic properties (Hofmann, 1991a,b; Grosshans, 1994b).

Grapes. In US studies carried out in 1991 (Nelsen *et al.*, 1995) phenoxy- and phenyl-labelled kresoxim-methyl (radiochemical purities 98.8 and 99.2%), formulated as BAS 490 F, were applied five times to mature Muscatine grape vines (variety Carlos) at rates of 0.5 kg/ha per application. Grapes were harvested 14 days after the final treatment. Samples were stored at <0°C for 1-7 months before analysis. Whole grapes were rinsed with methanol and then homogenized. The total radioactive residue was calculated at the sum of the ^{14}C in the methanol rinse and in the homogenized washed grapes, determined by combustion.

The extraction scheme is given in Figure 9. Homogenized grapes were extracted with either methanol or acetone/water. Residues in homogenates, grape rinses and unwashed samples were separated and identified by SPE, TLC, HPLC with UV and radiometric detection, GC-MS, and enzyme hydrolysis (β-glucosidase and hesperidinase). Confirmation of identifications by HPLC and TLC was by co-chromatography.

No significant differences were observed between the results for phenoxy- and phenyl-labelled kresoxim-methyl. About 40% of the TRR (1.6-1.91 mg/kg) was removed as surface residue by the methanol rinse (Table 15). There were no significant differences between the proportions extracted by methanol and acetone/water, indicating that cleavage of the molecule was unlikely. Less than 10% of the TRR remained unextracted. The total recovery of residues in the extracts used for characterization was about 90% of the TRR and the unextractable residue contained about 5%.

Table 15. Radioactive residues in grapes treated with phenoxy- and phenyl-labelled [^{14}C]kresoxim-methyl (mg/kg as parent equivalents based on weight of unwashed grapes).

Sample	Phenoxy label		Phenyl label	
	% of TRR	mg/kg	% of TRR	mg/kg
Methanol rinse	34.7, 40	1.32, 1.60	32.1, 40.5	1.13, 1.91
Homogenized rinsed grapes	65.3, 60	2.51, 2.40	67.9, 59.5	2.49, 2.81
TRR	100	3.83, 4.00	100	3.62, 4.72

Table 16. Fractionation of radioactive residues in grapes treated with phenoxy- and phenyl-labelled [^{14}C]kresoxim-methyl.

Sample	Phenoxy label		Phenyl label	
	Acetone/water	Methanol, mean %	Acetone/water	Methanol, mean %
TRR, mg/kg	3.83	3.94	3.62	4.35
% in rinse	34.7	38.2	32.1	37.7
% in homogenized grapes	52.4	50.7	56.7	52.0
% of TRR extracted	87.1	88.9	88.8	89.7
% unextractable	4.3	6.3	4.5	5.8
% of TRR recovered	91.4	95.1	93.3	95.5

Parent kresoxim-methyl was the main residue, 55.38% of the phenoxy TRR and 57.35% of the phenyl (Table 17). The alcohol-acid 490M2 was also prominent at 13.76% and 8.86% of the TRR (sum of free and conjugated). After β-glucosidation, levels of the phenolic acid 490M9 were 5.75% and 4.38% of the TRR. Small amounts of free 490M9 were originally present, at 1.25% and 1.4% of the TRR. The enzymatic conversion of conjugates to aglycones by ß-glucosidase was 85-88%. Approximately 3.5% and 5% of the TRR remained unidentified as polar or conjugated metabolites. A mixture of over 20 unhydrolysed conjugates and other polar materials were individually below 0.05 mg/kg. Those from the phenyl label were unaffected by the additional hesperidinase hydrolysis.

There were no major qualitative differences between the two labels.

Table 17. Characterization of radioactive residues in grapes treated with phenoxy- and phenyl-labelled [^{14}C]kresoxim-methyl.

Identity	phenoxy label		phenyl label	
	%TRR	mg/kg	%TRR	mg/kg
Unknown polar			0	0
Unknown polar			0.59	0.027
Unknown polar			1.40	0.066
Unknown polar	0.56	0.023	0.28	0.013

Identity	phenoxy label		phenyl label	
	%TRR	mg/kg	%TRR	mg/kg
Conjugate	3.18	0.127	2.78	0.130
490m2[1]	13.76	0.550	8.86	0.418
490m9[1]	5.75	0.230	4.38	0.206
490m54[1]	2.07	0.083	1.37	0.064
490M1[1] (acid)	0.48	0.019	0.13	0.006
Unknown	0.72	0.029	0.83	0.039
Unknown	1.03	0.041	1.11	0.052
Parent	55.38	2.215	57.35	2.707
Z-isomer	3.49	0.139	3.75	0.177
Unknown	0.58	0.023	0.42	0.019
(Background	3.70	0.148	2.98	0.140)
Total	90.70	3.63	86.23	4.07

[1]Sum of free and conjugated

Rotational crops. In trials in Germany during 1992/93 (Hoffmann, 1993a,b; Grosshans, 1994d) [*phenyl*-^{14}C]kresoxim-methyl (radiochemical purity 97-99%), was applied to bare soils at 0.3 kg/ha. After ageing for 30 days, the soils were diluted with untreated soil in the ratio of 1:9 in order to simulate ploughing. 30 days later spring wheat (Star, Ralle varieties), green beans (Maxi, Marona), carrots (Nantaise Frühbund) and lettuce (Ultra, Ovation) were sown or planted. Crops were harvested at interim stages to identify metabolites (as the final harvest samples would contain low levels of residues) and at maturity. Samples were stored at -18°C before analysis by combustion and LSC. The samples were apparently not washed before analysis.

The samples were extracted with methanol and then with dilute aqueous ammonia. The extractable radioactivity was separated by liquid/liquid partition (cyclohexane/ethyl acetate/water) and HPLC. Conjugates were cleaved by enzymes (hesperidinase and β-glucoside) and the structures of isolated metabolites and aglycones elucidated by chromatographic comparison with reference compounds.

The highest total radioactive residues found in the crops at harvest in mg/kg were 0.15 in wheat straw, 0.007 in wheat grain, 0.21 in bean forage, 0.009 in green beans, 0.006 in carrot roots, 0.047 in carrot foliage and 0.01 in lettuce heads (Table18). Methanol extracted 57 to 77% of the TRR and the subsequent dilute aqueous ammonia extraction released additional 20% to 34%. The total extraction was >85% of the TRR.

Table 18. The distribution of radioactivity in rotational crops after treatment of soil with 0.3 kg/ha phenyl-labelled [^{14}C]kresoxim-methyl. (Measured and calculated TRR, parent equivalents).

Sample	Type	Days after sowing or planting	TRR[1], in crops, mg/kg equiv	TRR[2], in crops, mg/kg equiv	TRR (column 4) as % of initial radioactivity in soil (mean 0.93 mg/kg)
Soil	initial		0.918, 0.83, 1.05		
Soil	after 30 days ageing		0.05, 0.066, 0.06		6.3
Wheat forage	interim	42, 61	0.067, 0.232	0.05	
Wheat straw	final harvest	124, 125	0.119, 0.068	0.077-0.146	10.0
Wheat grain	final harvest	124, 125	0.006, 0.007		0.7
Soil	final harvest	124, 125	0.050, 0.029		4.2
Green beans (pods)	interim	26, 56, 75	0.36, 0.004, 0.004	0.057-0.195	
Green beans (beans plus pods)	final harvest	77	0.009		1.0

Sample	Type	Days after sowing or planting	TRR[1], in crops, mg/kg equiv	TRR[2], in crops, mg/kg equiv	TRR (column 4) as % of initial radioactivity in soil (mean 0.93 mg/kg)
Bean forage	final harvest	77	0.21		22.6
Soil	final harvest	77	0.042		4.5
Carrots (plant)	interim	50	0.025	0.026	
Carrots (foliage)	interim	52, 90	0.061, 0.010		
Carrots (roots)	interim	52, 89, 90	0.052, 0.005, 0.003		
Carrots (foliage)	final harvest	111	0.047	0.035	5.0
Carrots (roots)	final harvest	111	0.006		0.6
Soil	final harvest	111	0.036		3.9
Lettuce (leaves/head)	interim	26, 30, 49, 56	0.053, 0.051, 0.02, 0.028	0.03-0.032	
Lettuce (head)	final harvest	66	0.010		1.0
Lettuce (roots)	final harvest	66	0.231		24.8
Soil	final harvest	66	0.032		3.4

[1]Measured by combustion
[2]Sum of extractable and unextractable radioactivity

In extracts of bean forage, carrot forage and lettuce conjugates were the main radioactive residues, accounting for about 30-40% of the TRR. Enzymatic treatments of the extracts and/or isolated conjugate fractions produced mainly the aglycones 490M2 and 490M9. The rest of the extractable radioactivity in these samples gave rise to several radioactive peaks representing up to 0.043 mg/kg (22% of the TRR). Mature lettuce also contained 9.4% of the TRR (0.003 mg/kg) as the unchanged parent compound and carrot forage 12.7% (0.005 mg/kg) as 490M1.

Wheat straw contained small amounts of the free hydroxy metabolites 490M2 and 490M9 (together about 10% of the TRR). Enzyme treatment produced 4.8% of the TRR as 490M2 and 10.4% as 490M9. The parent compound was detected in straw at 1.5% of the TRR (0.001 mg/kg). The results are shown in Table 19.

The results shown in Table 18 suggest that there is a slight uptake from soil into the crops, particularly wheat straw, bean forage and lettuce roots. Wheat straw and lettuce heads contained the parent compound at 0.15% and 0.09% of the initial radioactivity in the soil (Hofmann, 1993a,b; Grosshans, 1994d).

Table 19. Characterization of radioactivity in rotational crops after treatment of soil with 0.3 kg/ha phenyl-labelled [^{14}C]kresoxim-methyl. Where two figures are shown they are the results of separate uptake studies.

HPLC Peak	Identity	Wheat straw		Wheat forage		Bean forage		Carrot forage		Lettuce	
		mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR
1				0.003	6.0	0.002, 0.001	0.9, 1.4			0.003	8.9
2		0.01	7.6					0.0015	5.7		
3		0.001	0.9							0.0005	1.8
4		0.001	1.2			0.001	1.3	0.003	8.6		
5				0.009	17.1	0.043, 0.008	21.9, 13.4	0.002	6.9	0.001, 0.0006	4.2, 1.9
6		0.006	7.8								
7		0.001	1.1	0.003	6.3						

HPLC Peak	Identity	Wheat straw		Wheat forage		Bean forage		Carrot forage		Lettuce	
		mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR
8		0.021	16.0			0.017, 0.001	8.5, 2.4				
9		0.017, 0.004	13.2, 4.8	0.005	10.9						
10	unknown	0.034, 0.01	26.5, 12.5	0.017	33.5	0.008, 0.004	4.2, 6.8	0.0007 , 0.001	2.0, 3.2		
11		0.003	3.8								
12	conjugates	0.015, 0.004	11.6, 5.2								
13	conjugates	0.003	3.7	0.002	4.5	0.071, 0.018	36.7, 30.9	0.015, 0.004	43.6, 13.9	0.012, 0.015	41.5, 50.8
14		0.001	1.8			0.007, 0.008	3.4, 14.3	0.002, 0.004	5.7, 14.5	0.004	12.7
15						0.015, 0.002	7.7, 3.6				
16											
17								0.0003	1.1		
18	490M2	0.011, 0.001	8.5, 1.6								
19	490M9	0.0014	1.8							0.0006	2.1
20											
21		0.0008	1.1					0.0002	0.8		
22	409M1			0.001	1.5			0.004	12.7		
23		0.001	1.4								
24	Parent	0.001	1.5							0.003	9.4
25	(*Z*)-isomer										

Metabolic pathways in plants

The pathways proposed by the manufacturer for the metabolism of kresoxim-methyl in apples, wheat and following crops and in grapes are shown in Figures 10 and 11 respectively.

The manufacturer concludes that conjugates of 490M-2 and 490M-9 are incorporated into the starch and protein of wheat grain and the lignin of straw, and are further incorporated as bound residues in following crops.

Summary of metabolism

A total of 53 metabolites or degradation products of kresoxim-methyl have been identified in studies with rats, hens, goats, apples, wheat and grapes. A number of these have been identified in domestic animals and crop plants but not in rats: 16 in hens, 3 in goats and 1 in grapes.

Of these, only two are likely to occur in food commodities at significant levels (>0.05 mg/kg). These are 490M18, which was found at significant levels in several tissues in goats, and 490M54 which was found at significant levels in grapes. 490M18 is a postulated intermediate in rats.

The code names and chemical structures of the metabolites and degradation products are given in Figure 12 (at end of evaluation).

Environmental fate in soil and water/sediment systems

All the studies were carried out according to national or international guidelines and GLP.

Laboratory soil degradation studies

(a) In a study according to BBA guidelines Limbergerhof sandy loam soil was treated with [*phenoxy*-^{14}C]kresoxim-methyl (radiochemical purity (*Z*)- + (*E*)-isomers 100%, 0.5 mg/kg) and incubated at 40% maximum water holding capacity in the dark at 20°C. Volatile compounds were trapped in ethylene glycol, 0.5M H_2SO_4 and 0.5M NaOH. Soil samples were taken at nine intervals during 183 days and extracted with methanol and methanol/water. After clean-up the extracts were analysed by LSC and TLC and the identities of the compounds confirmed by HPLC and MS.

Recoveries were >92% of the applied radioactivity (AR) for the first 63 days but subsequently dropped to about 80% of the AR, which was attributed to loss of CO_2 and sorption of radioactivity to the filter paper during extraction. The degradation of kresoxim-methyl was very rapid (DT90 <3 days) and the free acid 490M1 reached 84% of the AR. This was subsequently degraded with a first-order half-life of 38 days. At the end of the experiment cumulative CO_2 production reached 27% of the AR whilst bound residues had reached a plateau of 47%. The bound residues were further examined and most of the radioactivity was found in the humin fraction. The only other compound identified during the experiment was 490M0 (the (*Z*)-isomer of kresoxim-methyl) and levels of this were very low in comparison with 490M1. No other compound exceeded 2.5% of the AR (Kellner, 1994a).

(b) In a study according to EPA guidelines Holly Springs sandy loam soil was treated with [*phenoxy*-^{14}C]kresoxim-methyl (radiochemical purity 95% (*E*)-isomer, >99% (*E*)- + (*Z*)- isomers, 0.5 mg/kg) and incubated at 75% water content in the dark at 20°C. Volatile compounds were trapped in ethylene glycol and 0.5M NaOH. Soil samples taken at nine intervals during 363 days were extracted and analysed as above.

Recoveries of radioactivity were 73-100% of the AR. Further work showed that the missing radioactivity was recoverable from the filter paper and was from the same compounds as in the main extract. The degradation of kresoxim-methyl was very rapid (DT90 about 2 days). The free acid 490M1 reached 66% of the AR and was subsequently degraded with a first-order half-life of 131 days. At the end of the experiment the cumulative CO_2 represented 2% of the AR. Bound residues reached a peak of 41% of the AR at day 272 and then decreased. Small amounts of the diacid 490M4 (max 3.3% of the AR) and 490M0 (4.4% of the AR) were also detected (Kellner, 1994b).

(c) This study was similar to (a), but the Limbergerhof sandy loam soil was treated with phenyl-labelled kresoxim-methyl (radiochemical purity >99%, 0.5 mg/kg). Volatile compounds were trapped in ethylene glycol and 0.5M NaOH. Soil samples were taken at ten intervals during 181 days and extracted and analysed as before.

Recoveries of radioactivity were >91% of the AR. The degradation of kresoxim-methyl was again very rapid (DT90 about 2 days). The free acid reached 81% of the AR before degradation with a first-order half-life of 57 days. The cumulative production of CO_2 was 43% of the AR. Bound residues reached a plateau of 36% of the AR with most of the radioactivity in the humin fraction. Other unidentified compounds reached a maximum of 1.6% of the AR (Kellner, 1994c).

(d) In a study according to BBA and Danish guidelines Speyer 2.2 sandy loam, Limbergerhof sandy loam, Limbergerhof clay loam and Versuchsstation sandy loam were treated with kresoxim-methyl (0.5 mg/kg) and incubated at 40% maximum water holding capacity in the dark at 20°C. Samples of the Limbergerhof sandy loam were also incubated under the same conditions at 0.05 mg/kg, and at 0.5 mg/kg with soil at 20 and 60% maximum water holding capacity and at 10 and 30°C. Soil samples taken at six intervals during 100 days were extracted by refluxing with buffered aqueous alkaline solution to hydrolyse the ester. After clean-up the acid was quantified by GLC. The mean

recovery was 83% and the limit of determination 0.005 mg/kg. First-order half-lives for the combined parent ester and acid are shown in Table 20.

Table 20. First-order half-lives of the combined kresoxim-methyl and its free acid metabolite (Keller 1993a).

Soil	Application rate, mg/kg	Temp., °C	% of max. water holding capacity	Half-life, days
Speyer 2.2 (sandy loam)	0.5	20	40	59 (r^2=0.95)
Limbergerhof (clay loam)	0.5	20	40	425 (r^2=0.25)
Versuchsstation (sandy loam)	0.5	20	40	22 (r^2=0.98)
Limbergerhof (sandy loam)	0.5	20	40	25 (r^2=0.99)
Limbergerhof (sandy loam)	0.5	20	20	192 (r^2=0.87)
	0.5	20	60	24 (r^2=0.99)
	0.5	10	40	122 (r^2=0.98)
	0.5	30	40	22 (r^2=0.94)
	0.05	20	40	20 (r^2=0.98)

(e) This study complied with Danish criteria. Limbergerhof sandy loam soil treated with 0.5 mg/kg [*phenoxy*- ^{14}C]kresoxim-methyl (radiochemical purity (*E*)- + (*Z*)- isomers >99%, (*Z*)-isomer about 5%) was incubated at 40% maximum water holding capacity in the dark at 20°C under a stream of nitrogen. Anaerobic conditions were regularly checked. Volatile compounds were trapped in ethylene glycol, 0.5M H_2SO_4 and 0.5M NaOH. Soil samples taken at seven intervals during 100 days were extracted and analysed as before.

Recoveries of radioactivity were 85-98% of the AR; the losses could be accounted for by sorption to filter paper during the extraction procedure. The degradation of kresoxim-methyl was very rapid (DT90 <3 days). The free acid 490M1 reached a maximum of 84% of the AR, but its subsequent degradation was too slow to calculate a half-life. At the end of the experiment the cumulative CO_2 accounted for 2.6% of the AR and bound residues for 20%. No other volatile compounds were detected (Kellner, 1993a).

(f) In a companion study Limbergerhof sandy loam soil was sterilized, treated with [*phenyl*- ^{14}C]kresoxim-methyl (radiochemical purity >98%, (*Z*)-isomer about 2%) at 0.5 mg/kg and incubated at 40% maximum water holding capacity in the dark at 20°C. Soil samples taken at five intervals during 181 days were analysed.

Recoveries of radioactivity were 87-120% of the AR. Kresoxim-methyl was so slowly degraded that after 181 days 68% was still present (degradation was too variable to calculate a half-life). The free acid 490M1 and bound residues (up to 4.8% of the AR) accounted for the remaining radioactivity. CO_2 was not measured (Kellner, 1992).

Soil dissipation under field conditions

(a) In a study according to BBA guidelines kresoxim-methyl (300 g ai/ha) was applied to bare soil at four sites in Germany (Niederhofen clay loam, Birkenheide sandy loam, Oberding clay loam and Brockhausen clay loam) in May 1992. Twenty soil cores were taken from each site at 0, 14, 28, 60, 100 and 182 days. These were sectioned into 0-10 and 10-25 cm layers and corresponding layers combined. Samples were extracted with iso-octane/phosphate buffer (1:1) and analysed by GLC for kresoxim-methyl only or combined kresoxim-methyl and 490M1, with procedural recoveries of 110% and 79% respectively and a limit of determination of 0.01 mg/kg in both cases. The samples were stored up to 18 months before analysis and there was some degradation of kresoxim-methyl during this period. CLICK HERE to continue

Kresoxim methyl accounted for 17% (day 0), 31% (day 0), 19% (day 14) and 0% of the combined residues at Niederhofen, Birkenheide, Oberding and Brockhausen respectively. Hence extensive degradation had occurred even on day 0 and half-life and DT90 values could not be calculated for kresoxim-methyl owing to the low residues and few early samples (there were no detectable residues of kresoxim-methyl after 14 days). Half-lives and DT90 values for the combined residues of kresoxim-methyl and 490M1 in the 0-10 cm layer were estimated graphically and are shown in Table 21. In the 10-25 cm layer, small amounts (0.03 mg/kg) of 490M1 were detected at day 0 in two samples.

Table 21. Graphically estimated half-life and DT90 values for combined kresoxim-methyl and 490M1 in the 0-10 cm layers of four soils (Hesse *et al.*, 1994).

Site	Half-life, days	DT90, days
Oberding	38	125
Oberding	35	117*
Niederhofen	11	36*
Niederhofen	16	38
Birkenheide	8	18
Brockhausen	8	- **

* Assumed first order
**Concentration too low for estimation

A proposed degradation route of kresoxim-methyl in soil is shown in Figure 14.

Photolysis in soil

In a study according to US EPA guidelines Holly Springs sandy loam soil at 33 kPa moisture content was treated with 11.1 mg/kg [*phenyl*-^{14}C]kresoxim-methyl (radiochemical purity (*E*)-isomer 95, (*Z*)-isomer 3%) and irradiated with a xenon lamp with a spectral distribution and intensity similar to sunlight in North Carolina, USA, at 25°C. Volatile compounds were trapped in carbitol, 0.5 M H_2SO_4 and 0.5M NaOH. Soil samples taken at seven intervals during 360 hours of illumination were extracted with methanol and methanol/water and analysed by LSC and HPLC.

Throughout the experiment recoveries of radioactivity were 98-103% of the AR. After 15 days continuous irradiation volatile compounds from the illuminated samples reached 1% of the AR whilst those from the dark control were <0.01%. Unextractable residues rose to 4.9% of the AR in irradiated samples and 2.1% in dark controls. First-order half-lives for kresoxim-methyl were 35 days in irradiated soils and 6.7 days in dark controls. In the irradiated samples 490M1 reached a maximum of 7.4 % of the AR and then decreased to 2.4 % by the end of the experiment and eleven other unidentified compounds (each <5.2% of the AR) were detected during the incubation. In the dark controls, 490M1 reached 60.6% of the AR at the last sampling. Small amounts (<7.6% of the AR) of six unidentified compounds were present but these were different from those in the irradiated samples. 490M0 remained at a constant level of about 3-5% of the AR throughout the study in both the illuminated and dark samples (McKenna, 1994).

Adsorption and desorption in soil

The adsorption and desorption of kresoxim-methyl and the free acid were measured in two studies according to OECD guidelines. [*Phenyl*-^{14}C]kresoxim-methyl (specific activity 227 MBq/mmol, radiochemical purity (*E*) + (*Z*) isomers >99%) was dissolved in 0.01M $CaCl_2$ (0.008 µg/ml, 0.04 µg/ml, 0.2 µg/ml and 1.0 µg/ml) and duplicate 25-ml aliquots were added to four different soils (5g) and equilibrated for 1h. Radioactivity in the solutions was quantified by LSC. Soil from the 1 µg/ml

experiment was also extracted with methanol and 91-101 % of the AR was accounted for. The results are shown in Table 22.

Table 22. Freundlich adsorption constants for kresoxim-methyl in four soils.

Soils	K_d	1/n	K_{oc}
Speyer 2.1 (sand)	2.6	0.97	372
Speyer 2.2 (loamy sand)	7.7	0.99	338
Speyer 2.3 (sandy loam)	3.6	0.95	301
Limbergerhof Ost (clay loam)	5.9	0.99	219

TLC of selected samples showed that a significant proportion of the radioactivity in the soil and solution after the experiment was due to the free acid 490M1. When two desorption steps, each of 16 h, were carried out 75-81% of the adsorbed radioactivity was desorbed (Keller, 1992).

In the second study [*phenyl*-^{14}C]490M1 (specific activity 101 MBq/mmol, radiochemical purity (*E*)- + (*Z*)-isomers 93%) was dissolved in 0.01M $CaCl_2$ (0.008 µg/ml, 0.04 µg/ml, 0.2 µg/ml and 1.0 µg/ml) and duplicate portions of 5 ml added to 1 g of the same four soils were equilibrated for 2 h. Radioactivity in the solutions was quantified by LSC. Soil samples equilibrated at 1 µg/ml were extracted with methanol and a recovery of 95-101% of the AR was obtained. The results are shown in Table 23.

Table 23. Freundlich adsorption constants for 490M1 in four soils.

Soils	K_d	1/n	K_{oc}
Speyer 2.1 (sand)	<0.1		
Speyer 2.2 (loamy sand)	0.62	0.94	24
Speyer 2.3 (sandy loam)	<0.1		
Limbergerhof Ost (clay loam)	0.55	0.91	17

TLC of selected samples showed that all the radioactivity in the aqueous solution after 24 h agitation was due to 490M1. Only 2.8-10% was sorbed to soil and almost all was desorbed after two desorption steps of 16 h (Keller, 1993b).

Mobility in soil (column leaching).

Four studies were carried out according to BBA guidelines, all with glass columns 30 cm by 5 cm i.d. filled with untreated soil and saturated with water from below. Duplicate columns were filled with Speyer 2.1, 2.2 or 2.3 soil and formulated kresoxim-methyl (BAS 490 04 F, 29.4 µg ai) was added to the tops of the columns which were leached with water (393 ml, equivalent to 200 mm rain) for 2 days. The leachates were analysed for combined kresoxim-methyl and 490M1 by GLC after alkaline hydrolysis. The proportions of the combined parent and acid in the leachates were 73.1-76.9%, <0.2-0.8% and 33.2-40.8% from the Speyer 2.1, 2.2 and 2.3 soils respectively (Keller, 1993c).

The second study was with the same soils. Formulated BAS 492 01 F containing kresoxim-methyl (20.6 µg ai) and fenpropimorph (41.2 µg ai) was added and the columns leached with water (393 ml, equivalent to 200 mm) for 2 days. The leachate was analysed for combined kresoxim-methyl and 490M1 as before and for fenpropimorph. The leachates contained 62.2-99.1%, 1.6-2.6% and 53.4-58.8% of combined kresoxim-methyl and acid from the Speyer 2.1, 2.2 and 2.3 soils respectively, and <0.8% of the fenpropimorph in all cases (Keller, 1994a).

The third study was identical except that formulated BAS 494 02 F containing kresoxim-methyl (24.5µg ai) and epoxiconazole (amount not stated) was added to the columns. The leachates

from the 2.1, 2.2 and 2.3 soils contained 41.2-48%, 14.7-24.3% and 43.3-62% of the combined ester and acid, and <0.2% of the epoxiconazole in all cases (Keller, 1994b).

In the fourth study Speyer 2.1 soil treated with [*phenyl*-^{14}C]kresoxim-methyl (radiochemical purity >99%, 0.5 mg/kg) was adjusted to 40% maximum water capacity and incubated in the dark at 20°C for 30 days with traps to collect volatile compounds. Samples of soil were extracted with acetonitrile/water and analysed by HPLC. Duplicate portions of the aged treated soil (113 g) were added to columns of the untreated soil which were leached with 200 mm water (393 ml) for 2 days. A similar experiment was undertaken with unaged soil.

Soil samples were extracted with methanol and methanol/water and water samples were acidified and partitioned with ethyl acetate. All extracts were then analysed by LSC and TLC.

In the unaged sample 40.2-56.1% of the AR was found in the leachate, mainly from 490M1. In the aged sample before leaching, 60% of the AR was extractable and most of this was due to 490M1, with small amounts of kresoxim-methyl and a more polar product. Unextractable residues accounted for 24.5% of the AR and volatile compounds for 4.5%. After leaching 56.7-58.4% of the AR was found in the leachate, mainly from 490M1. Of the 44-45% retained in the column, 26.1-30.7% of the AR was in the top 5 cm (Keller, 1991).

Mobility in soil (field leaching)

In a study according to BBA guidelines an SC formulation of [*phenoxy*- ^{14}C]kresoxim-methyl (radiochemical purity (*E*)- + (*Z*)-isomers 98.4%, 150 g ai/ha) was applied on 1 April and 4 May 1992 at Limbergerhof, Germany, to triplicate lysimeters (1 m² surface area, 1.2 m depth) containing Schifferstadt loamy sand in which barley was growing (growth stages 30/31 at the first application and 49/51 at the second application). In one of the lysimeters two further applications of 150 g ai/ha were made to winter wheat in April and May 1993 and a subsequent crop of oilseed rape was planted on 24 August 1993.

The lysimeters received 813 mm and 825 mm precipitation (rainfall + irrigation) in years one and two respectively. Leachate was collected regularly and except in one sample in June 1992 no leaching of radioactivity occurred before October of each year. Total radioactivity and $^{14}CO_2$ were measured and the nature of the remaining radioactivity was investigated. Where application was only in 1992 a total of 0.66-0.67% of the AR was leached over two years (mean concentration 0.4 µg/l). Where application was in 1992 and 1993, a total of 0.88% of the AR was leached over two years (mean concentration 0.62 µg/l). In all the lysimeters most of the radioactivity was in very polar unidentified fractions whilst CO_2 accounted for 0.03-0.09% of the AR. Kresoxim-methyl was not found (<0.01 µg/l) in any leachate sample. The annual average content of 490M1 was <0.01-0.04 µg/l and the highest individual concentration was 0.08 µg/l in April 1993.

At the end of the experiment the soil from one of the lysimeters treated in 1992 only was sectioned and the remaining radioactivity determined by combustion analysis. The whole profile contained 33.7% of the AR, and 25.9% of the AR was in the top 20 cm in which kresoxim-methyl concentrations were 0.38-0.79 µg/kg and 490M1 concentrations 0.25-0.33 µg/kg (Hamm, 1994).

Aqueous hydrolysis

In a study complying with EPA guidelines [*phenyl*-^{14}C]kresoxim-methyl (radiochemical purity (*E*)- + (*Z*)-isomer >98%, (*Z*)-isomer about 7%) was added to sterile buffer solutions at pH 5, 7 and 9 (0.23 mg/l) which were incubated at 25°C in the dark for periods up to 30 days and subsequently analysed by TLC. Recoveries were 97-106% of the AR and 490M1 was the only product. The first-order half-lives of kresoxim-methyl were 875, 34 and 0.29 days at pH 5, 7, and 9 respectively (Bieber 1992).

Aqueous photolysis

In a study according to BBA guidelines the absorbance in methanol was measured between 290 and 800 nm. There was little or no absorption above 340 nm, but at 292.5 nm the absorbance was 378 mol^{-1} cm^{-1} (Sarafin 1992a).

The quantum yield for kresoxim-methyl was determined over the range of incubation times. It varied with the duration of irradiation, which the author considered to show that the photoproducts were also absorbing. Quantitative details of the photoproducts obtained were not provided but compound 490M0 was detected (Sarafin 1992b).

In a study according to EPA guidelines [*phenyl*-^{14}C]kresoxim-methyl (radiochemical purity (*E*)-isomer 99.3%) was dissolved in sterilized 0.01M acetate buffer at pH5 (2 mg/l) and irradiated at 25°C with a xenon light source. The intensity of the source was the same as measured in December 1993 in North Carolina, USA, and wavelengths below 290 nm were filtered out. Samples were collected at six intervals during 370 h irradiation (volatile compounds were collected in appropriate traps) and analysed by LSC, HPLC and LC-MS.

The recovery of ^{14}C for all samples was 90-99% of the AR and no degradation occurred in the dark controls. After 370 h irradiation a total of 0.16% of the AR was found in the trapping solutions and six unknown compounds were detected in the main solution, none of which accounted for >5% of the AR at any time. The first-order half-life of kresoxim-methyl was calculated to be 716 h (r^2=0.9) (Goetz 1994).

The photolysis of 490M1 was studied in natural pond water (pH 8, 10 mg/l) and pure water (10 mg/l) irradiated at 20°C with a xenon light source. The intensity of the source was 3.0 mW/cm², which was stated to be consistent with the natural sunlight intensity on a clear sunny day, presumably in Germany, and wavelengths below 290 nm were filtered out. Samples were collected at six intervals during 15 days irradiation and compared with dark controls. Analysis was by HPLC and LC-MS.

No degradation of 490M1 took place in pond water stored in darkness for 15 days, but when the compound was irradiated in pure water and natural water, first-order half-lives were 37 days and 19 days respectively. In the natural water sample an additional compound occurred during irradiation which was found to be phthalic acid, but the author concluded that this was not likely to be formed by degradation of 490M1.

The absorbance spectra of the natural water solution were measured before and after irradiation and the absorbance was found to be lower at all wavelengths after irradiation, showing a consumption of potential photosensitizing compounds during the study period (Scharf, 1994).

Biodegradability

In studies complying with OECD guideline 301D the biodegradabilities of kresoxim-methyl and 490M1 were investigated using sewage plant effluent as the biological innoculum. Oxygen demand was found to be <20% and 0% respectively of the theoretical maximum values after 28 days, showing that neither kresoxim-methyl nor 490M1 is readily biodegradable under the conditions of the guideline (Lungershausen, 1993a).

Studies on the degradation of kresoxim-methyl in an aerobic aquatic environment (Beiber, 1993) and in air and the atmosphere (Sarafin 1993) were also submitted but not reviewed.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Methods for plants, plant products and feeding stuffs, soil and water, and animal products are summarized in Tables 24-26. Methods and chromatograms were acceptable unless otherwise stated. Low recoveries of 490M2 and 490M9 from wheat straw were observed at the lowest fortification level of 0.05 mg/kg. Variable recoveries of metabolites (up to 22.4% RSD) and low recoveries of 490M1 and 490M2 were reported for fat at the lowest fortification level. RSDs up to 34.8% were reported for 490M2 in milk although for all fortification levels the RSD averaged 13.9%. No methods were reported for residues in poultry products.

Table 24. Analytical methods and their validation for plants, plant products and feeding stuffs.

Sample	Analyte	Extraction	Partition, clean-up	Quantification	LOD, mg/kg	Spike, mg/kg	Mean recoveries %	RSD, % (n)	References
Apple, Wheat straw, wheat grain	Parent	methanol and KH_2PO_4	iso-octane, SPE silica gel, SPE C18	GC-ECD	0.05	0.05-5.0	92.8-105.5 92.4 87.5-96.5	6.4 (10). 18.4 7.8 (8)	Krotzky & Dams 1993; Schulz 1994a
Apple, Cereal straw, cereal grain Forage	Parent	aqueous methanol and KH_2PO_4	iso-octane, SPE silica gel, SPE C18	GC–MS and GC–ECD	0.05	0.05-5.0	79.3-93.8 91.8-111 97.9-98.5 104-106	5-7 (16). 7.6-11.2 (8). 12-16.4 (8). 5.6-9.2 (8)	Mackenroth & Krotzky 1994a
Apple	Parent	As above	As above	GC – ECD	0.05	0.05-5.0	103-109	7-9 (8)	Wayman 1994a
Wheat grain Apple[3]	Parent	acetone /water	sodium chloride/ dichloromethane, GPC (Bio Beads S-X3), silica gel	GC – ECD	0.01	0.01-0.1	100-101 99-100	0.7-1.4 (4). 2.1-3.5 (4)	Schmidt *et al.* 1994
Wheat forage Wheat straw	Parent 490M2 490M9 Parent 490M2 490M9	sequential aqueous methanol, aqueous ammonia/ methanol.	Iso-octane SPE silica gel, SPE C18 (parent only). Ethyl acetate/MTBE[2], enzyme hydrolysis (glucosidase, hesperinidase) with ascorbic acid, partition -dichloromethane, SPE NH2, HPLC RP-C18 (metabolites only).	GC – ECD or MS (parent). HPLC-UV (270 nm)	0.01[1] 0.05 0.05 0.01 0.05 0.05	0.05-5.0	89.2-104.1 74.9-89.4 78.8-84.5 91.8-111 61.8-73.7 60.7-73.4	1.8-9.2 (8). 2.8-8.7 (8). 3.2-6.6 (8). 7.6-11.2 (8). 7.6-12.6 (8). 8.6-12.7 (8)	Krotzky & Dams 1994a
Cereal plant Cereal grain Cereal straw	Parent 490M2 490M9 Parent Parent 490M2 490M9	As above	As above	As above	0.05	0.05-5.1 0.05-5.5 0.06-6.1 0.05-5.1 0.05-5.1 0.05-5.3 0.05-5.3	77-81 80-89 84 82-98 74-97 92-96 96-98	4.2-11 (8). 6-11 (8). 11 (8). 4.4-13 (8). 2.3-2.9 (8). 3.2-12 (8). 6-16 (8)	Flintham & Gillis 1994

[1]LOD quoted as 0.01 mg/kg, but lowest validation was 0.05 mg/kg
[2]Methyl *tert*-butyl ether
[3]Proposed for post-approval monitoring

Table 25. Analytical methods and their validation for soil and water.

Sample	Analyte	Extraction	Partition, clean-up	Quantification	LOD, mg/kg	Spike, mg/kg	Mean recoveries %	RSD, % (n)	References
Soil	Parent	KH_2PO_4 buffer/iso-octane	SPE silica gel	GC-MS	0.01	0.01-1.05	86.3-91.4	5.2-5.5 (8)	Mackenroth & Krotzky 1994b
Soil	Parent	As above	As above	GC-ECD	0.01	0.01-1.0	74.3-75.7	9-13 (8)	Wayman 1994b
Soil	Parent & 490M1, expressed as parent	KH_2PO_4 buffer	SPE Extrelut/ethyl acetate, SPE C18, esterification of 490M1 with methanol/H_2SO_4, further SPE C18	GC-ECD	0.01	0.01-1.0 0.01-1.0	66.3-76.1 71.9-83.6	9.8 (4). 0.8-9.2 (20)	Krotzky 1994a
Soil	Parent & 490M1, expressed as parent	As above	As above	As above	0.01	0.01-1.0 0.01-1.0	75-95.3 77.8-84.8	10.2-12.3(8). 8.6-10.3 (8)	Nigel & Matthew 1994
Water	Parent & 490M1, expressed as parent	Hydrolysis with NaOH, extraction of free acid on SPE C18	Esterification to parent with methanol/H_2SO_4, further SPE C18.	GC-ECD or MS.	0.05 µg/l	0.05-5.0 µg/l	73-75.9 80.2-97.2	3.0-3.4 (4). 6.3-8.7 (12)	Krotzky 1994b
Air	Parent 490M1	Tenax adsorbant, acetone extraction	Re-dissolved in acetonitrile	HPLC (Nucleosil C18)-UV (254 nm)	0.004 µg/l	0.004-0.407 0.004-0.377	75.8-93.7 86.6-96.6	7.4-10.8 (8). 4.2-9.1 8)	Sarafin 1994

Table 26. Analytical methods and their validation for animal products.

Sample	Analyte	Extraction	Partition, clean-up	Quantification	LOD, mg/kg	Spike, mg/kg	Mean recoveries %	RSD, % (n)	Ref.
Milk	490M2 490M9	acetone, extract centrifuged, (protein precipitated), addition of ascorbic acid and phosphate buffer	Iso-octane & DCM partitioning, SPE-NH_2, further DCM partition.	HPLC (NH_2,/ C18)-UV (270 nm)	0.001	0.001-0.025 0.001-0.025	88.3-108.3 93.0-100.3	4.8-4.9 (8) 2.3-5.8 (8)	Krotzky & Dams 1994b.
Milk	490M2 490M9	As above	As above	As above	0.002	0.001-0.1 0.001-0.1	68.4-96.5 83.5-91.0	2.4-34.8(12) 3.0-8.4 (12)	Maxwell 1994
Muscle	490M1 490M2	methanol, filtration	$Ca(OH)_2$-precipitation of non-polar compounds, dichloromethane partition, SPE NH_2, HPLC RP C18.	HPLC (NH2/CN)-UV (270nm)	0.01	0.01-1.0	83.6-88.9 88.4-88.7	2.5-21.2 (8) 2.8-7.4 (8)	Mackenroth Krotzky 1994c
Muscle	490M1 490M2	As above	As above	As above	0.01	0.01-1.0	88.0-94.7 80.9-95.7	4.4-4.7 (8) 10.2-11.0(8)	
Fat	490M1 490M2 490M9	As above	As above	As above	0.01	0.01-1.0	55.9-82.2 53.1-84.1 61.8-88.5	5.6-8.2 (8) 4.8-12.2 (8) 1.9-9.1 (8)	Mackenroth Krotzky 1994c
Fat	490M1 490M2 490M9	As above	As above	As above	0.01	0.01-1.0	63.9-81.3 64.7-89.0 72.2-108.7	13.3-22.4(8) 16.7-21.9(8. 18.2-21.9(8)	Maxwell 1994
Kidney	490M1 490M2 490M9	As above	As above	As above	0.01	0.01-1.0	79.5-97.4 80.4-91.0 82.1-109.4	6.2-17.4 (8) 4.5-6.5 (8) 3.4-3.9 (8)	Mackenroth Krotzky 1994c
Kidney	490M1 490M2 490M9	As above	As above	As above	0.01	0.01-1.0	81.0-82.4 76.3-91.5 81.7-85.0	5.2-15.6 (8) 6.2-8.8 (8) 10.4-16.7(8)	Maxwell 1994
Liver	490M1 490M9	As above	As above	As above	0.01	0.01-1.0	76.6-83.8 71.5-102.1	2.2-16.7 (8) 0.7-5.5 (8)	Mackenroth Krotzky 1994c
Liver	490M1 490M9	As above	As above	As above	0.01	0.01-1.0	73.6-74.8 82.6-97.1	2.5-7.9 (8). 6.4-17.8 (8)	Maxwell 1994

Stability of pesticide residues in stored analytical samples

(a) Trials with [^{14}C]kresoxim-methyl

Apples. Storage stability was determined in the apple metabolism study. After six applications of 0.4 kg/ha phenyl-labelled [^{14}C]kresoxim-methyl. to leaves, samples of peel were stored up to 14 months at -18°C before being extracted with methanol and analysed by HPLC and TLC. There was no marked change in the nature of the radioactive residues during storage as shown in Tables 27 and 28 (Hofmann, 1992a-c; Grosshans, 1994).

Table 27. Extractability of radioactivity from apple peel before and after storage, treated with phenyl-labelled [^{14}C]kresoxim-methyl.

	Before storage		After storage	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR (E+R)	1.577	100.0	1.865	100.0
MeOH extract (E)	1.499	95.1	1.783	95.6
Extraction residue (R)	0.078	4.9	0.082	4.4

Table 28. Composition of radioactivity in extracts of apple peel before and after storage.

HPLC peak no.	Identity	Before storage % of TRR	After storage at -18°C % of TRR	Extract at end of study, not stored % of TRR
A6	2.0	2.2	2.2	
A7	conjugates	6.3	9.2	8.3
A8	490Ml	3.9	3.6	3.6
A9		2.8	2.6	2.5
A10	parent	79.8	78.7	77.0
All	(*Z*)-isomer	5.2	2.5	4.1

Wheat. Storage stability data were available from the wheat metabolism study. After two applications of 0.4 kg/ha phenyl-labelled [^{14}C]kresoxim-methyl. to wheat, straw samples were stored at -18°C before being extracted with methanol. There was no marked change in the composition of the radioactive residues during 21 months storage as shown in Tables 29 and 30 (Hofmann, 1991a,b; Grosshans, 1994).

Table 29. Extractability of radioactivity from wheat straw before and after storage, after treatment with phenyl-labelled [^{14}C]kresoxim-methyl.

	Before storage		After storage	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR (E+R)	44.84	100	58.23	100
MeOH extract (E)	39.38	87.8	50.93	87.5
Extraction residue (R)	5.46	12.2	7.29	12.5

Table 30. Composition of radioactivity in extracts of wheat straw before and after storage.

TLC peak no.	Rf	Before storage % of TRR	After storage at -18°C % of TRR	Extract from end of study (not stored) % of TRR
1	origin	9.1	9.0	8.3
2	Rf of 490M1	2.6	2.3	2.0
3	Rf of parent	88.4	88.7	89.7

Grapes. In the grape plant metabolism study, after five applications of 0.5 kg/ha phenoxy and phenyl-labelled [^{14}C]kresoxim-methyl. to grapes, samples were stored at or below 0°C up to 15 months before analysis. There were small qualitative and quantitative differences in the composition of the TRR after 8 months storage. The results are shown in Tables 31 and 32 (Nelsen *et al.*, 1995).

Table 31. Extractability of radioactivity before and after storage from grapes treated with phenoxy- and phenyl-labelled [^{14}C]kresoxim-methyl.

	Phenoxy label				Phenyl label			
	Before storage		After 8 months storage		Before storage		After 8 months storage	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Acetone extract I	89.96	1.55	73.09	2.25	83.86	1.93	73.67	2.76
Acetone extract II	6.38	0.11	22.54	0.69	12.46	0.29	19.15	0.72
Unextracted	3.66	0.06	4.37	0.13	3.67	0.08	7.17	0.27
Total	100	1.73	100	3.07	100	2.30	100	3.75

Table 32. Composition of radioactive residues by TLC in extracts of grapes

	<30 days storage acetone/water extract, whole grapes	After 8 months storage at ≤0°C acetone/water extract, whole grapes	After 15 months storage at ≤0°C methanol extract, rinsed & homogenized grapes
% parent	68.32	75.01	58.4
% polar	15.81	18.04	23.6
% others	15.87	6.96	8.66

Poultry excreta and liver. Samples of excreta and liver from poultry treated with 180 mg/kg [^{14}C]kresoxim-methyl were stored at -18°C up to 21 months. The residues before and after storage are shown in Table 33. The extraction and composition of samples at the beginning and the end of the storage period showed comparable results (Burke, 1994; Grosshans, 1994c).

Table 33. Storage stability of residues in poultry samples taken after treatment of hens with [^{14}C]kresoxim-methyl.

Sample	Before storage		After storage		Reference
	% of TRR	mg/kg	% of TRR	mg/kg	
Liver		TRR = 6.90		TRR = 6.90	30942
Methanol extract	77.0	5.32	75.1	5.18	
Water extract	5.5	0.38	4.8	0.33	
Unextracted	17.5	1.21	20.1	1.39	
Excreta		TRR = 123		TRR = 113	30942
Methanol extract	84.3	103.7	85.0	96.5	
Unextracted	15.7	19.3	15.0	16.9	

Trials with unlabelled compounds

Crops. Apples, wheat grain, straw and forage were fortified with kresoxim-methyl, 490M2 and 490M9 at 1 mg/kg and stored at -20°C for 214 days. The stability of 490M2 and 490M9 was also determined in treated field samples. The results, corrected for procedural recoveries, are shown in Table 34.

Table 34. Storage stability of kresoxim-methyl and metabolites in wheat and apples.

Sample	Analyte	Type of residue	Storage period, days	Recovery, %	Reference
Grain	kresoxim-methyl	spiked	7	109.5	Krotzky 1994c
			30	91.3	
			93	98.3	
			214	104.9	
Straw	kresoxim-methyl	incurred	56	97.5	Krotzky 1994c
			91	100.3	
	490M2		56	96.5	
			91	109.8	
	490M9		56	53.3	
			91	142	
Forage	kresoxim-methyl	spiked	7	94.9	Krotzky 1994c
			35	97.8	
			168	86.2	
	490M2		35	-(<0.05 mg/kg)	
			168	-(<0.05 mg/kg)	
	490M9		35	96.7	
			168	108.7	
Apple	kresoxim-methyl	spiked	0	101	Mackenroth & Krotzky 1994d
			7	103	
			30	86.0	
			63	99.2	
			182	95.8	
			295	98.2	

Soil. Soil samples fortified separately with kresoxim-methyl and 490M1 at 0.5 mg/kg were stored at -20°C for one year. The residues found at intervals are shown in Table 35. The results were corrected for procedural recoveries.

Table 35. Storage stability of kresoxim-methyl and 490M1 added to soil at 0.5 mg/kg.

Analyte	Storage, months	Recovery, % (pH 6 soil)	Recovery, % (pH 8 soil)	Reference
kresoxim-methyl	0.5	82.6	99.0	Mann 1994
	1	87.0	101	
	3	86.1	101	
	6	73.9	78.6	
	12	72.2	76.7	
490M1	0.5	84.0	94.8	Mann 1994
	1	82.4	106.2	
	3	87.4	125.8	
	6	91.6	84.5	
	12	81.2	148.5	

USE PATTERN

Kresoxim-methyl was reported as being registered in many countries as shown in Tables 36-39. All the information was supplied by the manufacturer unless otherwise noted (BASF 1998, Regenstein 1998a-c).

Table 36. Registered uses of kresoxim-methyl on fruit (all field applications).

Commodity	Country	Form	Application			Max No[a]	PHI, days	Pest or disease, notes
			Spray conc., kg ai/hl	Water vol., l/ha	kg ai/ha			
Apple	Austria	WG	0.010	1000	0.100	6 (4)	35	ventura inaequalis
	Belgium	WG	0.007	1500	0.100	8 (4)	35	podosphaera leucotricha
	Belgium	WG	0.007	1500	0.100	8 (4)	35	venturia inaequalis
	Brazil	SC	0.01	1000	0.100	3	35	venturia inaequalis
	Chile	SC		1000	0.100	3	45	podosphaera leucotricha
	Chile	SC		1000	0.100	3	45	venturia inaequalis
	Chile	SC		1000	0.100	3	45	venturia pirina
	France	WG	0.010	1000	0.100	6 (4)	35	podosphaera leucotricha
	France	WG	0.010	1000	0.100	6 (4)	35	venturia inaequalis
	Hungary	WG	0.010	1000	0.100	4	35	podosphaera leucotricha
	Hungary	WG	0.010	1000	0.100	4	35	venturia inaequalis
	Israel	WG	0.008	1000	0.075		35	podosphaera leucotricha
	Israel	WG	0.008	1000	0.075		35	venturia inaequalis
	Italy	WG	0.005-0.007	1000		8 (4)	35	venturia inaequalis
	Italy	WG	0.005-0.007	1000		8 (4)	35	venturia pirina
	Japan	WG			1.880	3	30	alternaria mali
	Japan	WG			0.470	3	30	mycosphaerella pomi
	Japan	WG			0.470	3	30	podosphaera leucotricha
	Japan	WG			0.470	3	30	venturia inaequalis
	Netherlands	WG	0.010	1000	0.100	8 (4)	42	podosphaera leucotricha
	Netherlands	WG	0.010	1000	0.100	8 (4)	42	venturia inaequalis
	New Zealand	WG	0.005	2000	0.100	6	14	podosphaera leucotricha
	New Zealand	WG	0.005	2000	0.100	6	14	venturia inaequalis
	Norway	WG	0.01-0.015			4	21	podosphaera leucotricha
	Norway	WG	0.01-0.015			4	21	venturia inaequalis
	Poland	WG			0.100	6	35	podosphaera leucotricha
	Poland	WG			0.100	6	35	venturia inaequalis
	Poland	WG			0.100	6	35	venturia pirina
	Slovakia	WG	0.02			4		podosphaera leucotricha
	Slovakia	WG	0.02			4		venturia inaequalis
	South Africa	WG	0.007-0.01	500		6	45	podosphaera leucotricha
	South Africa	WG	0.007-0.01	500		6	45	venturia inaequalis
	Spain	WG	0.0075-0.010	1000	0.100	4	35	podosphaera leucotricha
	Spain	WG	0.0075-0.010	1000	0.100	4	35	
	Sweden	WG			0.100	6 (4)	42	podosphaera leucotricha
	Sweden	WG			0.100	6 (4)	42	venturia inaequalis
	Switzerland	WG			0.100	4		podosphaera leucotricha
	Switzerland	WG			0.100	4		venturia inaequalis
	UK	WG	0.050	200	0.100	5 (4)	35	venturia inaequalis
	Uruguay	SC	0.005	2000	0.100	3		venturia spp
Citrus	Japan	WG			1.410	3	14	botrytis cinerea
	Japan	WG			1.410	3	14	diaporthe citri
	Japan	WG			1.410	3	14	elsinoe fawcettii
	South Africa	WG	0.02	500			56	guidnardia citricarpa
Currant, black	Norway	WG	0.01-0.02			4	21	pseudopeziza ribis
	Norway	WG	0.01-0.02			4	21	sphaerotheca mors-uvae
	Switzerland	WG			0.15	4	21	glomerella cingulata
Currant, red	Norway	WG	0.01-0.02			4	21	pseudopeziza ribis

Commodity	Country	Form	Application			Max No[a]	PHI, days	Pest or disease, notes
			Spray conc., kg ai/hl	Water vol., l/ha	kg ai/ha			
	Norway	WG	0.01-0.02			4	21	sphaerotheca mors-uvae
	Switzerland	WG			0.15	4	21	glomeerella cingulata
Gooseberry	Norway	WG	0.01-0.02			4	21	pseudopeziza ribis
	Norway	WG	0.01-0.02			4	21	sphaerotheca mors-uvae
Grape	Austria	WG	0.0125	300-1000	0.0375-0.125	6 (3)	35	powdery mildew
	Austria	WG	0.0125	300-1000	0.0375-0.125	6 (3)	35	Uncinula necator
	Chile	SC			0.100	3	45	botrytis cinerea
	Chile	SC			0.100	3	45	uncinula necator
	Germany	WG	0.0075	*1600*	*0.12*	6 (3)	35	uncinula necator
	Hungary	WG	0.010	1000	0.100	5	35	uncinula necator
	Israel	WG	0.010	1000	0.100		21	uncinula necator
	Japan	WG			0.940	3	30	diaporthe spp.
	Japan	WG			0.940	3	30	gloeosporium ampelophagum
	Japan	WG			0.940	3	30	plasmopara viticola
	Slovakia	WG			0.02-0.03	3		botrytis cinerea
	Slovakia	WG			0.02-0.03	3		plasmopara viticola
	Slovakia	WG			0.02-0.03	3		uncinula necator
	South Africa	WG	0.023	250		6	14	uncinula necator
	Spain	WG	0.0075-0.015			3	35	uncinula necator
	Switzerland	WG	0.0075	*1600*	*0.12*	4	b	erwinia herbicola
	Switzerland	WG	0.0075	*1600*	*0.12*	4	b	guignardia bidwellii
	Switzerland	WG	0.0075	*1600*	*0.12*	4	b	plasmopara viticola
	Switzerland	WG	0.0075	*1600*	*0.12*	4	b	uncinula necator
Peach	Japan	WG			1.175	3	1	venturia carpophila
Pear	Austria	WG	0.010	1000	0.100	6 (4)	35	Venturia pirina
	Belgium	WG	0.007	1500	0.100	8 (4)		venturia pirina
	Chile	SC			0.100	3	45	podosphaera leucotricha
	Chile	SC			0.100	3	45	venturia inaequalis
	Chile	SC			0.100	3	45	venturia pirina
	France	WG	0.010	1000	0.100	6 (4)	35	venturia pirina
	Hungary	WG	0.010	1000	0.100	4	35	podosphaera leucotricha
	Hungary	WG	0.010	1000	0.100	4	35	venturia inaequalis
	Italy	WG	0.007	1000		8 (4)	14	stemphylium spp.
	Netherlands	WG	0.010	1000	0.100	8 (4)	42	venturia pirina
	Norway	WG	0.005-0.0075			4	21	phyllactinia guttata/pyri
	Norway	WG	0.005-0.0075			4	21	venturia pirina
	Poland	WG			0.100	6	35	podosphaera leucotricha
	Poland	WG			0.100	6	35	venturia pirina
	South Africa	WG	0.005	500		6	45	venturia pirina
	Spain	WG	0.0075-0.010	1000	0.100	4	35	venturia pirina
	Sweden	WG			0.100	6 (4)	42	phyllactinia guttata/pyri
	Sweden	WG			0.100	6 (4)	42	venturia pirina
	Switzerland	WG			0.100	4		podosphaera leucotricha
	Switzerland	WG			0.100	4		venturia inaequalis
	Uruguay	SC	0.005	2000	0.100	3		venturia spp
Pear, Oriental	Japan	WG			1.410	3	14	alternaria kikuchiana
	Japan	WG			0.470	3	14	venturia nashicola
Plum	Norway	WG				4	21	blumeriella jaapii
Plum, Kaki	Japan	WG			0.799	3	14	phyllactinia suffulta

Commodity	Country	Form	Application			Max No[a]	PHI, days	Pest or disease, notes
			Spray conc., kg ai/hl	Water vol., l/ha	kg ai/ha			
Pome fruits	Germany	WG	0.00625		~0.0625 per metre of tree top	8 (4)	35	podosphaera leucotricha Typically pome fruit trees 3m ~ 0.1875kg ai/ha
	Germany	WG	0.00625		~0.0625 per metre of tree top	8 (4)	35	venturia spp. Typically pome fruit trees 3m ~0.1875kg ai/ha
Small fruits	Switzerland	WG			0.150	4	21	powdery mildew
Strawberry	Israel	WG		1000	0.100		3	
	Norway	WG	0.01-0.02			4	14	diplocarpon earlianum
	Norway	WG	0.01-0.02			4	14	mycosphaerella fragariae
	Norway	WG	0.01-0.02			4	14	phomopsis obscurans
	Switzerland	WG			0.150	4	14	uncinula necator

[a] Numbers in parentheses represent the **proposed** maximum number of applications since GAP is to be changed (probably in 1999 season) for members of the European Community
[b] Use at 3-leaf stage – GS 13 – to berry touch – GS 77 to 79.
Figures in italics were not stated on the product label or in registration document but are estimated values supplied by the manufacturer.

Table 37. Registered uses of kresoxim-methyl on vegetables.

Commodity	Country	Form	F/G	Application			Max. No.	PHI, days	Pest or disease
				Spray conc., g ai/hl	Water, l/ha	kg ai l/ha			
Cucumber	Brazil	SC	F	0.030	500	0.150	3	7	erysiphe cichoracearum
	Japan	SC	F			0.415	3	1	sphaerotheca fuliginea
	Norway	WG	G	0.01-0.015			4	4	leveillula taurica
Cucurbits	Spain[a]	WG	G	0.01-0.015				3	-
Onion, Welsh	Japan	SC	F			0.623	3	7	puccinia allii
Onion	Nicaragua	SC	F			0.225			alternaria spp.
Pepper, Sweet	Spain[a]	WG	G	0.01-0.025				3	-
Potato	Brazil	SC	F	0.040	500	0.200	3	7	alternaria solani
Tomato	Brazil	SC	F	0.020	1000	0.200	3	3	alternaria solani
	Norway	WG	G	0.01-0.015			4	4	leveillula taurica
	Spain[a]	WG	G	0.01-0.025				3	-

F: field G: glasshouse
[a] Information quoted from the *Notification of Authorisation*, 24 July, 1998. Ministerio de Agricultura, Pesca y Alimentation, Spain. The product label detailed use only on pome fruit

Table 38. Registered uses of kresoxim-methyl on cereals (field applications).

Commodity	Country	Form	Application			Max No.	PHI days	Pest or disease
			Spray conc., kg ai/hl	Water, l/ha	kg ai/ha			
Cereals	Germany	SE	0.031-0.063	200-400	0.125	1	35	cercosporella herpotrichoides
	Germany	SE	0.031-0.063	200-400	0.125	1	35	cercosporella herpotrichoides
	Japan	SC			0.415	3	14	erysiphe graminis
	Japan	SC			0.415	3	14	fusarium nivale
	Japan	SC			0.415	3	14	fusarium roseum
Barley	Belgium	SC	0.063	200	0.125	2	35	erysiphe graminis hordei
	Belgium	SC	0.063	200	0.125	2	35	puccinia hordei
	Belgium	SC	0.063	200	0.125	2	35	puccinia striiformis

Commodity	Country	Form	Application			Max No.	PHI days	Pest or disease
			Spray conc., kg ai/hl	Water, l/ha	kg ai/ha			
	Belgium	SC	0.063	200	0.125	2	35	pyrenophora teres
	Belgium	SC	0.063	200	0.125	2	35	rhynchosporium secalis
	France	SE	0.053	200	0.0105	2	35	erysiphe graminia
	France	SC	0.063	200	0.125	2	35	cochliobolus sativus
	France	SC	0.063	200	0.125	2	35	erysiphe graminis avenae
	France	SC	0.063	200	0.125	2	35	puccinia hordei
	France	SC	0.063	200	0.125	2	35	puccinia striiformis
	France	SC	0.063	200	0.125	2	35	rhynchosporium secalis
	Germany	SE	0.027-0.053	200-400	0.105	2	35	erisyphe graminis/secalis
	Germany	SE	0.027-0.053	200-400	0.105	2	35	erysiphe graminis
	Germany	SE	0.027-0.053	200-400	0.105	2	35	erysiphe graminis/tritici
	Germany	SE	0.031-0.063	200-400	0.125	2	35	erysiphe graminis/tritici
	Germany	SE	0.031-0.063	200-400	0.125	2	35	puccinia hordei
	Germany	SE	0.031-0.063	200-400	0.125	2	35	pyrenophora teres
	Germany	SE	0.031-0.063	200-400	0.125	2	35	rhynchosporium secalis
	Germany	SC	0.031-0.063	200-400	0.125	2	35	erysiphe spp
	Germany	SC	0.031-0.063	200-400	0.125	2	35	puccinia hordei
	Germany	SC	0.031-0.063	200-400	0.125	2	35	pyrenophora teres
	Germany	SC	0.031-0.063	200-400	0.125	2	35	rhynchosporium secalis
	Luxembourg	SC	0.031-0.063	200-400	0.125	2	35	errysiphe graminishelminthosporium spp.puccinia hordeipuccinia striiformisrhynchosporium spp.
	Norway	SE			0.105		42	cercosporella herpotrichoides
	Norway	SE			0.105		42	leptosphaeria nodorum
	Norway	SE			0.105		42	mycosphaerella tassiana
	Switzerland	SC			0.126	1		erysiphe graminis/tritici
	Switzerland	SC			0.126	1		puccinia hordei
	Switzerland	SC			0.126	1		pyrenophora teres
	Switzerland	SC			0.126	1		septoria passerinii
Barley, Spring	Belgium	SE	0.053	200	0.105	2	35	erysiphe graminis hordei
	Belgium	SE	0.053	200	0.105	2	35	puccinia hordei
	Belgium	SE	0.053	200	0.105	2	35	pyrenophora teres
	Ireland	SC	0.063	200	0.125	2	-	cercosporella herpotrichoideserysiphe graminis hordeipuccinia hordeipuccinia striiformispyrenophora teresseptoria passerinii
	Netherlands	SE			0.105	2	35	erysiphe graminis
	Netherlands	SC			0.125	2	35	puccinia hordei
	Netherlands	SC			0.125	2	35	puccinia striiformis
	Netherlands	SC			0.125	2	35	pyrenophora teres
	Netherlands	SC			0.125	2	35	rhynchosporium secalis
	Poland	SE	0.053	200	0.105	1	35	erysiphe graminis
	Poland	SE	0.053	200	0.105	1	35	puccinia hordei
	Poland	SE	0.053	200	0.105	1	35	pyrenophora teres
	Poland	SE	0.053	200	0.105	1	35	rhynchosporium secalis
	Slovakia	SC			0.125	1		erysiphe graminis
	Slovakia	SC			0.125	1		pyrenophora teres
	Slovakia	SC			0.125	1		rhynchosporium secalis
	UK	SE			0.105	2		erysiphe graminis
	UK	SE			0.105	2		rhynchosporium secalis
	UK	SC	0.063	200	0.125	2		cercosporella herpotrichoides
	UK	SC	0.063	200	0.125	2		furarium spp
	UK	SC	0.063	200	0.125	2		leptosphaeria nodorum
	UK	SC	0.063	200	0.125	2		septoria tritici
Barley, Winter	Belgium	SE	0.053	200	0.105	2	35	erysiphe graminis hordei
	Belgium	SE	0.053	200	0.105	2	35	puccinia hordei
	Belgium	SE	0.053	200	0.105	2	35	pyrenophora teres
	Belgium	SC	0.063	200	0.125	2	35	erysiphe graminis hordei
	Belgium	SC	0.063	200	0.125	2	35	puccinia hordei

Commodity	Country	Form	Application			Max No.	PHI days	Pest or disease
			Spray conc., kg ai/hl	Water, l/ha	kg ai/ha			
	Belgium	SC	0.063	200	0.125	2	35	puccinia striiformis
	Belgium	SC	0.063	200	0.125	2	35	pyrenophora teres
	Belgium	SC	0.063	200	0.125	2	35	rhynchosporium secalis
	Ireland	SC	0.063	200	0.125	2	-	cercosporella herpotrichoideserysiphe graminis hordeipuccinia hordeipuccinia striiformispyrenophora teresseptoria passerinii
	Netherlands	SE			0.105	2	35	erysiphe graminis
	Netherlands	SE			0.105	2	35	erysiphe graminis
	Netherlands	SC			0.125	2	35	puccinia hordei
	Netherlands	SC			0.125	2	35	puccinia striiformis
	Netherlands	SC			0.125	2	35	pyrenophora teres
	Netherlands	SC			0.125	2	35	rhynchosporium secalis
	Poland	SE	0.053	200	0.105	1		erysiphe graminis
	Poland	SE	0.053	200	0.105	1		puccinia hordei
	Poland	SE	0.053	200	0.105	1		pyrenophora teres
	Poland	SE	0.053	200	0.105	1		rhynchosporium secalis
	UK	SE			0.105	2		erysiphe graminis
	UK	SE			0.105	2		rhynchosporium secalis
	UK	SE	0.063	200	0.125	2		cercosporella herpotrichoides
	UK	SE	0.063	200	0.125	2		fusarium spp
	UK	SE	0.063	200	0.125	2		leptosphaeria nodorum
	UK	SE	0.063	200	0.125	2		septoria tritici
	UK	SC	0.063	200	0.125	2		cercosporella herpotrichoides
	UK	SC	0.063	200	0.125	2		fusarium spp.
	UK	SC	0.063	200	0.125	2		leptosphaeria nodorum
	UK	SC	0.063	200	0.125	2		septoria tritici
	UK	SE	0.063	200	0.125	2		cercosporella herpotrichoides
	UK	SE	0.063	200	0.125	2		fusarium spp.
	UK	SE	0.063	200	0.125	2		leptosphaeria nodorum
	UK	SE	0.063	200	0.125			septoria tritici
Oats	France	SC	0.063	200	0.125	2	35	erysiphe graminis avenae
	France	SC	0.063	200	0.125	2	35	puccinia avenae
	Norway	SE			0.105		42	cercosporella herpotrichoides
	Norway	SE			0.105		42	leptosphaeria nodorum
	Norway	SE			0.105		42	mycosphaerella tassiana
Rye	Belgium	SE	0.053	200	0.105	2	35	erysiphe graminis/tritici
	Belgium	SE	0.053	200	0.105	2	35	leptosphaeria nodorum
	Belgium	SE	0.053	200	0.105	2	35	puccinia recondita
	Belgium	SE	0.053	200	0.105	2	35	puccinia striiformis
	Belgium	SE	0.053	200	0.105	2	35	septoria tritici
	Belgium	SC	0.063	200	0.125	1	35	erysiphe graminis/tritici
	Belgium	SC	0.063	200	0.125	1	35	puccinia recondita
	Belgium	SC	0.063	200	0.125	1	35	puccinia striiformis
	Belgium	SC	0.063	200	0.125	1	35	septoria tritici
	France	SC	0.063	200	0.125	2	35	puccinia recondita/recondita
	France	SC	0.063	200	0.125	2	35	rhynchosporium secalis
	Germany	SE	0.027-0.063	200-400	0.105	2	35	erisyphe graminis/secalis
	Germany	SE	0.027-0.063	200-400	0.105	2	35	erysiphe graminis
	Germany	SE	0.027-0.063	200-400	0.105	2	35	erysiphe graminis/tritici
	Germany	SE	0.027-0.063	200-400	0.125	2	35	erysiphe graminis/tritici
	Germany	SE	0.027-0.063	200-400	0.125	2	35	puccinia recondita/recondita
	Germany	SE	0.027-0.063	200-400	0.125	2	35	rhynchosporium secalis
	Germany	SC	0.027-0.063	200-400	0.125	2	35	erysiphe spp
	Germany	SC	0.027-0.063	200-400	0.125	2	35	puccinia recondita/recondita
	Germany	SC	0.027-0.063	200-400	0.125	2	35	rhynchosporium secalis
	Luxembourg	SC	0.027-0.063	200-400	0.125	1	35	puccinia recondita/triticiapuccinia striiformisseptoria spp.
	Poland	SE	0.053	200	0.105	1	35	erysiphe graminis
	Poland	SE	0.053	200	0.105	1	35	puccinia recondita
	Poland	SE	0.053	200	0.105	1	35	rhynchosporium secalis
	Poland	SE	0.053	200	0.105	1	35	septoria tritici

Commodity	Country	Form	Application			Max No.	PHI days	Pest or disease
			Spray conc., kg ai/hl	Water, l/ha	kg ai/ha			
	Switzerland	SC			0.126	1		puccinia recondita/recondita
Rye, Winter	Netherlands	SC			0.125	2	35	puccinia recondita/recondita
	Netherlands	SC			0.125	2	35	rhynchosporium secalis
Spelt	Belgium	SE	0.053	200	0.105	2	35	erysiphe graminis/tritici
	Belgium	SE	0.053	200	0.105	2	35	leptosphaeria nodorum
	Belgium	SE	0.053	200	0.105	2	35	puccinia recondita
	Belgium	SE	0.053	200	0.105	2	35	puccinia striiformis
	Belgium	SE	0.053	200	0.105	2	35	septoria tritici
	Belgium	SC	0.063	200	0.125	2	35	erysiphe graminis
	Belgium	SC	0.063	200	0.125	2	35	puccinia recondita
	Belgium	SC	0.063	200	0.125	2	35	puccinia striiformis
	Belgium	SC	0.063	200	0.125	2	35	septoria tritici
	Luxembourg	SC		200-400	0.125	2	35	puccinia reconditapuccinia striiformis
Triticale	Belgium	SE	0.053	200	0.105	2	35	erysiphe graminis/tritici
	Belgium	SE	0.053	200	0.105	2	35	leptosphaeria nodorum
	Belgium	SE	0.053	200	0.105	2	35	puccinia recondita
	Belgium	SE	0.053	200	0.105	2	35	puccinia striiformis
	Belgium	SE	0.053	200	0.105	2	35	septoria tritici
	Belgium	SC	0.063	200	0.125	1	35	erysiphe graminis/tritici
	Belgium	SC	0.063	200	0.125	1	35	puccinia recondita
	Belgium	SC	0.063	200	0.125	1	35	puccinia striiformis
	Belgium	SC	0.063	200	0.125	1	35	septoria tritici
	France	SC	0.063	200	0.150	2	35	cercosporella herpotrichoides
	France	SC	0.063	200	0.125	2	35	puccinia recondita
	France	SC	0.063	200	0.125	2	35	septoria tritici
	Germany	SE	0.031-0.063	200-400	0.125	1	35	leptosphaeria nodorum
	Germany	SC	0.031-0.063	200-400	0.125	1	35	leptosphaeria nodorum
	Luxembourg	SC	0.031-0.063	200-400	0.125	1	35	puccinia recondita/triticiapuccinia striiformisseptoria spp.
Wheat, Spring	Belgium	SE	0.053	200	0.105	2	35	erysiphe graminis/tritici
	Belgium	SE	0.053	200	0.105	2	35	leptosphaeria nodorum
	Belgium	SE	0.053	200	0.105	2	35	septoria tritici
	Ireland	SC	0.063	200	0.125	2	3/7	capnodium salicimiumcercosporella herpotrichoideserysiphe graminis/tritici
	Netherlands	SE			0.105	2	35	erysiphe graminis
	Netherlands	SC			0.125	2	35	erysiphe graminis/tritici
	Netherlands	SC			0.125	2	35	leptosphaeria nodorum
	Netherlands	SC			0.125	2	35	puccinia recondita/tritici
	Netherlands	SC			0.125	2	35	puccinia striiformis
	Netherlands	SC			0.125	2	35	septoria tritici
	Poland	SE	0.053	200	0.105	1	35	erysiphe graminis
	Poland	SE	0.053	200	0.105	1	35	leptosphaeria nodorum
	Poland	SE	0.053	200	0.105	1	35	puccinia graminis spp.
	Poland	SE	0.053	200	0.105	1	35	puccinia graminis/tritici
	Poland	SE	0.053	200	0.105	1	35	puccinia recondita
	Poland	SE	0.053	200	0.105	1	35	septoria tritici
Wheat, Soft	Belgium	SC	0.063	200	0.125	2	35	erysiphe graminis/tritici
	Belgium	SC	0.063	200	0.125	2	35	fusarium spp.
	Belgium	SC	0.063	200	0.125	2	35	leptosphaeria nodorum
	Belgium	SC	0.063	200	0.125	2	35	puccinia recondita
	Belgium	SC	0.063	200	0.125	2	35	puccinia striiformis
	Belgium	SC	0.063	200	0.125	2	35	septoria tritici
	France	SE	0.053	200	0.105	2	35	erysiphe graminis
	France	SC	0.075	200	0.150	2	35	cercosporella herpotrichoides
	France	SC	0.063	200	0.125	2	35	erysiphe graminis avenae
	France	SC	0.063	200	0.125	2	35	fusarium culmorum
	France	SC	0.063	200	0.125	2	35	puccinia recondita/tritici
	France	SC	0.063	200	0.125	2	35	puccinia striiformis
	France	SC	0.063	200	0.125	2	35	septoria tritici
	Germany	SE	0.027-0.053	200	0.105	2	35	erisyphe graminis/secalis

Commodity	Country	Form	Application			Max No.	PHI days	Pest or disease
			Spray conc., kg ai/hl	Water, l/ha	kg ai/ha			
	Germany	SE	0.027-0.053	200	0.105	2	35	erysiphe graminis
	Germany	SE	0.027-0.053	200	0.105	2	35	erysiphe graminis/tritici
	Germany	SE	0.031-0.063	200-400	0.125	1	35	cercosporella herpotrichoides
	Germany	SE	0.031-0.063	200-400	0.125	2	35	erysiphe graminis/tritici
	Germany	SE	0.031-0.063	200-400	0.125	2	35	leptosphaeria nodorum
	Germany	SE	0.031-0.063	200-400	0.125	2	35	puccinia recondita/tritici
	Germany	SE	0.031-0.063	200-400	0.125	2	35	puccinia striiformis
	Germany	SE	0.031-0.063	200-400	0.125	2	35	pyrenophora triciti-repentis
	Germany	SE	0.031-0.063	200-400	0.125	2	35	septoria tritici
	Germany	SC	0.031-0.063	200-400	0.125	1	35	cercosporella herpotrichoides
	Germany	SC	0.031-0.063	200-400	0.125	2	35	erysiphe graminis/tritici
	Germany	SC	0.031-0.063	200-400	0.125	2	35	helminthosporium spp
	Germany	SC	0.031-0.063	200-400	0.125	2	35	leptosphaeria nodorum
	Germany	SC	0.031-0.063	200-400	0.125	2	35	puccinia recondita/tritici
	Germany	SC	0.031-0.063	200-400	0.125	2	35	puccinia striiformis
	Germany	SC	0.031-0.063	200-400	0.125	2	35	septoria tritici
	Luxembourg	SC	0.031-0.063	200-400	0.125	2	35	erysiphe graminisfusarium oxysporumpuccinia recondita/triticiapuccinia striiformisseptoria spp.
	Norway	SE			0.105		42	cercosporella herpotrichoides
	Norway	SE			0.105		42	leptosphaeria nodorum
	Norway	SE			0.105		42	mycosphaerella tassiana
	Switzerland	SC			0.126	1		erysiphe graminis/tritici
	Switzerland	SC			0.126	1		leptosphaeria nodorum
	Switzerland	SC			0.126	1		puccinia recondita/tritici
	Switzerland	SC			0.126	1		puccinia striiformis
	Switzerland	SC			0.126	1		septoria tritici
Wheat, Winter	Belgium	SE	0.053	200	0.105	2	35	erysiphe graminis/tritici
	Belgium	SE	0.053	200	0.105	2	35	leptosphaeria nodorum
	Belgium	SE	0.053	200	0.105	2	35	septoria tritici
	Belgium	SC	0.075	200	0.150	1	35	cercosporella herpotrichoides
	Ireland	SC	0.063	200	0.125	2	-	capnodium salicimiumcercosporella herpotrichoideserysiphe graminis/triticileptosphaeria nodurumpuccinia recondita/triticipuccinia striiformisseptori tritici
	Luxembourg	SC		200-400	0.150	1	35	cercosporella herpotrichoides
	Netherlands	SE			0.105	2	35	erysiphe graminis
	Netherlands	SC			0.125	2	35	erysiphe graminis/tritici
	Netherlands	SC			0.125	2	35	leptosphaeria nodorum
	Netherlands	SC			0.125	2	35	puccinia recondita/tritici
	Netherlands	SC			0.125	2	35	puccinia striiformis
	Netherlands	SC			0.125	2	35	septoria tritici
	Poland	SE	0.053	200	0.105	1	35	erysiphe graminis
	Poland	SE	0.053	200	0.105	1	35	leptosphaeria nodorum
	Poland	SE	0.053	200	0.105	1	35	puccinia graminis spp.
	Poland	SE	0.053	200	0.105	1	35	puccinia graminis/tritici
	Poland	SE	0.053	200	0.105	1	35	puccinia recondita
	Poland	SE	0.053	200	0.105	1	35	septoria tritici
	Slovakia	SC			0.125	1		erysiphe graminis
	Slovakia	SC			0.125	1		leptosphaeria nodorum
	Slovakia	SC			0.125	1		puccinia spp.
	UK	SE			0.105	2		erysiphe graminis
	UK	SE			0.105	2		septoria tritici
	UK	SE	0.063	200	0.125	2		cercosporella herpotrichoides
	UK	SE	0.063	200	0.125	2		fusarium spp.
	UK	SE	0.063	200	0.125	2		leptosphaeria nodorum
	UK	SE	0.063	200	0.125	2		septoria tritici
	UK	SC	0.063	200	0.125	2		cercosporella herpotrichoides
	UK	SC	0.063	200	0.125	2		fusarium spp.

Commodity	Country	Form	Application			Max No.	PHI days	Pest or disease
			Spray conc., kg ai/hl	Water, l/ha	kg ai/ha			
	UK	SC	0.063	200	0.125	2		leptosphaeria nodorum
	UK	SC	0.063	200	0.125	2		septoria tritici

Table 39. Registered uses of kresoxim-methyl on ornamentals.

Commodity	Country	Form	F/G	Application			Max No	PHI, days	Pest or disease
				Spray conc., kg ai/hl	Water vol., l/ha	kg ai/ha			
Carnation	Colombia	SC	G	0.011	2000	0.220	10		botrytis cinerea
	Kenya	WG	F		1000	0.250	8	500	heterosporium spp.
	Kenya	WG	F		1000	0.250	-8	500	uromyces dianthi
	Switzerland	WG	F			0.100	4		uromyces dianthi
Cherry, Sweet	Norway	WG	F			0.005-0.01	4	21	blumeriella jaapii
Chrysanthemum	Colombia	SC	G		2000	0.220	10		botrytis cinerea
	Netherlands	SC	F	0.100					puccinia horiana
	Switzerland	WG	F			0.100	4		puccinia chrysanthemi
Deciduous trees, horticulture	Netherlands	SC	F						microsphaera alni/quercina
	Netherlands	SC	F						sphaerotheca pannosa
Gladiolus	Netherlands	SC	F			0.200	8		botrytis elliptica
	Netherlands	SC	F			0.200	8		botrytis gladiolorum
Larkspur, Rocket	Netherlands	SC	F						erysiphe spp.
	Netherlands	SC	F						sphaerotheca fuliginea
Lily, Orange	Netherlands	SC	F			0.200	8		botrytis elliptica
	Netherlands	SC	F			0.200	8		botrytis gladiolorum
Med. aromatic herbs spices, flavour	Netherlands	SC	F						erysiphe spp.
	Netherlands	SC	F						sphaerotheca fuliginea
Oak	Netherlands	SC	F	0.100					microsphaera alni/quercina
	Netherlands	SC	F	0.100					sphaerotheca pannosa
Ornamentals	Ecuador	WG	F			0.150			
Phlox, Annual	Netherlands	SC	F	0.100					erysiphe spp.
	Netherlands	SC	F	0.100					sphaerotheca fuliginea
Prunus-Ornamental Spp	Norway	WG	F	0.01-0.015			4		diplocarpon rosae
	Norway	WG	F	0.01-0.015			4		erysiphe cichoracearum
	Norway	WG	F	0.01-0.015			4		phragmidium mucronatum
Rose	Colombia	SC	G		2000	0.22	10		botrytis cinerea
	Colombia	SC	G		2000	0.22	10		sphaerotheca pannosa
	Ecuador	WG	F			0.105			
	Kenya	WG	F		1000	0.250	8	500	diplicarpon rosae
	Kenya	WG	F		1000	0.250	8	500	sphaerotheca pannosa
	Switzerland	WG	F			0.150			diplocarpon rosae
	Switzerland	WG	F			0.150			sphaerotheca pannosa
Sweet William	Switzerland	WG	F			0.150	4	21	uromyces dianthi
Tulip	Netherlands	SC	F			0.200	8		botrytis tulipae

RESIDUES RESULTING FROM SUPERVISED TRIALS

Trials were carried out under field conditions unless otherwise stated. They were reported in sufficient detail and acceptable analytical information was supplied. The residues were of parent kresoxim-methyl unless otherwise stated in the Tables or text. In some of the cereal trials “total” residues were determined. These were the sum of kresoxim-methyl and the metabolites 490M2 and 490M9 expressed as kresoxim-methyl. In selecting residues for the estimation of maximum residue levels and STMRs the trials according to maximum GAP (i.e. minimum PHI, maximum dose rate and

maximum number of treatments) have been used and the results from them underlined.

The residue trials were on apples, pears, grapes, bulb onions, cucumbers, melons, tomatoes, sweet peppers, wheat, barley, rye and pecans. The results are shown in Tables 40-53 CLICK HERE to continue

Table 40. Supervised residue trials on apples.

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. and Remarks
Nyíregyháza, Hungary	09/08/94	0.400	-	-	14	-	RAC	0.05	0	# 94/11727
							RAC	0.13	0	
							RAC	0.09	3	
							RAC	0.08	3	
							RAC	0.06	7	
							RAC	0.08	7	
							RAC	0.06	10	
							RAC	0.04	10	
							RAC	0.06	14	
							RAC	0.04	14	
							RAC	0.03	21	
							RAC	0.06	21	
							RAC	0.02	28	
							RAC	0.03	28	
							RAC	<0.01	35	
							RAC	0.01	35	
							RAC	<0.01	35	
Gualdo (FE), Italy	08/09/93	0.100	1500	0.007	12	ripening	RAC	0.05	0	# 94/11751
							RAC	<0.05	7	
							RAC	<0.05	14	
							RAC	<0.05	21	
							RAC	<0.05	28	
Verona, Italy	13/09/93	0.100	1200	0.008	12	ripening	RAC	<0.05	0	# 94/11751
							RAC	0.05	7	
							RAC	<0.05	14	
							RAC	<0.05	21	
							RAC	<0.05	28	
Voghenza, Italy	11/08/94	0.100	24	0.417	8	7 cm	RAC	0.14	0	# 95/10054
							RAC	<0.05	21	
							RAC	<0.05	28	
							RAC	<0.05	35	
							RAC	<0.05	41	
Belfiore, Italy	30/08/94	0.100	24	0.417	8	6 cm	RAC	0.08	0	# 95/10054
							RAC	<0.05	21	
							RAC	<0.05	28	
							RAC	<0.05	35	
							RAC	<0.05	42	
Don Benito (1), Spain	03/08/93	0.100	450	0.022	8	81	RAC	0.08	0	# 95/10082
							RAC	0.06	7	
							RAC	<0.05	14	
							RAC	<0.05	21	
							RAC	<0.05	28	
Don Benito (2), Spain	03/08/93	0.100	450	0.022	8	81	RAC	0.12	0	# 95/10082
							RAC	0.10	7	
							RAC	0.05	14	
							RAC	<0.05	21	
							RAC	<0.05	28	
Merville, France	27/08/93	0.100	450	0.022	8	79	RAC	0.20	0	# 95/10082
							RAC	0.19	7	
							RAC	0.06	14	
							RAC	0.07	21	
							RAC	<0.05	28	

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. and Remarks
Sayrac, France	27/09/93	0.100	450	0.022	8	79	RAC	0.16	0	# 95/10082
							RAC	0.18	7	
							RAC	0.14	14	
							RAC	<0.05	21	
							RAC	<0.05	28	
Merville, France	01/08/94	0.101	450	0.022	8	77	RAC	0.22	0	# 95/10418
							RAC	0.09	21	
							RAC	<0.05	28	
							RAC	<0.05	35	
							RAC	<0.05	42	
Sayrac, France	01/08/94	0.111	490	0.023	8	77	RAC	0.19	0	# 95/10418
							RAC	<0.05	21	
							RAC	<0.05	28	
							RAC	<0.05	35	
							RAC	<0.05	42	
Postfeld-Bormsdorf 9, Germany	01/10/93	0.100	450	0.022	8	81	RAC	0.12	0	# 95/10082
							RAC	0.08	6	
							RAC	<0.05	14	
							RAC	<0.05	21	
							RAC	<0.05	27	
Gundheim, Germany	31/08/93	0.100	450	0.022	8	81	RAC	0.26	0	# 95/10082
							RAC	0.21	7	
							RAC	0.16	14	
							washed apple	0.19	14	
							apple juice	<0.05	14	
							wet pomace	<0.05	14	
							apple sauce	<0.05	14	
							apple sauce	<0.05	14	
							RAC	0.08	21	
							RAC	<0.05	28	
Stetten, Germany	17/09/93	0.100	450	0.022	8	81	RAC	0.16	0	# 95/10082
							RAC	0.11	7	# 95/10082
							RAC	0.19	14	# 95/10082
							washed apple	0.07	14	# 95/10082
							apple juice	<0.05	14	# 95/10082
							wet pomace	0.09	14	# 95/10082
							apple sauce	<0.05	14	# 95/10082
							apple sauce	<0.05	14	# 95/10082
							RAC	<0.05	21	# 95/10082
							RAC	<0.05	28	# 95/10082
Rödersheim-Gronau, Germany	14/09/93	0.100	450	0.022	8	83	RAC	0.16	0	# 95/10082
							RAC	0.17	7	
							RAC	0.08	14	
							washed apple	0.16	14	
							apple juice	<0.05	14	

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. and Remarks
							wet pomace	0.17	14	
							apple sauce	<0.05	14	
							apple sauce	<0.05	14	
							RAC	0.09	21	
							RAC	<0.05	28	
Postfeld-Bormsdorf 9, Germany	02/08/94	0.100	447	0.022	8	77	RAC	0.09	0	# 95/10418
							RAC	<0.05	21	
							RAC	<0.05	28	
							RAC	<0.05	35	
							RAC	<0.05	42	
Stetten, Germany	27/07/94	0.102	447	0.023	8	77	RAC	<0.05	0	# 95/10418
							RAC	<0.05	21	
							RAC	<0.05	29	
							RAC	<0.05	35	
							RAC	<0.05	42	
Rödersheim-Gronau, Germany	31/08/94	0.102	455	0.022	8	85	RAC	0.12	0	# 95/10418
							RAC	0.07	21	
							RAC	<0.05	28	
							RAC	<0.05	35	
							RAC	<0.05	42	
Sint-Truiden, Belgium	02/09/93	0.100	450	0.022	8	84	RAC	0.34	0	# 95/10082
							RAC	0.16	7	
							RAC	0.15	14	
							RAC	0.11	21	
							RAC	0.05	28	
Sint-Truiden, Belgium	10/08/94	0.101	450	0.022	8	81	RAC	0.10	0	# 95/10418
							RAC	<0.05	21	
							RAC	<0.05	29	
							RAC	<0.05	35	
							RAC	<0.05	43	
Wyler-Groesbeek, Netherlands	02/09/93	0.100	450	0.022	8	84	RAC	0.36	0	# 95/10082
							RAC	0.27	7	
							RAC	0.07	14	
							RAC	0.11	21	
							RAC	0.11	28	
Wyler-Groesbeek, Netherlands	19/08/94	0.118	523	0.023	8	85	RAC	0.20	0	# 95/10418
							RAC	<0.05	21	
							RAC	<0.05	28	
							RAC	<0.05	35	
							RAC	<0.05	44	
East Malling, Kent, UK	19/08/94	0.104	469	0.022	8	80	RAC	0.41	0	# 95/10418
							RAC	0.11	20	
							RAC	0.14	27	
							RAC	0.06	34	
							RAC	0.06	41	
Toddington, UK	09/08/94	0.106	466	0.023	8	79	RAC	0.99	0	# 95/10418

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. and Remarks
							RAC	0.23	22	
							RAC	0.18	28	
							RAC	<0.05	36	
							RAC	0.11	42	
Storridge, UK	09/08/94	0.101	455	0.022	8	79	RAC	0.41	0	# 95/10418
							RAC	0.22	22	
							RAC	0.09	28	
							RAC	<0.05	36	
							RAC	0.05	42	
Otham, Kent, UK	21/07/94	0.099	443	0.022	8	80	RAC	0.25	0	# 95/10418
							RAC	<0.05	21	
							RAC	0.05	29	
							RAC	<0.05	36	
							RAC	<0.05	42	
Brenchley, Kent, UK	21/07/94	0.103	459	0.022	8	80	RAC	0.24	0	# 95/10418
							RAC	<0.05	21	
							RAC	<0.05	29	
							RAC	<0.05	36	
							RAC	<0.05	42	
Willingham, UK	20/07/94	0.101	449	0.022	8	80	RAC	0.43	0	# 95/10418
							RAC	0.15	20	
							RAC	0.06	28	
							RAC	0.05	34	
							RAC	<0.05	42	
Christchurch, New Zealand	18/10/93	0.100	2000	0.005	4	Late Blossom	RAC	<0.01	130	# 95/11022
							RAC	<0.01	137	
							RAC	<0.01	144	
Christchurch, New Zealand	30/11/93	0.100	2000	0.005	4	3rd Cover	RAC	<0.01	87	# 95/11022
							RAC	<0.01	94	
							RAC	<0.01	101	
Christchurch, New Zealand	04/02/94	0.100	2000	0.005	4	7th Cover	RAC	0.01	21	# 95/11022
							RAC	<0.01	28	# 95/11022
							RAC	<0.01	35	
Christchurch, New Zealand	04/02/94	0.100	2000	0.005	12	7th Cover	RAC	0.03	21	# 95/11022
							RAC	<0.01	28	
							RAC	<0.01	35	
Hastings, New Zealand	03/11/93	0.075	2000	0.004	3	*	RAC	<0.01	101	# 95/11022
							RAC	<0.01	108	
							RAC	<0.01	118	
							RAC	<0.01	132	
Hastings, New Zealand	13/12/93	0.075	2000	0.004	3		RAC	<0.01	46	# 95/11022
							RAC	<0.01	53	
							RAC	<0.01	63	
							RAC	<0.01	77	
Hastings, New Zealand	14/01/94	0.075	2000	0.004	2		RAC	0.04	14	# 95/11022
							RAC	0.04	21	
							RAC	<0.01	31	
							RAC	<0.01	45	
Hastings, New Zealand	02/03/93	0.100	1500	0.007	11		RAC	0.01	22	# 95/11022
							RAC	<0.01	29	
Hastings, New	02/03/93	0.200	1500	0.013	11		RAC	0.21	1	# 95/11022

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. and Remarks
Zealand										
							RAC	0.05	8	
							RAC	0.04	22	
							RAC	<0.01	29	
Lyndhurst, Rd Hastings, New Zealand	17/12/92	0.038	1000	0.004	9		RAC	0.07	1	#95/11022
							RAC	0.06	3	
							RAC	0.01	7	
							RAC	<0.01	16	
							RAC	<0.01	24	
							RAC	<0.01	33	
Lyndhurst, Rd Hastings, New Zealand	17/12/92	0.038	1000	0.004	5		RAC	0.04	1	#95/11022
							RAC	0.04	3	
							RAC	0.01	7	
							RAC	<0.01	16	
							RAC	<0.01	24	
							RAC	<0.01	33	
Christchurch, New Zealand	08/02/93	0.075	1500	0.005	12	6th Cover	RAC	0.60	1	#95/11022
							RAC	0.27	3	
							RAC	0.23	7	
							RAC	0.04	14	
							RAC	0.06	21	
							RAC	0.05	28	
							RAC	<0.01	35	
Christchurch, New Zealand	08/02/93	0.150	1500	0.010	12	6th Cover	RAC	1.26	1	#95/11022
							RAC	0.45	3	
							RAC	0.49	7	
							RAC	0.28	14	
							RAC	0.47	21	
							RAC	0.10	28	
							RAC	0.19	35	
Villiersdorp, South Africa	29/01/95	0.125	2500	0.005	12		RAC	0.27	0	# 95/10948
							RAC	0.12	12	
							RAC	0.13	24	
							RAC	0.09	35	
							RAC	<0.05	42	
Villiersdorp, South Africa	29/01/95	0.250	2500	0.01	12		RAC	0.63	0	# 95/10948
							RAC	0.40	12	
							RAC	0.18	24	
							RAC	0.18	35	
							RAC	0.09	42	
Vyeboom, South Africa	05/01/95	0.125	2500	0.005	10		RAC	0.15	0	# 95/10949
							RAC	0.13	12	
							RAC	<0.05	24	
							RAC	<0.05	35	
							RAC	<0.05	42	
Vyeboom, South Africa	05/01/95	0.250	2500	0.01	10		RAC	0.38	0	# 95/10949
							RAC	0.19	12	
							RAC	0.11	24	
							RAC	0.14	35	
							RAC	0.06	42	

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. and Remarks
Tiefkasfontein, Villiersdorp, South Africa	05/01/95	0.125	2500	0.005	10		RAC	0.21	0	#96/10831
							RAC	0.09	12	
							RAC	0.04	24	
							RAC	0.02	35	
Tiefkasfontein, Villiersdorp, South Africa	05/01/95	0.250	2500	0.010	10		RAC	0.48	0	#96/10831
							RAC	0.31	12	
							RAC	0.13	24	
							RAC	0.11	35	
Ashtabula County/OH, USA	16/05/95	1.120	1100	0.1	4		RAC	<0.05	90	#96/5118
							RAC	<0.05	90	490M2
							RAC	<0.05	90	490M9
							apple juice	<0.05	90	
							apple juice	<0.05	90	490M2
							apple juice	<0.05	90	490M9
							wet pomace	<0.05	90	
							wet pomace	<0.05	90	490M2
							wet pomace	<0.05	90	490M9
Tulare/CA, USA	28/03/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Tulare/CA, USA	19/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Tulare/CA, USA	28/03/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Tulare/CA, USA	19/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Mesa/CO, USA	07/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Mesa/CO, USA	28/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Delta/CO, USA	13/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Delta/CO, USA	04/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Stokes/NC, USA	12/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Stokes/NC, USA	03/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Alexander/NC, USA	13/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. and Remarks
							RAC	<0.05	90	
Alexander/NC, USA	03/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Carroll/VA, USA	13/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Carroll/VA, USA	03/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Ottawa/MI, USA	19/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Ottawa/MI, USA	09/06/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Kent/MI, USA	19/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Kent/MI, USA	09/06/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Ottawa/MI, USA	19/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Ottawa/MI, USA	09/06/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
								<0.05	90	
								<0.05	90	
Dunn/WI, USA	26/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Dunn/WI, USA	17/06/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Payette/ID, USA	22/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Payette/ID, USA	12/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Hood River/OR, USA	02/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Hood River/OR, USA	22/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Hood River/OR, USA	02/05/95	0.224	500	0.045	4		RAC	0.06	35	#96/5123
							RAC	<0.05	35	
							RAC	0.06	35	
Hood River/OR, USA	22/05/95	0.224	500	0.045	4		RAC	<0.05	35	#96/5123
							RAC	<0.05	35	
							RAC	<0.05	35	
Hood River/OR, USA	02/05/95	0.224	500	0.045	4		RAC	<0.05	75	#96/5123

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. and Remarks
							RAC	<0.05	75	
							RAC	<0.05	75	
Hood River/OR, USA	22/05/95	0.224	500	0.045	4		RAC	<0.05	75	#96/5123
							RAC	<0.05	75	
							RAC	<0.05	75	
Hood River/OR, USA	02/05/95	0.224	500	0.045	4		RAC	<0.05	147	#96/5123
							RAC	<0.05	147	
							RAC	<0.05	147	
Yakima/WA, USA	20/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Yakima/WA, USA	11/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Grant/WA, USA	26/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Grant/WA, USA	17/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Grant/WA, USA	18/04/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Grant/WA, USA	09/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Berks/PA, USA	03/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Berks/PA, USA	24/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Lehigh/PA, USA	01/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Lehigh/PA, USA	23/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Wayne/NY, USA	16/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Wayne/NY, USA	06/06/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Wayne/NY, USA	17/05/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Wayne/NY, USA	07/06/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
Wayne/NY, USA	17/05/95	0.224	500	0.045	4		RAC	<0.05	35	#96/5123
							RAC	<0.05	35	
							RAC	<0.05	35	
Wayne/NY, USA	07/06/95	0.224	500	0.045	4		RAC	<0.05	35	#96/5123
							RAC	<0.05	35	

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. and Remarks
							RAC	<0.05	35	
Wayne/NY, USA	17/05/95	0.224	500	0.045	4		RAC	<0.05	75	#96/5123
							RAC	<0.05	75	
							RAC	<0.05	75	
Wayne/NY, USA	07/06/95	0.224	500	0.045	4		RAC	<0.05	75	#96/5123
							RAC	<0.05	75	
							RAC	<0.05	75	
Wayne/NY, USA	17/05/95	0.224	500	0.045	4		RAC	<0.05	134	#96/5123
							RAC	<0.05	134	
							RAC	<0.05	134	
							RAC	<0.05	90	
							RAC	<0.05	90	
							RAC	<0.05	90	
Wayne/NY, USA	07/06/95	0.224	500	0.045	4		RAC	<0.05	90	#96/5123
							RAC	<0.05	90	
							RAC	<0.05	90	
British Columbia, Canada	22/05/95	0.230	1000		4		RAC	<0.05	90	#97/5036
							RAC	<0.05	90	490M2
							RAC	<0.05	90	490M9
Ontario, Canada	15/06/95	0.230	1000		4		RAC	<0.05	90	#97/5036
							RAC	<0.05	90	490M2
							RAC	<0.05	90	490M9
Nova Scotia, Canada	21/06/95	0.230	1000		4		RAC	<0.05	90	#97/5036
							RAC	<0.05	90	490M2
							RAC	<0.05	90	490M9
British Columbia, Canada	27/05/96	0.230	1000		4		RAC	<0.05	90	#97/5036
							RAC	<0.05	90	490M2
							RAC	<0.05	90	490M9
Ontario, Canada	19/06/96	0.230	1000		4		RAC	<0.05	90	#97/5036
							RAC	<0.05	90	490M2
							RAC	<0.05	90	490M9
Nova Scotia, Canada	20/06/96	0.230	1000		4		RAC	<0.05	90	#97/5036
							RAC	<0.05	90	490M2
							RAC	<0.05	90	490M9

Table 41. Supervised residue trials on pears.

Location	Date of last tr.	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report-No.
Don Benito (3), Spain	13/07/93	0.099	463	0.021	8	81	0.13	0	# 95/10082
							<0.05	7	
							<0.05	14	
							<0.05	21	
							<0.05	28	
Sanlucar la mayor, Spain	12/07/94	0.098	440	0.022	8	78	0.11	0	# 95/10418
							<0.05	20	
							<0.05	29	
							<0.05	36	
							<0.05	42	
Gibraleon, Spain	12/07/94	0.107	470	0.023	8	77-78	0.05	0	# 95/10418
							<0.05	21	

Location	Date of last tr.	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report-No.
							<0.05	29	
							<0.05	36	
							<0.05	42	
Aznalcazar, Spain	10/08/94	0.101	458	0.022	8	78	0.11	0	# 95/10418
							<0.05	22	
							<0.05	28	
							<0.05	35	
							<0.05	42	
Tiekasfontein, Villiersdorp, South Africa	22/12/95	0.125	2500	0.005	8	2.0 in. diam.	0.25	0	#96/10835
							0.07	12	
							0.03	24	
							0.01	35	
							<0.01	42	
Tiekasfontein, Villiersdorp, South Africa	22/12/95	0.250	2500	0.010	8	2.0 in. diam.	0.42	0	#96/10835
							0.23	12	
							0.08	24	
							0.07	35	
							0.06*	42	

* According to South African GAP for apples

Table 42. Supervised residue trials on grapes.

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
Ferdinando di Puglia, Italy	16/07/96	0.150	779	0.019	6	79	RAC	0.15	0	#97/10270
							RAC	<0.05	34	
							RAC	<0.05	41	
							RAC	<0.05	48	
							RAC	<0.05	55	
							RAC	0.06	0	490M2
							RAC	<0.05	34	490M2
							RAC	<0.05	41	490M2
							RAC	<0.05	48	490M2
							RAC	<0.05	55	490M2
							RAC	<0.05	0	490M9
							RAC	<0.05	34	490M9
							RAC	<0.05	41	490M9
							RAC	<0.05	48	490M9
							RAC	<0.05	55	490M9
S. Palomba, Italy	26/08/96	0.150	774	0.019	6	83	RAC	0.24	0	#97/10270
							RAC	0.15	36	
							RAC	0.13	42	
							RAC	0.06	49	
							RAC	0.10	56	
							RAC	0.08	0	490M2
							RAC	0.07	36	490M2
							RAC	0.10	42	490M2
							RAC	0.10	49	490M2
							RAC	0.09	56	490M2
							RAC	<0.05	0	490M9
							RAC	0.05	36	490M9
							RAC	0.06	42	490M9

Location	Applications						Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.				
							RAC	0.05	49	490M9
							RAC	0.06	56	490M9
S. Ferdinando di Puglia, Italy	14/07/95	0.150	767**	0.020	6	79	RAC	0.35	0	#97/10069 Table grape
							RAC	<0.05	35	
							RAC	<0.05	42	
							RAC	<0.05	49	
							RAC	<0.05	56	
							RAC	0.07	0	490M2
							RAC	0.05	35	490M2
							RAC	0.05	42	490M2
							RAC	<0.05	49	490M2
							RAC	<0.05	56	490M2
							RAC	<0.05	0	490M9
							RAC	<0.05	35	490M9
							RAC	<0.05	42	490M9
							RAC	<0.05	49	490M9
							RAC	<0.05	56	490M9
S. Ferdinando di Puglia, Italy	14/07/95	0.150	767**	0.020	6	79	RAC	0.28	0	Table variety 97/10069
							RAC	<0.05	35	
							RAC	<0.05	42	
							RAC	<0.05	49	
							RAC	<0.05	56	
							RAC	<0.05	0	490M2
							RAC	<0.05	35	490M2
							RAC	<0.05	42	490M2
							RAC	<0.05	49	490M2
							RAC	<0.05	56	490M2
							RAC	<0.05	0	490M9
							RAC	<0.05	35	490M9
							RAC	<0.05	42	490M9
							RAC	<0.05	49	490M9
							RAC	<0.05	56	490M9
S. Palomba, Pomezia, Italy	23/08/95	0.150	767**	0.020	6	35	RAC	0.12	0	Wine variety #97/10069
							RAC	<0.05	35	
							RAC	<0.05	42	
							RAC	<0.05	49	
							RAC	<0.05	56	
							RAC	0.12	0	490M2
							RAC	0.13	35	490M2
							RAC	0.09	42	490M2
							RAC	0.08	49	490M2
							RAC	0.09	56	490M2
							RAC	0.08	0	490M9
							RAC	0.08	35	490M9
							RAC	<0.05	42	490M9
							RAC	<0.05	49	490M9
							RAC	<0.05	56	490M9
S. Palomba, Pomezia, Italy	23/08/95	0.150	767**	0.020	6	35	RAC	0.09	0	Wine variety 97/10069
							RAC	<0.05	35	
							RAC	<0.05	42	
							RAC	<0.05	49	
							RAC	<0.05	56	
							RAC	0.09	0	490M2
							RAC	0.12	35	490M2
							RAC	0.12	42	490M2

Location	Applications					Growth stage at last tr.	Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.					
							RAC	0.11	49	490M2
							RAC	0.10	56	490M2
							RAC	0.05	0	490M9
							RAC	0.07	35	490M9
							RAC	0.07	42	490M9
							RAC	0.07	49	490M9
							RAC	0.06	56	490M9
S. Ferdinando di Puglia, Italy	14/07/95	0.150	767**	0.020	6	79	RAC	0.28	0	Table variety 97/10069
							RAC	<0.05	35	
							RAC	<0.05	42	
							RAC	<0.05	49	
							RAC	<0.05	56	
							RAC	<0.05	0	490M2
							RAC	<0.05	35	490M2
							RAC	<0.05	42	490M2
							RAC	<0.05	49	490M2
							RAC	<0.05	56	490M2
							RAC	<0.05	0	490M9
							RAC	<0.05	35	490M9
							RAC	<0.05	42	490M9
							RAC	<0.05	49	490M9
							RAC	<0.05	56	490M9
Jerez de la Frontera, Spain	14/07/95	0.149	562	0.027	6	81	RAC	0.81	0	#96/10830
							RAC	0.07	35	
							RAC	0.10	42	
							RAC	<0.05	49	
							RAC	<0.05	55	
							RAC	0.13	0	490M2
							RAC	0.27	35	490M2
							RAC	0.25	42	490M2
							RAC	0.21	49	490M2
							RAC	0.20	55	490M2
							RAC	<0.05	0	490M9
							RAC	0.09	35	490M9
							RAC	0.08	42	490M9
							RAC	0.07	49	490M9
							RAC	0.07	55	490M9
Jerez de la Frontera, Spain	14/07/95	0.150	565	0.027	6	81	RAC	0.88	0	#96/10830
							RAC	0.09	35	
							RAC	0.05	42	
							RAC	<0.05	49	
							RAC	<0.05	55	
							RAC	0.20	0	490M2
							RAC	0.22	35	490M2
							RAC	0.17	42	490M2
							RAC	0.16	49	490M2
							RAC	0.16	55	490M2
							RAC	0.06	0	490M9
							RAC	0.08	35	490M9
							RAC	0.06	42	490M9
							RAC	0.06	49	490M9
							RAC	0.07	55	490M9
Jerez de la Frontera, Spain	15/07/96	0.144	566	0.025	6	81/83	RAC	0.10	0	#96/10890
							RAC	<0.05	35	

Location	Applications Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
							RAC	<0.05	43	
							RAC	<0.05	49	
							RAC	<0.05	56	
							RAC	0.06	0	490M2
							RAC	0.05	35	490M2
							RAC	0.05	43	490M2
							RAC	0.05	49	490M2
							RAC	<0.05	56	490M2
							RAC	<0.05	0	490M9
							RAC	<0.05	35	490M9
							RAC	<0.05	43	490M9
							RAC	<0.05	49	490M9
							RAC	<0.05	56	490M9
Jerez de la Frontera, Spain	15/07/96	0.142	555	0.026	6	81/83	RAC	0.27	0	#96/10890
							RAC	<0.05	35	
							RAC	<0.05	43	
							RAC	<0.05	49	
							RAC	<0.05	56	
							RAC	0.09	0	490M2
							RAC	0.10	35	490M2
							RAC	0.08	43	490M2
							RAC	0.09	49	490M2
							RAC	0.07	56	490M2
							RAC	0.05	0	490M9
							RAC	<0.05	35	490M9
							RAC	<0.05	43	490M9
							RAC	<0.05	49	490M9
							RAC	<0.05	56	490M9
Pernand-Vergelesses, France	10/08/95	0.152	508	0.030	6	79	RAC	0.85	0	#96/10830
							RAC	0.18	36	
							RAC	0.20	42	
							RAC	0.27	49	
							RAC	0.20	55	
							RAC	0.14	0	490M2
							RAC	0.07	36	490M2
							RAC	<0.05	42	490M2
							RAC	0.05	49	490M2
							RAC	<0.05	55	490M2
							RAC	0.09	0	490M9
							RAC	0.06	36	490M9
							RAC	<0.05	42	490M9
							RAC	<0.05	49	490M9
							RAC	<0.05	55	490M9
Fronton, France	16/08/95	0.158	420	0.038	6	81	RAC	0.71	0	#96/10830
							RAC	0.36	34	
							RAC	0.39	41	
							RAC	0.26	49	
							RAC	0.14	56	
							RAC	0.14	0	490M2
							RAC	0.12	34	490M2
							RAC	0.14	41	490M2
							RAC	0.12	49	490M2
							RAC	0.11	56	490M2
							RAC	0.07	0	490M9
							RAC	0.06	34	490M9

Location	Applications						Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.				
							RAC	0.07	41	490M9
							RAC	0.06	49	490M9
							RAC	0.06	56	490M9
Lisle sur Tarn, France	01/08/95	0.153	400	0.038	6	81	RAC	0.62	0	#96/10830
							RAC	0.21	34	
							RAC	0.28	42	
							RAC	0.22	49	
							RAC	0.21	55	
							RAC	0.19	0	490M2
							RAC	0.28	34	490M2
							RAC	0.30	42	490M2
							RAC	0.17	49	490M2
							RAC	0.23	55	490M2
							RAC	0.11	0	490M9
							RAC	0.17	34	490M9
							RAC	0.18	42	490M9
							RAC	0.10	49	490M9
							RAC	0.14	55	490M9
Pernand-Vergelesses, France	12/08/96	0.147	508	0.029	6	79	RAC	0.25	0	#96/10890
							RAC	0.06	35	
							RAC	<0.05	42	
							RAC	0.08	49	
							RAC	0.06	56	
							RAC	0.07	0	490M2
							RAC	0.06	35	490M2
							RAC	<0.05	42	490M2
							RAC	<0.05	49	490M2
							RAC	<0.05	56	490M2
							RAC	0.14	0	490M9
							RAC	<0.05	35	490M9
							RAC	<0.05	42	490M9
							RAC	<0.05	49	490M9
							RAC	0.10	56	490M9
Fronton, France	09/08/96	0.153	586	0.026	6	81	RAC	0.95	0	#96/10890
							RAC	0.23	35	
							RAC	0.28	41	
							RAC	0.13	48	
							RAC	0.15	55	
							RAC	0.11	0	490M2
							RAC	0.06	35	490M2
							RAC	0.05	41	490M2
							RAC	<0.05	48	490M2
							RAC	<0.05	55	490M2
							RAC	0.10	0	490M9
							RAC	<0.05	35	490M9
							RAC	<0.05	41	490M9
							RAC	<0.05	48	490M9
							RAC	<0.05	55	490M9
Wiesloch, Germany	18/08/95	0.154	576	0.027	6	79	RAC	0.50	0	# 96/10698 white grape Müller-Thurgau
							RAC	0.11	0	490M2
							RAC	0.07	0	490M9
							RAC	0.25	34	
							RAC	0.15	34	490M2

Location	Applications						Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.				
							RAC	0.07	34	490M9
							must	<0.05	34	shortly after pressing
							must	0.05	34	490M2
							must	<0.05	34	490M9
							must	<0.05	34	after short heating
							must	<0.05	34	490M2
							must	<0.05	34	490M9
							wet pomace	0.57	34	
							wet pomace	0.42	34	490M2
							wet pomace	0.19	34	490M9
							wine	<0.05	34	
							wine	<0.05	34	490M2
							wine	<0.05	34	490M9
							wine	<0.05	34	after short heating
							wine	<0.05	34	490M2
							wine	<0.05	34	490M9
							RAC	0.35	42	
							RAC	0.16	42	490M2
							RAC	0.09	42	490M9
							RAC	0.19	49	
							RAC	0.15	49	490M2
							RAC	0.07	49	490M9
							RAC	0.16	56	
							RAC	0.15	56	490M2
							RAC	0.07	56	490M9
Wiesloch, Germany	12/09/95	0.155	580	0.027	6	83	RAC	0.64	0	# 96/10698 red grapes Spätburgunder
							RAC	0.10	0	490M2
							RAC	0.06	0	490M9
							RAC	0.73	35	
							RAC	0.08	35	490M2
							RAC	0.08	35	490M9
							must	0.06	35	after heating
							must	0.10	35	490M2
							must	0.06	35	490M9
							must	0.19	35	after cold pressing
							must	<0.05	35	490M2
							must	<0.05	35	490M9
							wet pomace	1.40	35	
							wet pomace	0.33	35	490M2
							wet pomace	0.18	35	490M9
							wine (rosé)	<0.05	35	
							wine (rosé)	0.05	35	490M2
							wine (rosé)	<0.05	35	490M9
							red wine	<0.05	35	after short heating
							red wine	0.11	35	490M2
							red wine	0.05	35	490M9

Location	Applications					Growth stage at last tr.	Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.					
							RAC	0.40	42	
							RAC	0.15	42	490M2
							RAC	0.10	42	490M9
							RAC	0.93	49	
							RAC	0.15	49	490M2
							RAC	0.10	49	490M9
							RAC	0.31	56	
							RAC	0.10	56	490M2
							RAC	0.07	56	490M9
Grünstadt-Sausenheim, Germany	16/08/95	0.155	582	0.027	6	79	RAC	0.63	0	# 96/10698 white grapes Müller-Thurgau
							RAC	0.11	0	490M2
							RAC	0.05	0	490M9
							RAC	0.44	35	
							RAC	0.11	35	490M2
							RAC	0.05	35	490M9
							must	0.08	35	directly after pressing
							must	<0.05	35	490M2
							must	<0.05	35	490M9
							must	0.07	35	after short heating
							must	<0.05	35	490M2
							must	<0.05	35	490M9
							wet pomace	0.38	35	
							wet pomace	0.21	35	490M2
							wet pomace	0.08	35	490M9
							wine	<0.05	35	
							wine	<0.05	35	490M2
							wine	<0.05	35	490M9
							wine	<0.05	35	after short heating
							wine	<0.05	35	490M2
							wine	<0.05	35	490M9
							RAC	0.16	41	
							RAC	0.07	41	490M2
							RAC	<0.05	41	490M9
							RAC	0.18	49	
							RAC	0.08	49	490M2
							RAC	<0.05	49	490M9
							RAC	0.33	56	
							RAC	0.09	56	490M2
							RAC	<0.05	56	490M9
Grünstadt-Sausenheim, Germany	16/08/95	0.153	580	0.026	6	79	RAC	0.39	0	# 96/10698 red grapes Portugieser
							RAC	0.07	0	490M2
							RAC	<0.05	0	490M9
							RAC	0.17	35	
							RAC	0.06	35	490M2
							RAC	<0.05	35	490M9
							must	<0.05	35	after heating
							must	0.07	35	490M2
							must	<0.05	35	490M9
							must	0.09	35	after cold pressing

Location	Applications						Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.				
							must	0.06	35	490M2
							must	<0.05	35	490M9
							wet pomace	0.52	35	
							wet pomace	0.11	35	490M2
							wet pomace	<0.05	35	490M9
							wine rosé	<0.05	35	
							wine rosé	<0.05	35	490M2
							wine rosé	<0.05	35	490M9
							red wine	<0.05	35	
							red wine	<0.05	35	490M2
							red wine	<0.05	35	490M9
							RAC	0.14	41	
							RAC	0.06	41	490M2
							RAC	<0.05	41	490M9
							RAC	0.20	49	
							RAC	0.05	49	490M2
							RAC	<0.05	49	490M9
							RAC	0.23	56	
							RAC	0.06	56	490M2
							RAC	<0.05	56	490M9
Wiesloch, Germany	26/08/96	0.147	573	0.026	6	79	RAC	0.73	0	#96/10890
							RAC	0.20	35	
							RAC	0.11	42	
							RAC	0.27	49	
							RAC	0.09	56	
							RAC	0.11	0	490M2
							RAC	0.06	35	490M2
							RAC	0.07	42	490M2
							RAC	0.06	49	490M2
							RAC	<0.05	56	490M2
							RAC	0.07	0	490M9
							RAC	<0.05	35	490M9
							RAC	<0.05	42	490M9
							RAC	0.05	49	490M9
							RAC	<0.05	56	490M9
Wiesloch, Germany	26/08/96	0.148	582	0.025	6	79	RAC	0.63	0	#96/10890
							RAC	0.15	35	
							RAC	0.21	42	
							RAC	0.21	49	
							RAC	0.18	56	
							RAC	0.11	0	490M2
							RAC	0.05	35	490M2
							RAC	0.10	42	490M2
							RAC	0.07	49	490M2
							RAC	0.09	56	490M2
							RAC	0.08	0	490M9
							RAC	0.05	35	490M9
							RAC	0.06	42	490M9
							RAC	0.05	49	490M9
							RAC	0.07	56	490M9
Grünstadt, Germany	14/08/96	0.150	574	0.026	6	76	RAC	0.17	0	#96/10890

Location	Applications					Growth stage at last tr.	Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.					
							RAC	0.09	35	
							RAC	<0.05	42	
							RAC	0.06	49	
							RAC	0.10	56	
							RAC	<0.05	0	490M2
							RAC	<0.05	35	490M2
							RAC	<0.05	42	490M2
							RAC	<0.05	49	490M2
							RAC	<0.05	56	490M2
							RAC	<0.05	0	490M9
							RAC	<0.05	35	490M9
							RAC	<0.05	42	490M9
							RAC	<0.05	49	490M9
							RAC	0.06	56	490M9
Roodezandt, Wellington, South Africa	11/12/95	0.038	750*	0.005	6		RAC	0.12	0	#96/10832 Mean of duplicate analyses
							RAC	0.06	16	Mean of duplicate analyses
							RAC	<0.01	30	Mean of duplicate analyses
							RAC	0.01	46	Mean of duplicate analyses
Roodezandt, Wellington, South Africa	11/12/95	0.075	750*	0.010	6		RAC	0.26	0	#96/10832 Mean of duplicate analyses
							RAC	0.09	16	Mean of duplicate analyses
							RAC	0.07	30	Mean of duplicate analyses
							RAC	0.01	46	Mean of duplicate analyses
Roodezandt, Wellington, South Africa	11/12/95	0.150	750*	0.020	6		RAC	0.36	0	#96/10832 Mean of duplicate analyses
							RAC	0.09	16	Mean of duplicate analyses
							RAC	0.03	30	Mean of duplicate analyses
							RAC	0.06	46	Mean of duplicate analyses
Kanaan, Wellington, South Africa	10/01/96	0.113	1125	0.010	7		RAC	0.26	0	#96/10833 average water volume Mean of duplicate analyses
							RAC	0.22	7	Mean of duplicate analyses
							RAC	0.06	15	Mean of duplicate analyses

Location	Applications					Growth stage at last tr.	Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.					
							RAC	0.03	30	Mean of duplicate analyses
							RAC	0.04	37	Mean of duplicate analyses
							RAC	<0.01	44	Mean of duplicate analyses
Kanaan, Wellington, South Africa	10/01/96	0.225	1125*	0.020	7		RAC	0.65	0	#96/10833 Mean of duplicate analyses
							RAC	0.44	7	Mean of duplicate analyses
							RAC	0.27	15	Mean of duplicate analyses
							RAC	0.15	30	Mean of duplicate analyses
							RAC	0.12	37	Mean of duplicate analyses
							RAC	0.03	44	Mean of duplicate analyses
Kanaan, Wellington, South Africa	10/01/96	0.450	1125*	0.040	7		RAC	0.24	0	#96/10833 Mean of duplicate analyses
							RAC	0.20	7	Mean of duplicate analyses
							RAC	0.10	15	Mean of duplicate analyses
							RAC	0.09	30	Mean of duplicate analyses
							RAC	0.06	37	Mean of duplicate analyses
							RAC	0.13	44	Mean of duplicate analyses Mean of duplicate analyses
Uitkyk, Paarl, South Africa	27/12/95	0.114	1140*	0.010	7		RAC	0.27	0	#96/10834 Mean of duplicate analyses
							RAC	0.24	7	Mean of duplicate analyses
							RAC	0.20	15	Mean of duplicate analyses
							RAC	0.06	30	Mean of duplicate analyses
							RAC	0.07	45	Mean of duplicate analyses
Uitkyk, Paarl, South Africa	27/12/95	0.228	1140*	0.020	7		RAC	0.70	0	#96/10834 Mean of

Location	Applications					Growth stage at last tr.	Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.					
										duplicate analyses
							RAC	0.49	7	Mean of duplicate analyses
							RAC	0.14	15	Mean of duplicate analyses
							RAC	0.21	30	Mean of duplicate analyses
							RAC	0.20	45	Mean of duplicate analyses
Uitkyk, Paarl, South Africa	27/12/95	0.456	1140*	0.040	7		RAC	1.55	0	#96/10834 Mean of duplicate analyses
							RAC	1.20	7	Mean of duplicate analyses
							RAC	0.62	15	Mean of duplicate analyses
							RAC	0.60	30	Mean of duplicate analyses
							RAC	0.64	45	Mean of duplicate analyses
Fresno County CA, USA	25/08/95	0.224			4		RAC	<0.05	30	#96/5137
							RAC	0.07	30	490M2
							RAC	<0.05	30	490M9
Tulare County CA, USA	01/09/94	0.224			4		RAC	<0.05	30	#96/5137
							RAC	<0.05	30	490M2
							RAC	<0.05	30	490M9
Kern County CA, USA	01/09/94	0.224			4		RAC	<0.05	30	#96/5137
							RAC	<0.05	30	490M2
							RAC	<0.05	30	490M9
Monterey County CA, USA	10/09/94	0.224			4		RAC	<0.05	30	#96/5137
							RAC	<0.05	30	490M2
							RAC	<0.05	30	490M9
Grant County WA, USA	13/09/94	0.224			4		RAC	0.18	30	#96/5137
							RAC	<0.05	30	490M2
							RAC	<0.05	30	490M9
							RAC	0.09	30	
							RAC	<0.05	30	490M2
							RAC	<0.05	30	490M9
Ontario County NY, USA	06/09/94	0.224			4		RAC	0.26	30	#96/5137 Mean of 4 analyses
							RAC	<0.05	30	490M2 Mean of 4 analyses
							RAC	<0.05	30	490M9 Mean of 4 analyses
Yates County NY, USA	02/09/94	0.224			4		RAC	0.18	30	#96/5137 Mean of 4 analyses

Location	Applications					Growth stage at last tr.	Sample	Residues. mg/kg	PHI, days	Report-No. and Remarks
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.					
							RAC	<0.05	30	490M2 Mean of 4 analyses
							RAC	<0.05	30	490M9 Mean of 4 analyses
Northampton County PA, USA	23/08/94	0.224			4		RAC	0.49	30	#96/5137 Mean of 4 analyses
							RAC	0.09	30	490M2 Mean of 4 analyses
							RAC	0.05	30	490M9 Mean of 4 analyses
Kent County MI, USA	16/08/94	0.224			4		RAC	0.43	30	#96/5137
							RAC	0.10	30	490M2
							RAC	0.07	30	490M9
Sampson County NC, USA	19/08/94	0.224			4		RAC	0.13	30	#96/5137
							RAC	0.07	30	490M2
							RAC	<0.05	30	490M9
							RAC	0.11	30	
							RAC	0.11	30	490M2
							RAC	<0.05	30	490M9
Matityahu, Israel	05/06/96	0.450	1500	0.030	7	fruit full size	RAC	0.27	21	#97/10668 5 replicates
Tulare County, CA, USA	08/09/94	0.672			4	mature	RAC	0.16	14	#97/5043 6 replicates
							RAC	0.05	14	490M2/6 replicates
							RAC	<0.05	14	490M9/6 replicates
							juice	<0.05	14	2 replicates
							juice	0.12	14	490M2/2 replicates
							juice	<0.05	14	490M9/2 replicates
							raisin	0.26	14	2 replicates
							raisin	0.08	14	490M2/2 replicates
							raisin	0.06	14	490M9/2 replicates
Ontario County, NY, USA	20/09/94	0.672			4	mature	RAC	1.82	14	#97/5043 4 replicates
							RAC	<0.05	14	490M2/4 replicates
							RAC	<0.05	14	490M9/4 replicates
							juice	0.13	14	2 replicates
							juice	0.08	14	490M2/2 replicates
							juice	<0.05	14	490M9/2 replicates
							raisin	2.82	14	2 replicates
							raisin	0.15	14	490M2/2 replicates
							raisin	0.16	14	490M9/2 replicates

* Average volume of the different treatments

Table 43. Supervised residue trials on bulb onions. Bulbs analysed.

	Applications					

Location	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI days	Report No. Residues determined
Üdemerbruch, Germany	04/09/95	0.205	255	0.080	7	48	<0.05	0	#97/10280
						48	<0.05	5	
						48	<0.05	7	
						48	<0.05	14	
						48	<0.05	21	
						48	<0.05	0	490M2
						48	<0.05	5	490M2
						48	<0.05	7	490M2
						48	<0.05	14	490M2
						48	<0.05	21	490M2
						48	0.10	0	490M9
						48	<0.05	5	490M9
						48	<0.05	7	490M9
						48	<0.05	14	490M9
						48	<0.05	21	490M9
Ottersum, Netherlands	04/09/95	0.203	252	0.081	7	48	<0.05	0	#97/10280
							<0.05	5	
							<0.05	7	
							0.06	14	
							<0.05	21	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	21	490M2
							<0.05	0	490M9
							<0.05	5	
							<0.05	7	490M9
							<0.05	14	490M9
							<0.05	21	490M9
Siebengewald, Netherlands	11/09/95	0.205	255	0.080	7	48	<0.05	0	#97/10280
							<0.05	5	
							<0.05	7	
							<0.05	14	
							<0.05	21	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	21	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	14	490M9
							<0.05	21	490M9
NN Haps, Netherlands	19/09/95	0.206	256	0.080	7	48	<0.05	0	#97/10280
							<0.05	5	
							<0.05	7	
							<0.05	13	
							<0.05	21	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	13	490M2
							<0.05	21	490M2

Location	Applications					Growth stage at last tr.	Residues mg/kg	PHI days	Report No. Residues determined
	Date of last treatment	kg ai/ha	Water l/ha	kg ai/hl	No.				
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	13	490M9
							<0.05	21	490M9
Üdemerbruch, Germany	21/08/86	0.203	253	0.080	7	48	<0.05	0	#97/10281
							<0.05	5	
							<0.05	7	
							<0.05	14	
							<0.05	21	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	21	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	14	490M9
							<0.05	21	490M9
PS Slijk-Ewijk, Netherlands	21/08/86	0.205	255	0.080	7	48	<0.05	0	#97/10281
							<0.05	5	
							<0.05	7	
							<0.05	14	
							<0.05	21	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	21	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	14	490M9
							<0.05	21	490M9
Millingen, Netherlands	21/08/86	0.200	249	0.080	7	47	<0.05	0	#97/10281
							<0.05	5	
							<0.05	7	
							<0.05	14	
							<0.05	21	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	21	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	14	490M9
							<0.05	21	490M9
Ottersum, Netherlands	12/08/96	0.200	249	0.080	7	48	<0.05	0	#97/10281
							<0.05	5	
							<0.05	7	
							<0.05	14	

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI days	Report No. Residues determined
							<0.05	21	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	21	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	14	490M9
							<0.05	21	490M9

Table 44. Supervised residue trials on cucumbers.

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
Sanlúcar de Barrameda, Spain	20/10/95	0.099	916*	0.011	4	69-87	<0.05	0	#97/10152
							<0.05	5	
							<0.05	7	
							<0.05	13	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	13	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	13	490M9
Sanlúcar, Spain	20/10/95	0.097	906*	0.011	4	69-85	<0.05	0	#97/10152
							<0.05	5	
							<0.05	7	
							<0.05	13	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	13	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	13	490M9
Sanlúcar, Spain	27/10/95	0.099	913*	0.011	4	69-88	<0.05	0	#97/10152
							<0.05	4	
							<0.05	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Sanlúcar, Spain	27/10/95	0.097	903*	0.011	4	69-86	0.46	0	#97/10152

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
							<0.05	4	
							<0.05	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Alcala de Guadaira, Spain	10/05/96	0.146	904*	0.016	4	69-75	<0.05	0	#97/10152
							<0.05	3	
							<0.05	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	3	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	3	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Alcala de Guadaira, Spain	20/05/96	0.128	778*	0.016	4	69-76	<0.05	0	#97/10152
							<0.05	4	
							<0.05	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Palacios, Spain	04/06/96	0.144	888*	0.016	4	69-75	<0.05	0	#97/10152
							<0.05	3	
							<0.05	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	3	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	3	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Palacios, Spain	04/06/96	0.144	888*	0.016	4	69-75	<0.05	0	#97/10152
							<0.05	3	
							<0.05	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	3	490M2
							<0.05	7	490M2
							<0.05	14	490M2

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
							<0.05	0	490M9
							<0.05	3	490M9
							<0.05	7	490M9
							<0.05	14	490M9

* Average volume of the different treatments

Table 45. Supervised residue trials on melons.

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
Alcala de Guadaira, Spain	14/06/96	0.150	900*	0.017	4	79	<0.05	0	#97/10155
							<0.05	4	
							<0.05	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Alcala de Guadaira, Spain	14/06/96	0.150	900*	0.017	4	78-79	<0.05	0	#97/10155
							<0.05	4	
							0.09	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	4	F 490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Palacios, Spain	14/06/96	0.150	900*	0.017	4	77-78	0.07	0	#97/10155
							0.11	4	
							0.07	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							0.06	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Palacios, Spain	07/08/96	0.150	900*	0.017	4	79-81	<0.05	0	#97/10155
							0.06	5	
							<0.05	7	
							<0.05	14	
							<0.05	0	

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
							<0.05	5	
							<0.05	7	
							<0.05	14	
							<0.05	0	
							<0.05	5	
							<0.05	7	
							<0.05	14	
Sanlúcar, Spain	23/07/96	0.150	900*	0.017	4	73-81	0.07	0	#97/10155
							0.06	3	
							<0.05	7	
							<0.05	13	
							<0.05	0	490M2
							<0.05	3	490M2
							<0.05	7	490M2
							<0.05	13	490M2
							<0.05	0	490M9
							<0.05	3	490M9
							<0.05	7	490M9
							<0.05	13	490M9
Sanlúcar, Spain	23/07/96	0.150	900*	0.017	4	73-80	<0.05	0	#97/10155
							<0.05	3	
							<0.05	7	
							<0.05	13	
							<0.05	0	490M2
							<0.05	3	490M2
							<0.05	7	490M2
							<0.05	13	490M2
							<0.05	0	490M9
							<0.05	3	490M9
							<0.05	7	490M9
							<0.05	13	490M9
Sanlúcar, Spain	23/07/96	0.150	900*	0.017	4	73-81	0.05	0	#97/10155
							0.08	3	
							<0.05	7	
							<0.05	13	
							<0.05	0	490M2
							<0.05	3	490M2
							<0.05	7	490M2
							<0.05	13	490M2
							<0.05	0	490M9
							<0.05	3	490M9
							<0.05	7	490M9
							<0.05	13	490M9
Palacios, Spain	07/08/96	0.150	900*	0.017	4	79-80	0.10	0	#97/10155
							0.16	5	
							<0.05	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	14	490M9
N-37-Esvres/Indre, France	26/07/96	0.150	900*	0.017	4	81	0.06	0	#98/10394

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
							0.06	4	
							<0.05	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
S-33-La Reole, France	25/07/96	0.150	900*	0.017	4	85	0.19	0	#98/10394
							0.08	4	
							0.09	6	
							0.06	13	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	6	490M2
							<0.05	13	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	6	490M9
							0.06	13	490M9
N-37-La Roche-Clermault, France	14/08/97	0.150	900*	0.017	4	mature	0.20	0	#98/10390
							0.16	4	
							0.08	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
N-37-Lemere, France	03/09/97	0.150	900*	0.017	4	83	<0.05	0	#98/10390
							0.05	5	
							<0.05	9	
							<0.05	15	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	9	490M2
							<0.05	15	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	9	490M9
							<0.05	15	490M9
Sanlúcar, Spain	10/10/97	0.150	900	0.017	4	89	0.13	4	#98/10218
							0.06	7	
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	4	490M9
							<0.05	7	490M9
Sanlúcar, Spain	10/10/97	0.150	900	0.017	4	89	0.07	4	

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
							0.07	7	
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	4	490M9
							<0.05	7	490M9

* Average volume of the different treatments.

Table 46. Supervised residue trials on tomatoes in Spain.

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
Alcala de Guadaira	16/10/95	0.100	900	0.011	4	69-83	<0.05	0	#97/10144
							<0.05	3	
							<0.05	7	
							0.07	14	
							<0.05	0	490M2
							<0.05	3	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	3	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Alcala de Guadaira	16/10/95	0.100	900	0.011	4	69-83	0.06	0	#97/10144
							0.05	3	
							0.06	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	3	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	3	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Sanlúcar	20/10/95	0.100	900	0.011	4	69-83	0.07	0	#97/10144
							0.08	5	
							<0.05	7	
							<0.05	13	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	13	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	13	490M9
Sanlúcar	27/10/95	0.100	900	0.011	4	68-82	<0.05	0	#97/10144
							0.06	4	
							0.05	7	
							0.11	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Alcala de Guadaira	10/05/96	0.250	900	0.028	4	68-82	0.35	0	#97/10144
							0.31	3	
							0.25	7	
							0.10	14	
							<0.05	0	490M2
							<0.05	3	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	3	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Alcala de Guadaira	20/05/96	0.250	900	0.028	4	69-83	0.20	0	#97/10144
							0.14	4	
							0.13	7	
							0.08	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Los Palacios	20/05/96	0.250	900	0.028	4	69-82	0.26	0	#97/10144
							0.25	4	
							0.12	7	
							0.10	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Los Palacios	20/05/96	0.250	900	0.028	4	69-82	0.11	0	#97/10144
							0.09	4	
							0.08	7	
							0.06	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Los Palacios	24/10/97	0.250	900	0.028	4	76-78	0.17	4	#98/10217
							0.20	7	
							<0.05	4	490M2
							<0.05	7	490M2

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
							<0.05	4	490M9
							<0.05	7	490M9
Los Palacios	24/10/97	0.250	900	0.028	4	76-79	0.27	4	#98/10217
							0.18	7	
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	4	490M9
							<0.05	7	490M9
Sanlúcar	23/10/97	0.250	900	0.028	4	77-79	0.23	4	#98/10217
							0.16	7	
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	4	490M9
							<0.05	7	490M9
Sanlúcar	23/10/97	0.250	900	0.028	4	75-76	0.13	4	#98/10217
							0.08	7	
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	4	490M9
							<0.05	7	490M9

Table 47. Supervised residue trials on sweet peppers in Spain.

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
Sanlúcar	20/10/95	0.100	900	0.011	4	68-77	<0.05	0	#97/10144
							<0.05	5	
							<0.05	7	
							<0.05	13	
							<0.05	0	490M2
							<0.05	5	490M2
							<0.05	7	490M2
							<0.05	13	490M2
							<0.05	0	490M9
							<0.05	5	490M9
							<0.05	7	490M9
							<0.05	13	490M9
Sanlúcar	27/10/95	0.100	900	0.011	4	69-75	<0.05	0	#97/10144
							<0.05	4	
							<0.05	7	
							<0.05	14	
							<0.05	0	490M2
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Alcala de Guadaira	14/06/96	0.250	900	0.028	4	77	0.15	0	#97/10144
							0.15	4	
							0.27	7	
							0.17	14	
							<0.05	0	490M2
							<0.05	4	490M2

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
							0.05	7	490M2
							0.05	14	490M2
							<0.05	0	490M9
							<0.05	4	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Alcala de Guadair a	26/06/96	0.250	900	0.028	4	77-79	0.41	0	#97/10144
							0.21	3	
							0.15	7	
							0.14	14	
							0.05	0	490M2
							<0.05	3	490M2
							<0.05	7	490M2
							<0.05	14	490M2
							<0.05	0	490M9
							<0.05	3	490M9
							<0.05	7	490M9
							<0.05	14	490M9
Los Palacios	24/10/97	0.250	900	0.028	4	75-76	0.44	4	#98/10217
							0.38	7	
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	4	490M9
							<0.05	7	490M9
Los Palacios	03/11/97	0.250	900	0.028	4	75-76	0.39	4	#98/10217
							0.32	8	
							<0.05	4	490M2
							<0.05	8	490M2
							<0.05	4	490M9
							<0.05	8	490M9
Los Palacios	24/10/97	0.250	900	0.028	4	78-80	0.37	4	#98/10217
							0.36	7	
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	4	490M9
							<0.05	7	490M9
Sanlúcar	23/10/97	0.250	900	0.028	4	75-76	0.10	4	#98/10217
							0.16	8	
							<0.05	4	490M2
							<0.05	8	490M2
							<0.05	4	490M9
							<0.05	8	490M9
Sanlúcar	03/11/97	0.250	900	0.028	4	75-77	0.19	4	#98/10217
							0.11	8	
							<0.05	4	490M2
							<0.05	8	490M2
							<0.05	4	490M9
							<0.05	8	490M9
Sanlúcar	23/10/97	0.250	900	0.028	4	75-76	0.10	4	#98/10217
							0.12	7	
							<0.05	4	490M2
							<0.05	7	490M2
							<0.05	4	490M9
							<0.05	7	490M9

Table 48. Supervised residue trials on wheat (winter sown).

Table 48. Supervised residue trials on wheat (winter sown).

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
Bothkamp, Germany	27/06/94	0.105	300	0.035	2	61/63	whole plant	1.03	0	#94/11004 total
							ears	<0.05	21	total
							haulm	0.10	21	total
							straw	0.22	35	total
							grain	<0.05	35	total
							straw	0.07	42	total
							grain	<0.05	42	total
							whole plant	1.03	0	parent
							ears	<0.05	21	parent
							haulm	0.10	21	parent
							straw	0.08	35	parent
							grain	<0.05	35	parent
							straw	0.06	42	parent
							grain	<0.05	42	parent
							whole plant	<0.05	0	490M9
							ears	<0.05	21	490M9
							haulm	<0.05	21	490M9
							straw	0.15	35	490M9
							straw	<0.05	42	490M9
							whole plant	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	<0.05	21	490M2
							straw	<0.05	35	490M2
							straw	<0.05	42	490M2
Lippetal, Germany	08/06/93	0.105	300	0.035	2	61	whole plant	1.40	0	#94/11005 total
							ears	0.05	21	total
							haulm	0.29	21	total
							ears	<0.05	37	total
							haulm	0.25	37	total
							ears	<0.05	44	total
							haulm	0.09	44	total
							grain	<0.05	50	total
							straw	0.16	50	total
							whole plant	0.06	0	490M9
							ears	0.05	21	490M9
							haulm	0.06	21	490M9
							ears	<0.05	37	490M9
							haulm	0.06	37	490M9
							ears	<0.05	44	490M9
							haulm	<0.05	44	490M9
							straw	<0.05	50	490M9
							whole plant	1.34	0	parent
							ears	<0.05	21	parent
							haulm	0.23	21	parent
							ears	<0.05	37	parent
							haulm	0.19	37	parent
							ears	<0.05	44	parent
							haulm	0.09	44	parent
							grain	<0.05	50	parent

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
							straw	0.09	50	parent
							whole plant	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	<0.05	21	490M2
							ears	<0.05	37	490M2
							haulm	<0.05	37	490M2
							ears	<0.05	44	490M2
							haulm	<0.05	44	490M2
							straw	0.07	50	490M2
Bothkamp, Germany	27/6/94	0.125	300	0.042	2	61/63	forage	1.72	0	#94/11004 total
							ears	0.09	21	total
							haulm	0.38	21	total
							straw	0.79	35	total
							grain	<0.05	35	total
							straw	0.60	42	total
							grain	<0.05	42	total
							forage	1.66	0	parent
							ears	0.09	21	parent
							haulm	0.29	21	parent
							straw	0.50	35	parent
							grain	<0.05	35	parent
							straw	0.44	42	parent
							grain	<0.05	42	parent
							forage	0.06	0	490M9
							ears	<0.05	21	490M9
							haulm	0.08	21	490M9
							straw	0.21	35	490M9
							straw	0.08	42	490M9
							forage	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	<0.05	21	490M2
							straw	0.08	35	490M2
							straw	0.07	42	490M2
Lippetal, Germany	8/6/93	0.125	300	0.042	2	61	forage	1.11	0	#94/11005 total
							ears	0.13	21	total
							haulm	0.19	21	total
							ears	<0.05	37	total
							haulm	0.24	37	total
							ears	<0.05	44	total
							haulm	0.09	44	total
							grain	<0.05	50	total
							straw	0.18	50	total
							forage	0.06	0	490M9
							ears	0.06	21	490M9
							haulm	<0.05	21	490M9
							ears	<0.05	37	490M9
							haulm	0.06	37	490M9
							ears	<0.05	44	490M9
							haulm	<0.05	44	490M9
							straw	<0.05	50	490M9
							forage	1.05	0	parent
							ears	0.07	21	parent
							haulm	0.19	21	parent
							ears	<0.05	37	parent
							haulm	0.18	37	parent
							ears	<0.05	44	parent
							haulm	0.09	44	parent
							grain	<0.05	50	parent
							straw	0.12	50	parent
							forage	<0.05	0	490M2
							ears	<0.05	21	490M2

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
							haulm	<0.05	21	490M2
							ears	<0.05	37	490M2
							haulm	<0.05	37	490M2
							ears	<0.05	44	490M2
							haulm	<0.05	44	490M2
							straw	0.06	50	490M2
Izel les Equerchin, France	01/06/93	0.105	300	0.035	2	65	whole plant	2.06	0	#94/11005 total
							ears	<0.05	20	total
							haulm	0.05	20	total
							ears	<0.05	35	total
							haulm	0.05	35	total
							ears	<0.05	43	total
							haulm	<0.05	43	total
							grain	<0.05	62	total
							straw	<0.05	62	total
							whole plant	<0.05	0	490M9
							ears	<0.05	20	490M9
							haulm	<0.05	20	490M9
							ears	<0.05	35	490M9
							haulm	<0.05	35	490M9
							ears	<0.05	43	490M9
							haulm	<0.05	43	490M9
							straw	<0.05	62	490M9
							whole plant	2.06	0	parent
							ears	<0.05	20	parent
							haulm	0.05	20	parent
							ears	<0.05	35	parent
							haulm	0.05	35	parent
							ears	<0.05	43	parent
							haulm	<0.05	43	parent
							grain	<0.05	62	parent
							straw	<0.05	62	parent
							whole plant	<0.05	0	490M2
							ears	<0.05	20	490M2
							haulm	<0.05	20	490M2
							ears	<0.05	35	490M2
							haulm	<0.05	35	490M2
							ears	<0.05	43	490M2
							haulm	<0.05	43	490M2
							straw	<0.05	49	490M2
Izel les Equerchin, France	1/6/93	0.125	300	0.042	2	65	forage	3.64	0	total
							ears	0.08	20	total
							haulm	0.16	20	total
							ears	<0.05	35	total
							haulm	0.17	35	total
							ears	<0.05	43	total
							haulm	0.07	43	total
							grain	<0.05	62	total
							straw	<0.05	62	total
							forage	0.08	0	490M9
							ears	0.08	20	490M9
							haulm	0.08	20	490M9
							ears	<0.05	35	490M9
							haulm	0.08	35	490M9
							ears	<0.05	43	490M9

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
							haulm	<0.05	43	490M9
							straw	<0.05	62	490M9
							forage	3.56	0	parent
							ears	<0.05	20	parent
							haulm	0.08	20	parent
							ears	<0.05	35	parent
							haulm	0.09	35	parent
							ears	<0.05	43	parent
							haulm	0.07	43	parent
							grain	<0.05	62	parent
							straw	<0.05	62	parent
							forage	<0.05	0	490M2
							ears	<0.05	20	490M2
							haulm	<0.05	20	490M2
							ears	<0.05	35	490M2
							haulm	<0.05	35	490M2
							ears	<0.05	43	490M2
							haulm	<0.05	43	490M2
							straw	<0.05	62	490M2
Neuville, France	16/6/92	0.150	300	0.050	2	65	forage.	3.23	0	# 94/11003 total
							ears	<0.05	31	total
							haulm	0.18	31	total
							straw	<0.05	51	total
							grain	<0.05	51	total
							forage.	3.15	0	parent
							ears	<0.05	31	parent
							haulm	0.12	31	parent
							straw	<0.05	51	parent
							grain	<0.05	51	parent
							forage.	0.08	0	490M9
							ears	<0.05	31	490M9
							haulm	0.06	31	490M9
							straw	<0.05	51	490M9
							forage.	<0.05	0	490M2
							ears	<0.05	31	490M2
							haulm	<0.05	31	490M2
							straw	<0.05	51	490M2
Montot, France	26/5/92	0.15	300	0.050	2	65	forage.	3.66	0	total
							ears	0.06	30	total
							haulm	0.59	30	total
							straw	0.50	51	total
							grain	<0.05	51	total
							forage.	3.37	0	parent
							ears	<0.05	30	parent
							haulm	0.28	30	parent
							straw	0.26	51	parent
							grain	<0.05	51	parent
							forage.	0.21	0	490M9
							ears	0.06	30	490M9
							haulm	0.20	30	490M9
							straw	0.07	51	490M9
							forage.	0.08	0	490M2
							ears	<0.05	30	490M2
							haulm	0.11	30	490M2
							straw	0.17	51	490M2
Villenouvelle,	19/5/92	0.15	300	0.050	2	65	forage.	6.24	0	total

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
France										
							ears	<0.05	31	total
							haulm	0.19	31	total
							straw	0.07	57	total
							grain	<0.05	57	total
							forage.	5.86	0	parent
							ears	<0.05	31	parent
							haulm	0.13	31	parent
							straw	0.07	57	parent
							grain	<0.05	57	parent
							forage.	0.30	0	490M9
							ears	<0.05	31	490M9
							haulm	0.06	31	490M9
							straw	<0.05	57	490M9
							forage.	0.08	0	490M2
							ears	<0.05	31	490M2
							haulm	<0.05	31	490M2
							straw	<0.05	57	490M2

Table 49. Supervised residue trials on wheat (spring sown).

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues, mg/kg	PHI, days	Report No. Residues determined
Alken-Vanco, Belgium	20/06/94	0.105	300	0.035	2	61	whole plant	5.07	0	#94/11004 total
							ears	0.12	21	total
							haulm	1.54	21	total
							straw	3.15	33	total
							grain	<0.05	33	total
							straw	1.80	42	total
							grain	<0.05	42	total
							whole plant	4.92	0	parent
							ears	0.12	21	parent
							haulm	1.11	21	parent
							straw	2.59	33	parent
							grain	<0.05	33	parent
							straw	1.51	42	parent
							grain	<0.05	42	parent
							whole plant	0.15	0	490M9
							ears	<0.05	21	490M9
							haulm	0.34	21	490M9
							straw	0.42	33	490M9
							straw	0.19	42	490M9
							whole plant	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	0.08	21	490M2
							straw	0.13	33	490M2
							straw	0.10	42	490M2
Birkenheide, Germany	09/06/93	0.105	300	0.035	2	61	whole plant	4.18	0	#94/11005 total
							ears	0.16	21	total
							haulm	1.60	21	total
							grain	<0.05	37	total
							straw	1.80	37	total

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues, mg/kg	PHI, days	Report No. Residues determined
							grain	<0.05	42	total
							straw	0.71	42	total
							whole plant	0.21	0	490M9
							ears	0.09	21	490M9
							haulm	0.25	21	490M9
							straw	0.17	37	490M9
							straw	<0.05	42	490M9
							whole plant	3.97	0	parent
							ears	0.07	21	parent
							haulm	1.25	21	parent
							grain	<0.05	37	parent
							straw	1.45	37	parent
							grain	<0.05	42	parent
							straw	0.65	42	parent
							whole plant	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	0.10	21	490M2
							straw	0.18	37	490M2
							straw	0.06	42	490M2
Borlo-Gingelom, Belgium	03/06/93	0.105	300	0.035	2	61	whole plant	2.19	0	#94/11005 total
							ears	0.07	21	total
							haulm	0.32	21	total
							ears	<0.05	35	total
							haulm	0.43	35	total
							grain	<0.05	42	total
							straw	0.36	42	total
							whole plant	0.13	0	490M9
							ears	<0.05	21	490M9
							haulm	0.07	21	490M9
							ears	<0.05	35	490M9
							haulm	0.17	35	490M9
							straw	0.07	42	490M9
							whole plant	2.06	0	parent
							ears	0.07	21	parent
							haulm	0.16	21	parent
							ears	<0.05	35	parent
							haulm	0.26	35	parent
							grain	<0.05	42	parent
							straw	0.24	42	parent
							whole plant	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	<0.05	21	490M2
							ears	<0.05	35	490M2
							haulm	<0.05	35	490M2
							straw	0.05	42	490M2
Niederbrechen, Germany	09/06/93	0.120	300	0.040	2	61	grain	<0.05	64	#94/11080
Niederbrechen, Germany	09/06/93	0.240	300	0.080	2	61	grain	<0.05	64	#94/11080
Niederbrechen, Germany	09/06/93	0.360	300	0.120	2	61	grain	<0.05	64	#94/11080
Alken-Vanco, Belgium	20/6/94	0.125	300	0.042	2	61	forage	5.83	0	#94/11004 total
							ears	0.30	21	total
							haulm	3.17	21	total
							straw	4.76	33	total
							grain	<0.05	33	total

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues, mg/kg	PHI, days	Report No. Residues determined
							straw	3.90	42	total
							grain	<0.05	42	total
							forage	5.73	0	parent
							ears	0.30	21	parent
							haulm	2.49	21	parent
							straw	4.00	33	parent
							grain	<0.05	33	parent
							straw	3.59	42	parent
							grain	<0.05	42	parent
							forage	0.11	0	490M9
							ears	<0.05	21	490M9
							haulm	0.53	21	490M9
							straw	0.60	33	490M9
							straw	0.19	42	490M9
							forage	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	0.16	21	490M2
							straw	0.17	33	490M2
							straw	0.12	42	490M2
Birkenheide, Germany	9/6/93	0.125	300	0.042	2	61	forage	4.17	0	#94/11005 total
							ears	0.16	21	total
							haulm	1.91	21	total
							grain	<0.05	37	total
							straw	1.64	37	total
							grain	<0.05	42	total
							straw	0.55	42	total
							forage	0.17	0	490M9
							ears	0.07	21	490M9
							haulm	0.20	21	490M9
							straw	0.17	37	490M9
							straw	<0.05	42	490M9
							forage	4.00	0	parent
							ears	0.09	21	parent
							haulm	1.61	21	parent
							grain	<0.05	37	parent
							straw	1.27	37	parent
							grain	<0.05	42	parent
							straw	0.47	42	parent
							forage	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	0.10	21	490M2
							straw	0.20	37	490M2
							straw	0.08	42	490M2
Borlo-Gingelom, Belgium	3/6/93	0.125	300	0.042	2	61	forage	1.65	0	#94/11005 total
							ears	0.12	21	total
							haulm	0.33	21	total
							ears	<0.05	35	total
							haulm	0.10	35	total
							grain	<0.05	42	total
							straw	0.12	42	total
							forage	0.13	0	490M9
							ears	0.06	21	490M9
							haulm	0.17	21	490M9
							ears	<0.05	35	490M9
							haulm	0.10	35	490M9

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues, mg/kg	PHI, days	Report No. Residues determined
							straw	0.06	42	490M9
							forage	1.52	0	parent
							ears	0.06	21	parent
							haulm	0.16	21	parent
							ears	<0.05	35	parent
							haulm	<0.05	35	parent
							grain	<0.05	42	parent
							straw	<0.05	42	parent
							forage	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	<0.05	21	490M2
							ears	<0.05	35	490M2
							haulm	<0.05	35	490M2
							straw	0.06	42	490M2

Table 50. Supervised residue trials on barley (winter sown).

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
Ven-Zelderheide and Netherlands	27/5/94	0.105	300	0.035	2	61	forage	2.02	0	#94/11004 total
							ears	0.09	21	total
							haulm	0.14	21	total
							ears	<0.05	34	total
							haulm	0.07	34	total
							straw	0.34	42	total
							grain	<0.05	42	total
							forage	2.02	0	parent
							ears	<0.05	21	parent
							haulm	0.14	21	parent
							ears	<0.05	34	parent
							haulm	0.07	34	parent
							straw	0.13	42	parent
							grain	<0.05	42	parent
							forage	<0.05	0	490M9
							ears	0.09	21	490M9
							haulm	<0.05	21	490M9
							ears	<0.05	34	490M9
							haulm	<0.05	34	490M9
							straw	0.12	42	490M9
							forage	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	<0.05	21	490M2
							ears	<0.05	34	490M2
							haulm	<0.05	34	490M2
							straw	0.08	42	490M2
Niederhofen, Germany	19/5/93	0.105	300	0.035	2	69	forage	2.43	0	#94/11005 total
							ears	<0.05	21	total
							haulm	0.38	21	total
							ears	<0.05	35	total
							haulm	0.13	35	total
							grain	<0.05	42	total
							straw	0.07	42	total

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
							forage	0.09	0	490M9
							ears	<0.05	21	490M9
							haulm	<0.05	21	490M9
							ears	<0.05	35	490M9
							haulm	<0.05	35	490M9
							straw	<0.05	42	490M9
							forage	2.34	0	parent
							ears	<0.05	21	parent
							haulm	0.29	21	parent
							ears	<0.05	35	parent
							haulm	0.08	35	parent
							grain	<0.05	42	parent
							straw	<0.05	42	parent
							forage	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	0.09	21	490M2
							ears	<0.05	35	490M2
							haulm	0.05	35	490M2
							straw	<0.05	42	490M2
Montot, France	15/5/93	0.105	300	0.035	2	65	forage	1.97	0	#94/11005 total
							ears	<0.05	20	total
							haulm	0.29	20	total
							grain	<0.05	33	total
							straw	0.20	33	total
							grain	<0.05	40	total
							straw	0.07	40	total
							forage	<0.05	0	490M9
							ears	<0.05	20	490M9
							haulm	<0.05	20	490M9
							straw	0.06	33	490M9
							straw	<0.05	40	490M9
							forage	1.97	0	parent
							ears	<0.05	20	parent
							haulm	0.29	20	parent
							grain	<0.05	33	parent
							straw	0.14	33	parent
							grain	<0.05	40	parent
							straw	0.07	40	parent
							forage	<0.05	0	490M2
							ears	<0.05	20	490M2
							haulm	<0.05	20	490M2
							straw	<0.05	33	490M2
							straw	<0.05	40	490M2

Table 51. Supervised residue trials on barley (spring sown).

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
Holzen, Germany	23/06/94	0.105	300	0.035	2	61	whole plant	1.47	0	#94/11004 total
							ears	0.06	21	total
							haulm	0.33	21	total
							straw	0.53	35	total
							grain	<0.05	35	total

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
							straw	0.37	42	total
							grain	<0.05	42	total
							whole plant	1.47	0	parent
							ears	0.06	21	parent
							haulm	0.26	21	parent
							straw	0.28	35	parent
							grain	<0.05	35	parent
							straw	0.15	42	parent
							grain	<0.05	42	parent
							whole plant	<0.05	0	490M9
							ears	<0.05	21	490M9
							haulm	0.07	21	490M9
							straw	0.11	35	490M9
							straw	0.10	42	490M9
							whole plant	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	<0.05	21	490M2
							straw	0.14	35	490M2
							straw	0.11	42	490M2
Bothcamp, Germany	07/06/93	0.105	300	0.035	2	63	whole plant	1.58	0	#94/11005 total
							ears	0.12	21	total
							haulm	0.39	21	total
							ears	<0.05	35	total
							haulm	0.28	35	total
							ears	<0.05	42	total
							haulm	0.26	42	total
							grain	<0.05	49	total
							straw	0.06	49	total
							whole plant	<0.05	0	490M9
							ears	0.06	21	490M9
							haulm	0.11	21	490M9
							ears	<0.05	35	490M9
							haulm	0.08	35	490M9
							ears	<0.05	42	490M9
							haulm	0.08	42	490M9
							straw	0.06	42	490M9
							whole plant	1.58	0	parent
							ears	0.06	21	parent
							haulm	0.23	21	parent
							ears	<0.05	35	parent
							haulm	0.20	35	parent
							ears	<0.05	42	parent
							haulm	0.18	42	parent
							grain	<0.05	49	parent
							straw	<0.05	49	parent
							whole plant	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	0.05	21	490M2
							ears	<0.05	35	490M2
							haulm	<0.05	35	490M2
							ears	<0.05	42	490M2
							haulm	<0.05	42	490M2
							straw	<0.05	49	490M2
Gennep, Netherlands	02/06/93	0.105	300	0.035	2	61	whole plant	2.84	0	#94/11005 total
							ears	<0.05	21	total

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
							haulm	0.71	21	total
							ears	<0.05	34	total
							haulm	0.60	34	total
							grain	<0.05	43	total
							straw	0.55	43	total
							whole plant	0.07	0	490M9
							ears	<0.05	21	490M9
							haulm	0.10	21	490M9
							ears	<0.05	34	490M9
							haulm	0.07	34	490M9
							straw	0.07	42	490M9
							whole plant	2.77	0	parent
							ears	<0.05	21	parent
							haulm	0.55	21	parent
							ears	<0.05	34	parent
							haulm	0.45	34	parent
							grain	<0.05	43	parent
							straw	0.36	43	parent
							whole plant	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	0.06	21	490M2
							ears	<0.05	34	490M2
							haulm	0.08	34	490M2
							straw	0.12	43	490M2
Hünstetten-Ketternschwalbach, Germany	21/06/93	0.120	300	0.040	2	61	grain	<0.05	46	#94/11158
Hünstetten-Ketternschwalbach, Germany	21/06/93	0.240	300	0.080	2	61	grain	<0.05	46	#94/11158
Hünstetten-Ketternschwalbach, Germany	21/06/93	0.360	300	0.120	2	61	grain	<0.05	46	#94/11158
Holzen, Germany	0.125	300	0.042	23/6/94	2	61	forage	1.94	0	#94/11004 total
							ears	0.18	21	total
							haulm	0.50	21	total
							straw	1.06	35	total
							grain	<0.05	35	total
							straw	0.80	42	total
							grain	<0.05	42	total
							forage	1.94	0	parent
							ears	0.12	21	parent
							haulm	0.37	21	parent
							straw	0.79	35	parent
							grain	<0.05	35	parent
							straw	0.63	42	parent
							grain	<0.05	42	parent
							forage	<0.05	0	490M9
							ears	0.06	21	490M9
							haulm	0.08	21	490M9
							straw	0.13	35	490M9
							straw	0.08	42	490M9
							forage	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	0.06	21	490M2
							straw	0.14	35	490M2
							straw	0.10	42	490M2

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
Bothcamp, Germany	0.125	300	0.042	7/6/93	2	63	forage	1.97	0	#94/11005 total
							ears	0.15	21	total
							haulm	0.25	21	total
							ears	0.06	35	total
							haulm	0.43	35	total
							ears	<0.05	42	total
							haulm	0.16	42	total
							grain	<0.05	49	total
							straw	0.06	49	total
							forage	<0.05	0	490M9
							ears	0.06	21	490M9
							haulm	<0.05	21	490M9
							ears	<0.05	35	490M9
							haulm	0.11	35	490M9
							ears	<0.05	42	490M9
							haulm	<0.05	42	490M9
							straw	0.06	49	490M9
							forage	1.97	0	parent
							ears	0.09	21	parent
							haulm	0.25	21	parent
							ears	0.06	35	parent
							haulm	0.26	35	parent
							ears	<0.05	42	parent
							haulm	0.16	42	parent
							grain	<0.05	49	parent
							straw	<0.05	49	parent
							forage	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	<0.05	21	490M2
							ears	<0.05	35	490M2
							haulm	0.06	35	490M2
							ears	<0.05	42	490M2
							haulm	<0.05	42	490M2
							straw	<0.05	49	490M2
Gennep, Netherlands	0.125	300	0.042	2/6/93	2	61	forage	4.16	0	#94/11005 total
							ears	0.11	21	total
							haulm	1.35	21	total
							ears	0.06	34	total
							haulm	1.17	34	total
							grain	<0.05	43	total
							straw	1.01	43	total
							forage	0.06	0	490M9
							ears	<0.05	21	490M9
							haulm	0.11	21	490M9
							ears	<0.05	34	490M9
							haulm	0.13	34	490M9
							straw	0.09	43	490M9
							forage	4.10	0	parent
							ears	0.11	21	parent
							haulm	1.16	21	parent
							ears	0.06	34	parent
							haulm	0.92	34	parent
							grain	<0.05	43	parent
							straw	0.75	43	parent
							forage	<0.05	0	490M2

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI, days	Report No. Residues determined
							ears	<0.05	21	490M2
							haulm	0.08	21	490M2
							ears	<0.05	34	490M2
							haulm	0.12	34	490M2
							straw	0.17	43	490M2
Castelnau d'Estr., France	0.150	300	0.050	22/5/92	2	75	forage	4.17	0	# 94/11003 total
							ears	<0.05	28	total
							haulm	0.19	28	total
							straw	0.22	42	total
							grain	<0.05	42	total
							forage	4.17	0	parent
							ears	<0.05	28	parent
							haulm	0.14	28	parent
							straw	0.22	42	parent
							grain	<0.05	42	parent
							forage	4.22	0	490M9
							ears	<0.05	28	490M9
							haulm	<0.05	28	490M9
							straw	<0.05	42	490M9
							forage	<0.05	0	490M2
							ears	<0.05	28	490M2
							haulm	0.05	28	490M2
							straw	<0.05	42	490M2

Table 52. Supervised residue trials on rye (winter sown).

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI days	Report No. Residues determined
Limburgerhof and Germany	14/5/93	0.105	300	0.035	2	69	forage	1.13	0	# 94/11005 total
							ears	0.15	21	total
							haulm	0.36	21	total
							ears	0.09	35	total
							haulm	0.27	35	total
							ears	0.06	42	total
							haulm	0.26	42	total
							grain	<0.05	49	total
							straw	0.18	49	total
							forage	0.06	0	490M9
							ears	0.08	21	490M9
							haulm	0.21	21	490M9
							ears	0.09	35	490M9
							haulm	0.19	35	490M9
							ears	0.06	42	490M9
							haulm	0.19	42	490M9
							straw	0.12	49	490M9
							forage	1.07	0	parent
							ears	0.07	21	parent
							haulm	0.07	21	parent
							ears	<0.05	35	parent
							haulm	0.08	35	parent
							ears	<0.05	42	parent
							haulm	0.07	42	parent

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Sample	Residues mg/kg	PHI days	Report No. Residues determined
							grain	<0.05	49	parent
							straw	<0.05	49	parent
							forage	<0.05	0	490M2
							ears	<0.05	21	490M2
							haulm	<0.05	21	490M2
							ears	<0.05	35	490M2
							haulm	<0.05	35	490M2
							ears	<0.05	42	490M2
							haulm	<0.05	42	490M2
							straw	0.06	49	490M2
Limburgerhof, Germany	14/5/93	0.125	300	0.042	2	69	forage	1.97	0	# 94/11005 total
							ears	0.16	21	total
							haulm	0.39	21	total
							ears	<0.05	35	total
							haulm	0.30	35	total
							ears	0.10	42	total
							haulm	0.35	42	total
							grain	<0.05	49	total
							straw	0.29	49	total
							forage	0.23	0	490M9
							ears	0.06	21	490M9
							haulm	0.22	21	490M9
							ears	0.19	35	490M9
							haulm	0.19	35	490M9
							ears	0.10	42	490M9
							haulm	0.20	42	490M9
							straw	0.13	49	490M9
							forage	1.60	0	parent
							ears	0.10	21	parent
							haulm	0.17	21	parent
							ears	<0.05	35	parent
							haulm	0.11	35	parent
							ears	<0.05	42	parent
							haulm	0.10	42	parent
							grain	<0.05	49	parent
							straw	0.08	49	parent
							forage	0.14	0	490M2
							ears	<0.05	21	490M2
							haulm	<0.05	21	490M2
							ears	<0.05	35	490M2
							haulm	<0.05	35	490M2
							ears	<0.05	42	490M2
							haulm	0.05	42	490M2
							straw	0.08	49	490M2

Table 53. Supervised residue trials on pecans, USA. Kernels analysed.

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
Mitchell County, GA	01/10/96	0.224	467	0.048	8	mature fruit	<0.05	35	#97/5064
							<0.05	35	490M2
							<0.05	35	490M9

Location	Date of last treatment	Applications kg ai/ha	Water l/ha	kg ai/hl	No.	Growth stage at last tr.	Residues mg/kg	PHI, days	Report No. Residues determined
							<0.05	45	
							<0.05	45	490M2
							<0.05	45	490M9
							<0.05	55	
							<0.05	55	490M2
							<0.05	55	490M9
							<0.05	65	
							<0.05	65	490M2
							<0.05	65	490M9
Mitchell County, GA	01/10/96	0.224	2335	0.010	8	mature fruit	<0.05	35	#97/5064
							<0.05	35	490M2
							<0.05	35	490M9
							<0.05	45	
							<0.05	45	490M2
							<0.05	45	490M9
							<0.05	55	
							<0.05	55	490M2
							<0.05	55	490M9
							<0.05	65	
							<0.05	65	490M2
							<0.05	65	490M9
Houston County, AL	01/10/96	0.224	467	0.048	8	mature fruit	<0.05	45	#97/5064
							<0.05	45	490M2
							<0.05	45	490M9
							<0.05	45	
							<0.05	45	490M2
							<0.05	45	490M9
Tift County, GA	13/09/96	0.224	467	0.048	8	nut fill	<0.05	45	#97/5064
							<0.05	45	490M2
							<0.05	45	490M9
							<0.05	45	
							<0.05	45	490M2
							<0.05	45	490M9
Washington County, MS	15/10/96	0.224	467	0.048	8	fruiting	<0.05	45	#97/5064
							<0.05	45	490M2
							<0.05	45	490M9
Washington County, MS	15/10/96	0.224	2335	0.010	8	fruiting	<0.05	45	#97/5064
							<0.05	45	490M2
							<0.05	45	490M9
Uvalde County, TX	27/08/96	0.224	467	0.048	8	nut past gel	<0.05	45	#97/5064
							<0.05	45	490M2
							<0.05	45	490M9
Uvalde County, TX	27/08/96	0.224	2335	0.010	8	nut past gel	<0.05	45	#97/5064
							<0.05	45	490M2
							<0.05	45	490M9
Lubbock County, TX	22/10/96	0.224	467	0.048	8	mature fruit	<0.05	45	#97/5064
							<0.05	45	490M2
							<0.05	45	490M9
Lubbock County, TX	22/10/96	0.224	2335	0.010	8	mature fruit	<0.05	45	
							<0.05	45	490M2
							<0.05	45	490M9

Livestock feeding trials

Cows. In a study in the UK during 1994, 11 lactating Friesian cows were dosed twice daily with kresoxim-methyl at 120, 360 or 1200 mg/cow/day, equivalent to 6, 18 or 60 ppm in the feed, for 28 or 29 days with an undosed control for each group. Three cows from each group were slaughtered on the day of the final dose. Two additional cows from the high-dose group were fed the basal diet for 2 or 7 days after the last dose.

Milk samples, taken twice daily and combined to give daily samples, were stored at 4°C before mixing and overnight before analysis. On days 1, 14 and 28 only, additional 5-litre samples were retained from the total 24-hour milk production of each cow and separated by centrifugation into cream and skimmed milk. Changes in milk yield were reported to be within normal limits. Residues of 490M2 and 490M9 in whole milk, cream and skimmed milk were all <0.002 mg/kg (<2 µg/l).

The residues in the tissues are shown in Table 54. The parent compound was not sought. Samples were stored up to 175 days before analysis. The highest residues occurred in the kidneys, principally as 490M1 which was present at slaughter in all cows. 490M1 also occurred in the highest dose group in the liver, peritoneal fat and subcutaneous fat, and in the 360 ppm group in the liver and peritoneal fat. 490M9 was found in the liver and kidneys at the higher doses. 490M2 residues were all <0.01 mg/kg. Residues generally increased with increasing dose.

After 2 days withdrawal only 490M1 was still present in the liver and kidneys. By seven days there were no residues of 490M1 or 490M9 above 0.01 mg/kg in the liver, but a single residue was found in the kidneys (Redgrave, 1994).

Table 54. Residues of kresoxim-methyl metabolites in cow tissues after dosing at 120, 360 and 1200 mg/day.

Metabolite	Group	Dose level mg/day	Residue concentration , mg/kg				
			Liver	Kidney	Muscle	Subcutaneous fat	Peritoneal fat
490M1	A	0	nd	<0.01	nd	nd	nd
	B	120	nd	0.021-0.028	<0.01	<0.01	<0.01
	C	360	0.012-0.028	0.054-0.13	<0.01	<0.01	<0.01-0.033
	D	1200	<0.01-0.036	<0.01-0.29	<0.01	<0.01-0.02	<0.01-0.091
490M2	A	0	nd	nd	nd	nd	nd
	B	120	<0.01	nd	<0.01	nd	nd
	C	360	<0.01	<0.01	nd	nd	nd
	D	1200	<0.01	<0.01	<0.01	<0.01	<0.01
490M9	A	0	nd	nd	nd	nd	nd
	B	120	nd	nd	<0.01	nd	nd
	C	360	<0.01-0.015	0.014-0.023	<0.01	nd	nd
	D	1200	<0.01-0.024	<0.01-0.049	<0.01	<0.01	<0.01

nd: not detectable, <0.002 mg/kg

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

Residues in processed products were determined in some of the residue trials on apples and grapes. The results are repeated, together with the corresponding processing factors, in Table 55.

Table 55. Residues of kresoxim-methyl in processed products of apples and grapes.

Residue, mg/kg, and (calculated processing factor)						
Raw apple	Washed apple	Apple juice	Wet pomace	Apple sauce		
0.16	0.19 (1.19)	<0.05 (<0.31)	<0.05 (<0.31)	<0.05 (<0.31)		
0.19	0.07 (0.37)	<0.05 (<0.26)	0.09 (0.47)	<0.05 (<0.26)		
0.08	0.16 (2)	<0.05 (<0.63)	0.17 (2.1)	<0.05 (<0.63)		
<0.05	-	<0.05	<0.05	-		
Mean factor	1.2	<0.4	≤1	<0.4		
Grapes	Must 1 after heating	Must 2 after pressing	Wet pomace	Wine	Rosé wine	Red wine
0.25	<0.05 (<0.2).	<0.05	0.57	<0.05 (<0.2). <0.05 (<0.2)	<0.05 (<0.2)	<0.05 (<0.2)
0.73	0.06 (0.08)	0.19	1.4			
0.44	0.07 (0.16).	0.08	0.38	<0.05 (<0.11)		
0.17	<0.05 (<0.29)	0.09	0.52		<0.05 (<0.29)	<0.05 (<0.29)
Mean factor	0.1	0.1	0.7	0.2	<0.2	<0.2
Grapes	Juice	Raisins				
0.16	<0.05 (<0.31)	0.26 (1.63)				
1.82	0.13 (0.071)	2.82 (1.55)				
Mean factor	0.07	1.6				

In a brewing study barley was treated at 0.25 kg ai/ha (twice the GAP application rate) with kresoxim-methyl. Two malts were used to prepare an ale beer in a 1:100 scale pilot brewery. Three brews were carried out for each malt with serial repitching of the yeast into the next brew of the series. Residues in the initial grain and in the beer were all <0.05 mg/kg (BASF, 1997).

Residues in the edible portion of food commodities

The only information on residues in the edible portion of commodities apart from the processing studies was on residues in the kernels of pecans (Table 53). The residues were all <0.05 mg/kg.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information.

NATIONAL MAXIMUM RESIDUE LIMITS

The national MRLs shown below were reported (BASF, 1998). There are no harmonised EU MRLs.

Country	MRL, mg/kg, and commodity
Austria	-
Belgium	0.05 pome fruits, other vegetable food
Brazil	-
Denmark	-
European Union	-
Finland	-
France	0.5 grapes 0.1 apple & pear 0.05 cereals
Germany	0.05 other vegetable food
Hungary	0.50 wine grapes, table grapes 0.05 apple
Ireland	-
Israel	0.5 wine grapes, table grapes 0.1 strawberries
Italy	0.05 apple, pear
Japan	15 grapes 10 orange & apricot 5 barley, kaki plum, apple & pear 2 mandarin, sweet pepper & welsh onion 1 kiwifruit 0.5 peach, cucumber & summer squash 0.1 wheat, sugar beet & garlic
Luxembourg	-
Netherlands	0.05 all vegetable food
Norway	-
Portugal	-
South Africa	0.10 apple, pear
Spain	0.5 grapes 0.05 apple, pear
Sweden	-
Switzerland	1 wine grapes, table grapes 0.05 cereals (grain), pome fruits
Taiwan	-
UK	0.05 barley (grain), wheat (grain) Estimated by UK on the basis of the trials data but not established in statute.
USA	-

- No MRLs

The definition of the residues for plant commodities is kresoxim-methyl for all the MRLs listed. Various definitions of the residue in animal products were reported by the manufacturer, all based on one or more of the metabolites 490M1, 490M2 and 490M9.

APPRAISAL

Kresoxim-methyl was considered for the first time by the current Meeting. It is used as a broad spectrum fungicide structurally related to Strobilurin A, a natural product of the wood-decaying fungus *Strobilurus tenacellus*. It is a member of a new class of biologically active compounds, the strobilurins, and is formulated as an SC, WG or SE.

Pure kresoxim-methyl is a white crystalline solid with a melting point of *c.* 102°C and low volatility. It has limited solubility in water with medium-high solubility in certain organic solvents. The log octanol-water partition coefficient of 3.4 suggests bioaccumulation may occur. Kresoxim-methyl does not dissociate at neutral pH, but the acid dissociation constant of the free acid 490M1 (pKa 4.2) indicates dissociation at neutral pH.

The main metabolites are identified by code numbers as shown below.

Code	Chemical name
parent	methyl (*E*)-methoxyimino[∀-(*o*-tolyloxy)-*o*-tolyl]acetate
490M0	methyl (*Z*)-methoxyimino[∀-(*o*-tolyloxy)-*o*-tolyl]acetate
490M1	(*E*)-methoxyimino[∀-(*o*-tolyloxy)-*o*-tolyl]acetic acid
490M2	∀-[(*o*-hydroxymethyl)phenoxy]-*o*-tolyl(methoxyimino)acetic acid
490M4	∀-(*o*-carboxyphenoxy)-*o*-tolyl(methoxyimino)acetic acid
490M8	∀-[*p*-hydroxy-(*o*-hydroxy)methylphenoxy]-*o*-tolyl(methoxyimino)acetic acid
490M9	α-(*p*-hydroxy-*o*-tolyloxy)-*o*-tolyl(methoxyimino)acetic acid
490M15	methyl α-(*p*-hydroxy-*o*-tolyloxy)-*o*-tolyl(methoxyimino)acetate
490M48	methyl hydroxyimino[∀-(2-methoxyphenoxymethyl)phenyl]acetate

Animal metabolism and environmental fate

Animal metabolism

Metabolism of absorbed kresoxim-methyl in rats was rapid and produced a large number of metabolites of which 34, including conjugates, were identified in the tissues and/or excreta. Ester cleavage to form the free acid 490M1 is a fast and important initial reaction. Other reactions involve cleavage of the oxime and benzyl ether bonds, ring hydroxylation, side chain oxidation and several conjugation reactions.

Goats were given daily doses of radiolabelled kresoxim-methyl equivalent to 7.1 or 450 ppm diet for 5 or 8 days respectively. Most of the dose was excreted (59-69% in the urine, 18-24% in the faeces). Apart from the excreta, the highest residue levels were in the kidneys and bile. Transfer into the milk and other edible tissues was low. The total radioactive residue (TRR) from the low dose was below 0.01 mg/kg as kresoxim-methyl in the milk, muscle and fat: 0.038 mg/kg in the liver and 0.142 mg/kg in the kidneys. The main metabolites identified in the liver and kidney extracts were 490M9 (1.9 and 4.0 mg/kg respectively), 490M1 (0.8 and 2.9 mg/kg) and 490M2 (0.5 and 4.6 mg/kg). 490M6, 490M18 and 490M19 were minor products. Three metabolites in the goats had not been identified in rats, of which the minor metabolite 490M18 was at the highest concentration (0.12 mg/kg in the ethyl acetate extract of the liver from the high-dosed goat), but the Meeting agreed that in practice concentrations of 490M18 would be very low (<0.01 mg/kg) in commodities of animal origin. Kresoxim-methyl itself was detected only in the faeces and fat.

Hens were given radiolabelled kresoxim-methyl in six daily doses equivalent to 10 or 180 ppm in the diet. 71-82.6% of the radioactivity recovered from the low dose was excreted and the total radioactive residue levels in the skin, kidneys and liver were 0.009, 0.065 and 0.082 mg/kg kresoxim-methyl equivalents respectively. The ^{14}C in eggs sampled at the end of the study was equivalent to 0.012 mg/kg and 0.215 mg/kg from the low and high doses respectively and did not appear to have reached a plateau. Metabolites were identified only in the high-dose group. A number of metabolites were produced, of which 490M9 was the most prominent with residues of 1.35 mg/kg in the liver. Two major metabolites in goats were 490M2 and 490M9. 490M2 was not identified in hens and 490M9 was found only in the eggs at 0.005 mg/kg. The parent compound was identified in the eggs, skin, muscle and fat at 0.01, 0.08, 0.005 and 0.31 mg/kg respectively.

Apples were sprayed with [p*henyl*-^{14}C]kresoxim-methyl at (1) 6 x 0.4 kg/ha, PHI 14 days (2) 2 x 0.4 kg ai/ha, PHI 149 days, or (3) 2 x 0.8 kg/ha, PHI 14 days. The total radioactive residues (TRR) in or on the apples were 0.36 mg/kg from (1), 0.04 mg/kg from (2) and 0.84 mg/kg from (3). When trees were sprayed with fruit present the radioactivity remained mainly on the peel (89%-98% of the TRR) and translocation to the pulp was low after 14 days. Extracts from all three experiments showed similar patterns of metabolites, containing predominantly unchanged kresoxim-methyl (74%-93% of

the TRR). The extracts from (1), in which the fruit was present at the time of treatment, contained kresoxim-methyl (78.3% of the TRR), 490M0 (3.3% of the TRR), the acid 490M1 (3.0%) and conjugates of the alcohol-acid 490M2 (1.8%) and phenol-acid 490M9 (2.1%). Kresoxim-methyl appeared to be translocated within the apple tree and to be persistent, since it was found in the fruit above the limit of determination 149 days after an early treatment when the fruit would not have been present. However, the Meeting concluded that this was not entirely consistent with the low water-solubility and the relatively low residues of the parent compound in crops shortly after treatment, and drew attention to the possibility that the parent compound found in the fruit 149 days after treatment may have been the result of methylation of the metabolite 490M1 during methanol extraction of the samples.

The metabolism of [*phenyl*-^{14}C]kresoxim-methyl was investigated in wheat treated twice at 0.25 kg ai/ha at an interval of 56 days. The total radioactive residues were 0.06 mg/kg in the grain and 9.21 mg/kg in the straw 64 days after the second application, and 1.31 mg/kg in the forage 55 days after the first. 30-99% of the TRR could be extracted with methanol, the extractability from mature grain being low. Subsequent extraction with dilute aqueous ammonia released an additional 31% of the TRR from grain and 16% from straw. Unextractable residues were 0.27 mg/kg in straw (2.9% of the TRR) and 0.025 mg/kg in grain (38.8% of the TRR).

Most of the radioactivity was due to unchanged parent compound at levels of 5.9 mg/kg in the straw after both treatments and 0.98 mg/kg in the forage one day before second (-1 day forage). Other compounds identified in the straw and -1 day forage were 490M0, the acid 490M1 and conjugates of the alcohol-acid 490M2 and the phenol-acid 490M9. The grain extract contained 0.011 mg/kg kresoxim-methyl and a variety of other metabolites constituting 0.3-5.6% of the TRR. Enzymatic treatment of conjugate fractions yielded 0.03 mg/kg 490M2 and 0.103 mg/kg 490M9 in -1 day forage, and 0.39 mg/kg 490M2 and 1.04 mg/kg 490M9 in straw. Samples from a 1.25 kg ai/ha treatment contained higher relative and absolute amounts of the parent compound. No cleavage of the phenyl or phenoxy rings was observed. Kresoxim-methyl was apparently translocated within the plant since grain contained determinable residues of the parent compound after two treatments although the grain was not present at the time of the second treatment (growth stage 52). As with apples the Meeting noted the possibility that the residues of kresoxim-methyl found in the grain at harvest may have been the result of methylation of 490M1 during methanol extraction. No experimental clarification was reported.

Grapes. The metabolism of phenyl- and phenoxy-labelled kresoxim-methyl was investigated in grapes treated at rates equivalent to a total dose of 2.5 kg/ha. The total radioactive residues from the phenoxy and phenyl labels were equivalent to 3.8-4.0 mg/kg and 3.6-4.7 mg/kg respectively. Kresoxim-methyl was the main compound in the residue: 55-57% of the TRR, 2.2-2.7 mg/kg. Conjugated 490M2 accounted for 8.8-13.8% of the TRR. After treatment with β-glucosidase, 490 M9 accounted for 4.4-5.7% of the TRR and 490 M54 for 1.4-2.1%. Unextractable residues accounted for 4.0-4.1%. There were no major qualitative differences between the metabolism of the phenyl and the phenoxy labels and no ring cleavage was observed. The metabolite 490 M54 was not identified as a product of wheat, apple or rat metabolism. The Meeting concluded that in practice concentrations of 490 M54 would be very low (<0.01mg/kg) in grapes treated according to GAP.

In studies carried out to assess metabolism in rotational crops, phenyl-labelled kresoxim-methyl was applied to bare soils at a rate of 0.3 kg/ha. After being aged for 30 days, the soils were diluted with untreated soils at a ratio of 1:9 to simulate ploughing, and spring wheat, green beans, carrots and lettuce were planted. The highest total radioactive residues at harvest, expressed as mg/kg kresoxim-methyl, were 0.15 in wheat straw, 0.007 in wheat grain, 0.21 in bean forage, 0.009 in green beans, 0.006 in carrot roots, 0.047 in carrot foliage and 0.01 in lettuce leaves. In bean forage, carrot forage and lettuce, conjugates constituted the main radioactive residue, accounting for 0.071 mg/kg, 0.015 mg/kg and 0.012 mg/kg respectively. Enzymatic cleavage yielded mainly the aglycones 490M2

and 490M9. Lettuce contained 0.003 mg/kg kresoxim-methyl and carrot forage 0.005 mg/kg 490M1. Wheat straw contained the free hydroxy metabolites 490M2 and 490M9 (together 0.011 mg/kg). Enzyme treatment of extracts of wheat straw produced 4.8% of the TRR as 490M2 and 10.4% as 490M9. No parent compound was detected in wheat, bean or carrot forage. Metabolites in grain extracts were not characterized. The results confirm the expectation that significant residues of kresoxim-methyl would not occur because of its rapid degradation in soil. (Half-lives in soils were 1-3 days for kresoxim-methyl and 38-131 days for 490M1, and DT90s for combined parent compound and 490M1 in the field were 18-25 days; see below).

Environmental fate in soil and water/sediment systems

Both aerobic and anaerobic degradation of kresoxim-methyl in soil produced 490M1 (the free acid) in amounts representing 66-84% of the applied radioactivity (AR). In aerobic conditions this was then degraded to CO_2 (27-43% of the AR in 180 days and 24% of the AR in 1 year in different experiments) or bound residues (a maximum of 36-47% of the AR) with 490M4 found in very small amounts as an intermediate. The bound radioactivity still unextractable after treatment with aqueous alkali was largely associated with the humin fraction.

In sterile conditions some degradation of kresoxim-methyl occurred but the rate was considerably slower than that in anaerobic or aerobic conditions. In anaerobic and sterile conditions the degradation of 490M1 was too slow to measure and levels of CO_2 and bound residues were considerably lower.

In aerobic conditions at 20°C and average moisture contents (usually 40% of the maximum water-holding capacity) the degradation of kresoxim-methyl, largely to 490M1, was extremely rapid with DT90 values of 2-3 days. The 490M1 was subsequently degraded with a half-life of 38-131 days.

In anaerobic conditions the DT90 for kresoxim-methyl was also <3 days. In photolysis studies degradation was more rapid in the dark controls than in the irradiated samples, which could have been caused by loss of moisture in the irradiated soil resulting in slower aerobic degradation.

In field studies undertaken in Germany in May, the DT50 values for the combined dissipation of kresoxim-methyl and 490M1 were 8-38 days and the DT90 values 18-125 days. The dissipation of 490M1 was mainly measured since substantial dissipation of kresoxim-methyl had already occurred in the samples taken on day 0 and no residues were determinable after 14 days.

The K_{oc} of kresoxim-methyl in four soils was found to be 219-372, indicating moderate mobility, although degradation to 490M1 occurred during the experiment. In a separate experiment the K_{oc} of 490M1 was found to be 17 and 24 in two soils, but sorption to two other soils was too low for quantification measurement. In column leaching studies with three standard soils up to 77% of the applied dose was leached as a mixture of kresoxim-methyl and 490M1. When the study was repeated with aged soil about 60% of the AR was found in the leachate and most of this was associated with 490M1.

Leaching was examined in more realistic conditions in a lysimeter study where a crop was planted and kresoxim-methyl was applied twice at 150 g ai/ha. No kresoxim-methyl was found in the leachate during the two years of the study and the annual average concentrations of 490M1 were <0.01-0.04 µg/l.

In a study of aqueous hydrolysis half-lives assuming first-order kinetics were 875, 34 and 0.29 days at pH 5, 7 and 9.

Methods of residue analysis

Satisfactory validation data were submitted for analytical methods for a number of commodities of plant and animal origin. Determinations of kresoxim-methyl and the metabolites 490M2 and 490M9 in apples, cereal grain, straw, soil and water were usually by GLC with an ECD after extraction with a variety of solvents and clean-up by solid-phase extraction. Commodities of animal origin were analysed by HPLC with UV detection. Limits of determination were 0.01-0.05 mg/kg in plant commodities, 0.01 mg/kg in soil, 0.05 µg/l in water, 0.001-0.002 mg/kg in milk and 0.01 mg/kg in animal products.

Stability of residues stored analytical samples

Kresoxim-methyl residues in samples of wheat (immature plants, grain and straw) and apples stored at –18°C were stable for the duration of the studies, namely up to 214 days for grain, 91 days for straw, 168 days for forage and 295 days for apples. There was no marked change in the qualitative or quantitative composition of radioactive residues in wheat samples stored frozen for 21 months, apple samples for 14 months, grape samples for 8 months or poultry samples for 21 months.

Definition of the residue

On the basis of the metabolism in apples, wheat and grapes, the Meeting agreed that the definition of the residue for compliance with MRLs for plant commodities should be kresoxim-methyl since this is the major component of the residue in primary crops. In several of the residue trials the metabolites 490M2 and 490M9 were also found but the Meeting considered these metabolites to be of low toxicity.

In ruminants the metabolite 490M9 is a major component of the residue and the parent compound is present only at very low relative concentrations. In poultry 490M9 would also be a suitable indicator compound since it was the main compound found in the liver.

The Meeting agreed to recommend the following residue definitions for both compliance with MRLs and the estimation of dietary intake.

Commodities of plant origin: *kresoxim-methyl*
Commodities of animal origin: a-*(p-hydroxy-o-tolyloxy)-o-tolyl(methoxyimino)acetic acid, expressed as kresoxim-methyl*

Supervised trials

Pome fruit. GAP for apples was reported for Austria, Belgium, Brazil, Chile, France, Germany (pome fruit), Hungary, Israel, Italy, Japan, The Netherlands, New Zealand, Norway, Poland, Slovakia, South Africa, Spain, Sweden, Switzerland, the UK and Uruguay.

Four Italian, four French and two Spanish trials were considered to comply with French and Spanish GAP (max. 0.1 kg ai/ha, PHI 35 days). The residues in all ten trials were <0.05 mg/kg. Seven German, two Belgian, six UK and two Dutch trials complied with GAP for Austria, Belgium, Hungary, Poland and the UK (also 0.1 kg ai/ha, PHI 35 days) with residues of <0.05 (11), 0.05 (3), 0.06 and 0.11 (2) mg/kg. Two New Zealand trials complied with New Zealand GAP (0.1 kg ai/ha; PHI 14 days) with residues in both of 0.04 mg/kg. Three South African trials according to South African GAP (0.01 kg ai/hl; PHI 45 days) yielded residues of 0.06, 0.09 and 0.11 mg/kg. Other trials were reported from the USA and Canada which included determinations of the metabolites 490M2 and 490M9, but no GAP was reported for the North American continent. The Meeting agreed that all

the results could be combined, as they were essentially from one population, to give residues of 0.04 (2), <0.05 (11), 0.05 (3), 0.06 (2), 0.09 and 0.11 (3) mg/kg.

GAP for pears was reported for Austria, Belgium, Chile, France, Germany, Hungary, Italy, Japan, The Netherlands, Norway, Poland, South Africa, Spain, Sweden, Switzerland and Uruguay. Separate GAP for "oriental pear" was reported for Japan.

Four Spanish trials were according to Spanish and French GAP (max. 0.1 kg ai/ha, PHI 35days) all with residues of <0.05 mg/kg. Two South African trials were reported, one of which complied with South African GAP for apples and the other with GAP for pears. The residues were 0.06 and 0.01 mg/kg respectively. The Meeting agreed that the data on pears and apples could be combined.

The combined residues in apples and pears were 0.01, 0.04 (2), <0.05 (15), 0.05 (3), 0.06 (3), 0.09 and 0.11 (3). The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.05 mg/kg for pome fruit.

Grapes. GAP was reported for Austria, Chile, Germany, Hungary, Israel, Japan, Slovakia, South Africa, Spain and Switzerland.

Seven Italian trials were according to Spanish GAP (max 0.015 kg ai/hl, PHI 35 days) with residues of <0.05 (6) and 0.15 mg/kg. Several French and German trials were reported at applications of 0.025-0.038 kg ai/hl which were higher than the German or Swiss GAP concentration of 0.0075 kg ai/hl and the Austrian concentration of 0.0125 kg ai/hl. Five French and seven German trials were considered to comply with the maximum Austrian GAP equivalent of 0.125 kg ai/ha however, with residues of 0.06, 0.09, 0.15, 0.17, 0.18, 0.20, 0.21, 0.23, 0.25, 0.36, 0.44 and 0.73 mg/kg. Three trials complied with South African GAP (0.023 kg ai/hl, PHI 14 days), with residues of 0.09, 0.14 and 0.27 mg/kg. Trials in the USA included analyses for the metabolites 490M2 and 490M9, but no GAP was reported for the North American continent. The Meeting agreed that the residues resulting from Austrian and South African GAP could be combined, since they appeared to be from the same population, to give 0.06, 0.09 (2), 0.14, 0.15, 0.17, 0.18, 0.20, 0.21, 0.23, 0.25, 0.27, 0.36, 0.44 and 0.73 mg/kg. The residues from the trials according to Spanish GAP were considered to be from a different population since six of the seven results were below the limit of determination. The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.2 mg/kg.

Onions. GAP for onions was reported for Nicaragua and for Welsh onions for Japan, but as trials were reported only from Germany and The Netherlands there was no basis for an evaluation.

Cucumbers. GAP was reported for Brazil, Japan, Spain and Norway.

The residues in eight Spanish indoor trials which complied with Spanish GAP (0.01-0.015 kg ai/hl; PHI 3 days) were all <0.05 mg/kg, and in seven of the trials <0.05 mg/kg even on the day of application. The Meeting estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.05 mg/kg.

Melons. No GAP was reported.

Tomatoes, sweet peppers. Eight indoor trials in Spain on each commodity complied with Spanish glasshouse GAP (max. 0.025 kg ai/hl; PHI 3 days), with residues of 0.09, 0.13, 0.14, 0.20, 0.23, 0.25, 0.27 and 0.31 mg/kg in tomatoes, and 0.10 (2), 0.15, 0.19, 0.21, 0.37, 0.39 and 0.44 mg/kg in peppers. As none of the trials were identified as complying with GAP until late in the Meeting however, neither maximum residue levels nor STMRs were estimated.

Wheat. GAP for wheat was reported for Belgium, Ireland, Luxembourg, The Netherlands, Poland, Slovakia and the UK, and for cereals for Germany and Japan.

The residues in winter and spring wheat were evaluated together because the levels were similar and the latest time of application was described as a pre-harvest interval not a growth stage. Seven German, three Belgian and five French trials accorded with Belgian, Polish, German, Dutch and Luxembourg GAP (0.105-0.150 kg ai/ha, PHI 35 days) with residues all <0.05 mg/kg in the grain or ears and <0.05, 0.05, 0.08, 0.09, 0.12, 0.13, 0.18, 0.19, 0.26, 0.28, 0.50, 1.27, 1.45, 2.59 and 4.00 mg/kg in the straw or haulm. Residues of the metabolites 490M9 and 490M2 were also measured and the total residue calculated. The Meeting estimated maximum residue levels of 0.05* and 5 mg/kg and STMRs of 0.05 and 0.19 mg/kg for the grain and straw respectively.

Barley. GAP for barley was reported for Belgium, France, Germany, Luxembourg, Norway, Switzerland, Ireland, The Netherlands, Poland and the UK, and for cereals for Germany and Japan.

The trials on winter and spring barley were evaluated together for the reasons given above. Three Dutch, two French and six German trials complied with GAP in Belgium, France, Germany, Luxembourg, The Netherlands, Norway and Poland (max. rate 0.105 or 0.125 kg ai/ha, PHI 35 or 42 days) with residues of <0.05 (9) and 0.06 (2) mg/kg in the grain or ears and 0.07, 0.08, 0.14 0.20, 0.22, 0.26, 0.28, 0.45, 0.79 and 0.92 mg/kg in the straw or haulm. The Meeting estimated maximum residue levels of 0.1 and 2 mg/kg and STMRs of 0.05 and 0.24 mg/kg for grain and straw respectively.

Rye. GAP was reported for Belgium, France, Germany, Luxembourg, Poland, Switzerland and The Netherlands, with maximum application rates of 0.105 or 0.125 kg ai/ha and PHIs of 35 days.

Only two trials were reported, both in Germany and according to GAP, with residues of <0.05 mg/kg in the ears and 0.08 and 0.11 mg/kg in the haulms. The Meeting agreed that the data for wheat could be extrapolated to rye, giving combined residues of <0.05 (17) mg/kg in the grain and <0.05, 0.05, 0.08 (2), 0.09, 0.11, 0.12, 0.13, 0.18, 0.19, 0.26, 0.28, 0.50, 1.27, 1.45, 2.59 and 4.00 mg/kg in the straw or haulm. The Meeting estimated maximum residue levels of 0.05* and 5 mg/kg, and STMRs of 0.05 and 0.18 mg/kg for grain and straw respectively.

The Meeting agreed that it was appropriate to recommend a group MRL for cereal straws rather than separate MRLs for the individual straws. Accordingly the Meeting recommended an MRL of 5 mg/kg and estimated an STMR of 0.24 mg/kg for “straw and fodder (dry) of cereal grains” since these represented the highest estimates for any individual cereal.

Pecans. A number of trials in the USA were reported but the Meeting was informed that there was no current GAP for pecans.

Processing studies

Apples were processed to washed fruit, apple juice, wet pomace and apple sauce, and grapes to juice, must, wine, wet pomace, and raisins. The mean processing factors were <0.4, <1 and <0.4 for apple juice, wet apple pomace and apple sauce, and 0.1, 0.7, <0.2 and 1.6 for must, wet grape pomace, wine and raisins respectively.

From these factors the Meeting estimated a maximum residue level of 2 mg/kg for dried grapes and STMRs of 0.05, 0.02 and 0.02 mg/kg for wet apple pomace, apple sauce and apple juice and 0.14, 0.02, 0.04 and 0.32 mg/kg for wet grape pomace, grape must, wine and dried grapes respectively. A study of the effects of brewing on residues in barley was difficult to interpret since

the residues were <0.05 mg/kg in the initial grain although the barley had been treated at twice the GAP rate.

Farm animal feeding studies

Dairy cows were dosed twice daily with kresoxim-methyl at rates equivalent to 6, 18 and 60 ppm in the feed for 28 or 29 days. Residues of 490M2 and 490M9 in whole milk, cream and skimmed milk were <0.002 mg/kg; 490M1 was not determined. Residues in the tissues of the low-dose group were all <0.01 mg/kg, except those of 490M1 which appeared in the kidneys at 0.021-0.028 mg/kg. In the high-dose group the highest residue concentrations were 490M1 in the kidneys (<0.01-0.29 mg/kg) and peritoneal fat (<0.01-0.091 mg/kg), and 490M9 in the liver (<0.01-0.024 mg/kg) and kidneys (<0.01-0.049 mg/kg).

The highest residue levels in the feed items were in wheat straw for which the Meeting estimated a maximum residue level of 5 mg/kg. This leads to a theoretical maximum dietary level of 2.5 ppm, based on a 50% level of straw in the diet. The Meeting concluded that no residues above the practical limits of determination (0.01 mg/kg for milk and 0.05 mg/kg for other animal products) would occur in animal commodities from this dietary level. The Meeting estimated maximum residue levels of 0.01* mg/kg for milks and 0.05* mg/kg for mammalian meat, edible offal and fats, and corresponding STMRs of 0.002 and 0.01 mg/kg. The STMRs are based on the validated limits of determination of the analytical methods for these commodities.

The only poultry feed item containing determinable residues was barley grain with residues in the trials of ≤0.06 mg/kg and an estimated maximum residue level of 0.1 mg/kg. The Meeting concluded that the intake for poultry would be ≤0.1ppm in the feed. In the poultry metabolism study TRRs were very low in the skin (0.009 mg/kg), kidneys (0.065 mg/kg) and liver (0.082 mg/kg) at doses equivalent to 10 ppm in the feed. The Meeting concluded that no residues above the practical limit of determination (0.05 mg/kg) would occur in edible poultry tissues, and estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.01 mg/kg for poultry meat. The STMR is based on the validated limit of determination for the reported methods of analysis.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and for the estimation dietary intake for plant commodities: kresoxim-methyl.

For compliance with MRLs and for the estimation dietary intake for animal commodities: α-(*p*-hydroxy-*o*-tolyloxy)-*o*-tolyl(methoxyimino)acetic acid, expressed as kresoxim-methyl

Commodity		Recommended MRL, mg/kg		STMR
CCN	Name	New	Previous	
JF 0226	Apple juice			0.02
	Apple pomace, wet			0.05
JF 0226	Apple sauce			0.02
GC 0640	Barley	0.1		0.05
VC 0424	Cucumber	0.05*		0.05
DF 0269	Dried grapes (= currants, raisins and sultanas)	2		0.32
MO 0105	Edible offal (Mammalian)	0.05*		0.01
	Grape must			0.02

Commodity		Recommended MRL, mg/kg		STMR
CCN	Name	New	Previous	
	Grape pomace, wet			0.14
FB 0269	Grapes	1		0.2
MF 0100	Mammalian fats (except milk fats)	0.05*		0.01
MM 0095	Meat (from mammals other than marine mammals)	0.05*		0.01
ML 0106	Milks	0.01*		0.002
FP 0009	Pome fruits	0.2		0.05
PM 0110	Poultry meat	0.05*		0.01
GC 0650	Rye	0.05*		0.05
AS 0081	Straw and fodder (dry) of cereal grains	5		0.24
GC 0654	Wheat	0.05*		0.05
	Wine			0.04

FURTHER WORK OR INFORMATION

Desirable

1. Information on residues in food in commerce or at consumption (monitoring or total diet data).

2. Experimental determination of whether (*E*)-methoxyimino[∀-(*o*-tolyloxy)-*o*-tolyl]acetic acid (490M1) is methylated to kresoxim-methyl when methanol is used as an extractant in metabolism studies or the analysis of samples from supervised trials.

DIETARY RISK ASSESSMENT

STMRs have been estimated for 18 commodities of which the 11 commodities for which there are consumption data have been used in the estimate of dietary intake.

The International Estimated Dietary intakes for the five GEMS/Food regional diets were 0% of the ADI. The Meeting concluded that the intake of residues of kresoxim-methyl resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

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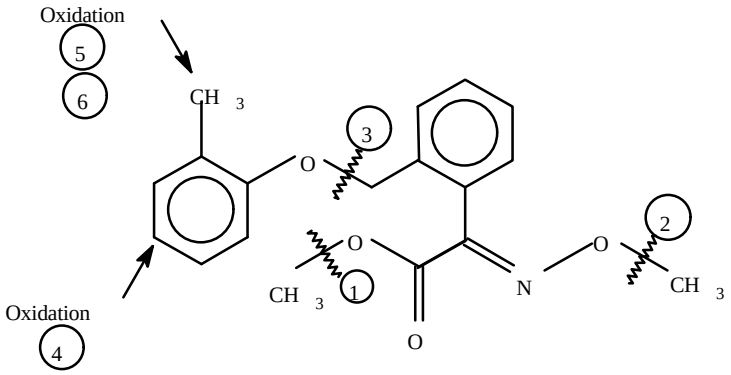
KRESOXIM-METHYL FIGURES 1-13

Figure 1. Metabolic reactions of kresoxim-methyl in rats.



1. Ester cleavage
2. Oxime ether cleavage
3. Benzyl ether cleavage
4. Oxidation on the phenoxy ring
5. Oxidation of methyl group on the phenoxy ring
6. Subsequent oxidation to the carboxylic acid

Figure 2. Metabolic pathways of kresoxim-methyl in goats.

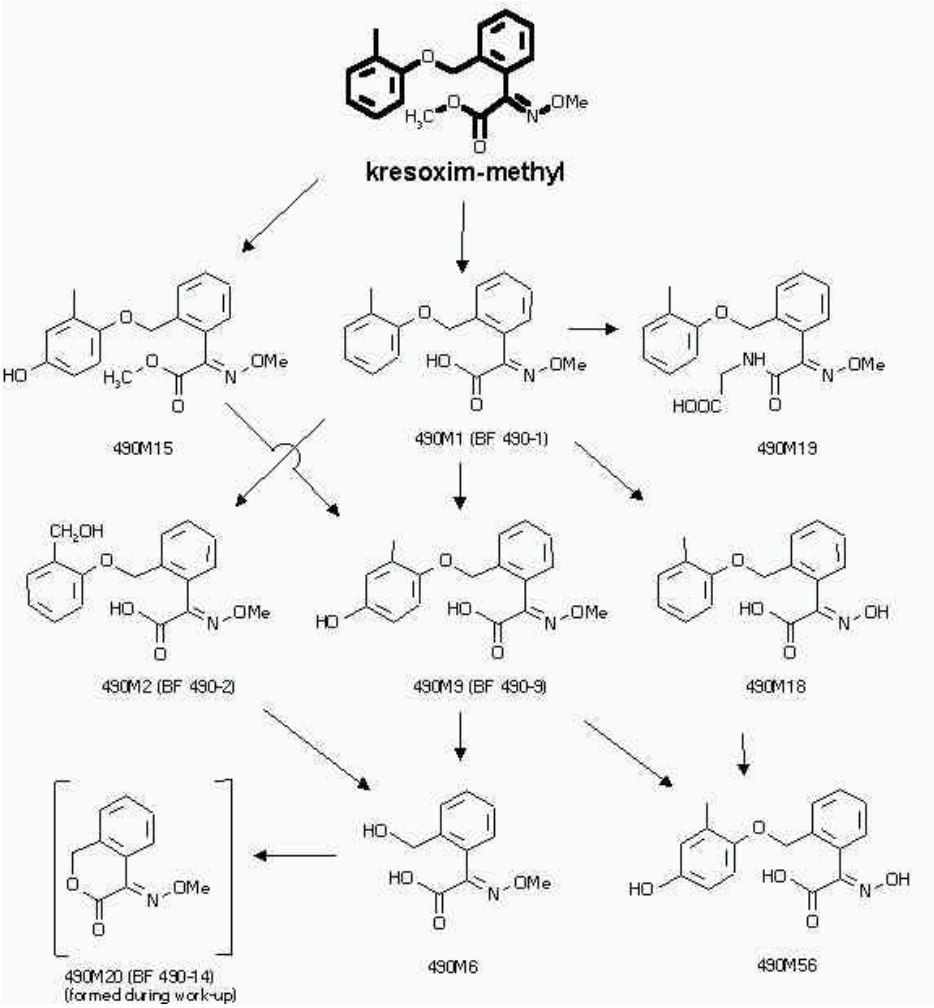


Figure 3. Metabolic pathways of kresoxim-methyl in poultry.

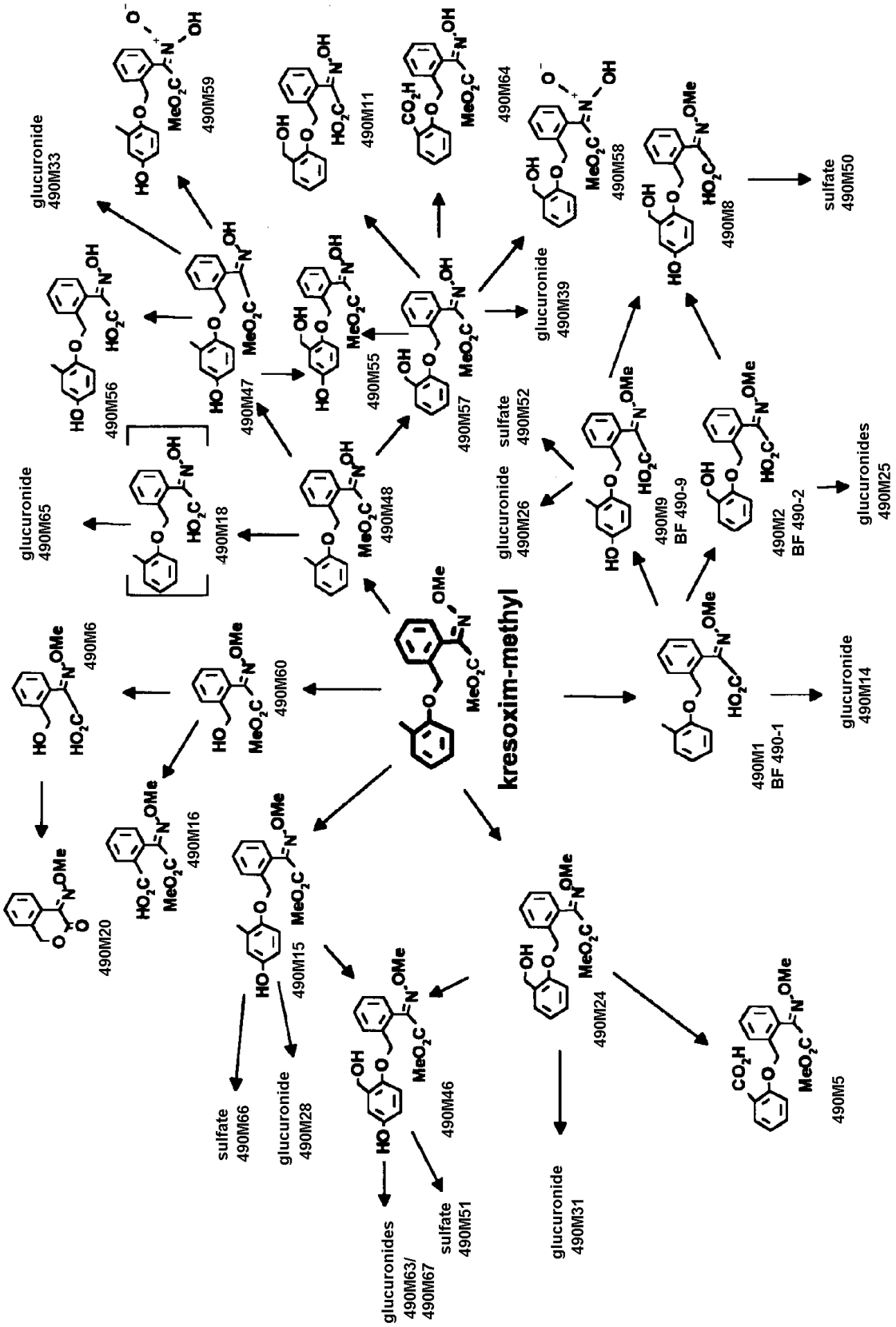


Figure 4. Extraction and characterization of apple peel samples.

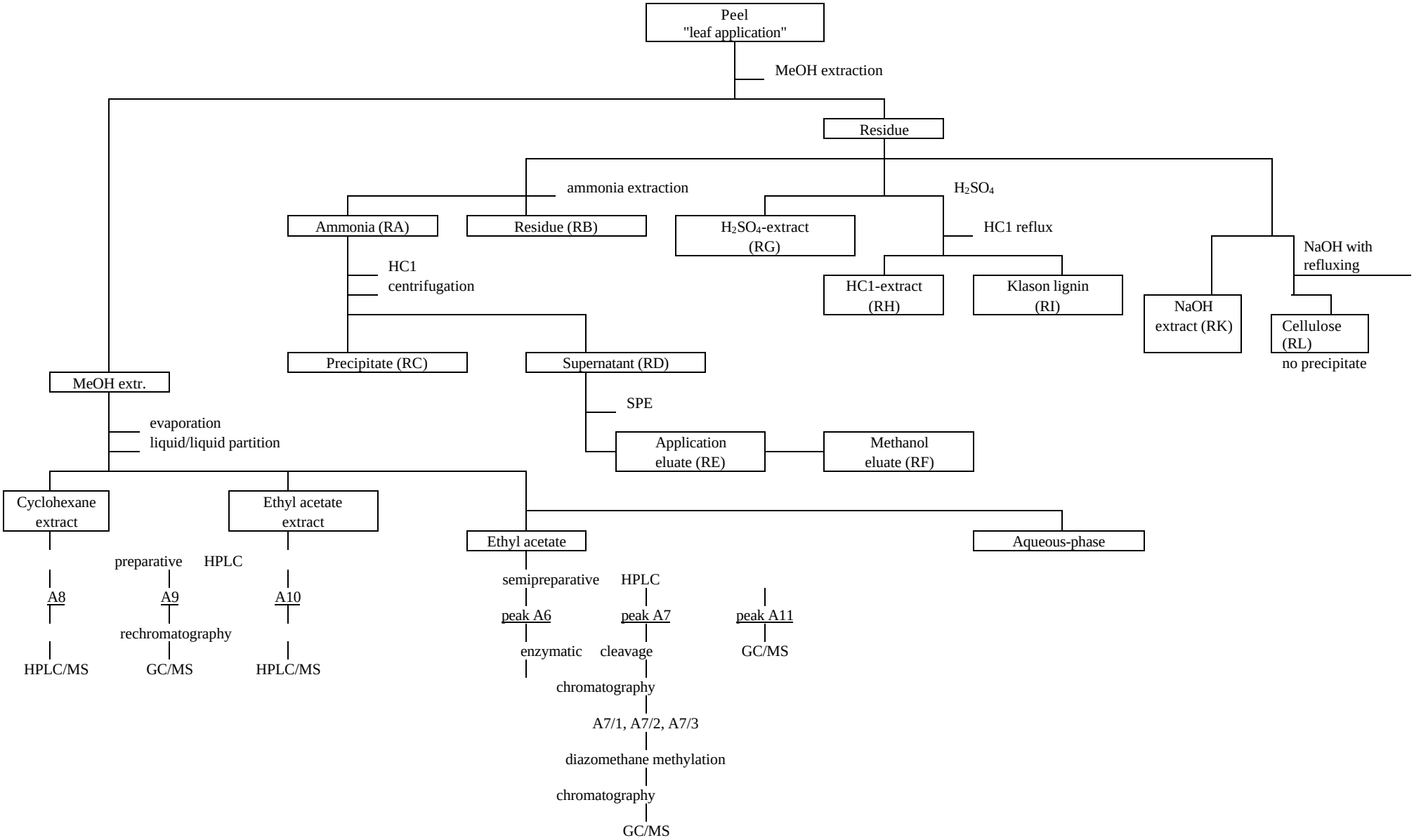


Figure 5. Extraction and characterization of apple pulp samples.

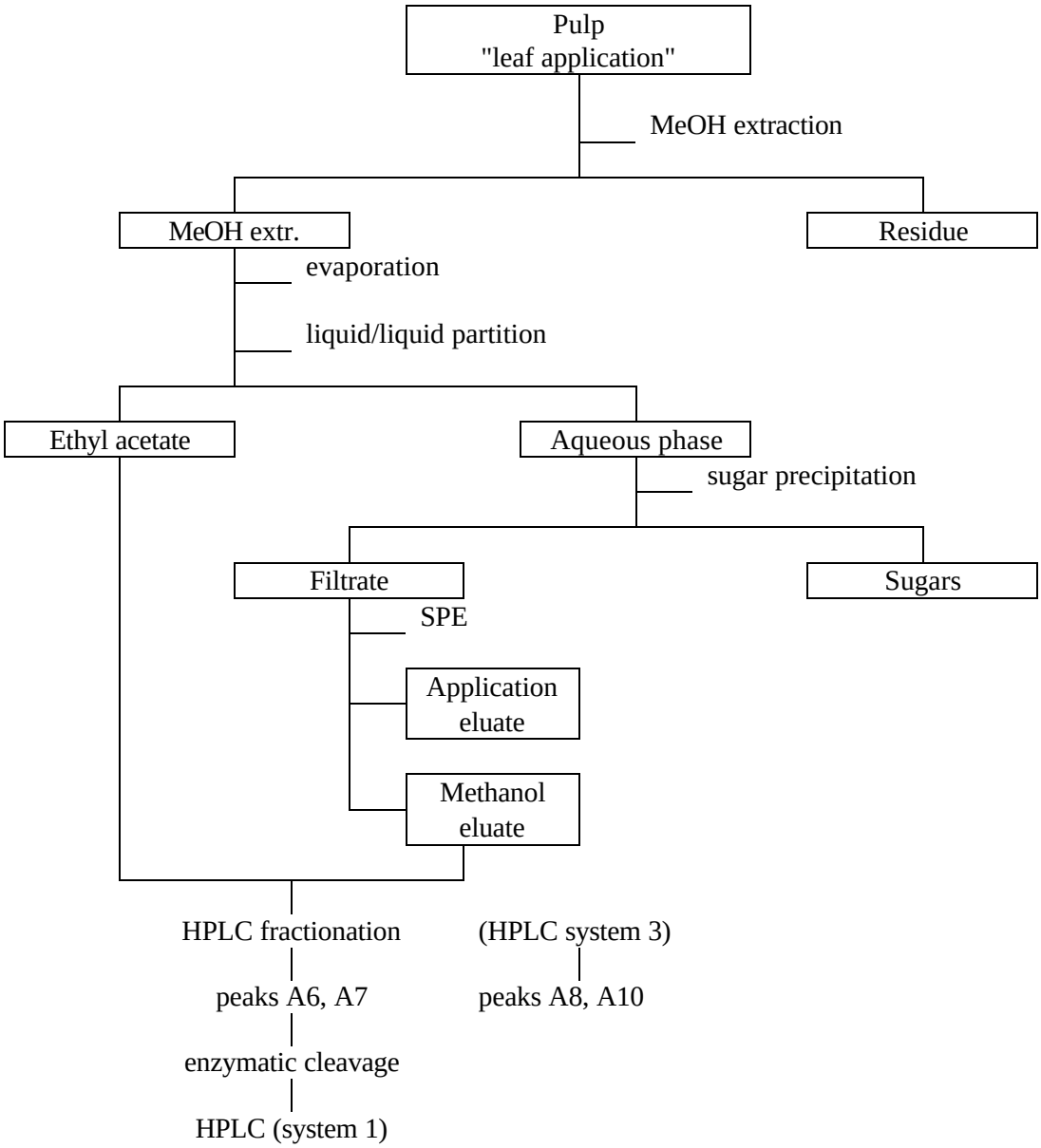
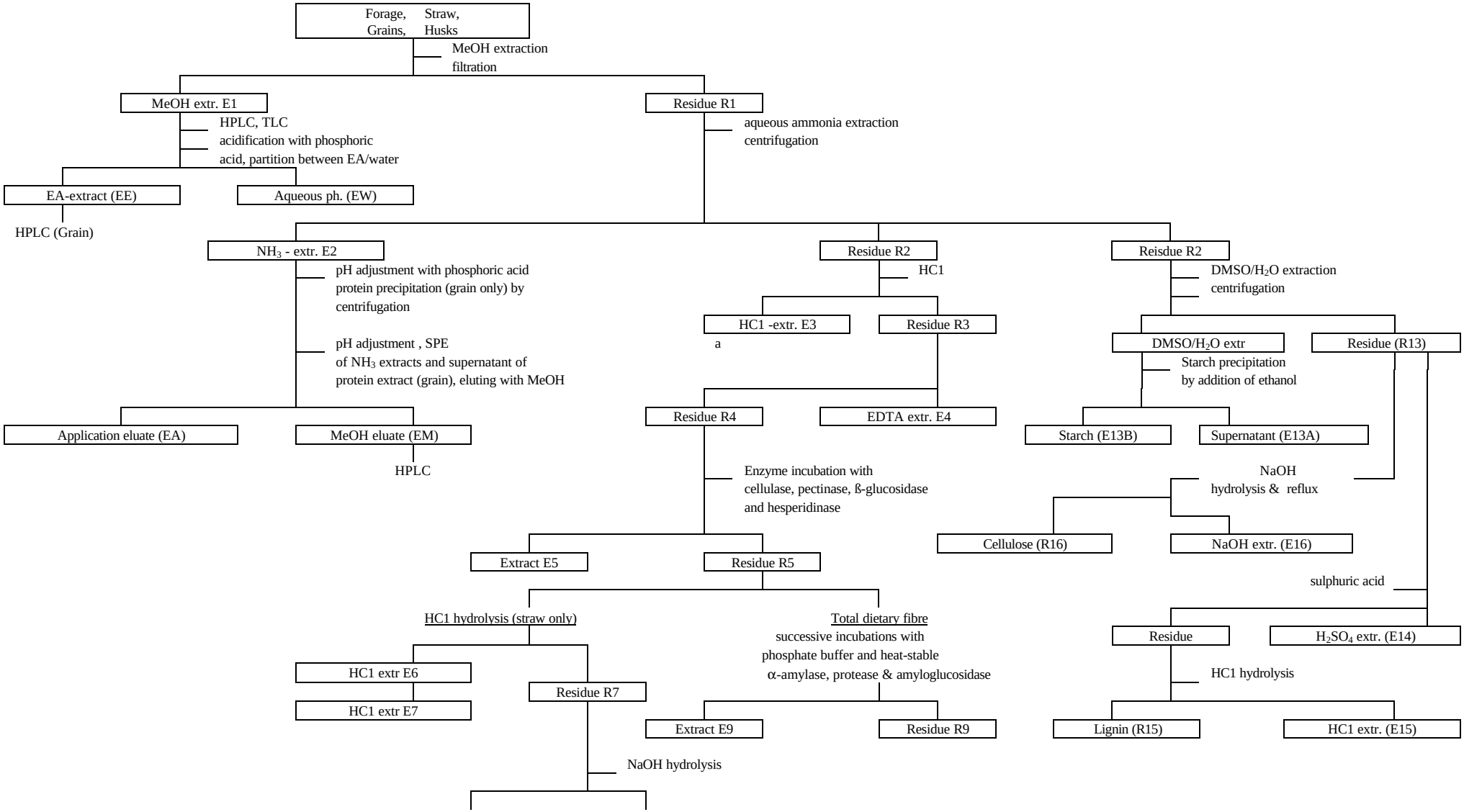


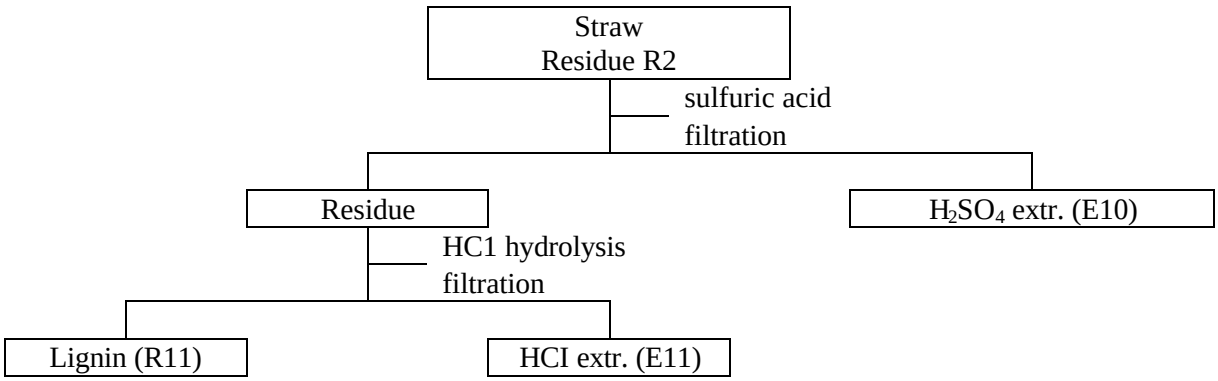
Figure 6. Extraction and characterization of radioactive residues in wheat forage, straw and grain.



aqueous NaOH extr. E8	Residue R8

Figure 7. Characterization of unextractable residues in wheat straw.

A) Klason Lignin



B) Cellulose fractionation

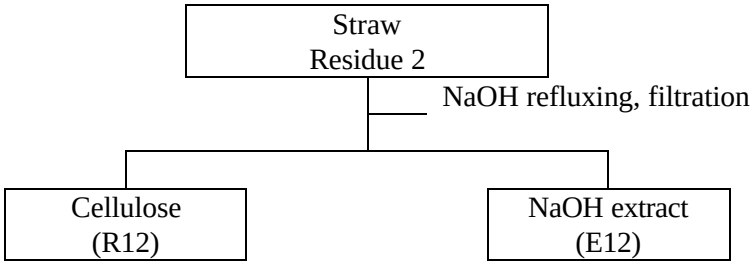
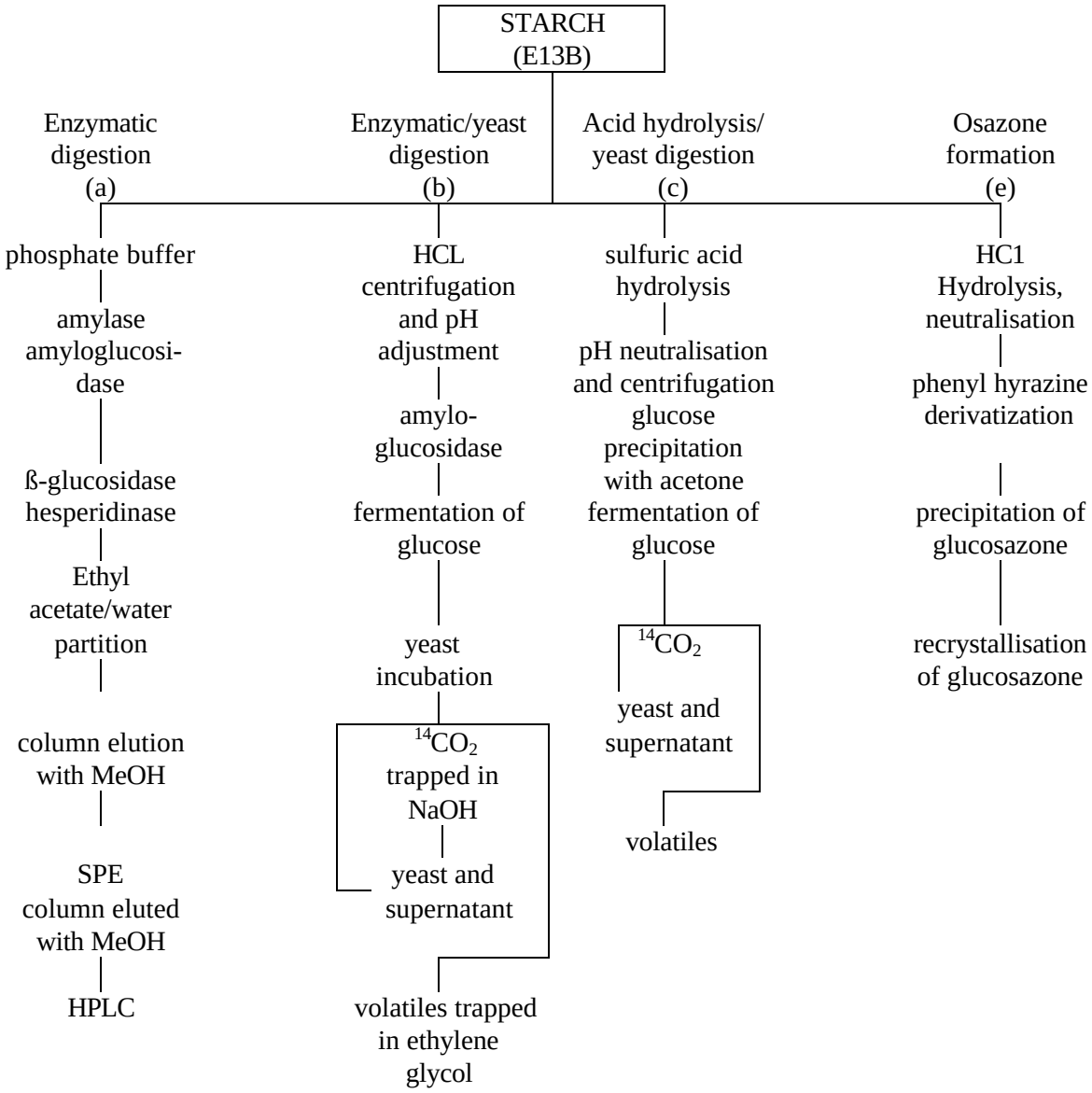


Figure 8. Fractionation of wheat starch.



(d): as trial (c), but with commercially available ^{14}C glucose

Figure 9. Extraction and characterization of ^{14}C residues in grapes.

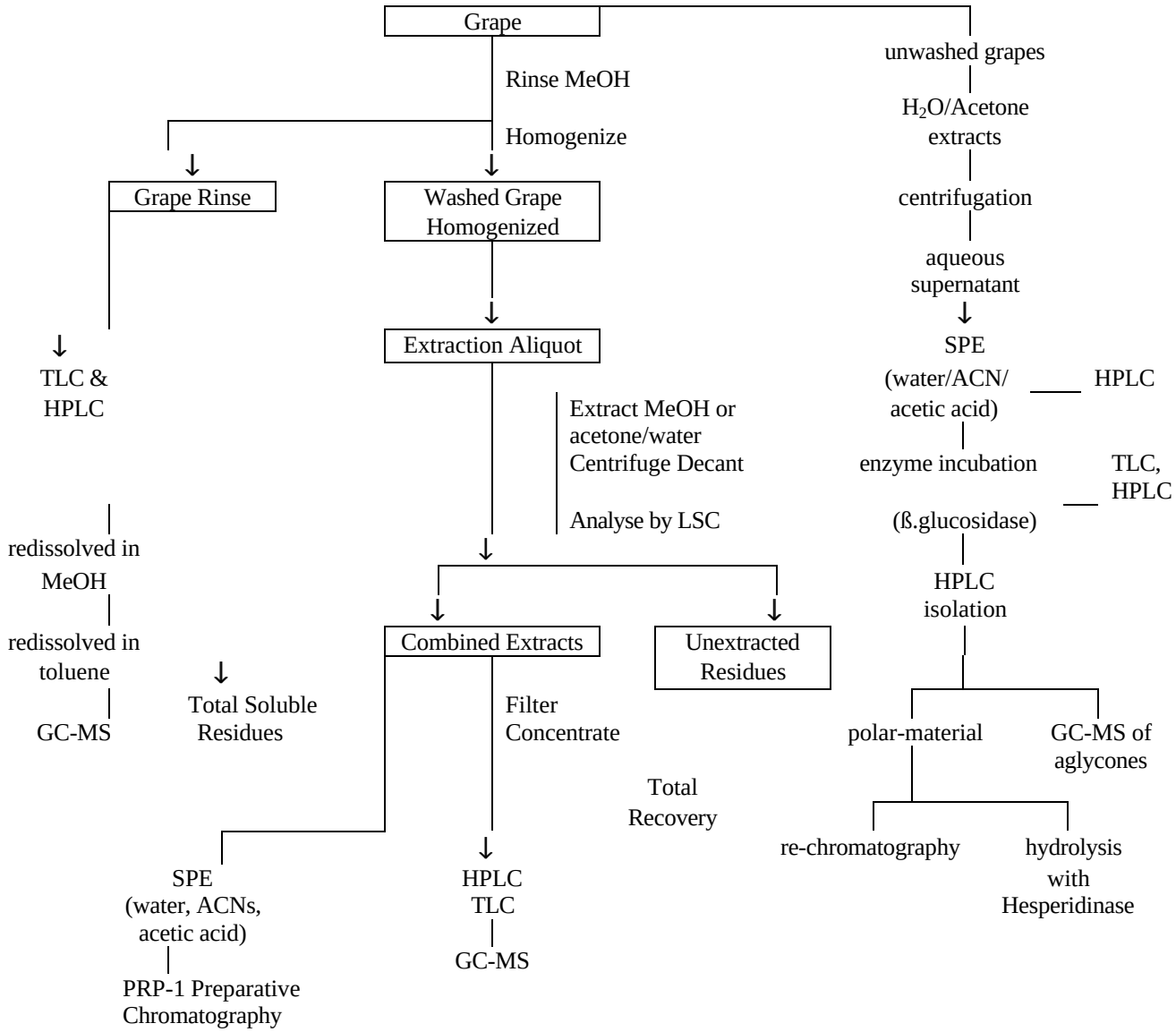


Figure 10. Metabolic pathways of kresoxim-methyl in apples, wheat and following crops

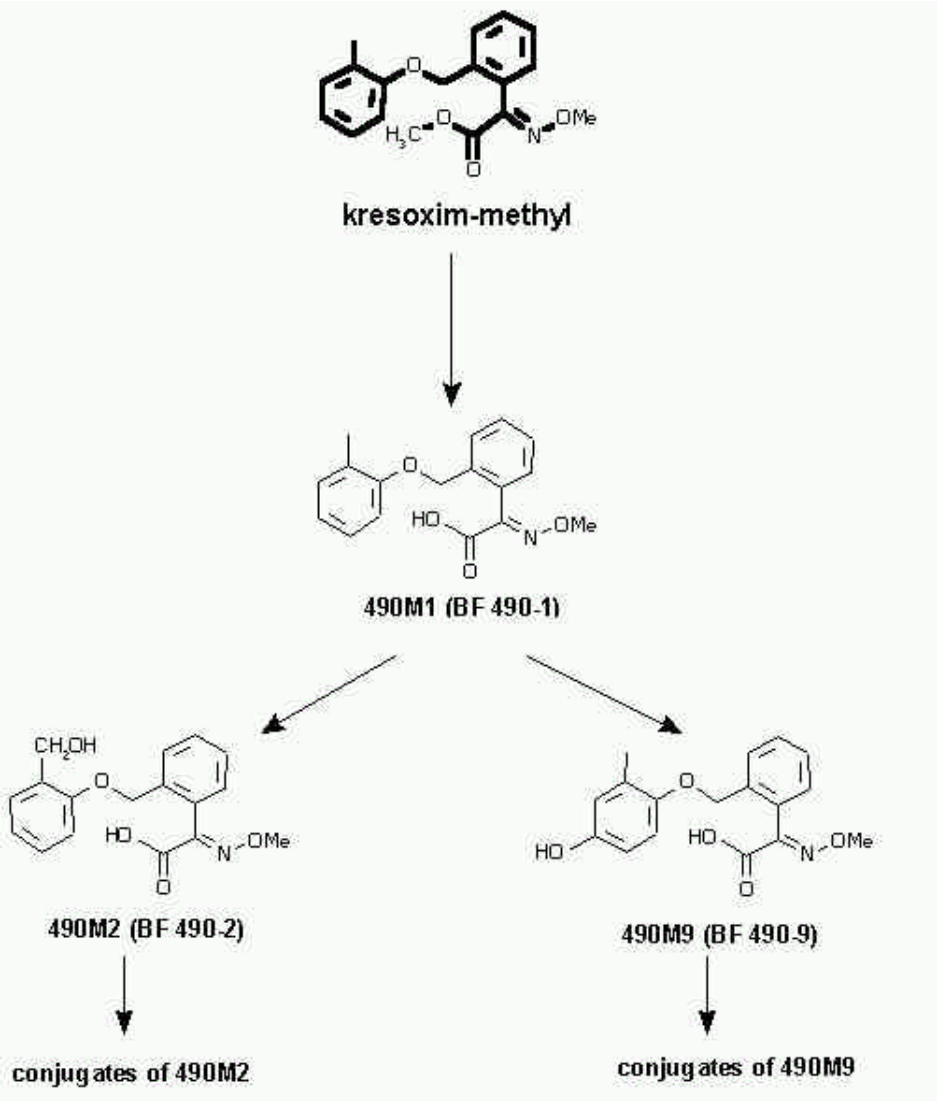


Figure 11. Metabolic pathways of kresoxim-methyl in grapes.

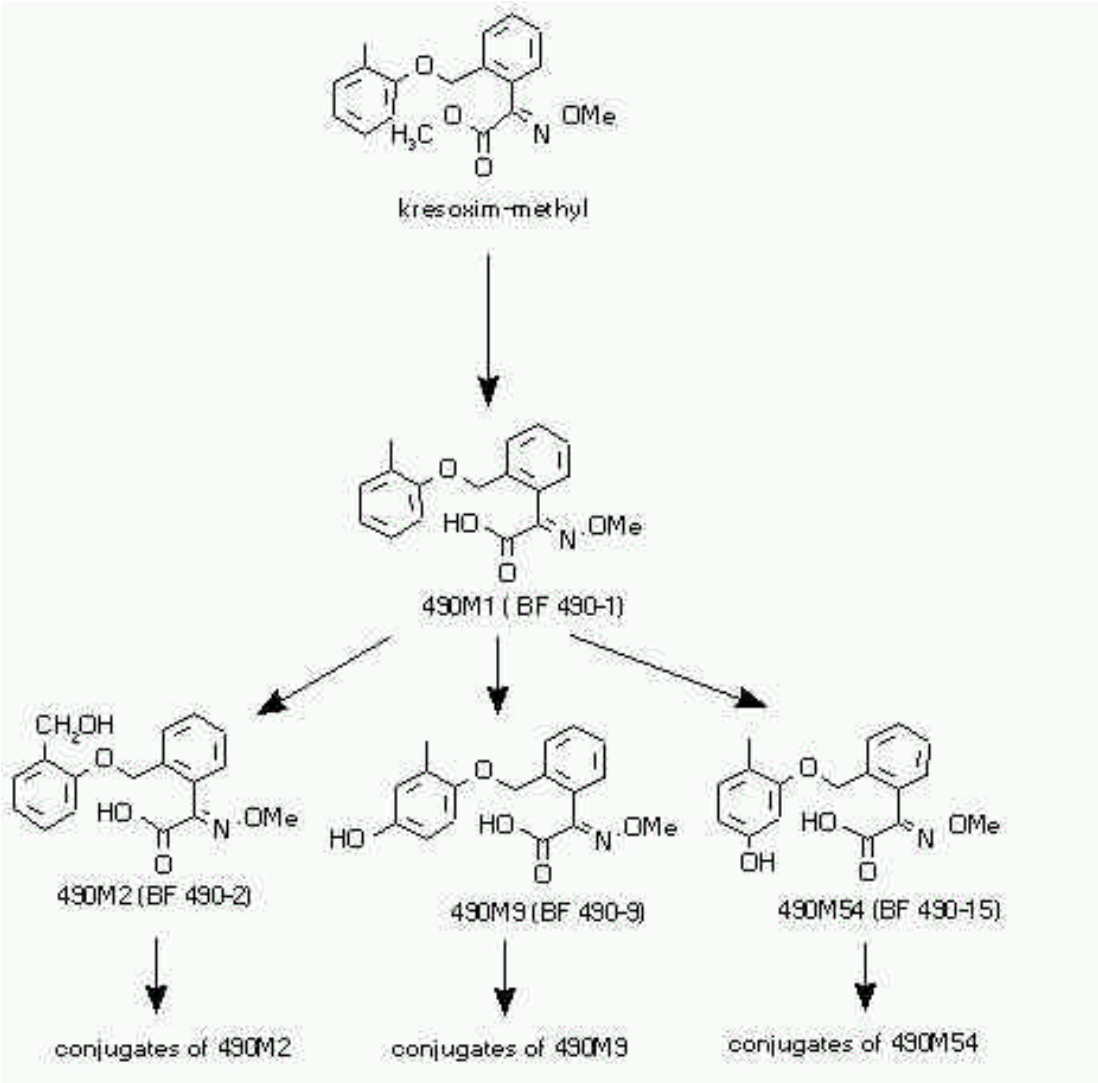
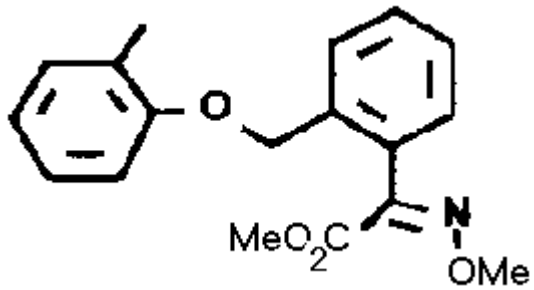
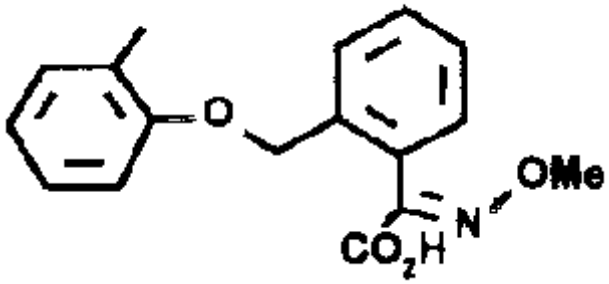
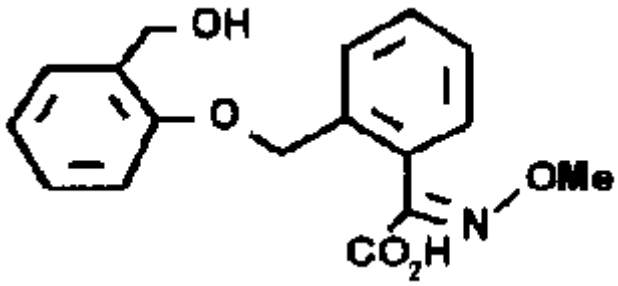
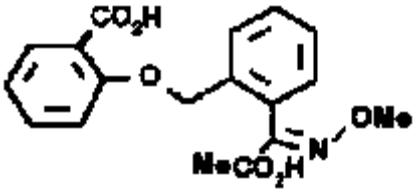
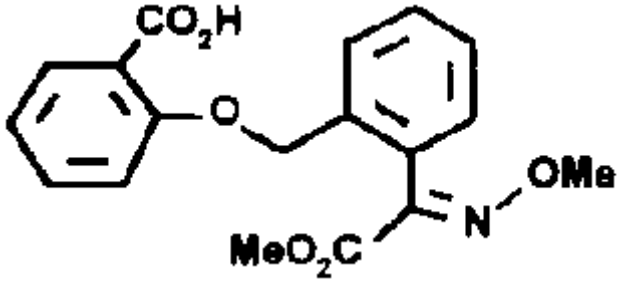
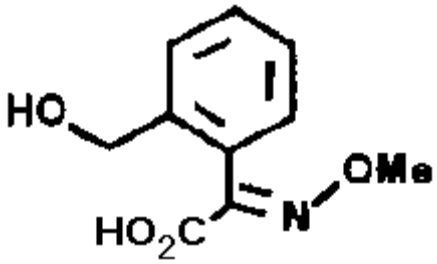
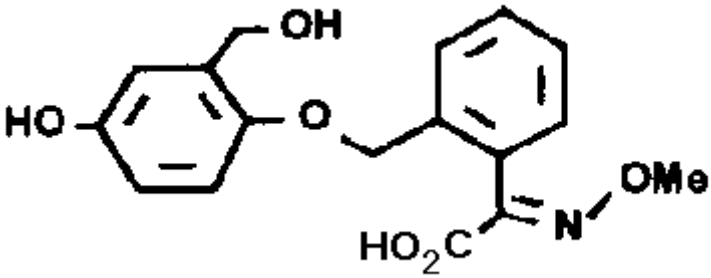
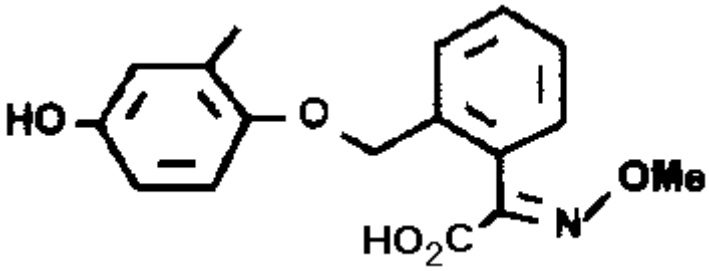
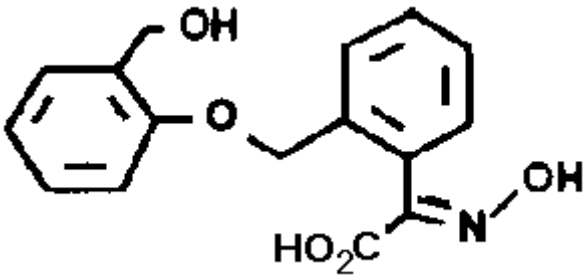
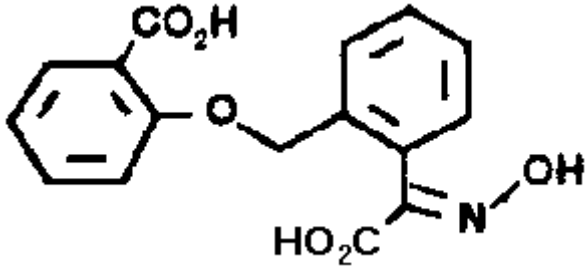
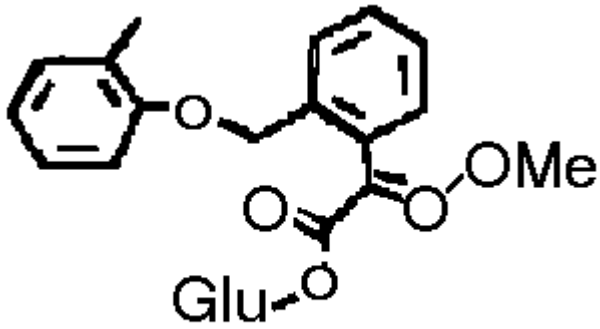
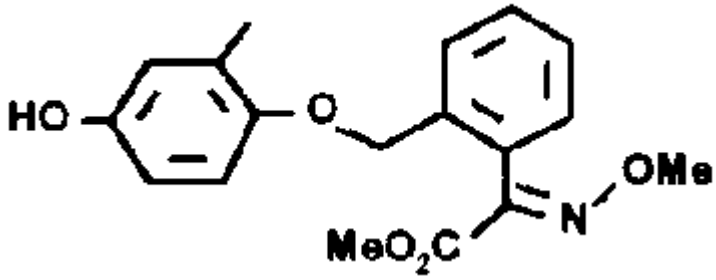
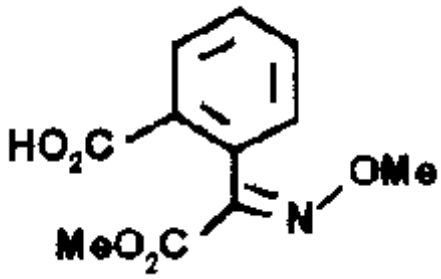
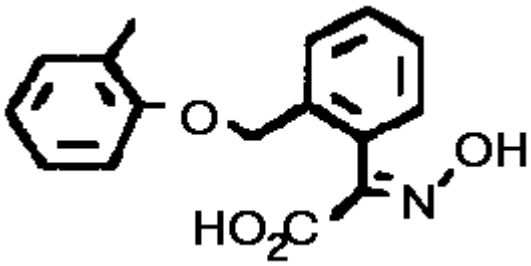
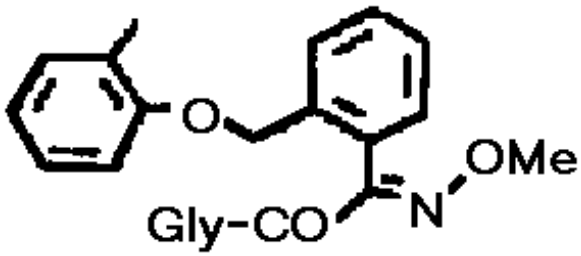
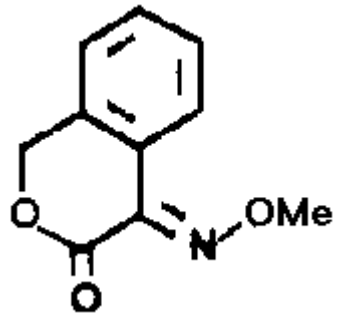
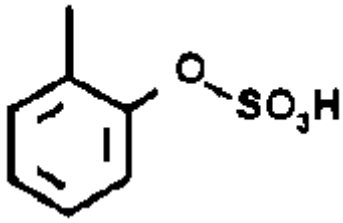
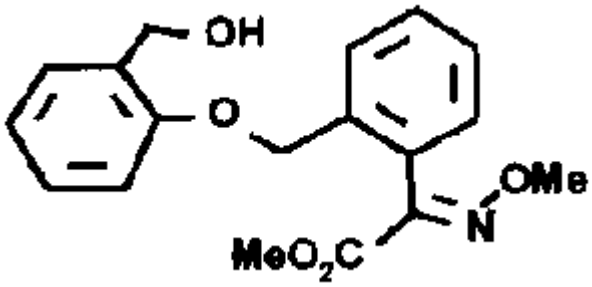
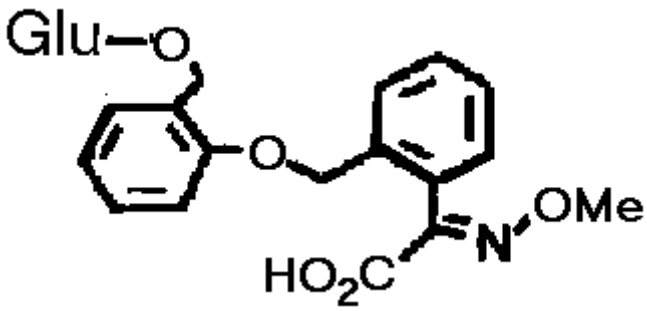
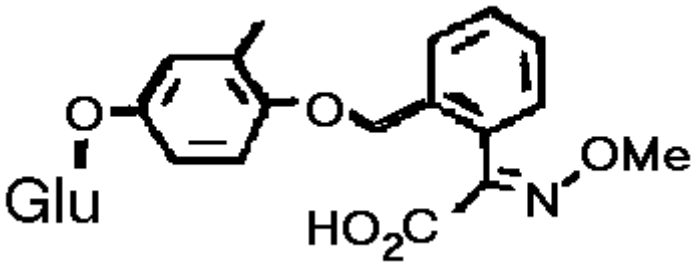


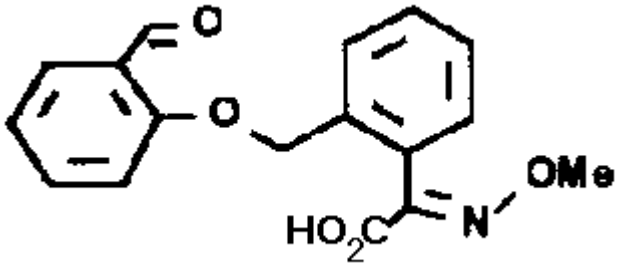
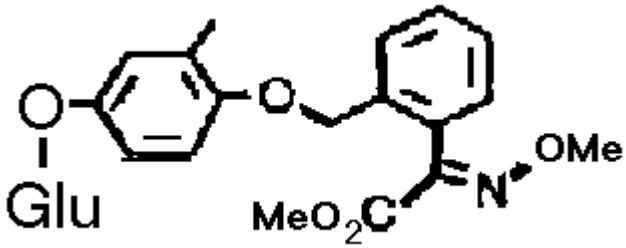
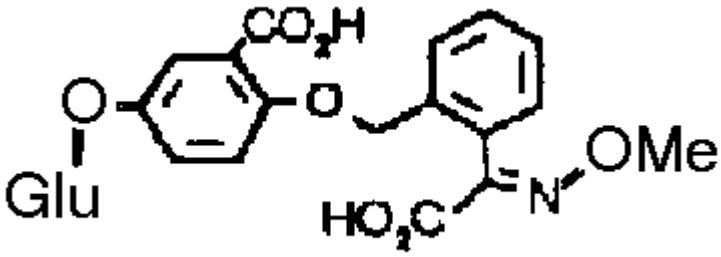
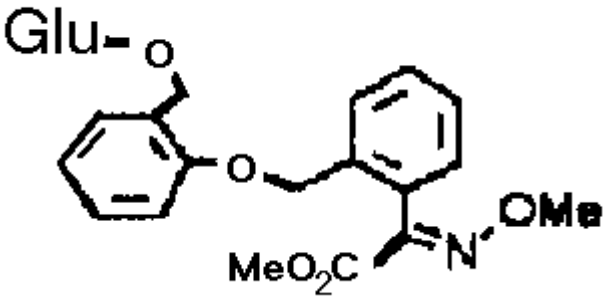
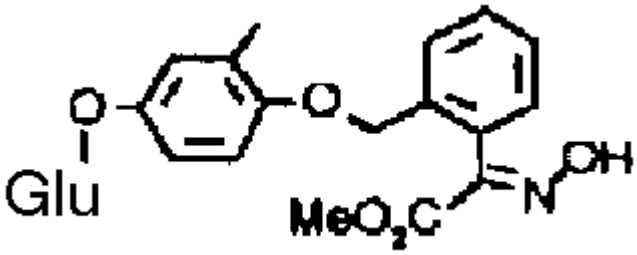
Figure 12. Code names and structures of degradation products and metabolites of kresoxim-methyl.

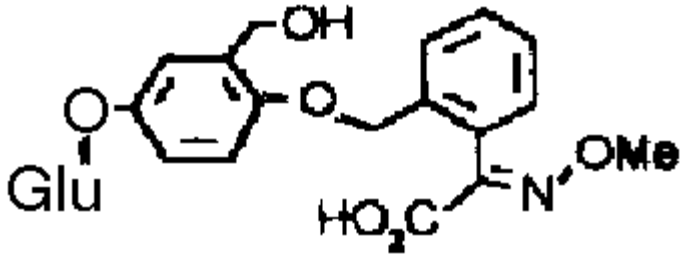
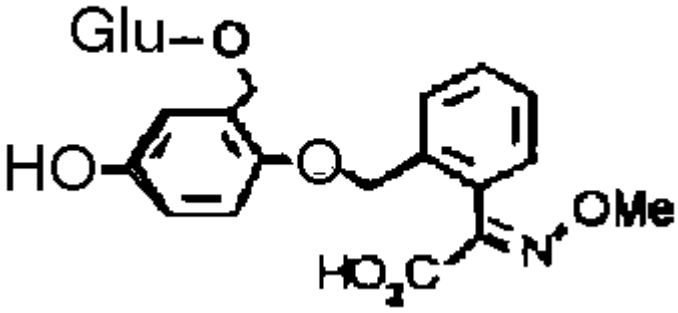
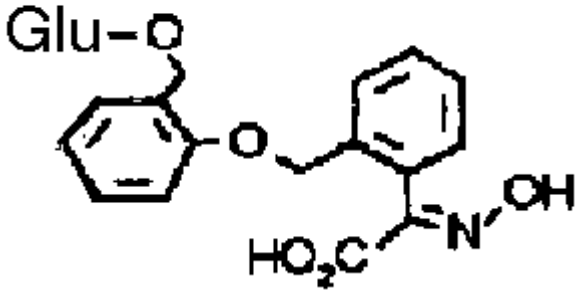
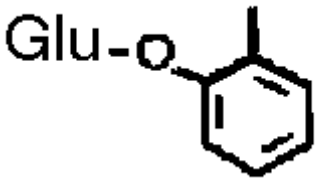
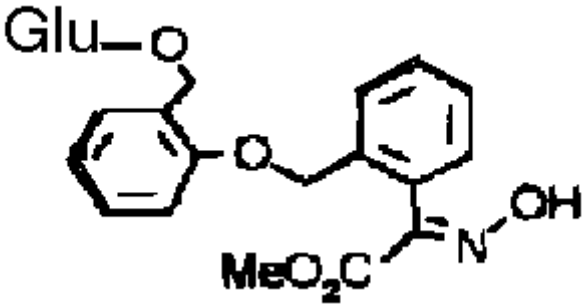
Code	Structure	Occurrence
490M0 (Z)-Isomer (242010)		Rat
490M1 BF 490-1 (262451)		Rat Goat Hen Apple Wheat Soil Water
490M2 BF 490-2 (291685)		Rat Goat Apple Wheat Grape
490M4 BF 490-5 (286404)		Rat Soil
490M5		Rat Hen

Code	Structure	Occurrence
490M6		Rat Goat Hen
490M8 BF 490-11 (303218)		Rat Hen
490M9 BF 490-9 (292932)		Rat Goat Hen Apple Wheat Grape
490M11		Rat Hen
490M12		Rat

Code	Structure	Occurrence
490M14		Rat Hen
490M15 BF 490-4 (299446)		Rat Goat Hen
490M16		Rat Hen
490M18 BF 490-8 (299153)		Goat
490M19		Goat

Code	Structure	Occurrence
490M20 BF 490-14		Rat Hen
490M22		Rat
490M24		Rat Hen
490M25		Rat Hen
490M26		Rat Hen

Code	Structure	Occurrence
490M27		Rat
490M28		Rat Hen
490M29		Rat
490M31		Rat Hen
490M33		Rat Hen

Code	Structure	Occurrence
490M34		Rat
490M35		Rat
490M36		Rat
490M37		Rat
490M39		Rat Hen

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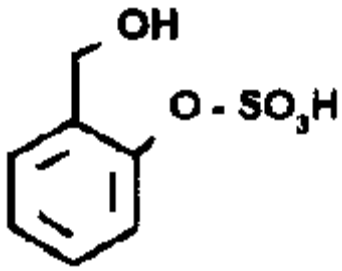
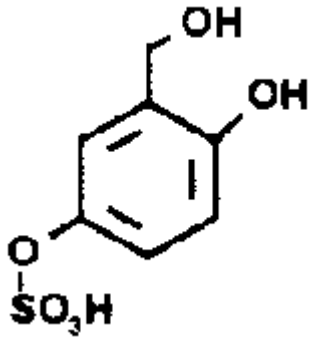
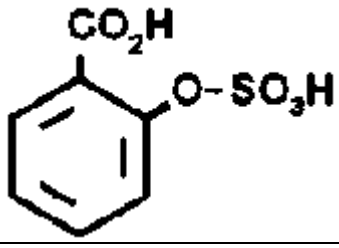
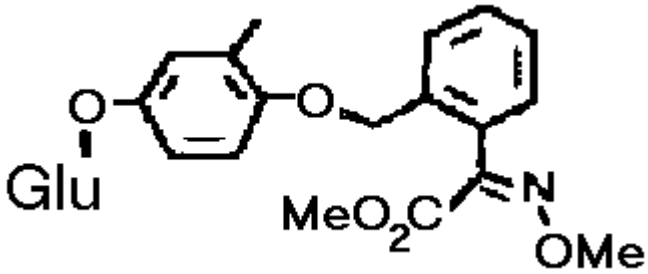
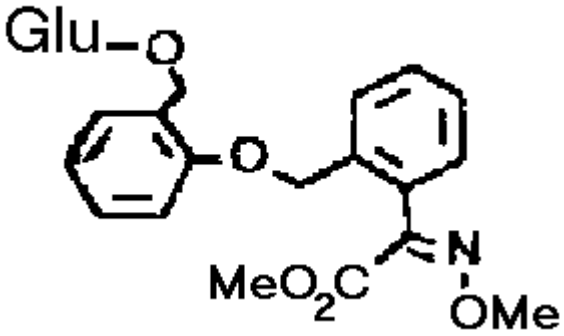
490M41		Rat
490M42		Rat
490M43		Rat
490M44		Rat
490M45		Rat

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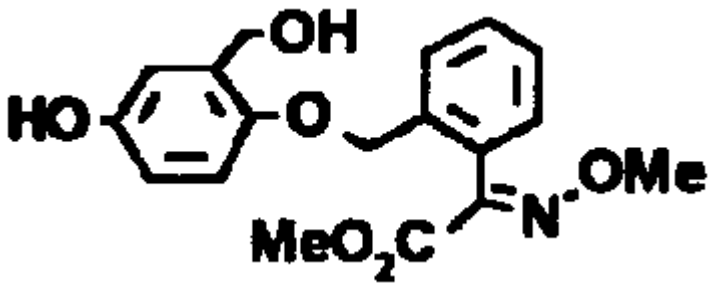
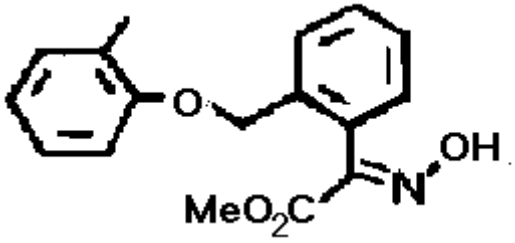
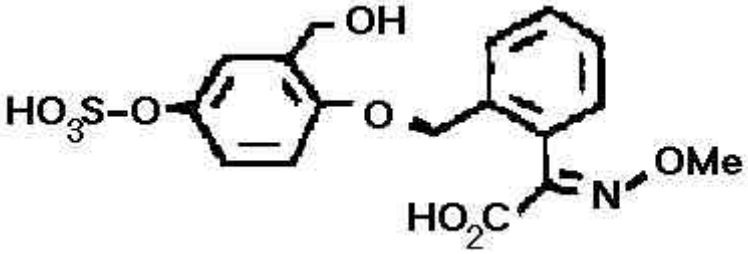
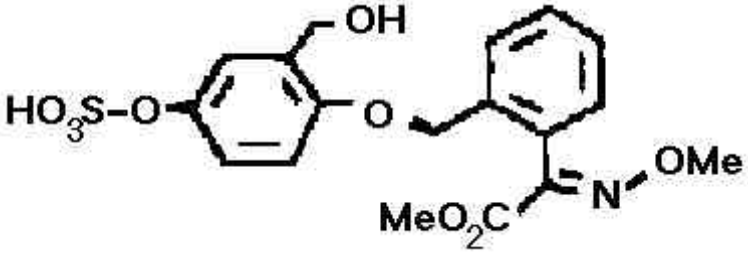
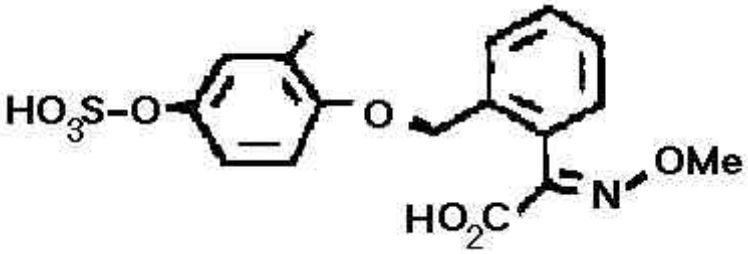
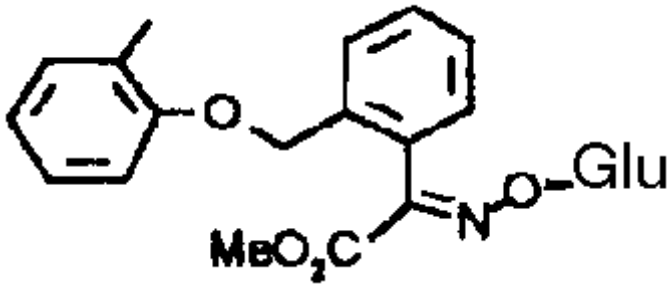
490M46		Hen
490M48 BF 490-3 (266042)		Hen
490M50		Hen
490M51		Hen
490M52		Hen
490M53		Rat

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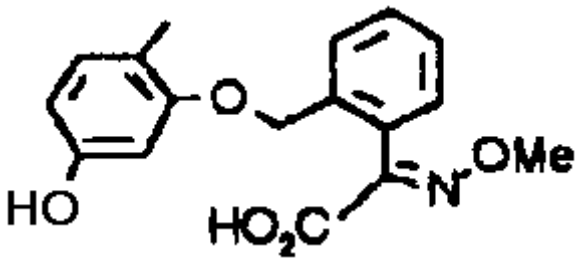
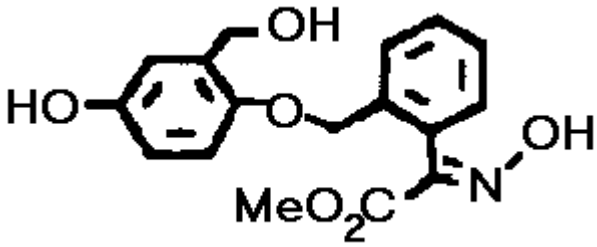
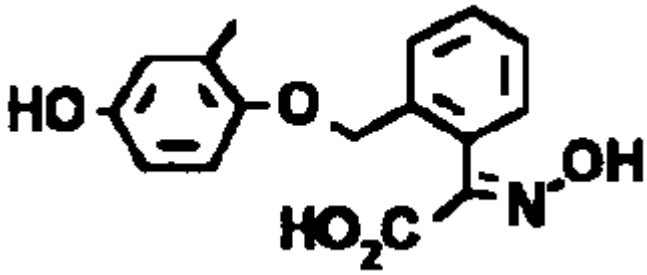
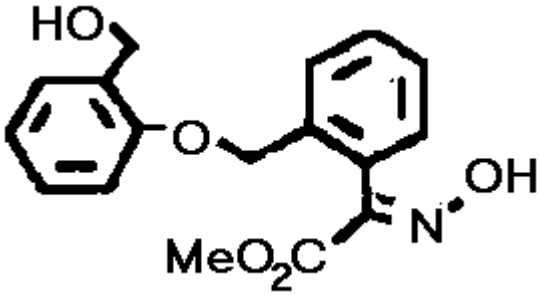
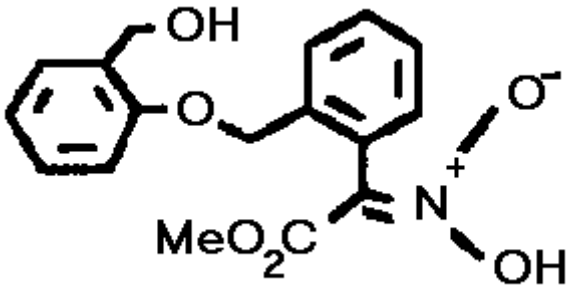
490M54 BF 490-15		Grape
490M55		Hen
490M56		Goat Hen
490M57		Hen
490M58		Hen

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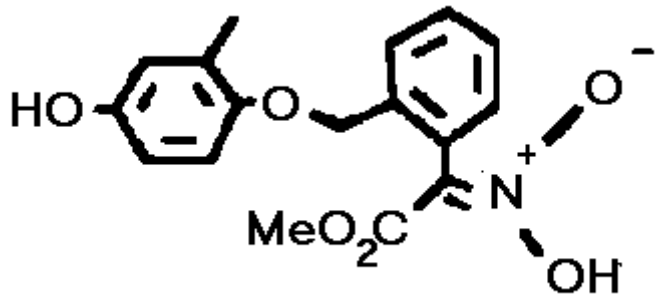
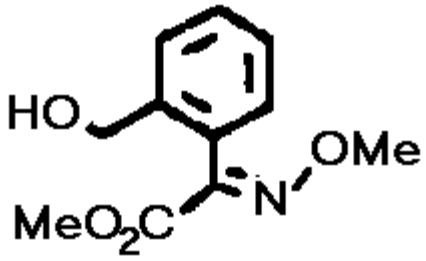
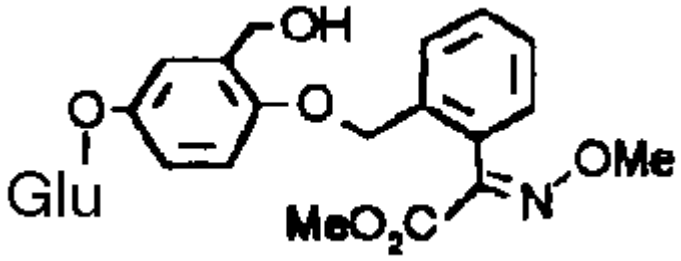
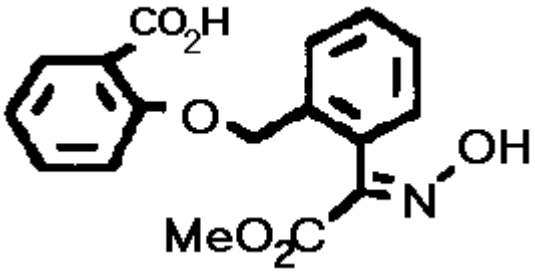
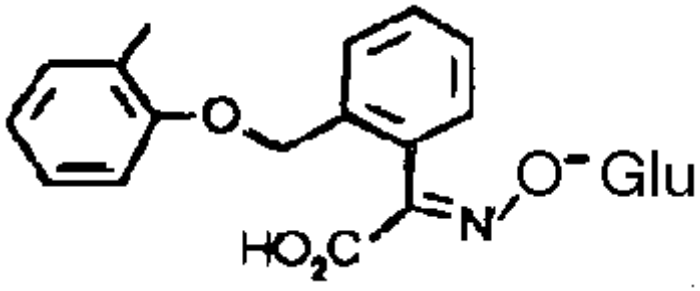
490M59		Hen
490M60		Hen
490M63		Hen
490M64		Hen
490M65		Hen

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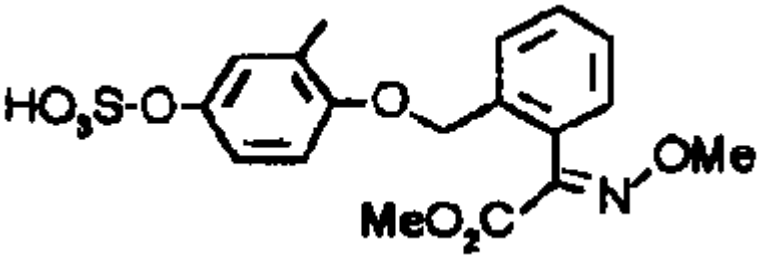
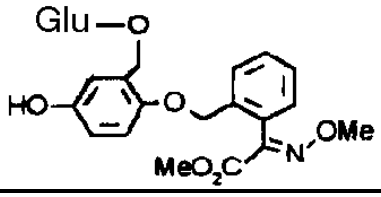
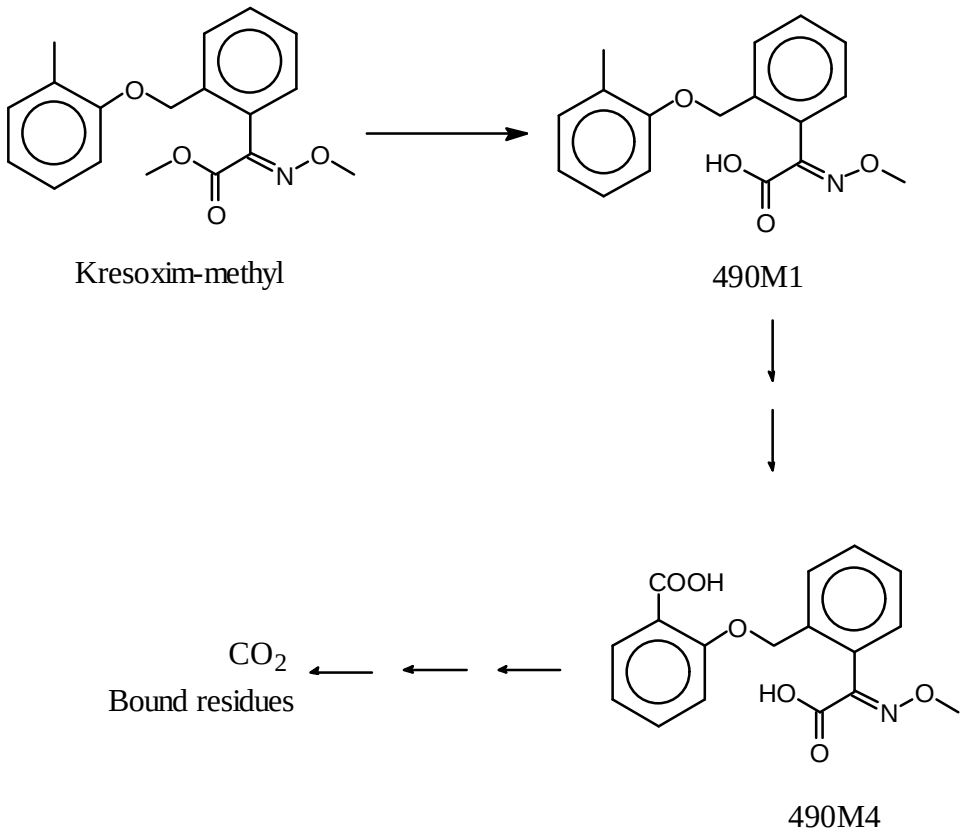
490M66		Hen
490M67		Hen

Figure 13. Proposed degradation pathway of kresoxim-methyl in soil.



MALEIC HYDRAZIDE (102)

EXPLANATION

The compound was first evaluated in 1976. The review of its toxicology in 1996 and the present review of residue aspects are within the CCPR Periodic Review Programme.

The manufacturer submitted information on metabolism and environmental fate, analytical methods, use patterns, supervised trials, and the effects on residues of storage and processing. The Netherlands supplied information on analytical methods, residue trials, and national GAP and MRLs. Germany and Poland provided information on GAP and MRLs.

IDENTITY

ISO common name: maleic hydrazide

Chemical name
IUPAC: 6-hydroxy-2*H*-pyridazin-3-one; 1,2-dihydropyridazine-3,6-dione
CA: 6-hydroxy-3(2*H*)-pyridazinone; 1,2-dihydro-3,6-pyridazinedione

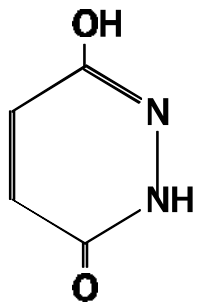
CAS No: 123-33-1

CIPAC No: 310

Synonymes: MH

Molecular formula: $C_4H_4N_2O_2$

Structural formula:



Molecular weight: 112.1

Physical and chemical properties

Pure active ingredient

Vapour pressure: $<10^{-5}$ Pa at 25°C, purity 99.7% (Knauppila *et al.*, 1989)

Melting point: 298-300°C at 99.9% purity (Anon., 1989a)

Octanol/water partition coefficient (log P_{OW}):		-0.68 at pH 5 -2.01 at pH 7 -2.42 at pH 9, purity 99.6% (Kerish and Parkins, 1985)
Solubility:	methanol	4.179 g/l
	water	4.507 g/l
	toluene	<1 mg/l
	hexane	<1 mg/l
		at 25-26°C, 99.6% purity (Jewell, 1989)
Specific gravity:	1.61 g/cm^3 (Sweetapple, 1988)	
Hydrolysis (45°C, dark):	stable at pH 3, 6 and 9 after 61 days (Lacadie, 1976)	
Hydrolysis (80°C, dark):	stable at pH 3, 6 and 9 after 30 days (Lacadie, 1976)	
Photolysis (water, at 25°C):	essentially stable at pH 5 and 7 for 30 days, half-life 15.9 days at pH 9 (Fackler, 1993) degradation products: maleic acid, succinic acid (Schocken, 1994)	
Photolysis (in air):	stable at 20°C after irradiation for 7 days (Riggs, 1995a)	
Dissociation constant:	pK_a 5.62 at 20 ± 1°C (Book and Thomas, 1988)	
pH (25°C):	3.61 at 0.4% in water 4.32 of 1% in water/dioxane, 50:50 (Mattschei, 1989)	
Oxidation:	Slight increase in temperature during the first 30 min after mixing with $KMnO_4$ (Sanders, 1990)	

Technical material

Purity:	>99%
Melting range:	300-302°C (Riggs, 1995b)
Thermal stability in air:	stable at 55°C in water-saturated air for 14 days (Riggs, 1995c)
Stability in presence of 315L stainless steel:	stable at 20°C for 16 weeks (Riggs, 1995d)
Storage stability:	stable at 25°C for 1 year (Thomson, 1990)

Formulations

Maleic hydrazide (as the potassium salt) is formulated as dispersible granules (SG, GR) and as liquid formulations (SL, SC).

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Caley and Cameron (1990) and Caley *et al.* (1990a) studied the metabolism of [^{14}C]maleic hydrazide in male and female Sprague-Dawley rats at a target level of 2 mg/kg bw given as a single intravenous dose, a single oral dose or an oral dose after 14 daily doses of unlabelled maleic hydrazide at 2 mg/kg/day, and given at a target level of 100 mg/kg as a single oral dose.

After either intravenous or oral administration radioactivity was eliminated rapidly during the first 24 hours (Table 1). The main route of elimination was via the urine with more than 40% of the administered dose excreted within 4 hours. Excretion in the urine was faster initially after intravenous dosing but the mean total excretion was similar in all dose groups (76.71 to 86.97%). The total elimination in the faeces was between 9.4 and 14.4% of the oral doses and 6.3% and 5.1% of the intravenous dose in males and females respectively. Radioactivity in the expired air accounted for less than 0.5% of the administered dose. The levels of radioactivity in all the tissues and organs combined accounted for less than 0.01% of the total administered dose. Less than 0.5% of the administered radioactivity remained in the carcase.

Table 1. Excretion of [^{14}C]maleic hydrazide after oral and intravenous administration to rats.

Ref.	Administration method, Dose	Time, h	Mean % of administered dose					
			Urine		Faeces		Total	
			Male	Female	Male	Female	Male	Female
Caley *et al.*, 1990;	Intravenous 2 mg/kg	0-4 0-24 0-168	65.2 78.2 80.3	59.5 85.3 87.0	X 5.3 6.3	X 4.4 5.1	65.2 83.4 86.6	59.5 89.7 92.1
Caley and Cameron, 1990	Oral 2 mg/kg	0-4 0-24 0-168	43.8 82.8 83.4	54.8 77.1 78.5	X 12.4 13.0	X 9.7 10.5	43.8 95.1 96.3	54.8 86.8 89.0
	Multiple Oral 2 mg/kg	0-4 0-24 0-168	44.4 75.8 77.1	53.3 74.8 76.7	X 13.3 14.4	X 11.2 13.5	44.4 89.1 91.5	53.3 86.0 90.2
	Oral 100 mg/kg	0-4 0-24 0-168	47.5 78.9 80.0	45.0 78.4 80.7	X 9.0 9.4	X 11.0 11.5	47.5 87.9 89.4	45.0 89.4 92.3

X = no faeces available

The urine contained two compounds: the major component was maleic hydrazide and the minor was tentatively identified as its sulfate conjugate. Because of poor chromatography the identification of faecel metabolites could not be confirmed but there were at least two components, possibly maleic hydrazide and fumaric acid.

Hawkins *et al.* (1984) studied the percutaneous absorption of [^{14}C]maleic hydrazide in rabbits. A liquid formulation of the potassium salt was applied to the shaved backs of New Zealand White rabbits for a 4-hour exposure period at 16 mg/kg bw. Urine was collected for periods of 0-4, 4-24, 24-48, 48-72 and 72-96 hours. Faeces were collected at 24-hour intervals for 96 hours. The rabbits were killed at 96 hours. ^{14}C was measured in the urine, faeces, cotton wool swabs (used for removing the residual material from the dose sites after completing the exposure), dressings and carcases. Most of the radioactivity was eliminated in the urine, 24% and 39% of the total applied dose in males and females respectively (Table 2). Urinary elimination was rapid during the first 24

hours, accounting for 22% and 38% of the administered dose in males and females respectively. Less than 0.2% was excreted in the faeces. The total absorption of maleic hydrazide was calculated to be 26% and 40% of the applied dose in males and females respectively. Most of the urinary radioactivity (88% to 96.5%) was associated with unchanged maleic hydrazide.

Table 2. Mean excretion of radioactivity in the urine and faeces of rabbits after topical application of [^{14}C]maleic hydrazide (Hawkins *et al.*, 1984).

Time, h	^{14}C, % of applied					
	Male		Female		Male and female	
	Mean	SD	Mean	SD	Mean	SD
Urine						
0-4	2.6	4.5	12.5	22	7.5	15
4-24	19	13.5	25	14	22	13
24-48	1.6	0.38	0.77	0.38	1.2	0.57
48-72	0.38	0.18	0.89	1.15	0.64	0.79
72-96	0.14	0.12	0.11	0.06	0.13	0.09
Cage washings						
0-48	1.4	2.4	0.00	0.00	0.69	1.7
48-96	0.84	1.3	0.58	0.76	0.71	0.94
Faeces						
0-24	0.19	0.17	0.13	0.10	0.16	0.13
24-48	0.00	0.00	0.02	0.04	0.01	0.03
48-72	0.00	0.00	0.00	0.00	0.00	0.00
72-96	0.00	0.00	0.02	0.04	0.01	0.03
Dressings	11	5.7	12	8.9	11.5	6.7
Dose washings[1]	54	14	40	16.1	47	16
Total	91.15		92.02		91.55	
Systemic absorption[2]	26.15		40.02		33.05	

[1] Recovered from cotton wool swabs
[2] Urine, faeces and cage washings
SD = standard deviation

Lactating goats. Cameron *et al.* (1992) examined the metabolism of maleic hydrazide in a non-pregnant lactating goat dosed twice daily by gavage with 7.5 mg/kg bw [^{14}C]maleic hydrazide after milking for 32 days. Urine and faeces were collected 12 hours after each dosing and milk immediately before each dosing and immediately before slaughter. Liver, kidney, fat (renal and subcutaneous), muscle, bile and plasma were collected at slaughter and whole blood immediately before slaughter. All tissues were sequentially extracted with methanol/water (90:10) and acetonitrile/water (90:10). After concentration, the extracts were heated at 60°C for 4 hours with 4 M HCl, then evaporated and reconstituted in 90:10 methanol/water. A sample of liver was hydrolysed by incubation with 4 N NaOH at 60°C for 24 hours. Liver was also digested with protease by incubating with pepsin in 0.1 M HCl for 96 hours at 37°C. A subsample of milk extract was combined with 0.1 M sodium acetate (pH 5) containing β-glucuronidase with sulfatase activity added and incubated at 37°C for 17 hours.

Approximately 87% of the administered dose was recovered in the urine, faeces, cage wash, tissues and milk (Table 3). The main route of elimination was in the urine, which accounted for approximately 63% of the administered dose.

Table 3. ^{14}C in urine, faeces, cage wash, milk and tissues from a goat administered [^{14}C]maleic hydrazide.

Ref.	Sample	Interval, h	Total recovered, % of administered dose
Cameron, *et al.*, 1992	Urine	12 24 48 72 84 (total)	8.02 7.30 16.87 18.63 12.12 (62.94)
	Faeces	12 24 48 72 84 (total)	0.06 1.65 6.10 7.31 8.03 (23.15)
	Cage wash	12 24 48 72 84 (total)	0.04 0.09 0.08 0.08 0.21 (0.50)
	Milk	12 24 36 48 60 72 84 96 108 (total)	0.00 0.002 0.015 0.008 0.025 0.011 0.027 0.014 0.022 (0.13)
	Tissues	(total)	(0.06)
	TOTAL		86.78

The ^{14}C in milk increased from 0.2 mg/kg as maleic hydrazide (pm, day 1) to 0.88 mg/kg (am, day 4), and decreased to 0.67 mg/kg within 24 hours of the final dose. Only 0.06% of the administered dose was recovered from the tissues, in which the highest levels of radioactivity were observed in the liver (1.3 mg/kg) and kidneys (3.3 mg/kg). The results are shown in Table 4.

Table 4. ^{14}C in milk, blood, bile and tissues from a goat administered [^{14}C]maleic hydrazide.

Ref.	Sample	Interval, h	^{14}C, mg/kg as maleic hydrazide
Cameron *et al*., 1992	Milk	12	0.00
		24	0.20
		36	0.54
		48	0.61
		60	0.79
		72	0.79
		84	0.88
		96	0.85
		108	0.67
	Subcutaneous fat	slaughter	0.19
	Renal fat	slaughter	0.11
	Muscle (fore)	slaughter	0.44
	Muscle (hind)	slaughter	0.44
	Kidney	slaughter	3.3
	Liver	slaughter	1.3
	Whole blood	slaughter	0.63
	Bile	slaughter	1.3
	Plasma	slaughter	0.71

The nature of the radioactive residues in the tissues and milk in extracted and hydrolysed samples is shown in Table 5. In the kidneys the major metabolite, accounting for 91% of the ^{14}C, was a polar compound, postulated to be a conjugate. Acid hydrolysis of this yielded maleic hydrazide and a relatively non-polar component with an HPLC retention time of 15 min. In liver approximately 43% of the ^{14}C was not extractable with methanol or acetonitrile, but protease treatment increased the extractable residues to approximately 98%. After acid hydrolysis, the level of the polar conjugate in liver decreased with a corresponding increase in maleic hydrazide and two metabolites with HPLC retention times of 10 and 15 minutes. The 10 minute retention time is similar to that of fumaric acid. Maleic hydrazide and the polar conjugate were also identified in muscle and fat after acid hydrolysis. Approximately 13% of the ^{14}C in milk was identified as maleic hydrazide, and enzyme treatment indicated that the major polar components were sulfate conjugates. Maleimide did not co-chromatograph with any unknown metabolites in milk.

Table 5. Radioactive residues in extracted and hydrolysed tissues and milk from a goat treated with [^{14}C]maleic hydrazide.

Report	Sample	^{14}C, mg/kg as maleic hydrazide						
		MH [1]	Conjugate[2]	Unknown 1[3]	Unknown 2[4]	Other	Un-extractable	Total
Cameron *et al.*, 1992	Extracted							
	Kidney	nd	2.77	nd	nd	0.19	0.07	3.03
	Liver	nd	0.51	nd	0.04	0.06	0.56	1.17
	Muscle	0.03	0.26	nd	0.05	<0.01	0.01	0.36
	Fat	nd	0.16	nd	0.01	0.01	<0.01	0.19
	Milk	0.11	0.39	0.06	0.14	<0.01	0.03	0.74
	Acid-hydrolysed							
	Kidney	0.96	1.79	nd	0.13	0.03	0.07	2.98
	Liver	0.16	0.16	0.10	0.13	0.07	0.56	1.18
	Muscle	0.15	0.05	0.05	0.15	0.02	0.01	0.43
	Fat	0.05	0.07	0.01	0.03	0.02	<0.01	0.19
	Enzyme-hydrolysed							
	Milk	0.38	0.05	0.05	0.25	0.02	0.03	0.78
	Protease-hydrolysed							
	Liver	0.25	0.43	nd	0.09	0.01	0.06	0.84
	Protease- and acid-hydrolysed							
	Liver	0.30	0.28	nd	0.27	0.03	0.06	0.94

nd = not detected
[1] maleic hydrazide
[2] Conjugate had a retention time of approximately 8 min
[3] HPLC retention time 10 min, later identified as fumaric acid
[4] HPLC retention time 15 min, tentatively identified as pyridazinone

Cameron and Johnston (1995) subjected goat milk extracts to HPLC analysis after storing the milk at about -20°C for periods up to 18 months. The stability of the radiolabelled components under these storage conditions was determined and a major unknown metabolite was identified as 3-pyridazinone.

The profile of radioactivity observed in enzyme-deconjugated milk extracts confirmed the stability of the radiolabelled components. Three main components were detected by radio-HPLC after each storage period. The main compound was eluted at the same retention time as maleic hydrazide and represented about 50.5% of the radioactivity after 1 month and 67.5% after 18 months. A less polar compound now known to be 3-pyradizinone accounted for 32.8% after 1 month and 22.1% after 18 months and the third, more polar, component represented 7.2% after 1 month and 10.4% after 18 months. A further component seen in milk extracts at 1 month and representing 6.8% of the injected radioactivity was not observed at the later time: its disappearance was considered to result from the breakdown of polar conjugated material, probably as a result of more efficient enzymatic deconjugation.

Lactating cows. Jackson and Hall (1992a) dosed twelve lactating cows intrarumenally in 4 groups of 3 animals each twice daily for 28 days at 0, 0.45, 1.36 and 4.5 mg/kg bw/day with [^{14}C]maleic hydrazide. Milk was collected daily throughout the dosing period and the cows were slaughtered 6 hours after the final dose. The levels of ^{14}C in the milk are shwon in Table 6 and in the edible tissues in Table 7.

The ^{14}C in the milk reached a plateau after 3-4 days of about 0.02 mg/kg as maleic hydrazide from the low dose, 0.06 mg/kg from the medium dose, and 0.2 mg/kg from the high dose, indicating a linear relationship between dose and residue.

Table 6. ^{14}C in milk from lactating cows.

Ref.		Mean ^{14}C, mg/kg as maleic hydrazide		
	Days	0.45 mg/kg bw/day	1.35 mg/kg bw/day	4.5 mg/kg bw/day
Jackson and Hall, 1992a	1-3	0.011-0.016	0.033-0.049	0.12-0.2
	4	0.018	0.055	0.21
	8	0.02	0.062	0.2
	9-28	0.019-0.021	0.052-0.064	0.19-0.22

Table 7. ^{14}C in tissues from lactating cows.

Ref.	Sample	Mean ^{14}C, mg/kg as maleic hydrazide		
		0.45 bw/day	1.35 bw/day	4.5 bw/day
Jackson and Hall, 1992a	Liver	0.08[a]	0.24[c]	0.8[d]
	Kidney	0.34[a]	1.0[c]	3.9[d]
	Muscle	0.02[a]	0.09[c]	0.2[d]
	Fat	0.05[b]	0.1[d]	0.4[e]

LOD a 0.0, b 0.03, c 0.04, d 0.1, c 0.3 mg/kg

Jackson and Hall (1992b) dosed groups of ten hens (average body weight 2 kg) dosed with [^{14}C]maleic hydrazide at 1, 3 and 10 mg/kg bw/day. The test solution was administered by gavage twice daily for 28 days. Eggs were collected daily and liver, kidneys, muscle (breast and thigh), abdominal fat and skin with associated fat were collected at slaughter.

Egg yolks and whites were separated and daily samples in each dose group were pooled. Tissue samples were also pooled. The levels of ^{14}C are shown in Tables 8 and 9. The residue levels were too low for the identification of metabolites.

Table 8. ^{14}C in pooled samples of egg whites and yolks from hens treated with ^{14}C-maleic hydrazide for 28 days.

Ref.	Days	Mean ^{14}C, mg/kg as maleic hydrazide					
		1 mg/kg bw/day		3 mg/kg bw/day		10 mg/kg bw/day	
		White	Yolk	White	Yolk	White	Yolk
Jackson and Hall, 1992b	1	0.0028	<0.001	0.028	0.001	0.156	0.01
	2	0.0088	0.001	0.045	0.010	0.181	0.04
	3	0.0115	0.004	0.051	0.019	0.192	0.07
	4	0.0124	0.007	0.054	0.031	0.189	0.10
	5	0.013	0.010	0.057	0.042	0.210	0.14
	6	0.0127	0.013	0.061	0.051	0.208	0.17
	7 to 14	0.013 to 0.0152	0.015 to 0.018	0.053 to 0.057	0.057 to 0.062	0.19 to 0.203	0.20 to 0.23
	15 to 28	0.0126 to 0.0147	0.018 to 0.019	0.055 to 0.069	0.060 to 0.073	0.190 to 0.203	0.20 to 0.23

Table 9. ^{14}C in tissues from hens treated with [^{14}C]maleic hydrazide for 28 days.

Ref.	Sample	Mean ^{14}C, mg/kg as maleic hydrazide		
		1 mg/kg bw /day	3 mg/kg bw/day	10 mg/kg bw/day
Jackson and Hall, 1992b	Liver	0.016	0.059	0.19
	Kidney	0.059	0.235	0.78
	Breast muscle	0.022	0.080	0.27
	Thigh muscle	0.014	0.059	0.18
	Abdominal fat	0.006	0.020	0.06
	Skin and fat	0.022	0.060	0.18

Maleic hydrazide is rapidly metabolized by hens. The ^{14}C reached plateaux in egg whites after 5 days and yolks after about 8 days of 0.01-0.02 mg/kg from the low dose, 0.05-0.07 mg/kg from the mid dose, and 0.19-0.23 mg/kg from the high dose. The tissue residues were highest in the kidneys (0.06-0.8 mg/kg) and lowest in abdominal fat (0.006-0.06 mg/kg). Radioactive residues in the muscle, liver and skin ranged from 0.01-0.02 mg/kg at the low dose yo 0.18-0.27 mg/kg at the high dose. The residues were not high enough to identify metabolites.

Johnston *et al.* (1993) dosed six laying hens twice daily for 3½ days by gavage with [^{14}C]maleic hydrazide at 15 mg/kg bw/day (equivalent to 196 ppm in the diet). The excreta were collected daily and the cage rinse was retained. Eggs were collected daily and separated into whites and yolks. Liver, kidney, muscle (breast and thigh), abdominal fat pad, skin with associated fat, heart, lungs, spleen, whole blood and plasma were collected at slaughter.

The ^{14}C levels in the eggs, tissues, excreta and cage rinse are shown in Table 10. The maximum residues in egg whites and yolks were 0.33 and 0.23 mg/kg as maleic hydrazide respectively. The residues in the tissues ranged from 0.04 to 0.2 mg/kg. Approximately 98% of the administered dose was recovered in the excreta and cage rinse within 24 h after the final dose. The distribution of extractable and unextractable ^{14}C in tissues and eggs is shown in Table 11.

Table 10. ^{14}C in eggs, tissues, excreta and cage rinse from hens treated with [^{14}C]maleic hydrazide for 3½ days.

Report	Sample	Hours after first dose	^{14}C	
			mg/kg as maleic hydrazide	% of administered dose
Johnston et al., 1993	Egg white	24 78 72 96 120	0.023 0.295 0.293 0.334 0.201	0.001 0.008 0.009 0.010 0.006
	Egg yolk	24 48 72 96 120	<0.01 0.07 0.12 0.18 0.23	<0.001 0.002 0.001 0.002 0.003
	Abdominal fat	slaughter[1]	0.04	<0.001
	Heart	slaughter	0.10	<0.001
	Kidney	slaughter	0.20	0.002
	Liver	slaughter	0.13	0.005
	Lung	slaughter	0.12	0.001
	Breast muscle	slaughter	0.11	
	Thigh muscle	slaughter	0.09	
	Spleen	slaughter	0.10	<0.001
	Skin with fat	slaughter	0.07	
	Plasma	slaughter	0.13	
	Whole blood	slaughter	0.09	
	Excreta	24 48 72 96 (total)		27.16 27.09 27.63 14.42 (96.30)
	Cage wash	24 48 72 96 (total)		0.35 0.38 0.67 0.58 (1.98)

[1] 24 hours after final dose

Table 11. Extractable and unextractable radioactive residues from hen tissues and eggs.

Ref.	Sample	mg/kg as maleic hydrazide	% of ^{14}C in sample		
			Extractable	Unextractable	Total
Johnston *et al.*, 1993	Kidney	0.18	74.6	29.9	104.5
	Liver	0.13	71.5	19.2	90.7
	Breast muscle	0.11	78.5	12.7	91.2
	Egg white	0.197	73.4	32.4	105.8
	Egg yolk	0.26	112.1	25.7	137.8

The residues were determined by HPLC. Their distribution is shown in Table 12. In the kidneys after extraction about 21% of the TRR was associated with a nonpolar metabolite, <5% was maleic hydrazide, and about 25% was an unidentified polar compound. The major extractable residue in liver (58% of the ^{14}C) and muscle (64%) was the nonpolar metabolite found in the kidneys. In egg white, the polar metabolite constituted about 32% of the TRR and the nonpolar metabolite about 33%. Maleic hydrazide accounted for about 51% of the ^{14}C in egg yolk, which also contained the unknown polar and nonpolar metabolites. After acid treatment, the level of the polar compound in the kdineys, egg white and yolk extracts decreased with a corresponding increase in maleic hydrazide and/or other compounds. Maleimide did not co-chromatograph with any of the metabolites. Mass spectrometry of the nonpolar metabolite isolated from egg white indicated that it was a conjugate of a methylated maleic hydrazide, probably the O-methyl derivative.

Table 12. Distribution of radioactive residues in tissues and eggs.

Ref.	Sample	Radioactive residues, mg/kg as maleic hydrazide					
		MH	Polar metabolite[1]	Nonpolar metabolite[2]	Other compounds	Unextractabl	Total
Johnston et al., 1993	After extraction						
	Kidney	<0.01	0.06	0.05	0.02	0.10	0.24
	Liver	nd	<0.01	0.07	0.02	0.02	0.12
	Muscle	<0.01	<0.01	0.07	<0.01	0.01	0.11
	Egg white	nd	0.061	0.063	0.004	0.064	0.192
	Egg yolk	0.18	0.03	0.02	0.05	0.07	0.35
	After acid hydrolysis						
	Kidney	0.05	<0.01	0.06	0.01	0.10	0.23
	Liver	<0.01	<0.01	0.06	0.01	0.02	0.11
	Muscle	<0.01	nd	0.05	0.01	0.01	0.08
	Egg white	0.061	nd	0.066	0.005	0.027	0.159
	Egg yolk	0.18	nd	0.05	0.03	0.07	0.33

nd = no HPLC peak MH = maleic hydrazide

[1] Unknown compound with HPLC retention time 8 min.

[2] HPLC retention time 15 min. tentatively identified as conjugae of O-methyl maleic hydrazide

Plant metabolism

The metabolism of [4,5- ^{14}C]maleic hydrazide was investigated in potatoes and onions.

Lengen (1988) treated potato plants with single applications of two maleic hydrazide formulations spiked with 0.007 g of the radiolabelled compound. Tubers and vines were collected 1 and 12 weeks after treatment. The tubers were washed with cold water to remove surface soil and debris and peeled, and the vines were air-dried. The peeled tubers were extracted twice with 20% aqueous methanol and twice with 0.1 N formic acid (pH 4.5). The ^{14}C levels were highest in the vines (mean 202 mg/kg as maleic hydrazide) and at similar levels the tubers and peels (26 and 25 mg/kg). The results are shown in Table 13.

Table 13. ^{14}C in potato tubers, peel and vines harvested 1 and 12 weeks after treatment with two formulations of [^{14}C]maleic hydrazide.

Ref.	Formulation	PHI, weeks	^{14}C, mg/kg as maleic hydrazide		
			Tubers	Peels	Vines
Lengen, 1988	SG	1	32	40	211
		12	24	19	215
	SL	1	19	16	198
		12	30	26	183

About 90% of the ^{14}C in the peeled tubers was extractable with aqueous methanol and formic acid. Maleic hydrazide was the major residue, indicating that only limited metabolism occurred. The glucose conjugate of maleic hydrazide was the main metabolite. The identities were confirmed by thermospray mass spectrometry. Fumaric acid, maleimide and maleic acid were also identified. The results are shown in Table 14.

Table 14. Compounds identified in extracts of potato tubers.

Ref.	Compound	Extractable residues as % of total residues			
		SG		SL	
		1 wk	12 wk	1 wk	12 wk
Lengen, 1988	Maleic hydrazide	84.2	52.0	78.7	75.3
	Maleic acid	nd	1.5	<0.1	0.2
	Fumaric acid	0.7	1.5	1.2	1.8
	MH glucoside	9.4	13.3	7.3	6.4
	Maleimide	0.2	nd	0.2	0.2

nd = not detected

In summary, maleic hydrazide was translocated from the potato foliage to the tubers which contained maleic hydrazide and its glucoside as the major residues. Maleic acid, fumaric acid and maleimide were minor metabolites.

A single application (hand-held sprayer) of [^{14}C]maleic hydrazide at a rate equivalent to 2.3 kg/ha was applied to potato plants which were harvested 1 hour, 2 weeks and 8 weeks after

treatment (Caley *et al.*, 1990b). Excess soil was brushed off and discarded and the tubers were washed in distilled water. Vines were not washed. Potato tubers and vines were radio-assayed. The results are shown in Table 15. After 1 hour virtually 100% of the ^{14}C was in the vines with only 0.04% the tubers. After 8 weeks about 10% of the ^{14}C was in the vines and 90% in the tubers.

Table 15. ^{14}C in rinsed potatoes, wash water and vines at intervals after treatment with [^{14}C]maleic hydrazide.

Ref.	PHI	Sample	Mean ^{14}C, mg/kg as maleic hydrazide
Caley *et al.*, 1990b	1 h	tubers: tissue wash	 0.035 0.009
		vines	109
	2 wks	tubers: tissue wash	 57 0.064
		vines	24.55
	8 wk	tubers: tissue wash	 67 36.4
		vines	7.73

Six tuber samples from the treated plots were harvested at 2 and 8 weeks. Individual and pooled samples (composites of treated tubers and vines) were extracted sequentially with 20% aqueous methanol and 0.1 N formic acid (Table 16). About 80-85% of the ^{14}C was extractable with methanol. HPLC and TLC of the methanol extract yielded single radioactive peaks shown by co-chromatography to be due to maleic hydrazide.

Table 16. Extractable and unextractable radioactive residues in pooled samples of potatoes harvested at intervals after treatment with [^{14}C]maleic hydrazide.

Ref.	PHI, weeks	% of ^{14}C in sample			
		Extracted by		Unextractable	Total
		20% aqueous methanol	0.1 N formic acid		
Caley *et al.*, 1990b	2	85.74	7.41	7.26	100.4
	8	80.77	4.22	12.39	97.4

In summary, maleic hydrazide was translocated from potato leaves to the tubers, with about 60% translocation in 8 weeks. All the radioactivity in the methanol extracts of the tubers was due to maleic hydrazide.

Caley *et al.* (1990c) treated onion tops with a single application of [^{14}C]maleic hydrazide by hand-held sprayer at a rate equivalent to 2.3 kg/ha when about half the tops had fallen. Plants were sampled 1 hour and 2 weeks after treatment. Excess soil was brushed off and discarded. The leaves and bulbs collected 1 hour after treatment were washed with distilled water. The leaves of plants

sampled after 2 weeks were discarded and the bulbs were washed. Samples were oven-dried to a constant weight at 40°C and the radioactivities were expressed on a dry-weight basis. Six of the samples harvested 2 weeks after application and a pooled sample (about 2 g of each) were extracted with 20% aqueous methanol and 0.1 N formic acid.

The results are shown in Table 17. The levels of radioactivity in the bulbs after 2 weeks were about ten times the initial levels.

Table 17. ^{14}C in onion leaves and bulbs after treatment with ^{14}C-maleic hydrazide.

Ref.	PHI	Sample	Mean ^{14}C[1]
Caley *et al.*, 1990c	1 h	leaves	528
		bulbs	14.8
	2 wks	bulbs	113

[1] mg maleic hydrazide equivalents/kg dry weight

^{14}C found in rinsed leaves and bulbs and the wash water is shown in Table 18. The mean proportions of the ^{14}C found in the wash water were about 22 and 51% from the leaves and bulbs respectively after 1 hour and 0.2% from the bulbs after 2 weeks

Table 18. ^{14}C in rinsed onions and wash water 1 hour and 2 weeks after treatment with [^{14}C]maleic hydrazide.

Ref.	Sample harvest	Sample	Mean ^{14}C[1]
Caley *et al.*, 1990c	1 h	Leaves: rinsed tissue wash	 2764 774
		Bulbs: rinsed tissue wash	 240 254
	2 wks	Bulbs: rinsed tissue wash	 2390 4.1

[1] Expressed as total µg maleic hydrazide equivalents

The distribution of ^{14}C in the analytical fractions from the bulbs after 2 weeks is shown in Table 19. About 90% of the ^{14}C was extractable with methanol. The methanol extracts contained a single radioactive compound identified by HPLC and thin-layer co-chromatography as maleic hydrazide.

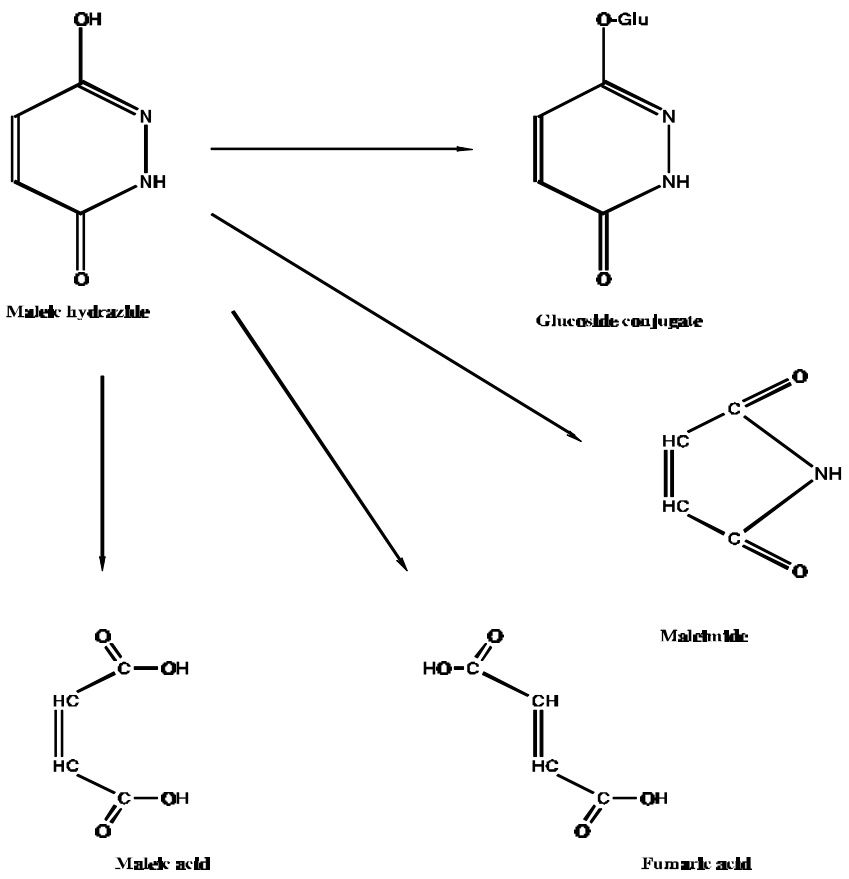
Table 19. Extractable and unextractable radioactive residues in onion bulbs harvested 2 weeks after treatment with [^{14}C]maleic hydrazide.

Sample no.	% of ^{14}C in sample		
	Extracted by	Unextractable	Total

	20% aqueous methanol	0.1 N formic acid		
1	87.19	6.71	1.65	95.55
2	89.45	6.86	1.89	98.20
3	85.71	6.64	1.46	93.81
4	87.43	7.32	1.73	96.48
5	85.38	5.68	1.15	92.21
6	82.32	8.76	2.08	93.16
1-6 pooled	90.62	5.95	2.60	99.17

In summary, maleic hydrazide was translocated from onion tops to the bulbs. The methanol-extractable metabolite in the bulbs harvested 2 weeks after treatment was maleic hydrazide. Proposed metabolic pathways in plants are shown in Figure 1.

Figure 1. Proposed metabolic pathways of maleic hydrazide in plants.



Environmental fate in soil

<u>Aanaerobic degradation</u>

Mackie *et al.* (1991a) investigated the degradation of [^{14}C]maleic hydrazide aged aerobically in loamy sand for 12 hours and then incubated under flooded anaerobic conditions for 60 days. Overall mean recoveries were 93.6-98.3% over the aerobic and anaerobic incubation periods. $^{14}CO_2$ evolution increased to 70.3% 60 days after flooding. Volatile organic ^{14}C was very low (mean ≤0.08%). The proportion of ^{14}C extractable with methanol/water decreased with time from 56.6% at day 0 to 3.5% 60 days after flooding. The proportion of the radioactivity in the water decreased from 30% at 30 days to 0.86% at 60 days. Bound radioactivity at 60 days accounted for 22.65% of the applied dose. Maleic hydrazide was degraded steadily to maleic acid, maleimide and an unidentified component, which were detected throughout the incubation period, as well as to $^{14}CO_2$.

Lengen (1986) investigated the distribution of radioactivity in a sandy loam soil incubated with 4.35 mg/kg [^{14}C]maleic hydrazide under anaerobic conditions (Table 20). When anaerobic conditions were established, 13 days of aerobic incubation 19-27% of the applied radioactivity had been evolved as $^{14}CO_2$.

Table 20. Distribution (%) of radioactivity in anaerobic soils treated with [^{14}C]maleic hydrazide.

Ref.	Days incubation	^{14}C, % of TRR					
		CO_2	Other volatiles	Water	Extracted from soil	Bound in soil	Total
Lengen, 1986	0	27.2[1]	<0.01	0.32	16.74	39.04	83.3
	32	19.9	<0.01	4.22	4.65	45.30	74.07
	60	23.8	<0.01	3.72	2.42	44.75	74.69

[1] One sample analysed, duplicate lost

The water phase of the anaerobic samples on day 0 contained less than 0.4% of the radioactivity, suggesting that the ^{14}C residues would not be readily desorbed from the soil. Extraction with isopropanol/water/ammonia removed 16.7% of the applied radioactivity and 39% remained bound. The soil extract was cleaned up on reverse-phase columns and the eluate analysed by HPLC. Additional residues were eluted with 1*N* formic acid and chromatographed on silica gel TLC plates. HPLC showed less than 2% of the ^{14}C as maleic hydrazide and TLC an additional 0.1%. Four other components, each less than 3% of the TRR were also detected.

The extractable soil residues decreased during the 60-day anaerobic incubation to less than 5%, while bound material increased to about 45%. The level of maleic hydrazide decreased to 1.3%, with other products (maleamic acid, maleic/fumaric acids, succinic acid and lactic acid) generally not exceeding 0.6%. The water phase showed a slight increase in ^{14}C activity to about 4% and TLC analysis indicated that it contained less than 1% of the initial ^{14}C as maleic hydrazide.

Aerobic degradation

Mackie *et al.* (1991b) studied the degradation of [^{14}C]maleic hydrazide in soil under aerobic conditions. $^{14}CO_2$, ^{14}C in organic volatiles and levels of radioactivity in the soil were determined throughout the 90-day incubation. Overall mean recoveries ranged from 95.6% to 101% during this period. Cumulative $^{14}CO_2$ evolution rose to 71.6% at 90 days. Organic volatile evolution was <5%. Radioactivity extractable with 1:1 methanol/water decreased from 62.4% at day 0 to 0.44% at 90 days. Bound radioactivity at 90 days accounted for 24.5% of the applied dose.

TLC indicated that maleic hydrazide was rapidly degraded. Maleic acid, maleimide and up to 5 unidentified components were detected in soil extracts throughout the incubation period. The proportions of these compounds were low because of further degradation to $^{14}CO_2$. HPLC analysis

of methanol/water extracts of samples taken during the first 5 days confirmed the presence of maleic hydrazide, maleimide and 3 unidentified components.

The half-life of maleic hydrazide under these conditions was 11 hours.

Mobility

Lengen (1985) determined the adsorption of the potassium salt of [^{14}C]maleic hydrazide to four soils. At equilibrium, log plots of the concentrations in soil against those in the aqueous phase conformed (with correlation co-efficients >0.9) to the Freundlich equation

$$\log S = \log k + 1/n \log C$$

where S is the maleic hydrazide adsorbed to the soil, C the concentration of maleic hydrazide in solution and k and n are the y-intercept and slope, respectively, of the curve. The results were as follows.

Soil	$k_{adsorption}$ (28 h)	$k_{desorption}$ (60-72 h)
Wisconsin sand	0.21	0.39
Washington silt loam	0.23	14.45
Connecticut sandy loam	2.61	2.97
Texas sandy clay loam	0.14	0.6

The k values determined by linear regression analysis indicated low adsorption to soil and thus a rather high potential for leaching.

In the same paper Lengen reported the mobility of [^{14}C]maleic hydrazide (potassium salt) in four leaching columns packed with the same soils. The test material was allowed to age aerobically for 14 days and the treated soils were then added to the tops of the soil columns and leached with 50 cm of water. Only 4.9% of the applied radioactivity was leached from the sandy loam column, and most of the radioactivity remained in the top 15 cm.

Haig *et al.* (1991) obtained different results. The treated soil was allowed to age for 12 hours only (about the half-life of maleic hydrazide under aerobic conditions). Overall mean recoveries from the loamy sand and sand were 102.2% and 103.1% of the applied radioactivity respectively including $^{14}CO_2$ evolved during the 7-day leaching period ($\leq$25%). Leaching was greatest from the sand with 100.8% of the ^{14}C recovered in the leachate, but only 39.8% from the loamy sand. The total extractable radioactivity was generally low for the loamy sand (5.37%) and negligible for the sand (0.22%). Bound residues accounted for 29.3% of the applied dose for the loamy sand and 1.1% for the sand. The results indicate that maleic hydrazide has the potential to leach, but will be degraded rapidly by ageing to products which bind strongly to the soil and are therefore not readily leached.

Field dissipation

Studies were conducted at several sites with the potassium salt.

Lengen and Batorewicz (1986, 1987) showed that maleic hydrazide formulated as an SG dissipated rapidly from field sites in Connecticut and New Mexico (USA). The half-life was estimated to be less than two weeks in a sandy clay loam and 5 days in a clay loam soil.

Dykman (1993 a,b,c) conducted field dissipation studies in California, Washington and North Carolina.

In California a turf sandy loam soil with about 0.6% organic matter was treated at 6.7 kg a.i/ha (1993a). The half-life was 5.3-6 days. The concentration was 3 mg/kg at day 0 and <0.01 mg/kg (the LOD) after 30 days. Residues at 15-30 cm were below the LOD after 14 days.

A Washington state potato field of sandy loam soil with about 0.7% organic matter was treated at 3.4 kg ai/ha (1993b). The half-life was 2.6 days. The concentration started at 0.66 mg/kg and became below the LOD after 14 days. Levels of maleic hydrazide near the LOD were found at 15-30 cm.

In North Carolina a tobacco field of sandy loam clay soil, organic matter about 1.4 %, was treated at 5.04 kg ai/ha (1993c). The half-life was 5.8-7.3 days. The initial maleic hydrazide concentration was 1.6 mg/kg and became lower than the LOD after 27 days.

None of the sites showed residues of maleic hydrazide below 30 cm.

Photolysis

Lengen and Frederick (1985) exposed ^{14}C-maleic hydrazide in sandy loam soil to simulated sunlight. The compound was very stable with about 80% recovery as intact maleic hydrazide after 34 days of exposure.

Environmental fate in water

Lacadie (1976) determined the hydrolysis of [^{14}C]maleic hydrazide in buffered solutions at pH 3, 6 and 9 at 7.2°C and 26.7°C. No hydrolysis was seen in two months.

Lengen and Frederick (1985) found a half-life of 34-52 days under photolytic conditions with simulated sunlight. The main photoproduct was maleic acid.

Fackler (1993) repeated the study by Lengen and Frederick and found a half-life of 15.9 days at pH 9. Maleic hydrazide was stable in all dark control solutions.

Schocken (1994) exposed aqueous solutions of [^{14}C]maleic hydrazide at a nominal concentration of 12 mg/l in pH 9 buffer to artificial sunlight for 85 days with a 12-hour light and 12-hour dark cycle each day. The main photoproducts were maleic and succinic acids.

Residues in rotational crops

Caley *et. al*. (1990) investigated the degradation of [4,5-^{14}C]maleic hydrazide in field-grown rotational wheat. The compound was applied once to a sandy loam soil at a rate of 0.3 g/m^2 (equivalent to 3 kg/ha) and wheat was planted 30 and 92 days after treatment. Forage was collected 5 weeks after emergence, and whole plants were collected at maturity of the grain and separated into grain, chaff and straw. Soil cores (22 cm) were taken before and after application, before sowing, and at each harvest. The cores were separated into 0-11 cm and 12-22 cm sections. The TRRs in the soil samples on a dry weight basis are shown in Table 21. Most of the recovered radioactivity was in the upper core sections (top 11 cm).

Table 21. ^{14}C in soil sampled at various intervals after treatment with [^{14}C]maleic hydrazide.

Ref.	Time of sampling	^{14}C, mg/kg as maleic hydrazide, mean and (range)			
		92-day planting		30-day planting	
		Upper section	Lower section	Upper section	Lower section

Ref.	Time of sampling	^{14}C, mg/kg as maleic hydrazide, mean and (range)			
		92-day planting		30-day planting	
		Upper section	Lower section	Upper section	Lower section
Caley *et al.*, 1990d	Before sowing wheat	1.25 (0.32-1.94)	0.10 (0.01-0.22)	2.28 (0.03-5.52)	0.05 (0.02-0.12)
	At first harvest	0.88 (0.21-1.55)	0.06 (0.01-0.16)	1.18 0.4-1.51)	0.03 (0.01-0.13)
	At final harvest	2.25 (0.62-7.08)	1.13 (0.03-5.96)	1.13 (0.17-2.71)	0.06 (0.02-0.1)

Whole plants from the 92-day planting contained radioactive residues similar to the controls and those from the 30-day planting showed that the uptake of [^{14}C]maleic hydrazide was limited. The radioactivity was distributed throughout the plants with slightly higher levels in the straw and chaff than the grain. The results are shown in Table 22.

Table 22. ^{14}C in wheat harvested from plots treated with [^{14}C]maleic hydrazide 92 and 30 before planting.

Ref.	Planting interval	Time of sampling	Mean total ^{14}C, mg/kg dry wt as maleic hydrazide			
			Straw	Grain	Chaff	Whole plant
Caley *et al.*, 1990d	92 days	5 weeks post emergence	X	X	X	0.03
		maturity	0.08	0.02	0.02	0.06[1]
	30 days	5 weeks post emergence	X	X	X	0.29
		maturity	0.04	0.02	0.05	0.04[1]

X No analysis
[1] Calculated from residdues in individual plant components

The mean levels of radioactivity in the soil decreased from 2.5 mg/kg as maleic hydrazide at application to 0.88 mg/kg at the first harvest of the wheat. The residues in the wheat were too low for identification. The ^{14}C in whole plants planted 92 and 30 days after soil treatment corresponded to 0.03 and 0.29 mg/kg respectively 5 weeks after emergence and 0.06 and 0.04 mg/kg at maturity of the grain. The straw, grain and chaff contained 0.04-0.08 mg/kg, 0.02 mg/kg and 0.02-0.05 as mg/kg respectively at maturity.

Ling and Burnett (1995) treated sandy loam soil at the maximum combined label rate of 6.6 kg ai/ha. ^{14}C residues were 0.26 mg/kg as maleic hydrazide in the forage of wheat planted 30 days after treatment (DAT) and 0.08 mg/kg in forage after planting 120 DAT. Residues were not detected in forage from 274 DAT and 364 DAT plantings.

^{14}C residues in the straw were 0.52 mg/kg from 30 DAT plantings and 0.22 mg/kg from 120 DAT. Residues in the straw from 274 and 364 DAT plantings were 0.03 and 0.02 mg/kg respectively.

^{14}C residues in the grain were 0.36 mg/kg from 30 DAT, 0.2 mg/kg from 120 DAT, 0.024 mg/kg from 274 DAT and 0.019 mg/kg from 364 DAT plantings.

In the grain samples from 30 DAT and 120 DAT crops, 47.5% and 56% of the ^{14}C respectively was shown to be incorporated into glucose. An additional 12% was released from each sample by hydrolysis with a proteinase enzyme, indicating incorporation into or association with protein.

The extracted radioactive material was found to be very polar, nonionic and of low molecular weight. The parent compound could not be conclusively identified, but may have been present at levels of no more than 0.02 mg/kg in the 30 DAT forage and straw.

Acid hydrolysis with 1*N* HCL released a significant amount of activity from forage and straw, but the component(s) could not be separated from the matrix. This may again indicate incorporation into the tissues.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Crops

The method of Lane (1963) involves reduction with zinc and hydrolysis in hot alkali to hydrazine. The hydrazine is isolated by distillation and determined colorimetrically as the azine after the addition of *p*-dimethylaminobenzaldehyde. The procedure is useful for determining residues of total maleic hydrazide and its conjugates. The available recovery data are shown in Table 23.

Table 23. Recovery of maleic hydrazide from various crops (Lane, 1963).

Sample	Fortification level, mg/kg	Recovery range, %	Mean recovery, %	Standard deviation	
				%	mg/kg
Cranberries	4	53 - 95	70	15	0.6
French fries	85	75 - 95	87	8.6	7.3
Mashed potatoes	28	74 - 87	83	3.9	1.1
Onions	10	70 - 106	81	15	1.5
Peaches	1.3	54 - 115	92	23	0.3
Potatoes	39	67 - 113	85	18	6.9
Potato chips	44	84 - 96	91	5	2.2

Newsome (1980) analysed plant material for residues of maleic hydrazide and its ß-D-glucoside by HPLC. Both maleic hydrazide and the glucoside were extracted with methanol and the extract was concentrated. The residues were cleaned up by passage through different cation-exchange columns (Amberlite XAD-2 and Dowex 50 resins for maleic hydrazide; Amberlite XAD-2, Dowex 1 and Dowex 50 resins for the glucoside) to separate the compounds from one another and from co-extractives. The glucoside was then hydrolysed with ß-glucosidase and the maleic hydrazide residues were determined by HPLC with detection by light absorption at 313 nm. The

average recoveries of maleic hydrazide at 1-50 mg/kg and of the glucoside at 2-50 mg/kg from beets, carrots, potatoes and turnips were both 87%. The LOD was 1 mg/kg.

King (1983) determined residues of maleic hydrazide in potatoes by gas chromatography after oxidation with aqueous lead dioxide to 3,6-pyridazinedione in the presence of cyclopentadiene. Potato samples were extracted with methanol and partitioned with chloroform containing cyclopentadiene and a suspension of freshly precipitated lead dioxide. The chloroform layer was removed and the aqueous fraction again partitioned with chloroform. The chloroform fractions were combined and evaporated to dryness. Residues maleic hydrazide were determined by GLC with EC detection on a DB17 packed column. Recoveries from potato samples fortified at 0.1, 0.5, 1, 5 and 10 mg/kg were 95.7, 94.0, 91.5, 87.9 and 90.4% respectively. The mean recovery of maleic hydrazide (as the Diels-Alder adduct) was 91.7% and the coefficient of variation was 3.1%. The limit of determination was 0.1 mg/kg. Samples containing conjugates were not analysed.

Harrison *et al.* (1989) used two monoclonal antibodies specific for maleic hydrazide to develop an enzyme immunoassay. Detection limits ranged from 0.11 to 1.3 mg/kg maleic hydrazide but the method was not validated for plants.

The official method of analysis for maleic hydrazide in The Netherlands (Anon., 1996) is based on the method of Lane (1963). The hydrazine produced by treatment with zinc in strong alkali is steam-distilled and the *p*-dimethylaminobenzaldehyde derivative is measured by spectrophotometry at 455 nm. In onions the LOD was 1 mg/kg with a mean recovery of 68.5% (n = 16, standard deviation 6%).

Animal products

Doran and McGuire (1996) employed proteolytic enzymes to solubilize maleic hydrazide from its bound form in animal tissues. The extracted maleic hydrazide was then determined by HPLC with UV detection. At fortification levels of 0.2 mg/kg, recoveries were 90-96% from cow milk and 68-88% from eggs. Beef liver spiked with 1 mg/kg showed recoveries of 52-79%.

Soil

Batoroewicz (1986) developed an HPLC method with electrochemical detection. The compound was soxhlet-extracted with water, the extract was concentrated to an appropriate volume, centrifuged and injected onto the HPLC column. Recoveries from clay loam and sandy clay loam soils fortified at 1 mg/kg were 60-70%.

Kennedy (1997a) extracted maleic hydrazide from soil with methanol/water (50:50) and quantified the residue by direct injection onto a reversed-phase HPLC column with an electrochemical detector. The mean recovery was 105% at fortification levels of 0.005, 0.025, 0.05 and 0.1 mg/kg with a relative standard deviation of 6.9%. The LOD was 0.005 mg/kg.

Water

Kennedy (1997b) cleaned up ground-water samples by liquid/liquid partition with dichloromethane. After concentration the residue was determined by HPLC with electrochemical detection. Validation at fortification levels of 0.0001, 0.0005, 0.001 and 0.002 mg/l showed a mean recovery of 92% with a relative standard deviation of 8.8%.

Stability of pesticide residues in stored analytical samples

Dykeman (1993d) tested the stability of maleic hydrazide in potato tubers stored for 12 months at about -20°C (Table 24).

Table 24. Stability of maleic hydrazide in frozen potatoes (Dykeman, 1993).

Months storage	Fortification level, mg/kg	% remaining	% remaining mean
0	25	96	100
	40	104	
1	30	84	79
	30	73	
3	20	107	110
	20	113	
6	20	111	113
	20	115	
12	20	76	84
	20	92	

Jacobson and Wight (1992a,b) tested the stability of maleic hydrazide in frozen onions and potatoes fortified at 20 mg/kg (Table 25).

Table 25. Stability of maleic hydrazide in frozen onions and potatoes fortified at 20 mg/kg (Jacobson and Wight, 1992a,b). Controls showed <1.2 mg/kg in potatoes and <0.2 in onions in all samples.

Months storage	Sample	% remaining	
		potatoes	onions
0	stored 1	113	98
	stored 2	79	98
	analytical[1] 1	77	118
	analytical 2	93	107
1	stored 1	86	53
	stored 2	103	49
	analytical 1	93	76
	analytical 2	87	73
2	stored 1	113	115
	stored 2	100	115
	analytical 1	56	113
	analytical 2	87	99
4	stored 1	80	115
	stored 2	113	83
	analytical 1	101	77
	analytical 2	72	111
6	stored 1	97	121
	stored 2	116	116
	analytical 1	97	81
	analytical 2	118	121

[1]Control sample spiked at 20 mg/kg and analysed immediately

Cameron and Johnston (1995) determined the profile of radioactivity in enzyme-deconjugated goat milk extracts during storage at about -20°C for about 18 months. Three main components were observed in the extracts at each analysis by radio-HPLC. The major component was eluted at the same retention time as maleic hydrazide and represented about 50.5% of the injected ^{14}C after 1 month and 67.5% after 18 months. A less polar component now known to be 3-pyradizinone accounted for 32.8% after 1 month and 22.1% after 18 months and a third more polar component represented 7.2% after 1 month and 10.4% after 18 months. The results confirmed the stability of the radiolabelled components in goat milk stored under these conditions.

Johnston and Cameron (1996) dosed laying hens with [^{14}C]maleic hydrazide at 3 mg/kg bw/day, extracted samples of pooled liver, kidney and egg yolk from selected hens with methanol or methanol/water (80:20) then analysed them by HPLC. The extracts were stored at about -20°C for 30 months. The profiles of radioactivity in samples analysed within about 1 month of collection and after storage for about 30 months were very similar, indicating that no deterioration of the ^{14}C residues had occured during storage.

USE PATTERN

The potassium salt of maleic hydrazide as the potassium salt is a growth regulator used to suppress sprouting in storage bulb vegetables and potatoes, to control suckers on tobacco and volunteer potatoes in following crops, and as a grass growth retardant in amenity and non-crop situations. It is also used on carrots. Tables 26 summarizes the use patterns.

Table 26. Registered uses of maleic hydrazide, application rates expressed as free maleic hydrazide.

Crop/Country	Form	Application				PHI, days
		Timing	Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
Carrots Denmark	SL	BBCH 49	1.8-2.2		1	14
Garlic France	SG	when 10% leaves fallen but still green	2.4		1	10
Grass (non-fodder) Denmark	SL	BBCH 21-25, grass 5-10 cm high	5.4		1	NA
UK	SC	when grass is beginning to grow	4.6			NA
Onions France	SG	before leaves fall over (necking) and still green	2.4		1	10
Greece	SL	mature plants	2.3		1	15
Denmark	SL	BBCH 49	1.4-1.6		1	14
Netherlands	SL	at necking when tops are still green	2.3		1	28
Poland	EC SG	about 2 weeks before harvest	2.0 2.4	0.68 0.8	1 1	
Spain	SL	late stage	2.7	0.45	1	
UK	SG SC	10-50% necking 50 % necking	1.5-2.4 2.3-3.0		1 1	7 4
Potatoes France	SG	when 80% of tubers have reached 35-40mm	3.0		1	21
Denmark	SL	BBCH 49	3.1		1	14
Poland	EC SG	about 4-6 (EC) or 3-5 (SG) weeks before harvest	2.6 3	0.43-0.87 0.5-1.0	1 1	
UK/Ireland	SG	when smallest tubers are not less than 2.5 cm long, not for use on seed potatoes	3.0		1	21

Crop/Country	Form	Application				PHI, days
		Timing	Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
Shallots France	SG	before leaves fall over (necking) and still green	2.4		1	10
Tobacco Greece	SL	mature plants	1.1-1.6		1	7
Italy	SC GR	after flowering	1.8-2.3 1.7-2.5	0.3-0.37 0.3-0.5	1 1	
Spain	SL	late stage	2.7	0.45	1	

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of supervised residue trials on crops are shown in Tables 27-31. Residues, application rates and spray concentrations have been expressed as maleic hydrazide and have generally been rounded to two significant figures or, for residues below 0.1 mg/kg, to one significant figure. Only when residues were detected in control samples are they recorded in the Tables. Multiple values from single trials are from replicate field samples. Underlined residue values were used for the estimation of maximum residue levels and/or STMRs.

Bulb vegetables

Garlic. Critical GAP: 1 x 2.4 kg ai/ha, PHI 10 days (France). One trial was conducted in France in 1992 with single applications of maleic hydrazide at either 2.4 or 3.6 kg ai/ha (Table 27).

Table 27. Residues of maleic hydrazide in garlic, France.

Year	Application				PHI, days	Residues, mg/kg	Reference, analytical method
	Form	No	kg ai/ha	kg ai/hl			
1985	600 SG	1	2.4		10 30 (S) 60 (S) 90 (S)	 5.5 7.0 5.0	Anon., 1990a; (S) = Storage, days, before analysis no information on analytical method
1992	600 SG	1 1	2.4 3.6		7 7 control	2.4, 2.7 5.4, 6.3 0.22, 0.13	Anon., 1993a; GLC

Shallots. Critical GAP: 1 x 2.4 kg ai/ha, PHI 10 days (France). Five trials were conducted in France (1998-1992). In the trial in 1988, samples were analysed by GLC and by a colorimetric method. In three of the trials the samples were analysed or re-analysed after storage for 5-11 months (Table 28).

Table 28. Residues of maleic hydrazide in shallots, France, 1988-92.

Year	Application				PHI, days	Residues, mg/kg	Reference, remarks analytical method
	Form	No	kg ai/ha	kg ai/hl			
1988	600 SG	1	2.4		5 17 18 19 28	9.5 (8.4) 2.4 (5.0) 8.5 (6.3) 10 (7.0) 2.6 (4.1)	Anon., 1989b, 1993b,c GLC () 2nd analysis colorimetric

Year	Application				PHI, days	Residues, mg/kg	Reference, remarks analytical method
	Form	No	kg ai/ha	kg ai/hl			
1989	600 SG	1	2.4		52 (S) 240 (S)	7.6 4.0	Anon., 1990a; (S) = Storage, days, before analysis no information on analytical method
		1	2.4		52 (S) 240 (S)	11 2.8	
		1	2.4		52 (S) 240 (S)	8.6 4.0	
1990, site 1	600 SG	1	2.4	0.3	18 150 (S) 270 (S) 330 (S)	 14 <0.1 8.7	Anon., 1990b; (S) = Storage, days, before analysis No information on analytical method
		1	2.4		26 150 (S) 270 (S) 330 (S)	 13 14 13	
		1	2.4		35 150 (S) 270 (S) 330 (S)	 5.0 20 10	
1990, site 2		1	2.4	0.3	21 150 (S) 270 (S) 330 (S)	 13 <0.1 4.9	Anon., 1990b; (S) = Storage, days, before analysis no information on analytical method
		1	2.4		30 150 (S) 270 (S) 330 (S)	 <0.5 <0.5 <0.5	
		1	2.4		38 150 (S) 270 (S) 330 (S)	 7.0 21 4.2	
1992	600 SG	1	2.4	0.48	7	2.6, 3.9 4.0, 4.2 4.3, 4.5	Anon., 1993b, c; GLC
		1	3.6	0.72	7	7.7, 7.9 5.7, 7.8 6.9, 7.1	

Onions. Critical GAP: 1 x 3.0 kg ai/ha, PHI 4 days (UK). The results of trials in France, The Netherlands, the UK and the USA are shown in Table 29.

Table 29. Residues of maleic hydrazide in onions. The results in parentheses are suspect.

Country Year	Application				PHI, days	Residues, mg/kg	Reference, remarks, analytical method
	Form	No	kg ai/ha	kg ai/hl			
UK, 1983	600 SG	1	2.3	0.75	15	<0.5, 0.8, 3.6, 3.7	Tomkins, 1983 Colorimetric
	180 SL	1	2.3	0.75	15	3.0, 3.4, 6.2, 7.5	

Country Year	Application Form	No	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference, remarks, analytical method
UK, 1984	600 SG	1	2.1	1.5	(21 25	2.8) (control 3.7) 2.7	Tomkins, 1984 Colorimetric SG and SL were applied to separate plots in the same trial
	SL	1	3.0	1.5	(21 25	4.0) (control 3.7) 2.2	
UK, 1985	600 SG	1	3.0	0.75	(23 (128 S 12 129 (S) 212 (S)	16) 4.9) (control 20) 5.5 7.0 7.7	Tomkins, 1985a Colorimetric (S) = Storage, days, before re-analysis Samples at days 12, 129, 212 are replicates
UK, 1993	800 SG	1 1	2.4 3.6		7 7	2.7,4.6, 4.8 5.9, 6.4, 7.0	Anon., 1993d, 1994 GLC
USA, 1992 CA OR (No1) OR (No2) OR (No3) WA ID CO (No1) CO (No2) CO (No3) TX MI (No1) MI (No2) NY (No1) NY (No2) NY (No3)	269SL	 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	 2.2 2.2 2.2 2.2 2.2 2.2 2.2 2.2 2.2 2.2 2.2 2.2 2.2 2.2 2.2 2.2	 0.19 0.76 0.77 1.5 0.77 0.24 0.19 0.19 2.4 0.24 0.19 0.19 0.24 1.9 0.24	 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10	 1.0 6.3 0.38 0.40 1.1 4.0 0.95 0.89 1.3 0.94 4.3 3.9 3.0 4.8 7.5	Jacobson and Wight, 1992a Colorimetric
Netherlands 1977		1 1	2.3 2.3	0.46 0.46	35 191 (S) 39 187 (S)	3.8 3.7 4.2 3.4	Olthof, 1998 Colorimetric (S) = Storage, days, before analysis
Netherlands 1989	180 SL	1 1 1	1.1 1.1[1] 1.1[2]	0.22 0.22 0.22	29 29 29	0.38,0.43 1.1, 1.2 0.50,0.84	Pritchard, 1993 GLC
		1 1 1	1.6 1.6[1] 1.6[2]	0.32 0.32 0.32	29 29 29	7.3, 11 2.0, 2.0 1.6, 1.9	
		1 1 1	2.3 2.3[1] 2.3[2]	0.45 0.45 0.45	29 29 29	1.6, 4.9 0.84, 3.2 2.1, 3.1	
Netherlands 1990	180 SL	1 1 1	1.1 1.1[1] 1.1[2]	0.22 0.22 0.22	21 21 21	1.2, 1.3 0.15,0.68 0.43,0.51	Pritchard, 1993 GLC
		1 1	1.6 1.6[2]	0.32 0.32	21 21	0.51,0.54 0.68,1.4	
		1 1	2.3 2.3[2]	0.45 0.45	21 21	2.1, 2.8 1.6, 1.7	
	un- known	1 1 1	4[3] 6[3] 8[3]		21 21 21	0.73,0.78 0.93, 2.3 0.76, 1.4	
Netherlands 1991	600 SG	1 1	1.5 1.5[1]	0.3 0.3	30 30	0.54,0.92 0.84, 1.5	Pritchard, 1993 GLC
		1 1	2.4 2.4[1]	0.48 0.48	30 30	0.62, 1.7 2.4, 5.4	

Country Year	Application				PHI, days	Residues, mg/kg	Reference, remarks, analytical method
	Form	No	kg ai/ha	kg ai/hl			
	180 SL	1 1 1	1.1 1.1[1] 1.1[1]	0.22 0.22 0.22	30 30 30	0.49,0.61 0.75,1.2 0.43,0.92	
		1 1 1	1.6 1.6[1] 1.6[2]	0.32 0.32 0.32	16 30 16 30 30	2.4, 3.3 0.36,0.83 1.1, 1.6 0.47, 1.8 0.82, 1.3	
		1 1 1	2.3 2.3[1] 2.3[2]	0.45 0.45 0.45	16 30 16 30 30	0.61,<u>2.4</u> 1.0, 1.7 2.0, <u>2.3</u> 1.0, 2.3 1.5, 7.8	
	un- known	1 1 1	4[3] 6[3] 8[3]		30 30 30	0.55, 1.0 1.1, 2.2 0.95, 4.0	
France, 1987	600 SG	1	2.4	0.48	8 150 (S) 210 (S) 8 150 (S) 210 (S) 13 150 (S) 210 (S)	 9.0 0.05 5.3 0.41 5.0 0.25	Anon., 1987 analytical method: no information PHI 8 or 13 days, (S) = Storage, days, before analysis
France, 1992	600 SG	1 1	2.4 3.6	0.48 0.72	7 7	0.1, 0.17 3.4, <u>3.7</u> 2.9, 3.5 3.3, 3.8 4.8, 5.0 3.3, 4.0	Anon., 1993b,c; GLC

[1] + Surfactant Primawett (0.125 l)
[2] + Surfactant Exell (0.5 l)
[3] 4, 6 and 8 kg of formulated product “Allirem”. No further information

<u>Root and tuber vegetables</u>

<u>Carrots</u>. Critical GAP: 1 x 2.2 kg ai/ha, PHI 14 days (Denmark). No residue data were received.

<u>Parsnips</u>. No information on GAP was received. Residue trials were carried out in the UK (Table 30).

Table 30. Residues of maleic hydrazide in parsnips.

Country Year	Application Form	No	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference, remarks analytical method
UK, 1987	600 SG	1	3.0 3.0 6.0 9.0	0.9 1.2 1.8 2.7	23 23 23 23	19 (2) 26, 27 13, 45 31, 45	Tomkins, 1987 Colorimetric method

Potatoes. Critical GAP: 1 x 3.1 kg ai/ha, PHI 14 days (Denmark). Residue trials were conducted in the UK and the USA (Table 31).

Table 31. Residues of maleic hydrazide in potatoes.

Country Year	Application Form	No	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference, remarks analytical
UK, 1982 Cambridge- shire, site 1	600 SG	1	3	0.75	unknown 0 (S) 30 (S) 90 (S) 180 (S)	 14 15 6.8 7.2	Anon., 1983 Colorimetric PHI unknown (S) = storage, days, before analysis
UK, 1982 Cambridge- shire, site 2	600 SG	1	3		unknown 0 (S) 30 (S) 90 (S) 180 (S)	 22 29 14 17	Anon., 1983 Colorimetric PHI unknown (S) = storage, days, before analysis
UK, 1982 Essex	600 SG	1	3		unknown 0 (S) 30 (S) 90 (S) 180 (S)	 17 13 13 12	Anon., 1983 Colorimetric PHI unknown (S) = storage, days, before analysis
UK, 1982 Kent, site 1	600 SG	1	3		unknown 0 (S) 30 (S) 90 (S) 180 (S)	 10 15 11 7.7	Anon., 1983 Colorimetric PHI unknown (S) = storage, days, before analysis
UK, 1982 Kent, site 2	600 SG	1	3		unknown 0 (S) 30 (S) 90 (S) 180 (S)	 8.2 8.6 4.7 7.9	Anon., 1983 Colorimetric PHI unknown (S) = storage, days, before analysis
UK, 1982 Midlands	600 SG	1	3	2.3	unknown 0 (S) 30 (S) 90 (S) 180 (S)	 25 34 14 13	Anon., 1983 Colorimetric PHI unknown (S) = storage, days, before analysis
UK, 1985 Worcester- shire	600 SG	1 1 1 1 1 1	 0.5 0.5 0.5 0.5 0.5 0.5		28 150 (S) 32 150 (S) 150 (S) 150 (S) 150 (S) 150 (S)	 5.3 1.0 1.6 2.7 2.1 2.2	Anon., 1985 Colorimetric (S) = storage, days, before analysis

Country Year	Application				PHI, days	Residues, mg/kg	Reference, remarks analytical
	Form	No	kg ai/ha	kg ai/hl			
UK, 1985 Cambridge-shire, site 1	600 SG	1 1	3 3	9.1 aerial 0.66 ground	36 166 (S) 36 180 (S)	7.0 4.6 8.5 7.0	Tomkins, 1985b Colorimetric (S) 5 = storage, days, before re-analysis
UK, 1985 Cambridge-shire, site2	600 SG	1	3	0.75 ground	53 170 (S)	14 12	
UK, 1985 Cambridge-shire	600 SG	1 1	3 3	9.1 aerial 0.66 ground	36 166 (S) 36 180 (S)	4.8 2.3 11 7.3	
UK, 1985 Notting-hamshire	600 SG	1	3	1.1 ground	34 170 (S)	29 36	
UK, 1985 Lincoln-shire, site 1	600 SG	1 1	3 3	9.1 aerial 0.53 ground	40 162 (S) 40 180 (S)	12 16 8.0 9.5	
UK, 1985 Lincoln-shire, site 2	600 SG	1	3	0.75 ground	40 180 (S)	3.9 3.0	
UK, 1985 Lincoln-shire, site 3	600 SG	1	3	0.75 ground	55 182 (S)	14 12	
UK, 1985 Lincoln-shire, site 4	600 SG	1	3	0.75 ground	48 182 (S)	6.5 11	
UK, 1985 Norfolk	600 SG	1	3	1.5 ground	40 197 (S)	16 15	
UK, 1985 Derby, site2	600 SG	1	3	1.4 ground	32 control 170 (S) control	20 4.2 12 10	
UK, 1985 Derby, site1	600 SG	1	3	0.67 ground	21 162 (S)	8.9 19	
UK, 1991 York	600 SG	1	3	0.67	45	5.5[1] 4.7[2]	Anon., 1991 [1] GLC [2] Colorimetric
UK, 1991 Lincolnshire	600 SG	1	3	0.75	41	8.7[1] 5.4[2]	
UK, 1991 Doncaster	600 SG	1	3	0.75	42	9.5[1] 6.5[2]	
UK, 1991 Cambridge-shire, site 1	600 SG	1	3	0.75	23	9.5[1] 8.4[2]	
UK, 1991 Cambridge-shire, site 2	600 SG	1	3	0.75	69	11[1] 9.4[2]	
UK, 1991 Cambridge-shire, site 3	600 SG	1	3	0.77	57	14[1] 11[2]	
UK, 1993 Gloucester-shire, 2 sites	134 SL	1 1	3.1 3.1	0.78 0.78	28 29	13 9.3	Patel, 1994 GLC

Country Year	Application				PHI, days	Residues, mg/kg	Reference, remarks analytical
	Form	No	kg ai/ha	kg ai/hl			
UK, 1992 Kent, 2 sites	600 SG	1 1	3 3	0.86 0.86	30 30	5.7 4.3	Knight, 1994 GLC
UK, 1992 Doncaster	600 SG	1	3	0.6	44	8.7	
UK, 1992 York	600 SG	1	3	0.67	68	10	
UK, 1992 Northamp-tonshire	600 SG	1	3	0.75	55	5.9	
UK, 1992 Suffolk	600 SG	1	3		32	13	
USA, 1991 CA	269 SL	1	3.4	0.8	21	2.7, 3.8, 12	Jacobson and Wight, 1992b Colorimetric
OR		1	3.4	1.1	21	5.2, 6.4, 1.7	
WA (No 1)		1	3.5	1.1	21	11, 15, 20	
WA (No 2)		1	4.4	1.5	21	6.4, 8.4, 15	
WA (No 3)		1	3.0	3.6	21	<1.2, 2.3, 3.0	
ID (No 1)		1	3.3	1.2	21	18, 22, 26	
ID (No 2)		1	3.4	1.2	21	7.7,11, 11	
ID (No 3)		1	3.1	3.6	21	6.5, 8.5, 9.1	
ND		1	2.9	1.2	21	13,26,36	
WI		1	3.4	0.98	21	<1.2, 2.6, 2.7	
MI		1	3.4	1.0	21	10, 15, 15	
NY		1	3.4	1.2	21	15, 20, 35	
ME		1	3.4	1.2	21	34, 48, 61	
ME		1	3.4	3.6	21	36, 41, 41	

Animal products

Feeding studies with unlabelled maleic hydrazide were not reported but metabolism studies on cows (Jackson and Hall, 1992a) and hens (Jackson and Hall, 1992b) were conducted for 28 days with dosing at 0.45, 1.35 or 4.5 mg/kg bw/day. Residues of maleic hydrazide reached a plateau in the milk after 3-4 days of 0.02 mg/kg and in eggs after 5-8 days of 0.01-0.02 mg/kg.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

The post-harvest storage stability of maleic hydrazide was determined in shallots, onions and potatoes. The storage conditions were not reported in detail for most of the trials but were equivalent to commercial practice. The results are shown above in Tables 28, 29 and 31.

Shallots. Table 28 includes 3 storage trials for 8 months (Anon., 1990a) and 6 for 5, 9 or 11 months (Anon., 1990b).

Onions. Table 29 includes 1 storage trial for 5 months (Tomkins, 1985a), 2 for 6 months (Olthof, 1998) and 3 for 5 -7 months (Anon., 1987).

Potatoes. Table 31 includes 17 storage trials for 6 months (Anon., 1983; Tomkins, 1985b).

In a storage study by Dykeman (1993d) potatoes were sprayed at an application rate of 4.4 kg ai/ha and harvested 21 days later. Samples were placed in refrigerated storage for 1 year. The recorded temperatures were 7-12°C for 6 months and 3-9°C for 6 months. Residues of maleic hydrazide were determined by a colorimetric method (Table 32).

Table 32. Effect of refrigerated storage on residues of maleic hydrazide in potatoes (Dykeman. 1993d).

Storage period, months	Residues, mg/kg, in replicate samples			Mean, mg/kg (Std. Dev.)
	1	2	3	
0	30, 36	25, 26	33	30 (4.6)
1	23	24	20	22.3 (2.1)
3	25	26	30	27 (2.6)
6	21	17	18	18.7 (2.1)
12	16	17	17	16.7 (0.58)

Byast (1988) determined the residues of maleic hydrazide in peeled tubers and potato peels before and after storage for 1 year (Table 33). T-tests to compare the means of fresh and stored samples revealed no significant differences among the means. The residues were determined by the HPLC method of Newsome (1980).

Table 33. Residues of maleic hydrazide in peeled potatoes and peels at harvest an after 1 year storage (Byast, 1988).

Field site (UK)	Sample	No. of samples	Mean residues, mg/kg	
			at harvest	after storage
Scott	Peeled tubers	3	8.0	8.9
	Peels	3	4.4	1.8
Renshaw	Peeled tubers	3	11	16
	Peels	3	7.5	6.9
Richardson	Peeled tubers	3	8.8	8.4
	Peels	3	5.2	4.8
Hay	Peeled tubers	3	10	7.7
	Peels	3	3.9	2.5
Greens	Peeled tubers	3	3.6	3.8
	Peels	3	1.4	2.6

In processing

Potatoes from supervised trials carried out in the UK (Table 31) were processed. Analyses were by the GLC method of King (1983).

(Anon., 1991). For boiling, whole potatoes were washed in flowing water for 2 min at room temperature, steam peeled, mechanically sliced and boiled for 5 min at 100°C. For crisping, whole potatoes were washed for 2 min, steam peeled, mechanically chipped, blanched at 80°C for 1.5 min and fried for 9 min at 180°C.

(Patel, 1994). Whole potatoes were washed for 2 min at room temperature, pricked with metal forks and microwaved in ½ kg batches for 15 min at 1800 watts.

(Knight, 1994). To produce baked potatoes, whole potatoes were washed in flowing water for 2 min at room temperature and baked in 12 kg lots in electric ovens for 80 min at 200°C. For crisping, whole tubers were washed for 2 min, steam peeled, re-washed for 3 min, mechanically sliced, blanched in water at 80°C for 1.5 min and fried in 1 kg lots for 9 min at 180°C. Chips were produced similarly, but fried in 4 kg lots in fresh oil for 10 min at 180°C.

The results are shown in Table 34. The mean processing factors were boiled tubers 0.52, microwaved tubers 1.2, baked tubers 1.35, crisps 0.0265 and chips 0.92.

Table 34. Processing studies on potatoes.

Ref.	Sample	Residues, mg/kg	Processing factor
Anon., 1991	RAC	5.5	
	boiled tuber	3.5	0.64
	RAC	8.7	
	boiled tuber	3.5	0.40
	RAC	9.5	
	Crisps	0.23	0.02
	RAC	9.5	
	Crisps	0.33	0.03
	RAC	11	
	Chips	15	1.36
	RAC	14	
	Chips	13	0.92
Patel, 1994	RAC	13	
	microwaved tuber	16	1.23
	RAC	9.3	
	microwaved tuber	11	1.18
Knight, 1994	RAC	5.7	
	baked tuber	4.5, 7.1, 7.3, 9.5	0.79, 1,2, 1.3, 1.7
	RAC	4.3	
	baked tuber	4.4, 6.3, 6.6, 7.8	1.02, 1.5, 1.5, 1.8
	RAC	8.7	
	Crisps	<0.1, 0.18, 0.38, 0.64	<0.01, 0.02, 0.04, 0.07
	RAC	10	
	Crisps	0.26, 0.29	<0.01 (2), 0.026, 0.029
	Chips	7, 10, 11, 12	0.7, 1, 1.1, 1.2
	RAC	5.9	
	Chips	4.7, 5.5,	0.8, 0.92, 0.93, 1.05

Ref.	Sample	Residues, mg/kg	Processing factor
		5.4, 6.2	
	RAC	12.8	
	Chips	7.6, 9.3, 10 (2)	0.59, 0.73, 0.78 (2)

Jacobson and Wight (1992c) carried out trials in the USA. The potatoes were sprayed with 3.4 kg ai/ha and tubers were harvested after a PHI of 21 days. The samples were steamed-peeled and washed. 18 and 56 kg were used for producing chips and potato granules respectively. The wet peel was dried. The RAC and peel samples were analysed by the colorimetric method after distillation and the processed fractions by HPLC with electrochemical detection (Table 35). The processing factors for producing granules and chips were 3-4, notably higher than the processing factors for chips in the studies summarized in Table 34.

Table 35. Processing studies on potatoes (Jacobson and Wight, 1992c).

Location	Sample	Residues, mg/kg	Processing factor
Washington	RAC[1]	5.4	
	RAC[2]	7.4	
	Wet peel	1.5	0.2
	Dry Peel	23	3.1
	Granules	29	3.9
	Chips	22	2.97
North Dakota	RAC[1]	23	
	RAC[2]	19	
	Wet peel	3.2	0.17
	Dry Peel	64	3.4
	Granules	70	3.7
	Chips	63	3.3

[1]Samples collected and frozen at harvest
[2]Sampled after cool storage immediately before processing. Processing factors derived from these residues

Byrd and Patel (1992) processed potatoes to crisps. The frozen tubers were thawed for 18 hours at room temperature, washed in flowing water for 2 min, peeled, mechanically chipped, blanched at 80°C for 1.5 min and fried for 9 min at 180°C in vegetable oil. The residues (Table 36) were determined by the GLC method of King, 1983.

Table 36. Processing studies on potatoes (Byrd and Patel, 1992).

Sample	Sample weight, kg	Residues		Processing Factor
		mg/sample	mg/kg	
Raw potato	5.74	5.47	31.4	
Thaw water	0.3	30.9	9.3	
Washed potato	5.5	8.25	45.4	1.4
Peeled potato	4.9	8.76	42.9	1.3
Peel	0.5	0.44	0.2	0.006
Water from peeling	100	0.25	25	
Sliced potato	4.8	2.18	10.5	0.33
Holding water	16	1.79	28.6	
Blanched potato	4.85	0.50	2.4	
Blanch water	15	1.8	27	
Cooling water	65	0.31	20.1	

Sample	Sample weight, kg	Residues		Processing Factor
		mg/sample	mg/kg	
Crisps	0.55	0.33	0.18	0.0057
Oil	18.4	0.30	5.52	

Residues in the edible portion of food commodities

Residues in peeled potato tubers are included in the processing studies described above. All the other residues reported in the Tables of supervised trials were in the edible fractions. No other studies of residues in edible portions of commodities were reported.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Data on residues in ware potatoes (Table 37) were received from The Netherlands (Olthof, 1998).

Table 37. Residues of maleic hydrazide in potatoes in commerce; Netherlands, 1996.[1]

Samples analysed	Samples whithout residues (LOD = 1 mg/kg)	Samples with residues <MRL	Samples with residues >MRL	MRL,mg/kg
43	42	1	-	50

[1] Report AM9511GF7 (1997), Inspectorate of Public Health, Amsterdam, The Netherlands

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported to the Meeting.

Country	Definition of the residue	Commodity	MRL, mg/kg
European Union		Carrots Spring onions Other bulb vegetables Early potatoes Ware potatoes Other fruit and vegetables	0.2* 0.2* 10 1* 50 1*
Germany	Maleic hydrazide and its conjugates, expressed as maleic hydrazide	Bulb vegetables except spring onions Stored potatoes Other food of plant origin	10 50 1
Netherlands	Maleic hydrazide	Garlic Onions Shallots Ware potatoes Other food commodities	10 10 10 50 1*
Poland	Maleic hydrazide	Onion. Bulb Other food commodities of plant origin	10 1

* at or about the LOD

APPRAISAL

Maleic hydrazide (6-hydroxy-2*H*-pyridazin-3-one) was first reviewed in 1976. At the request of the manufacturer, it was scheduled for the CCPR Periodic Review Programme. Its toxicology was evaluated in 1996 and it is now evaluated for residues.

The Meeting received information on animal and plant metabolism, environmental fate, analytical methods, updated GAP, supervised residue trials and the effect on residues of processing.

Maleic hydrazide is a plant growth regulator. It is formulated (as the potassium salt) as dispersible granules (SG, GR) and as liquid formulations (SL, SC). It main uses are for suppression of sprouting in stored potatoes and bulb vegetables, the control of suckers on tobacco and of volunteer potatoes in following crops and as a grass growth retardant in non-crop situations.

The absorption, distribution, metabolism and excretion of [^{14}C]maleic hydrazide has been studied in rats, rabbits, cows, a goat and hens.

Maleic hydrazide was well absorbed when administered orally to rats. Elimination was rapid and mainly via the urine (77-87% of the administered dose). Elimination via the faeces and expired CO_2 was less than 14% and 0.5% respectively. Very low levels of the test material were found in the carcase (<0.5% of the dose). No differences in the rate or route of elimination were noted between males and females. The major urinary component was maleic hydrazide (45-70%) and a minor metabolite was tentatively identified as its sulfate conjugate.

Maleic hydrazide was absorbed through rabbit skin at a rapid rate after a 4-hour topical exposure. The absorbed radioactivity was rapidly eliminated, almost entirely in the urine and in most cases during the first 24 hours after application. Approximately 90% of the urinary radioactivity excreted in the first 24 hours was identified as maleic hydrazide. The total dermal absorption of the radiolabelled material was calculated to be 26% of the total applied dose in males and 40% in females.

Most of the total radioactive residue (TRR) in cows dosed with [^{14}C]maleic hydrazide at 3 levels (0.45, 1.36, 4.5 mg/kg bw/day) was found in the kidneys. In milk, radioactive residues reached a plateau after 3-4 days of treatment, at a level of 0.02 mg/kg in the low-dose group. Radioactive residues in the low-dose animals were 0.34 mg/kg in the kidneys and ranged from <0.05 mg/kg in the fat and muscle to 0.08 mg/kg in the liver.

In a goat [^{14}C]maleic hydrazide was excreted in the urine (approximately 63% of the administered dose), faeces (23%) and milk (0.13%). Only 0.06% of the administered dose was recovered from the tissues (fat, muscle, kidneys, liver, blood and bile). Most of the radioactivity in the tissues and milk was in a conjugate, which was hydrolysed to maleic hydrazide and 2 relatively nonpolar compounds. One of these, observed in the liver, muscle and fat, co-chromatographed with fumaric acid. The residues of the parent before hydrolysis were 0.11 mg/kg in milk, 0.03 mg/kg in muscle and undetectable in the kidneys, liver and fat. More maleic hydrazide was identified after enzymatic hydrolysis in the milk (0.38 mg/kg) and after acid hydrolysis in the tissues (kidneys 0.96, liver 0.16, muscle 0.15 and fat 0.05 mg/kg).

Maleic hydrazide was rapidly metabolized by hens. Approximately 98% of the administered ^{14}C was recovered in the excreta within 24 hours after dosing laying hens for 3.5 days. Maleic hydrazide was the major component of egg yolk (0.18 mg/kg, 69% of the TRR) but was not present in muscle. An unidentified nonpolar metabolite was the major component of the residue in the liver (60% of the TRR) and was also present in the kidneys, muscle, egg white and egg yolk. Mass spectrometry of the nonpolar metabolite isolated from egg white indicated that it was a conjugate of a methylated maleic hydrazide. A polar compound was present in the kidneys and eggs. After acid

treatment, the level of this compound in extracts decreased, with a corresponding increase in maleic hydrazide and some unidentified compounds.

Six hens were dosed daily for 28 days with [^{14}C]maleic hydrazide at 1, 3 and 10 mg/kg bw/day. The TRR reached a plateau in egg whites after 5 days of administration and in egg yolks after about 8 days. The plateau levels in egg whites and yolks were 0.01-0.02 mg/kg from the low dose, 0.05-0.07 mg/kg from the mid dose and 0.19-0.23 mg/kg from the high dose. The highest TRR was observed in the kidneys (0.06 mg/kg in the low-dose group) and the lowest in abdominal fat (0.006 mg/kg in the low-dose group). Radioactive residues in muscle, liver and skin were 0.01 to 0.02 mg/kg from the low dose.

Information on the metabolism of maleic hydrazide in plants was provided for potatoes and onions. Maleic hydrazide is rapidly absorbed by foliage and translocated to growing shoots and roots.

Approximately 99% of the radioactivity in potato plants harvested 1 hour after treatment was in the vines. In plants harvested 8 weeks after treatment 61% was in the tubers. Most of the TRR in potato tubers consisted of maleic hydrazide (52-84%), with lower levels of a glucose conjugate (6.4-13%).

Leaves of onions harvested 1 hour after treatment contained approximately 87% of the total radioactivity. At 2 weeks after application, the levels of radioactivity in the bulbs were about 10 times those at the first harvest. The residues in the methanol-extractable fraction were identified as maleic hydrazide (no glucose conjugate was identified).

Maleic hydrazide is degraded rapidly in soil and is efficiently mineralized to CO_2 under aerobic conditions (half-life 11 hours). Degradation proceeds via the initial formation of maleamide resulting from the elimination of one of the nitrogens, followed by further conversion to maleamic acid, maleic and fumaric acids which will yield lactic acid and succinic acid and finally CO_2. Most of the radioactivity remaining in the soil is in the form of firmly bound residues. Maleic hydrazide has a high leaching potential but if it is allowed to age for a number of days after application it will be degraded rapidly and bind strongly to the soil, which will minimize leaching. The dissipation of maleic hydrazide in the environment is attributed to both aerobic and anaerobic degradation. Photolysis and hydrolysis may make limited contributions.

In a metabolism study on rotational crops wheat was planted 30 and 92 days after treatment of the soil with [^{14}C]maleic hydrazide in the field. Total radioactive residues in wheat forage, grain, chaff and straw ranged from 0.02 mg/kg to 0.29 mg/kg expressed as maleic hydrazide. The residues were too low to permit identification.

A further rotational wheat study showed that the residues in the grain are incorporated into glucose or associated with protein.

Analytical methods for total residues of maleic hydrazide in plants are based on reduction with zinc and hydrolysis in hot alkali to hydrazine. The hydrazine is isolated by distillation and determined colorimetrically as the azine by the addition of *p*-dimethylaminobenzaldehyde. These procedures are useful for determining total maleic hydrazide. The LOD for onions was 1 mg/kg.

Maleic hydrazide and its ß-D-glucoside can be determined by HPLC. Both maleic hydrazide and the glucoside are extracted from plant tissue with methanol and the extract is concentrated. Maleic hydrazide and the glucoside are cleaned up separately by passage through different cation-exchange columns. The glucoside is then hydrolysed with ß-glucosidase and maleic hydrazide is determined by HPLC with detection by light absorption at 313 nm. The average recovery of maleic

hydrazide from beets, carrots, potatoes and turnips fortified at 1 to 50 mg/kg was 87%. The LOD was 1 mg/kg. The same average recovery of the glucoside was obtained at levels from 2 to 50 mg/kg.

A gas-chromatographic method involves oxidation of maleic hydrazide with aqueous lead dioxide to 3,6-pyridazinedione in the presence of cyclopentadiene. The reaction product is determined by GLC with an ECD. The mean recovery of maleic hydrazide (as the Diels-Alder adduct) from potato samples fortified at 0.1, 0.5, 1, 5 and 10 mg/kg was 92% and the coefficient of variation was 3.1%. The limit of determination was 0.1 mg/kg. This method quantifies free extractable maleic hydrazide but not its conjugates.

An enzyme immunoassay based on two monoclonal antibodies specific for maleic hydrazide has been developed but the method has not been validated for plant samples.

HPLC with electrochemical detection has been used for the determination of maleic hydrazide in soil and water. The LODs were 0.005 mg/kg for soil and 0.0001 mg/l for water.

Proteolytic enzymes have been employed to solubilize maleic hydrazide from its bound residues in animal products, which occur as glucuronide and sulphate conjugates. Both types of conjugate will release maleic hydrazide on acid hydrolysis, so methods for the analysis of maleic hydrazide are also suitable for some of its conjugates if these are first hydrolysed. In view of the susceptibility of both conjugates to hydrolysis, it was assumed that maleic hydrazide glucoside would serve as a standard for the validation of methods for the glucuronide and sulphate conjugates. The extracted maleic hydrazide was analysed by HPLC with UV detection. Recoveries at fortification levels of 0.2 mg/kg of maleic hydrazide and its glucose conjugate (expressed as maleic hydrazide) were 90-114% for cow milk, 72-94% for liver and 68-80% for eggs.

The Meeting noted that the method was validated by fortifying animal products with the glucoside conjugate of maleic hydrazide, a plant metabolite. Furthermore, metabolism in goats indicated that a large proportion of conjugated metabolites were not released by acid hydrolysis. The Meeting could not confirm the validity of the method, based on HCL/pepsin hydrolysis, for residues in animal products arising from residues in feed.

In a study of the storage stability of maleic hydrazide and its metabolites in milk at -20°C, 33 and 22% of the applied radioactivity was identified as 3-pyridazinone after 1 and 18 months storage respectively.

Information was submitted on the stability of maleic hydrazide residues in stored analytical samples of potatoes and onions. The Meeting concluded that the compound is stable for at least six months in potatoes and onions.

The metabolism studies with a root or tuber vegetable (potato) and a bulb vegetable (onion) showed that the metabolic pattern is similar in these crops. Maleic hydrazide is degraded slowly in plants and is the major residue identified in studies of plant metabolism. Maleic hydrazide glucoside was the main metabolite in potatoes (6-13% of the total ^{14}C) and did not occur in onions.

The Meeting concluded that the definition of the residue in plants for compliance with MRLs and for the estimation of dietary intake should be maleic hydrazide *per se.*

For animal products an appropriate definition would be the sum of free and conjugated maleic hydrazide, but metabolism in goats produced a large proportion of conjugated metabolites from which the exocons were not released by acid hydrolysis.

In a storage stability study of maleic hydrazide and its metabolites in milk, 3-pyridazinone accounted for 33 and 22% of the applied radioactivity after 1 and 18 months storage but the relevance of free and conjugated pyridazinone to the definition of the residue could not be estimated from the data submitted. Furthermore, no validated analytical method for the metabolites, including pyridazinone, is available. From the limited data reported the Meeting could not recommend a definition of the residue in animal products.

The octanol/water partition coefficient of maleic hydrazide at natural pH (log P_{OW} = –0.68 at pH 5 and –2.01 at pH 7) shows that the compound is hydrophilic. The Meeting concluded that the compound is not fat-soluble.

Information was made available to the Meeting on registered uses of maleic hydrazide and on supervised residue trials on garlic, shallots, onions and potatoes.

Garlic, shallots and bulb onions. The reported GAP is 1 x 2.3-3.0 kg ai/ha, with PHIs (days) of 4 or 7 in the UK, 10 in France, 15 in Greece and 28 in The Netherlands. Labels give the following directions.

Apply one or two weeks before harvest and not later than 50% necking.
Do not apply less than one week before harvesting.
Avoid spraying edible onions too early, if spraying is done earlier than two weeks before maturity, spongy bulbs may result.

One trial on garlic (1 x 2.4 kg ai/ha, PHI 10 days) approximated French GAP (1 x 2.4 kg ai/ha, PHI 10 days). The residues in duplicate samples were 2.4 and 2.7 mg/kg. In one further trial, residues of 5.0 to 7.0 mg/kg were determined after storage times of 30-90 days, but no information on the analytical method used was available.

Five trials on shallots in France were carried out at the registered application rate of 1 x 2.4 kg ai/ha. In two of them, the residues were 9.5 and 4.5 mg/kg after PHIs of 5 and 7 days. No information on the analytical method used was available for the other trials.

Seven residue trials on onions were carried out in the UK (1 x 2.1-3.6 kg ai/ha, PHI 7-25 days). Ten of 37 Dutch trials were at approximately the registered application rate (1 x 2.3 kg ai/ha), but the PHIs ranged from 16 to 39 days. Three French trials at 1 x 2.4-3.6 kg ai/ha were reported. Fifteen trials were conducted in the USA (1 x 2.2 kg ai/ha, PHI 10 days), but no GAP was reported.

In general, the residues after short and long PHIs were of the same order, as the decrease of the residues is offset by translocation of the compound from the onion tops to the bulbs and the uptake of residues by roots from the soil. No degradation of residues was observed after storing bulbs for 5-11 months after harvest.

Because the use pattern and growing conditions of bulb onions, garlic and shallots are alike, the Meeting agreed to extrapolate the residue data for onions (application 1 x 2.3-3 kg ai/ha) to garlic and shallots.

On the basis of the label recommendation that application should be at the earliest two and at the latest one week before harvest, the residues at PHIs from 5 to 17 days were used for the evaluation. In the case of replicates, only the highest result was selected. The residues in onions, shallots and garlic in rank order were 2.3, 2.4, 2.7, 3.7, 3.7, 4.5, 4.8, 5.5, 7.5 and 9.5 mg/kg. The Meeting estimated STMRs of 4.1 mg/kg and maximum residue levels of 15 mg/kg for garlic, bulb onions and shallots. The estimate of 15 mg/kg confirms the current CXL for onion, bulb.

Potatoes. The reported GAP is 1 x 2.6-3.1 kg ai/ha, with PHIs of 14 days in Denmark and 21 days in France and the UK. The label recommendation for application states: "The last few flowers may still be apparent but most of the blossom will already have fallen. A few of the lowest leaves may be turning yellow but the haulm must be predominantly green and actively growing."

The label recommendation indicates that the PHI could range from about 4 to 10 weeks. The metabolism studies on potatoes show that the residue level in the tubers depends on the time available for translocation of maleic hydrazide from the treated leaves to the tubers, so the critical GAP should not be linked to the registered PHIs of 14 or 21 days.

A total of 14 trials were carried out in the USA (1 x 2.9-3.5 kg ai/ha, PHI 21 days) but no GAP was reported. A number of trials from 1985 to1992 in the UK complied with GAP (1 x 3.0 kg ai/ha). The residues in the tubers at PHIs from 21 to 69 days were 3.9, 4.3, 4.8, 5.5, 5.7, 5.9, 6.5, 7.0, 8.0, 8.5, 8.7, 8.7, 8.9, 9.3, 9.5, 9.5, 10, 11, 11, 12, 13, 13, 14, 14, 14, 16 and 29 mg/kg. In the 1985 trials the residues were determined again after storage for about six months. The residues in the stored samples were 2.3, 3.0, 4.6, 7.0, 7.3, 9.5, 11, 12, 12, 15, 16, 19 and 36 mg/kg.

In six trials in the UK in 1982 residues were measured during the storage of field-treated potatoes for 180 days. The field treatment complied with UK GAP but the PHIs were not reported. The residues in rank order at the four sampling intervals 0 days 8.2, 10, 14, 17, 22 and 25 mg/kg, 30 days 8.6, 13, 15, 15, 29 and 34 mg/kg, 90 days 4.7, 6.8, 11, 13, 14 and 14 mg/kg and 180 days 7.2, 7.7, 7.9, 12, 13 and 17 mg/kg. The median values were 15.5, 15, 12 and 9.95 mg/kg for the 0, 30, 90 and 180 days storage periods respectively.

The Meeting based its evaluation on the highest data population, the residues in stored potatoes in the 1985 UK trials, and estimated an STMR of 11 mg/kg and a maximum residue level of 50 mg/kg.

No residue data were reported on carrots.

Animal feeding studies

The exposure of farm animals to maleic hydrazide residues will arise from its use on potatoes with a maximum residue level of 50 mg/kg and an STMR of 11 mg/kg.

Dairy and beef cattle. Because the residue could not be satisfactorily defined the Meeting could not estimate maximum residue levels for cattle milk, meat or edible offal.

Poultry. A 28-day feeding study with [^{14}C]maleic hydrazide at dose levels of 1, 3 and 10 mg/kg bw/day was submitted. As potatoes are a minor feedstuff (less than 10% of diet, according to US data), the Meeting concluded that further studies and the estimation of maximum residue levels for residues in poultry commodities resulting from feed were not necessary.

Processing studies were conducted on potatoes in the UK to determine the effect of washing, peeling, microwave baking, oven baking, boiling and frying on residues of maleic hydrazide. Mean processing factors were 0.52 for boiling, 1.2 for microwave baking, 1.35 for oven baking, 0.0265 for frying crisps and 0.92 for frying chips. A further study in the USA showed a mean processing factor for granules and chips of 3.5 and for dry peels of 3.25. A third study demonstrated that washing and peeling do not reduce the residues (processing factors were 1.4 or 1.3).

Since washing, peeling and microwave or oven baking do not change the residue content substantially, the Meeting estimated only STMRs of 5.7 mg/kg (0.52 x 11) for boiled potatoes and 0.29 mg/kg for crisps (0.0265 x 11). As fried potatoes may be prepared in widely varying ways with

different processing factors (means 3.5 and 0.92 in the trials), the Meeting estimated STMRs for chips of 38.5 mg/kg (3.5 x 11) for US commercial practice and 10.12 (0.92 x 11) for UK commercial practice for the assessment of dietary intake.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting estimated the maximum residue levels and STMR levels listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue in plant commodities for compliance with MRLs and for estimation of dietary intake: maleic hydrazide.

Commodity		Recommendation		
CCN	Name	New	Previous	STMR, STMR-P
VA 0381	Garlic	15	-	4.1
VA 0385	Onion, Bulb	15	15	4.1
VR 0589	Potato	50	50	11
	Potato crisps			0.29
	Potato chips			38.5[1] 10.12[2]
	Potato, boiled			5.7
VA 0388	Shallot	15		4.1

[1]US commercial practice
[2]UK commercial practice

FURTHER WORK OR INFORMATION

Desirable

Further information on the nature of the residues in farm animals.

DIETARY RISK ASSESSMENT

The International Estimated Dieatary Intakes of maleic hydrazide for the five GEMS/Food regional diets based on the STMRs for garlic, bulb onions, shallots and boiled potatoes, were in the range of 1 to 8% of the ADI. The Meeting concluded that the intake of residues of maleic hydrazide resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

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MYCLOBUTANIL (181)

EXPLANATION

Myclobutanil was evaluated in 1992 and 1997. In 1997 the JMPR evaluated six field trials on hops conducted in the UK but the four trials which complied with GAP were considered insufficient to estimate a maximum residue level. Several post-harvest trials on bananas were according to proposed GAP, but since only proposed GAP was reported the 1997 Meeting could not estimate a maximum residue level. The present Meeting was informed that further trials in Germany were in progress which included processing studies, and that there was now registered GAP for bananas which would allow the recommendation of an MRL

The manufacturer requested the present Meeting to evaluate additional data on hops and re-evaluate the data on bananas in the light of the recently established GAP.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The analytical method used to determine myclobutanil and its hydroxy metabolite RH-9090 in hops in the trials reported to the present Meeting was described in the 1992 evaluation.

The method involves maceration with methanol or alkaline methanol followed by liquid-liquid partition with petroleum ether and hexane, then transfer into dichloromethane. The extracts are purified by silica gel, Florisil and/or C18 column chromatography, and the residues are determined by GLC with an ECD or NPD (Brackett, 1984). The method was validated for many plant commodities (Gilbert, 1998a)

The LOD was 0.02 mg/kg for green hops, spent hops, trubs and yeast, 0.5 mg/kg for dried hops and 0.01 mg/kg for beer. Mean recoveries for dried hops fortified with 0.5 to 5.0 mg/kg were 79% for myclobutanil and 88% for RH-9090, for spent hops at 0.02 to 2.0 mg/kg 76% and 84%, for green hops at 0.02 to 2.0 mg/kg 76% and 86%, and for beer at 0.02 to 2.0 mg/kg 83-101% and 76-92%.

USE PATTERN

The UK GAP for hops was recorded in the 1997 evaluation. The new GAP for bananas in Costa Rica was reported to the present Meeting and is shown in Table 1.

Table 1. Registered uses of myclobutanil on hops and bananas.

Crop	Country	Form.	Application				PHI, days
			Method	kg ai/ha	kg ai/hl	No.	
Banana	Costa Rica	WP	Spray/dip or cascade		0.02-0.04 (200-400 mg/l)		
Hops	UK	SC	F	0.045-0.135	0.0045	6	10

RESIDUES RESULTING FROM SUPERVISED TRIALS

Hops. Six trials in England were evaluated in 1997. The residues in the dried cones ranged from 0.3 to 1.2 mg/kg.

Eight supervised field trials were carried out in Germany in 1996 and 1997, in which myclobutanil 20 EW was applied four times at 10-14-day intervals with a total application of 1.02 to 1.15 kg ai/ha. In four trials 0.006 kg ai/hl was sprayed at high volume almost to run-off, and in the other four 0.009 kg ai/hl was sprayed at medium volume. The plots were 4 rows of 30 or 15 m. Sampling-to-analysis intervals ranged from 12 to 519 days.

The residues of myclobutanil in dried hops ranged from 0.3 to 1.54 mg/kg. The results of the UK and German trials are shown in Table 2.

Table 2. Myclobutanil residues in hops from supervised trials. The underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Country Year	Application				Sample	PHI, days	Residues, mg/kg		Ref.
	Form.	No.	kg ai/ha	kg ai/hl			Myclob.	RH-9090	
UK 1991	EW	6	0.101	0.0045	dried cones	7	0.5	<0.2	Nat. Hop 1995
UK 1991	EW	6	0.101	0.0045	dried cones	13	0.3	<0.2	
UK 1992	EW	6	0.103	0.0045	dried cones	8	1.2	<0.2	
UK 1992	EW	6	0.103	0.0045	dried cones	9	0.27	<0.2	
UK 1991	EW	6	0.103	0.0045	dried cones	3	1.8	<0.2	
UK 1991	EW	6	0.103	0.0045	dried cones	4	1.6	<0.2	
Germany 1996	EW	4	0.18-0.30	0.006	green hops	0	0.27	0.07	Gilbert 1998b
			1.02[1]			7	0.15	0.04	
						14	0.28	0.09	
					dried hops	14	1.02	<0.5	
Germany 1996	EW	4	0.18-0.3	0.006	green hops	0	0.22	0.02	Gilbert 1998b
			1.03[1]			7	0.46	0.1	
						14	0.22	0.03	
					dried hops	14	0.53	nd	
Germany 1996	EW	4	0.2-0.31	0.009	green hops	0	0.63	0.14	Gilbert 1998b
			1.15[1]			7	0.49	0.04	
						14	0.41	0.07	
					dried hops	14	1.54	<0.5	
Germany 1996	EW	4	0.19-0.31	0.009	green hops	0	0.97	0.13	Gilbert 1998b
			1.06[1]			7	0.17	<0.02	
						14	0.35	0.04	
					dried hops	14	1.06	<0.5	
Germany 1997	EW	4	0.18-0.3	0.006	green hops	0	2.42	0.23	Gilbert 1998c
			1.05[1]			7	0.25	0.07	
						14	0.35	0.16	
					dried hops	14	1.08	<0.5	
Germany 1997	EW	4	0.18-0.3	0.006	green hops	0	2.63	0.13	Gilbert 1998c
			1.02[1]			7	0.89	0.11	
						14	0.49	0.05	
					dried hops	14	<0.5	<0.5	
Germany 1997	EW	4	0.18-0.3	0.009	green hops	0	2.41	0.1	Gilbert 1998c
			1.02[1]			7	1	0.16	
						14	0.16	0.03	
					dried hops	14	0.63	<0.5	
Germany 1997	EW	4	0.18-0.3	0.009	green hops	0	0.82	0.05	
			1.03[1]			7	0.21	0.06	

Country Year	Application				Sample	PHI, days	Residues, mg/kg		Ref.
	Form.	No.	kg ai/ha	kg ai/hl			Myclob.	RH-9090	
						14	0.33	0.09	
					dried hops	14	0.73	<0.5	

[1] Total application

Bananas. Residue trials in which myclobutanil was used post-harvest at 200 and 400 mg/l in the USA (California and Hawaii) and Costa Rica were reviewed by the 1997 JMPR. The present Meeting re-evaluated the data in the light of the recently established GAP in Costa Rica.

Myclobutanil residues in whole bananas from trials which complied with the new GAP ranged from 0.64 to 1.7 mg/kg. The residues in the edible pulp were 0.1, 0.17, 0.19, 0.2, 0.21, 0.22, 0.27, 0.35, 0.39 and 0.41 mg/kg.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Hops. In processing studies in Germany green hops (5 kg) from supervised trials were dried just after harvest and processed in a pilot plant by simulated commercial procedures. The steps in the process were as follows.

1. Boiling the wort from malted barley with hops.
2. Separation of trubs (flocs).
3. Fermentation.
4. Cool storage and maturing.
5. Filtration and bottling.

Each processing step was planned to simulate "worst case" conditions to keep possible residues of the test substance as high as possible, reducing the processing steps to a minimum. The hops were added to the boiling wort as dry hops instead of as hop extracts, the proportion of dry hops (450 g/100 l) was relatively high, the period of boiling the wort (75 minutes) was as short as possible, and fermentation was carried out under pressure to shorten the following cool storage. The residues of myclobutanil and its metabolite in beer were below the LOD (0.01 mg/kg). The results of these studies are shown in Table 3.

Table 3. Residues of myclobutanil in hops and brewing fractions in Germany, 1996 and 1997 (Gilbert, 1998b,c).

Application				PHI, days	Sample	Residues, mg/kg	
Form.	kg ai/ha	kg ai/hl	No.			Myclobut.	RH-9090
EW	0.18-0.3	0.006	4	14	dried hops	1.02	<0.5
	1.02 (total)				spent hops	0.09	<0.02
					trub	<0.02	<0.02
					yeast	<0.02	<0.02
					beer	<0.01	<0.01
EW	0.18-0.30	0.006	4	14	dried hops	1.08	<0.5
	1.05 (total)				spent hops	0.04	n.d.
					trub	<0.02	<0.02
					yeast	n.d.	<0.02
					beer	<0.01	<0.01

APPRAISAL

Myclobutanil was evaluated in 1992 and 1997. In 1997 the JMPR evaluated six field trials on hops conducted in the UK but the four trials which complied with GAP were considered insufficient to estimate a maximum residue level. Several post-harvest trials on bananas were according to proposed GAP, but since only proposed GAP was reported the 1997 Meeting could not estimate a maximum residue level. The present Meeting was informed that further trials in Germany were in progress which included processing studies, and that there was now registered GAP for bananas which would allow the recommendation of an MRL.

The manufacturer requested the present Meeting to evaluate additional data on hops and re-evaluate the data on bananas in the light of the recently established GAP.

The analytical methods for myclobutanil and its hydroxy metabolite RH-9090 used in the trials on hops and bananas reported in 1997 were described in the 1992 and 1997 monographs. The method used in the hop trials in Germany was described in the 1992 evaluation. The LODs for dried hops and beer were 0.5 and 0.01 mg/kg respectively. This method was validated for many plant commodities.

Four of the six UK trials reported in 1997 complied with GAP (6 applications, 0.0045 kg ai/hl, 10 days PHI). The residues of myclobutanil on hops (dried cones) ranged from 0.27 to 1.2 mg/kg. Eight supervised trials on hops were conducted in Germany in 1996 and 1997, four of which can be considered to comply with UK GAP. The residues of myclobutanil in dried hops in these trials ranged from <0.5 to 1.08 mg/kg.

The residues of myclobutanil in dried hops in the eight trials according to GAP in rank order (median underlined) were 0.27, 0.3, <0.5, 0.5, 0.53, 1.02, 1.08 and 1.2 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR of 0.515 mg/kg for dried hops.

Bananas. The trials evaluated by the 1997 JMPR showed myclobutanil residues in whole bananas treated according to Costa Rica GAP from 0.64 to 1.7 mg/kg. The residues in the edible pulp in rank order (median underlined) were 0.1, 0.17, 0.19, 0.2, 0.21, 0.22, 0.27, 0.35, 0.39 and 0.41 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg (whole fruit) and an STMR of 0.215 mg/kg for banana.

Processing studies. Dried hops from two supervised trials containing residues of 1.02 and 1.06 mg/kg were brewed into beer. The residues in the beer in both studies were below the LOD. The calculated processing factor for hops to beer is 0 (<0.009), and the estimated STMR for beer is 0 mg/kg.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue level listed below is suitable for establishing maximum residue limit.

Definition of residue for compliance with MRL and for estimation of dietary intake: myclobutanil

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	new	previous	
FI 0327	Banana	2	-	0.215
	Beer			0
DH 1100	Hops (dry)	2	-	0.515

DIETARY RISK ASSESSMENT

Recommendations for myclobutanil MRLs on bananas and hops have been added to the previous recommendations and STMRs have been estimated for these commodities. The other values used for the intake estimation were previously estimated STMRs for six commodities and CXLs established for ten commodities. The International Estimated Daily Intakes of myclobutanil for the five GEMS/Food regional diets were 0 to 4% of the ADI. The Meeting concluded that the intake of residues of myclobutanil resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

REFERENCES

Gilbert, J. 1998a. Myclobutanil and its Metabolites RH-9090. Validation of the Method of Analysis for the Determination of Residues in Green Hops, Beer, Dry and Spent Hops, Trub and Yeast, Cherries, Cherries, Grapes, GRAPE Juice and wine, Apples, Artichokes, Strawberry Preserves and Jam, Tomatoes, Tomato Puree, Juice and Preserves, Peppers and Cucumbers. Rohm & Haas Report No. 49.5/TR34-98-16.

Gilbert, J. 1998b. To Determine the Magnitude of Residues of Myclobutanil and the Metabolite RH-9090 During the Fourteen Days Following the Final Application in the Raw and Processed Agricultural Commodity of Hops Resulting from Sequential Directed Application of Systhane 20EW in Germany. Rohm & Haas Report No. 99.3/TR-34-98-22.

Gilbert, J. 1998c. Myclobutanil and its Metabolite Rh-9090. To Determine the Magnitude of Residues During the Fourteen Days Following the Final Application in the Raw Agricultural and Processed Commodity of Hops Resulting from Sequential Directed Application of Systhane 20EW in Germany. Rohm & Haas Report No. ER 99.4/TR-34-98-23.

OXYDEMETON-METHYL (166)

DEMETON-S-METHYL (073)

EXPLANATION

Oxydemeton-methyl (ODM) was evaluated for residues by the JMPR in 1968, 1973, 1979, 1984, 1989, and 1992. The 1992 review was a complete re-evaluation. It reviewed extensive residue data from supervised trials on all major crops and associated data on use patterns, storage stability, processing, and methods of residue analysis were reviewed and numerous MRLs were recommended. The MRLs are expressed as the sum oxydemeton-methyl, demeton-S-methyl, and demeton-S-methylsulphon, expressed as oxydemeton-methyl. The ADI was established in 1989 at 0.0003 mg/kg body weight and is for the sum of the three compounds.

Demeton-S-methyl is an insecticide. The sulfoxide of demeton-S-methyl is ODM. It currently has no MRLs.

The 1995 CCPR scheduled ODM and demeton-S-methyl for periodic review of residue aspects by the 1997 JMPR (ALINORM 95/24A). This was changed by the 1997 CCPR, which scheduled ODM and demeton-S-methyl for periodic review by the 1998 JMPR.

Bayer AG has submitted data in support of the Periodic Review which included information on crops and regions of interest to that company. The governments of Germany and The Netherlands have also submitted information.

IDENTITY

Common name (ISO): Oxydemeton-methyl

Chemical name:
IUPAC: *S*-2-ethylsulfinylethyl *O,O*-dimethyl phosphothioate
CA: *S*-[2-ethylsulfinyl)ethyl] *O,O*-dimethyl phosphothioate

CAS number: 301-12-2

EU-index number: 015-046-00-7

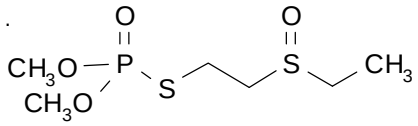
EINECS number: 206-110-7

CIPAC number: 171

Molecular formula: $C_6 H_{15} O_4 P S_2$

Synonyms: Metasystox R

Structural formula:



Molecular weight: 246.3 g/mol

Physical and chemical properties

Pure active ingredient:

Vapour pressure: 3.8×10^{-5} hPa at 20°C; 5.1×10^{-5} hPa at 25°C (Sevekow, 1980, Bayer AG Report PC884)

Boiling point: 106°C at 0.013 hPa
Melting point: < -10°C

Octanol/water partition coefficient: log P_{ow} = -0.74 at 21°C (Hellbusch, 1983)

Solubility:		
	water:	miscible in any ratio
	n-hexane:	0.025 g/l
	toluene:	>200 g/l
	dichloromethane:	>200 g/l
	2-propanol:	>200 g/l
	1-octanol:	>200 g/l
	polyethyleneglycol:	>200 g/l
	acetone:	>200 g/l
	dimethylformamide:	>200 g/l
	ethyl acetate:	>200 g/l
	acetonitrile:	>200 g/l
		(all at 20°C) (Krohn, 1987a,b)

Specific gravity: 1.29 g/cm^3 at 20°C (Krohn, 1986)

Hydrolysis:

Half-life, days of ODM in sterile aqueous buffer solution

pH	25°C	40°C
5	94	22
7	40	7.5
9	2.5	<1

(Pither and Puhl, 1978, 1989)

Photolysis: Half-life in pH 5 buffer in natural sunlight 137 days, in the absence of light 194 days. Photolytic processes contribute little to the decomposition (Kesterson *et al.*, 1988)

Technical material:

Purity: Oxydemeton-methyl (TGAI), batch 808306101-103, purity 89.0%.

Stability: Stable for 8 months at ambient temperature (as a 50% solution). The technical material is unstable (Bayer AG)

Formulations

Bayer AG provided a list of formulations for itsproducts. The list does not include products manufactured or distributed by other companies.

Product	Country	Formulation	Common name of ai	g ai/l
Metasystox R 50	Austria	48.5 EC	oxydemeton-methyl	50
Metasystox R 100	Sweden	100 EC	oxydemeton-methyl	100
Aphitox R 250 EC	South Africa	250 EC	oxydemeton-methyl	250
Metasystemox R	France		oxydemeton-methyl	
Metasystox 250	Ireland		oxydemeton-methyl	
Metasystox R	Austria Finland Germany Portugal Spain		oxydemeton-methyl	
Metasystox R EC 25	Morocco		oxydemeton-methyl	
Metasystox R 25	Mexico		oxydemeton-methyl	
Metasystox R 250 EC	South Africa		oxydemeton-methyl	
Enduro	France	258 EC	oxydemeton-methyl beta-cyfluthrin	250 8
Metasystox R 25 EC	Turkey	265 EC	oxydemeton-methyl	265
Ecombi	Germany	375 EC	oxydemeton-methyl parathion	200 175
Metasystox R 50 SL	Greece	50 SL	oxydemeton-methyl	50
Metasystox R spezial	Austria Germany	100 SL	oxydemeton-methyl	100
Metasystox R	Italy	188.7 SL	oxydemeton-methyl	188.7

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

The metabolism of [*ethylene*-1-^{14}C]oxydemeton-methyl was investigated with male and female Sprague-Dawley rats (Walter and Kane, 1989). The compound dissolved in deionized water was administered orally and intravenously at different dose levels to groups of 5 rats. In a pilot experiment doses of 20.0 mg/kg body weight were administered to 3 male and 2 female rats in order to measure radioactivity in the expired air.

Both oral and intravenous studies showed that <1% of the dose was present in the tissues and blood 72 hours after the final dosing. The highest concentrations, 0.15 mg/kg as ODM or 0.02% of the administered dose, were found in the blood of both female and male rats from a single oral dose of 20 mg/kg bw. Transformation to volatiles was a very minor pathway, 0.059%-0.062% of the dose. The major route of elimination was in the urine, reaching 89–105% at 72 hours after the final dose. More than 80% of the urinary radioactivity was eliminated during the first 24 hours.

Urine samples taken at 0–24 hours were combined and fractionated by reverse-phase HPLC. Isolated compounds were purified by HPLC, extraction or TLC and identified by mass spectrometry (direct chemical ionization and GC electron impact) and comparison with reference compounds.

Pooled faeces samples were extracted with methanol in a Soxhlet unit. The extracts were analysed by TLC and compared to authentic standards. Only the high dose (20 mg/kg bw) provided enough material (3% of the administered ^{14}C) for useful analysis.

The identified compounds are shown in Table 1.

Table 1. Compounds identified in urine and faeces of rats dosed orally or intravenously with ODM.

Sample	Compound	% of dose
Urine	ODM	50
	ODM sulfone [M 01]	2.2
	1-(ethylsulfinyl)-2-(methylsulfinyl)ethane [“sulfinyl” M 03]	16
	1-(ethylsulfonyl)-2-(methylsulfinyl)ethane [“sulfonyl” M 04]	16
	Demethyl ODM [M 06]	2.9
	Demethyl ODM sulfone [M 07]	2.1
	Unknown A	11
	Unknowns B–D	3.7
	Total identified	89%
Faeces	ODM	0.24
	ODM sulfone	0.21
	ODM sulfide	0.80
	Unknowns 1–3	0.62
	Unextracted	0.42
	Total identified	1.2%

The identified metabolites are consistent with a metabolic pathway that starts with hydrolysis of the thioester followed by *S*-methylation of the free thiol. Further oxidation of the sulfur results in metabolites M 03, 1-(ethylsulfinyl)-2-(methylsulfinyl)ethane, and M 04, 1-(ethylsulfonyl)-2-(methylsulfinyl)ethane.

The metabolism of [*ethylene*-1-^{14}C]ODM in a lactating Swiss Alpine goat was studied by Merricks (1987). The treated goat (39 kg) and a control (29 kg) each received 1.5 kg of feed per day, which was completely consumed. The test goat was given one capsule containing lactose and [^{14}C]ODM diluted with natural abundance ODM to a specific activity of 22,543 dpm/µg each day after the morning milking for three consecutive days. Each capsule contained lactose and. Each capsule contained 273 mg of total ODM, corresponding to 7 mg ODM/kg body weight. The control goat received a placebo capsule each day. Milk was collected twice each day, and the pm milk of one day was added to the am milk of the following day. Urine and faeces were collected daily and stored frozen. The goats were slaughtered 2 hours after the third dosing, and liver, kidney, muscle (composite of loin, round, and flank) and fat (composite of omental, renal, and subcutaneous) were collected and stored frozen.

Tissues were homogenized, and subsamples (10 g) were mixed with water (15 ml) and centrifuged. The water extracts were purified on C-18 “Sep-pak” cartridges eluted with methanol. The water extracts contained virtually all of the radioactivity from all tissues except fat, where about 14% remained in the post-extraction solid. The C-18 clean-up recovered 83% (from fat) to 94% (from muscle) of the radioactivity in the extracts.

Milk samples were centrifuged and the supernatants again purified on C-18 “Sep-pak” cartridges. Virtually all of the radioactivity was transferred to the aqueous phase. The C-18 clean-up recovered about 80% of it.

Extracts were analysed by TLC and co-chromatographed with authentic reference standards (ODM, ODM sulfone, sulfonic acid, demethyl-sulfone). A linear analyser was used to scan the developed plates. Kidney tissue was subjected to repeated extractions and preparative TLC. All components accounting for more than 10% of the dose in the original tissue extract were isolated and subjected to mass spectrometry. References to the mass spectra were provided, but no actual spectra or data.

The results are shown in Table 2. The maximum residue in milk was found on day 2 pm, 3.83 mg/kg ODM equivalents.

Table 2. Distribution of radioactive residues in tissues and milk after oral administration of [^{14}C]ODM to a lactating goat.

Compound	% of total radioactive residue				
	Kidney (13 mg/kg)	Liver (4.2 mg/kg)	Muscle (4.0 mg/kg)	Fat (0.62 mg/kg)	Milk (3.8 mg/kg)
ODM	23.2	25.7	42.2	41.3	61.0
ODM sulfone	13.9	0.8	23.4	16.1	7.0
Unknown 1 (TLC origin; polar, 6 compounds)	16.2	34.5	7.5	11.1	2.5
Unknown 2	4.3	6.7	2.2	3.8	5.9
Unknown 3	13.3	21.4	10.0	15.2	23.6
Unknown 4	29.1	9.8	14.3	12.0	0.0
Identified, %	37.1	26.5	65.6	57.4	68.0

Marsh *et al.* (1987) dosed a group of laying hens with [*ethylene*-^{14}C]ODM, diluted to a specific activity of 8 mCi/mmol by the addition of natural abundance ODM, for three consecutive days at 6.9 mg/kg body weight. Eggs were collected each day at 7:30 and 20:00, pooled by day and refrigerated. Hens were killed within four hours of the final dosing and appropriate tissues were collected and pooled for the group. Homogenized samples of eggs and tissues were combusted and radio-assayed.

Homogenized tissue subsamples (5 g) were extracted with water or chloroform or sequentially with acetonitrile and water and the extracts were analysed by HPLC. Subsamples of eggs, fat and skin were extracted with methylene chloride/acetone (1:1) and the extracts purified by gel permeation chromatography. Extraction efficiencies before GPC were 93% for breast, 93% for thigh, 83% for liver, 93% for kidney, 70% for eggs and apparently 160% for fat. Appropriate fractions, as determined by radio-assay, were subjected to HPLC and TLC.

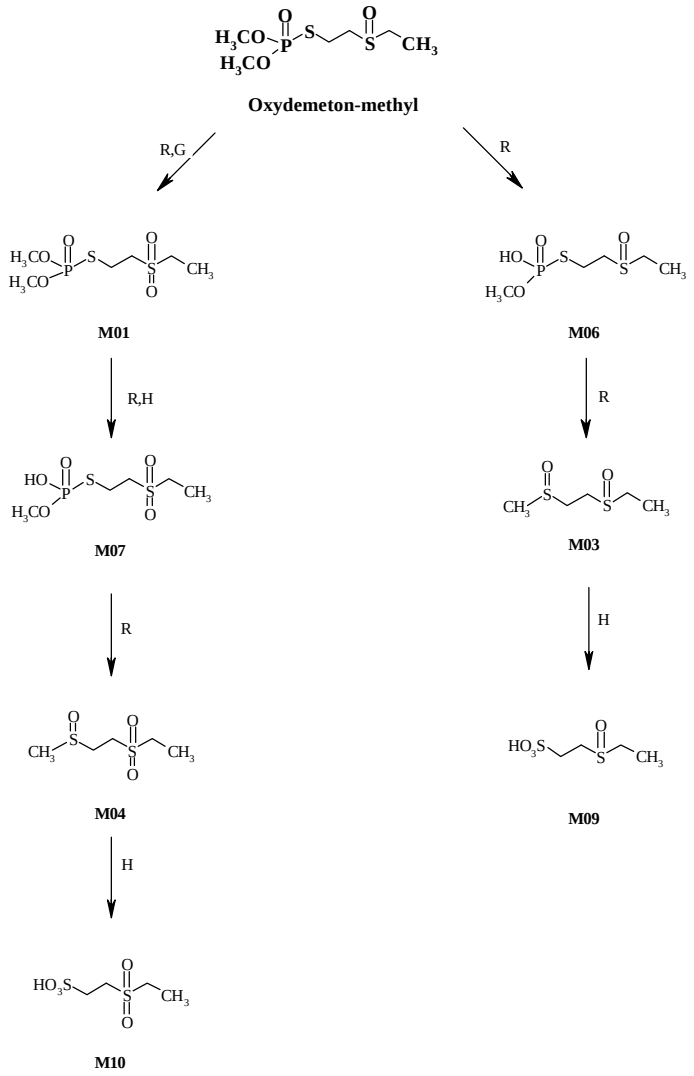
The results are shown in Table 3. Demethyl-ODM sulfone (M 07) was the major or only residue present in eggs, skin, heart, liver, breast and thigh muscle. The two sulfonic acid metabolites 2-(ethylsulfinyl)ethanesulfonic acid (M 09) and 2-(ethylsulfonyl)ethanesulfonic acid (M 10) were the main metabolites in the kidney and gizzard.

Table 3. Distribution of residues in tissues[1] and eggs after oral administration of ODM to laying hens.

Compound	% of total radioactive residue					
	Breast (0.51 mg/kg)	Thigh (0.43 mg/kg)	Liver (0.60 mg/kg)	Kidney (1.4 mg/kg)	Skin (0.41 mg/kg)	Eggs[2] (0.36 mg/kg)
ODM	3.3	n.d.	5.3	n.d.	n.d.	n.d.
M 07 (demethyl-ODM sulfone)	70.1	79.6	48.4	n.d.	100.0	100.0
M 09 + M 10 (2-(ethylsulfinyl) ethanesulfonic acid + 2-(ethylsulfonyl)ethane sulfonic acid)	26.6	n.d.	42.1	83.7	n.d.	n.d.
Unknown	0.0	20.4	4.3	16.3	0.0	0.0
Identified, %	100.0	80	96	84	100.0	100.0

[1]Fat was not successfully analysed.
[2]Day 3. Day 2 eggs = 0.20 mg/kg; day 1 eggs = 0.086 mg/kg.

Figure 1: Proposed metabolic pathways of ODM in animals (R = rats, G = goat, H = hen)



Plant metabolism

Metabolism studies were reported for ODM in sugar beets (Wagner *et al.*, 1989) and cabbages (Smyser and Halpin, 1987), demeton-S-methylsulphon in apples (Wagner *et al.*, 1984), and demeton-S-methyl in wheat (Wagner and Oehlmann, 1987).

Cabbages were treated with three foliar applications of [*ethylene*-1-^{14}C]oxydemeton-methyl at rates corresponding to 0.8 kg ai/ha each and harvested six weeks after the first application. About 97% of the radioactivity was extractable with acetone and aqueous acetone. ODM accounted for 12% of the recovered radioactivity and ODM sulfone (M 01) for 8% (TLC; MS). About 70% of the recovered radioactivity was characterized as being from acidic, very polar, water-soluble metabolites (TLC; HPLC; derivatizations). TLC analysis revealed at least 5 components.

[*Ethylene*-^{14}C]ODM (87.8 µci/mg) was applied with a microlitre syringe to three sugar beet plants. Roots and tops were sampled after 28 and 42 days, and tops also after 6 days. The samples were homogenized and extracted sequentially with chloroform, methanol and water. Most of the radioactivity was removed by the solvents (80–95% from foliage, 82–94% from roots). Extracts were analysed by TLC. Some identifications were confirmed by isolation and MS (EI and CI). The results are shown in Table 4.

Table 4. Distribution and identification of the radioactive residue from the application of [^{14}C]ODM to sugar beets.

Sample	Foliage[1] (% of ^{14}C)	Roots [1](% ^{14}C)
Surface washing	2.70	---
Organosoluble	61.40	8.10
Water-soluble	18.72	3.26
Unextractable	3.09	2.71
Total	85.91	14.07
Compound		
ODM	2.21	---
M 01 (ODM sulfone)	1.71	---
M 06 (demethyl-ODM)	14.19	3.39
M 11 (bis[2-(ethylsulfinyl)ethyl] disulfide)	11.53	1.03
M 12 (2-hydroxy-3-[(2-ethylsulfinyl)ethyl)thio]propionic acid)	13.71	1.61
M 13 (2-hydroxy-3-[(2-ethylsulfonyl)ethylthio]propionic acid)	10.09	0.61
M 14 (2-hydroxy-3-[(2-ethylsulfonyl)ethylsulfinyl]propionic acid)	10.91	2.13
Identified, %	64.34	8.68

[1] % of the sum of the radioactivity found in the root and foliage, NOT % of applied radioactivity. The total radioactivity in the foliage was 61% of the applied, and in the root 9.9% of the applied

[*Ethylene*-1-^{14}C]demeton-S-methyl was applied to spring wheat grown in a greenhouse. The test substance (241.5 µci in 2 ml benzene) was applied with a chromatography sprayer to wheat plants growing on 0.05 m^2 in a 10 l bucket. The actual radioactivity applied to the plants, excluding that on the soil, was 126.8 µci. 12 plants were harvested after 3 and 14 days, and 18 plants after 42 and 60 days. The plants were separated into kernels, chaff, straw and roots. No kernels existed at the 3-day sampling.

Straw, chaff, kernels and roots were washed with water and extracted sequentially with chloroform, acetone, methanol and water. The rinse water for straw was extracted with chloroform. The extracts were analysed by TLC. Radioactive zones located with X-ray film were scraped and determined by scintillation counting. MS was used to confirm tentative TLC identifications. The radioactivity levels, as demeton-S-methyl equivalents, were 10–17 mg/kg in the straw and 0.7–1.6 mg/kg in the kernels. In the 60-day samples, 76% of the residue was extractable from straw (13.6 mg/kg) and 24% from grain (0.72 mg/kg). The results are shown in Table 5.

Table 5: Identification of the radiolabelled residue in the straw and grain of wheat harvested 60 days after the application of [^{14}C]demeton-S-methyl (^{14}C in the plant at 60 days = 100%)

Compound	^{14}C, % of total in straw	^{14}C, % of total in grain
Demeton-S-methyl (test compound)	1.2	0.12
M 01 (ODM sulfone)	9.8	0.11
ODM	11.7	0.01
M 03 (1-(ethylsulfinyl)-2-(methylsulfinyl)ethane)	8.9	0.02
M 10 (2-(ethylsulfonyl)ethanesulfonic acid)	8.2	0.07
M 11 (bis[2-(ethylsulfinyl)ethyl] disulfide)	1.1	0.18
M 15 (*S*-2-(ethylsulfonyl)ethyl dihydrogen phosphorothioate	5.2	0.04
M 16 (1-(ethylsulfinyl)-2-(methylthio)ethane)	4.5	0.06
M 17 (2-ethylsulfinylethanol)	5.1	---
M 18 (2-ethylsulfonylethanol)	0.6	0.02
M 19 (2-ethylsulfinylethylene)	1.2	0.03
Unknown	5.8	0.07
Unextracted	23.8	3.8
Total Identified	58%	0.66%

[*Ethylene*-^{14}C]demeton-S-methylsulphon was applied to five apples on one tree of the James Grieve variety with an Eppendorf pipette (Wagner *et al.*, 1984). The exact application rate could not be ascertained from the information provided. Single apples were harvested at 0, 6, 13, 20 and 27 days after the application. The apples were rinsed with water to remove surface residues, peeled and the peel and pulp were each lyophilized and homogenized with dichloromethane. The residue was extracted sequentially with acetone, ethanol, methanol and water, and the residual solid was combusted and radio-assayed. Forty one per cent of the applied radioactivity was solvent-extractable on day 27 from both peel and pulp and 1.9% was recoverable from a surface water rinse. The extractable percentage was constant at each sampling, but the proportion in the surface rinse decreased from 13% on day 6. Extracts were analysed by TLC and tentative identifications were confirmed by MS. The results are shown in Table 6. Neither radioactive residue concentrations (mg/kg as parent compound) nor the data needed to calculate them were supplied.

Table 6. Identification of the residues from the application of [^{14}C]demeton-S-methylsulfon to apples.

Compound	Day 6 (% of applied)		Day 13 (% of applied)		Day 20 (% of applied)		Day 27 (% of applied)	
	Pulp	Peel	Pulp	Peel	Pulp	Peel	Pulp	Peel
(Parent M 01)	25	35	30	21	26	25	24	24
M 07 (demethyl M 01)	2.0	4.5	2.4	1.9	1.3	3.2	2.6	2.9
M 15 (*S*-2-(ethylsulfonyl)ethyl dihydrogen phosphorothioate	2.0	1.5	1.7	1.9	0.6	3.3	1.2	3.4
Demeton-S-methyl sulfone (M 01)	0.9	3.5	0.9	3.3	1.4	3.1	0.9	0.9
2-(ethylsulfonyl)ethanesulphonic acid	1.4	0.9	1.3	1.1	3.9	1.4	3.2	2.2
1-(ethylsulfonyl)-2-(methylsulfinyl)ethane	1.1	1.5	2.5	1.3	0.7	1.9	1.6	1.3

Compound	Day 6 (% of applied)		Day 13 (% of applied)		Day 20 (% of applied)		Day 27 (% of applied)	
	Pulp	Peel	Pulp	Peel	Pulp	Peel	Pulp	Peel
1-(ethylsulfonyl)-2-(methylsulfonyl)ethane	0.6	0.6	0.9	0.7	0.4	0.9	0.7	0.6
2-(ethylsulfonyl)ethanol (M 18)	1.1	2.4	6.2	3.1	0.5	2.3	2.9	0.2
Unknown	0.4	0.7	1.2	1.9	0.6	4.3	0.2	3.3
Total identified	34	50	46	34	35	41	37	39

The four metabolism studies were inadequately detailed. The data needed to verify ^{14}C concentrations and to convert counts to mg equivalents per kg substrate were not provided. The qualitative identification steps were not detailed, but the mass spectra used to confirm identifications were provided. Two of the studies were conducted with compounds closely related to ODM, but not with ODM. The studies taken together indicate the metabolic pathways shown in Figure 2.

Environmental fate in soil

Stevenson (1989) applied [*ethylene*-1-^{14}C]oxydemeton-methyl to a sandy loam soil at a rate corresponding to 3.4 kg ai/ha and incorporated it to a depth of 15 cm in Stilwell, Kansas, USA (1988–1989). The soil consisted of 56% sand, 36% silt, 8% clay, 2.6% organic matter and the pH was 5.1. The treated soil was aged under aerobic conditions for 34 days. Kale, wheat and red beets were planted in the first rotation. The second and third rotational crops were planted 184 and 351 days after treatment. The crops were harvested at normal maturity and radio-assayed.

The radioactive residues in the soil decreased from 0.5 mg/kg on the day of application to 0.07 mg/kg at harvest 351 days after treatment. No residues (<0.01 mg/kg) were detectable in the rotational leafy and root crops. Residues in rotational wheat were low (0.03 mg/kg in straw) in the first rotation, highest (0.06 mg/kg in chaff) in the second rotation and undetectable (<0.01 mg/kg) in the third rotation. Because of the rapid decline of oxydemeton-methyl in soil, very low or negligible amounts of residues were taken up by the rotational crops. The results are shown in Table 7.

Figure 2. Proposed metabolic pathways of oxydemeton-methyl, demeton-S-methyl and demeton-S-methylsulphon in plants.

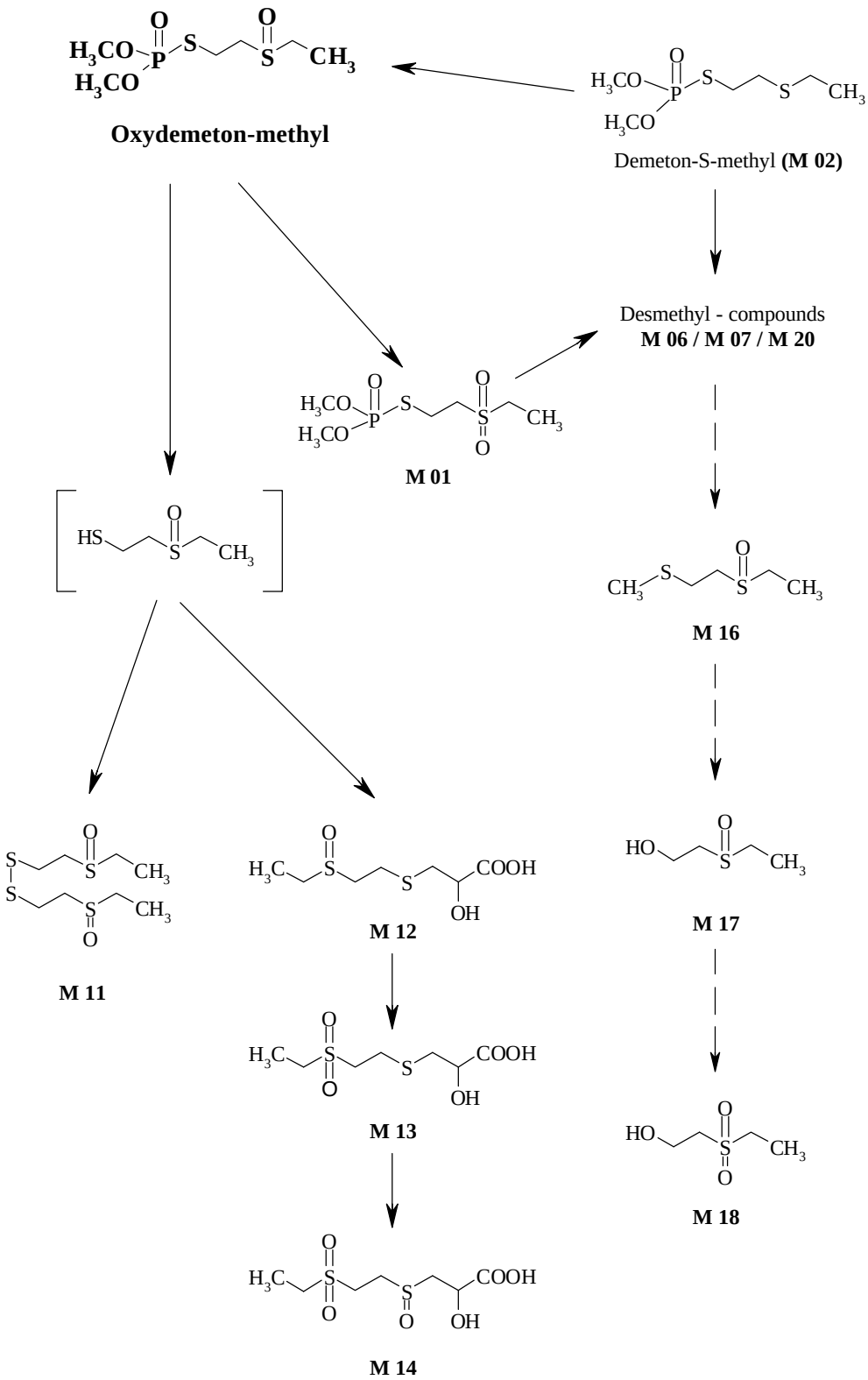


Table 7: Total radioactive residue concentrations in soil and rotational crops after application of [^{14}C]ODM to soil at 3.4 kg ai/ha.

Sample type	Planting interval, days/Sampling interval, days, after application of [^{14}C]ODM								
	First rotation (mg ai equivalent/kg)			Second rotation (mg ai equivalent/kg)				Third rotation (mg ai equivalent/kg)	
	34/	34/73	34/140	184/	184/204	184/227	184/267	305	305/351
Soil	0.14	0.01	0.01	0.10	0.08	0.08	0.08	0.07	0.07
Immature wheat (boot stage)		0.02		<0.01					
Kale		<0.01			<0.01			<0.01	
Red beet top			<0.01				<0.01		<0.01
Red beet root			<0.01				<0.01		<0.01
Wheat straw			0.03			0.02			<0.01
Wheat chaff			0.02			0.06			<0.01
Wheat grain			0.01			0.02			<0.01

As the radioactive residues in all the crop samples were very low, <0.01-0.06 mg/kg, they could not be characterized or identified. Wheat grain, chaff and straw from the first and second rotations were extracted with methanol/water and refluxed with 1 N HCl. Neither solvent nor acid extracted the radiolabel.

The photolysis of ODM on soil was studied by Jackson *et al.* (1988). [*Ethylene*-1-^{14}C]oxydemeton-methyl was applied to a sandy loam soil and irradiated under natural sunlight conditions for 30 days. The resulting half-lives of 61 days of the irradiated samples and 53 days of the dark controls indicated that degradation was not due to photolysis. At the end of the study about 76% of the applied radioactivity was due to unchanged parent compound. The products identified were demethyl-ODM sulfone (M 07, 1.9%) and the sulfonic acids M 09 (2-ethylsulfinylethanesulfonic acid) and M 10 (2-ethylsulfonylethanesulfonic acid), their sum 22.1%. The products and their proportions were the same for the irradiated and unexposed soils at each time interval. None of the unknown products accounted for >4% of the applied radioactivity

The adsorption and desorption of [*ethylene*-1-^{14}C]oxydemeton-methyl was investigated by Daly (1987, revised 1988). A batch equilibrium procedure was used to determine the K_d and K_{oc} values in four soils equilibrates at 25 $\pm$ 1ºC with an aqueous solution of the radiolabelled ODM. The mass balance was >98%. The results are shown in Table 8. The soils were sand (88% sand, 7% silt, 5% clay, 0.52% organic carbon, pH 4.3), sandy loam (56% sand, 30% silt, 14% clay, 0.58% organic carbon, pH 6.6), silt loam (17% sand, 66% silt, 17% clay, 1.53% organic carbon, pH 5.9), and clay loam (21% sand, 50% silt, 29% clay, 1.16% organic carbon, pH 6.4). The low K_{oc} values suggest that oxydemeton-methyl is not significantly bound to soil.

Table 8. Adsorption of [^{14}C]ODM on different soil types.

Soil	Adsorption	
	K_d (ml/g)	K_{oc} (ml/g)
Sand	0.09	17
Sandy loam	0.01	2
Silt loam	0.89	58
Clay loam	0.45	39

In a study of the leaching of aged ODM in a sandy clay loam soil after incubation under greenhouse conditions (Obrist and Thornton, 1978) the soil was treated with [*ethylene*-1-^{14}C]oxydemeton-methyl and aged aerobically for 30 days, by which time almost 50% of the originally applied radioactivity was lost as CO_2. After the ageing period samples were placed on the top of three soil columns (30 cm long and 4.8 cm i.d.) containing fresh soil. The rate of addition of leaching water was adjusted to equal approximately the rate of discharge. 1.25 cm of simulated rainfall was applied each day for 45 days. The results are shown in Tables 9 and 10. ODM and its degradation products showed little tendency to leach through the soil.

Table 9. Leaching of [*ethylene*-1-^{14}C]oxydemeton-methyl in a sandy clay loam soil (56% sand, 23% silt, 21.0% clay, 0.36% org. C, pH6.0) during 45 days.

	% of radioactivity recovered from column		
	I	II	III
Layer 1 (0-1.25 cm)	36.2	1.1	0.3
Layer 2 (1.25-2.5 cm)	50.6	80.7	79.4
Layer 3 (2.5-5.0 cm)	1.4	3.4	6.5
Layer 4 (5-7.5 cm)	0.7	2.2	0.9
Layer 5 (7.5-12.5 cm)	1.0	1.1	1.1
Layer 6 (12.5-17.5 cm)	0.6	0.6	0.8
Layer 7 (17.5-22.5 cm)	<0.1	<0.1	<0.1
Layer 8 (22.5-27.5 cm)	<0.1	<0.1	<0.1
Layer 9 (27.5-30.0 cm)	<0.1	<0.1	<0.1
Total in soil	90.5	89.1	89.0
Leachate	9.5	10.9	11.0
Total	100.0	100.0	100.0

Table 10. Distribution of degradation products of [*ethylene*-1-^{14}C]oxydemeton-methyl in the leachate from aged soil column II.

Compound	^{14}C, mg/kg as ODM, at days					Total
	1-9	10-18	19-27	28-36	37-45	
oxydemeton-methyl	0.13	0.24	0.09	0.03	0.02	0.51
M 01 (ODM sulfone)	0.03	0.06	0.02	trace	trace	0.27
M 09 (2-ethylsulfinylethanesulfonic acid)	0.21	0.32	0.09	trace	trace	0.62
M 10 (2-ethylsulfonylethanesulfonic acid)	0.26	0.40	0.24	0.06	trace	0.90
M 21 (2-ethylsulfinylethanethiol)	0.07	0.13	0.05	0.02	trace	0.27
Unknown	0.64	0.78	0.29	0.13	0.13	1.73
Unextractable	0.41	2.58	1.89	0.89	0.69	6.76

The degradation of oxydemeton-methyl was investigated under aerobic conditions on a sandy loam soil (Schmidt *et al.*, 1993). Soil samples were treated with [*ethylene*-1-^{14}C]oxydemeton-methyl under dark conditions at a temperature of 25 $\pm$ 1°C at a nominal concentration of 25 mg/kg corresponding to 5 kg ai/ha, 10 times the maximum recommended US rate. Samples were collected at 0, 1, 3, 7, 14 and 21 days and 1, 2, 3, 4, 6, 9 and 12 months after treatment. Extractable residues (methanol and water/methanol) decreased from 87.1% of the applied radioactivity at day 0 to 52.6% at 12 months, and unextractable increased from 0.4% on day 0 to 21% after 12 months. Volatile residues increased to 9.3% after 12 months and were shown to be CO_2. The mean recovery of ^{14}C was 93%. The main products observed by HPLC at all sampling points were the sulfonic acids M 09 and M 10 at maximum levels of 30% of the applied radioactivity after 2 months and 26% after 12 months respectively. ODM decreased to 50% of the applied amount within 3 days and to 1% within 21 days. No compound exceeded 10% of the applied ^{14}C at any time. Minor products were ODM sulfone (M 01, 6% maximum), 1-(ethylsulfinyl)-2-(methylsulfinyl)ethane (M 03, 1% maximum), 1-(ethylsulfonyl)-2-(methylsulfinyl)ethane (M 04, 1% maximum) and 2(ethylthio)ethane sulfonic acid (M 22, 3% maximum). Volatiles accounted for 9% of the applied radioactivity.

The half-life of oxydemeton-methyl under these conditions was calculated to be 3.2 days using first order degradation kinetics. Its degradation pathways are shown in Figure 3.

The results reported in the Schmidt experiment were in good agreement with those of an earlier study (Olson *et al.*, 1989) under dark conditions at a temperature of 25 $\pm$ 0.6°C. Soil samples were treated with [*ethylene*-1-^{14}C]oxydemeton-methyl at a nominal concentration of 8.3 mg/kg, corresponding to about 1.7 kg ai/ha. Samples were collected after 0 and 6 hours, 1, 3, 7, 14 and 21 days and 1, 2 and 3 months. As in the Schmidt study, the main products observed at all sampling points were the sulfonic acids M 09 and M 10. No other product exceeded 10% of the applied ^{14}C at any time, but about 30% was recovered as carbon dioxide after 3 months. The half-life of oxydemeton-methyl was calculated to be 9.6 hours.

In a supplementary study (Kasper and Shadrick, 1993) on degradation under field conditions two sandy loam soils from two sites in California (Fresno and Chualar) were treated with [*ethylene*-1-^{14}C]oxydemeton-methyl at a rate corresponding to 1.12 kg ai/ha. Samples were analysed in triplicate immediately after application and in duplicate after 6 and 12 hours and 1, 2, 4 7, 10, 18, 29 and 60 days. At each sampling, the top 3 cm of soil was analysed for degradation products.

During the 60-day experiment, the residues of the parent compound decreased to 2.1% of the applied radioactivity in the Fresno soil and 0.3% in the Chualar soil. Residues of M 09 and M 10 reached maximum levels of 28.5% and 14.0% on day 4 in the Fresno soil. The corresponding levels in the Chualar soil were approximately 20% and 10% between 2 and 18 days.

The total radioactive residues decreased in both soils throughout the experiment with most of the radioactivity remaining in the top 3 cm layer. Residues extracted from the top soil layers decreased as the bound residues increased. The distribution of the residues as a function of time is shown in Table 11.

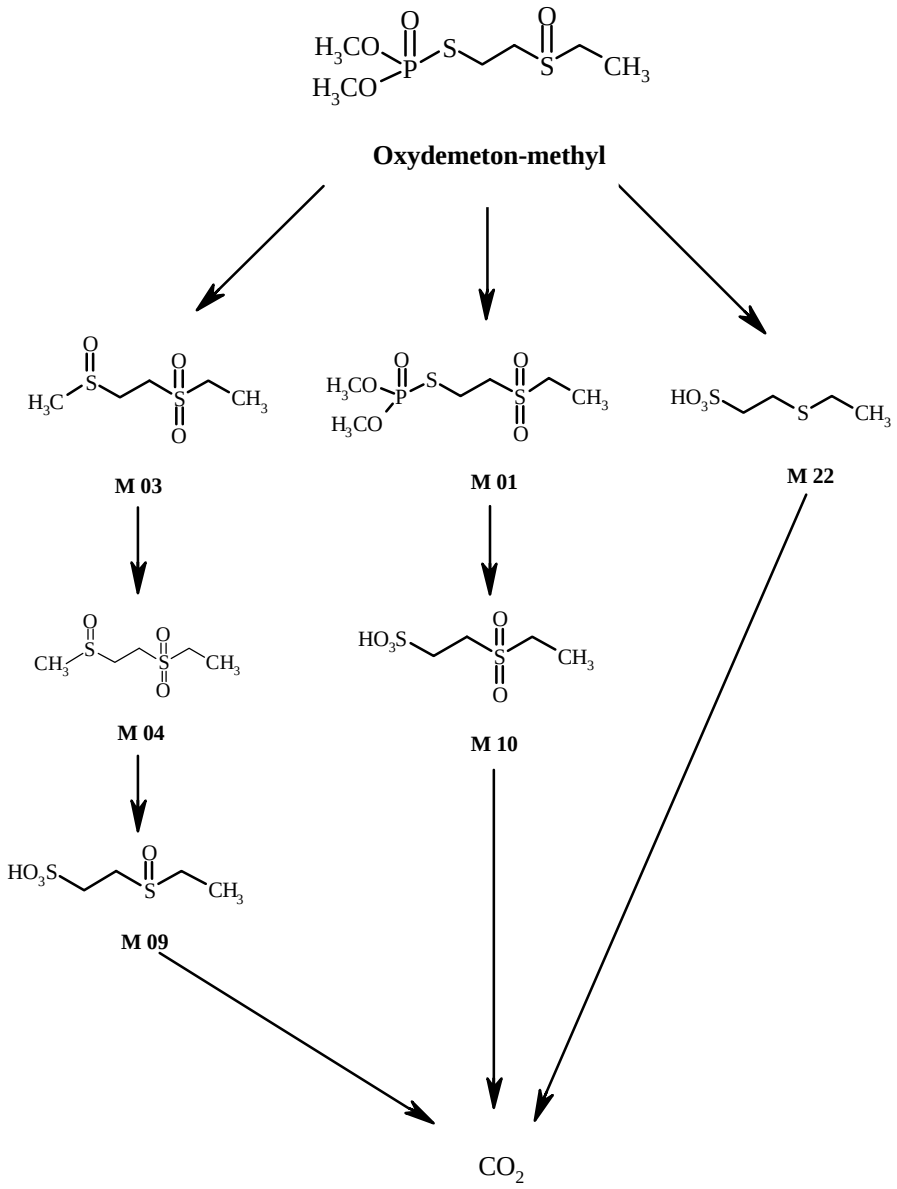
Table 11. Distribution of residues in 0-3 cm soil layers at intervals after application of [*ethylene*-1-^{14}C]oxydemeton-methyl in Fresno and Chualar, California.[1]

Elapsed time, days	^{14}C, % of applied			
	ODM	M 09	M 10	Unknowns
Fresno				
0	94.6	3.5	nd	nd
0.25	78.9	6.5	nd	4.0
0.50	84.3	6.8	nd	1.3
1	50.2	15.6	9.1	nd
2	52.8	6.6	2.1	7.5
4	11.1	28.5	14.0	6.7
7	nd	8.9	4.7	nd
10	nd	9,0	5.6	nd
18	1.4	3.6	5.2	nd
39	1.9	8.7	6.8	3.0
60	2.1	8.7	5.6	3.6
Half-life, days	10.3	5.3	4.5	
Chualar				
0	92.1	1.8	nd	nd
0.25	84.2	2.9	nd	nd
0.50	84.1	3.4	nd	1.2
1	76.0	7.4	nd	nd
2	50.6	20.2	7.0	nd
4	49.7	11.0	3.0	6.2
7	24.1	19.0	10.8	5.1
10	19.9	16.5	9.7	5.0
18	8.5	15.6	10.7	2.9
39	0.1	0.9	1.1	0.5
60	0.3	4.2	1.1	1.1
Half-life, days	6.1	6.4	8.5	

[1] Average of duplicates, except time 0 which is average of triplicates

In a study of the degradation of oxydemeton-methyl in soil under anaerobic conditions (Olson, 1989b) [*ethylene*-1-^{14}C]oxydemeton-methyl was applied to a sandy loam soil at a nominal concentration of 10.0 mg/kg, corresponding to 2 kg ai/ha. The incubation temperature was 25 $\pm$ 0.4°C. The flasks were flushed with nitrogen to maintain anaerobic conditions. Samples were taken at 0 and 10 hours and 30 and 60 days. Oxydemeton-methyl was rapidly degraded. The major degradation products were the sulfonic acids M 09 and M 10, the sum of which reached a maximum of 27% of the applied radioactivity after 10 hours. The only other identified product was M 22, 2-(ethylthio)ethanesulfonic acid, at 4% of the applied radioactivity. The sampling times were too few to calculate a half-life for ODM.

Figure 3: Proposed degradation pathways of oxydemeton-methyl in soil.



In a dissipation study under field conditions (Jacobsen, 1989; Grace and Cain, 1990) oxydemeton-methyl was applied to soil cropped with sugar beets at two sites in California (Fresno and Chualar). Two plots were treated at each site, one with a single application of 1.12 kg ai/ha and the other with six applications of 0.84 kg ai/ha. These rates represent the highest label single rate and the highest seasonal rate of 5.05 kg ai/ha/season respectively. Fifteen soil core samples were taken at each sampling.

At the multiple-application plots, core samples were taken to a depth of 15 cm directly after each of the first five applications and composited by field section to give three replicate samples per application. Cores for all the other samples were driven to a depth of 122 cm and divided into 15 cm segments. For all samples after the final or single applications the 15 cm soil segments were analysed separately and all lower segments were composited by field section to give three replicates per segment for analysis.

First-order dissipation rate constants (k) and half-life values of oxydemeton-methyl were calculated from the single-application plots. Calculations were also made from the analytical results from all the plots to indicate possible leaching of the compound and its sulfone M 01. The k values for ODM were calculated to be 0.31499 at Chualar and 0.44415 at Fresno with half-lives of 2.2 and 1.6 days respectively. At no time were any measurable residues ($\geq$0.01 mg/kg, dry weight basis) of oxydemeton-methyl or its sulfone found in soil below the 0–15 cm segments.

Environmental fate in water/sediment systems

The behaviour of [*ethylene*-1-^{14}C]oxydemeton-methyl in sterile buffer solutions pH 5, 7 and 9 at 25° and 40°C and concentrations of 5 and 50 mg/l was reported by Pither and Puhl (1978, revised 1989). The half-life of oxydemeton-methyl varied from less than one day at pH 9 and 40°C to 94 days at pH 5. Degradation was dependent on both pH and temperature. The results are given in Table12. The degradation products identified by TLC were demethyl-ODM (M 06) and 2-(ethylsulfinyl)ethamethiol (M 21). At pH 7 on day 35, M 06 and M 21 accounted for 34% and 13% of the recovered radioactivity at 25°C and for 67% and 28% at 40°C.

Table 12. Half-life values for the hydrolysis of [*ethylene*-1-^{14}C]ODM in sterile aqueous buffer solutions.

pH	Half-life, days	
	25°C	40°C
5	93.7	21.7
7	39.6	7.5
9	2.5	<1

Kesterson *et al.* (1985) exposed [*ethylene*-1-^{14}C]oxydemeton-methyl in sterile buffer solution at pH 5 to natural sunlight for 30 days. Duplicate irradiated and dark control samples were taken at 0, 5, 10, 15, 20 and 30 days. The half-life of ODM was 137 days for irradiated samples and 194 days for dark controls. Thus, photolytic processes account for little if any of the degradation. The major degradation products identified were demethyl-ODM sulfone (M 07; 7.4% on day 30, 2.8% in control) and the sulfonic acids M 09 and M 10 (3.7% on day 30, 8.3% in control). The recovery of the applied radioactivity was >94% from all samples.

A study of the behaviour of [*ethylene*-1-^{14}C]oxydemeton-methyl in two water/sediment systems was reported by Anderson (1987). Water and sediment were collected from on orchard drainage ditch (IJzendoorn) and from a fishpond (Lienden) in The Netherlands. Both systems were treated with 0.5 mg ai/l. Samples were taken on days 1, 7, 20 ,41 and 91.

The distribution of radioactivity between the aqueous phase and the sediment was similar in the two test systems (Table 13).

Table 13. Distribution of radioactivity from [*ethylene*-1-^{14}C]oxydemeton-methyl in water/sediment systems.

System	Sampling interval, days	^{14}C, % of applied (mean of duplicates)				
		Aqueous phase	Sediment extracts incl. HCl	Sediment unextractable	Volatile compounds	
					$^{14}CO_2$	others
IJzendoorn	1	75.8	15.2	9.6	<0.1	<0.1
	7	33.5	20.6	39.4	0.8	<0.1
	20	18.4	18.3	52.6	4.3	<0.1
	41	4.4	5.6	67.5	15.2	<0.1
	91	1.9	4.2	65.9	22.3	<0.1
Lienden	1	82.9	7.5	9.2	<0.1	<0.1
	7	45.3	11.0	35.3	0.6	<0.1
	20	32.5	8.9	45.8	3.8	<0.1
	41	22.7	6.1	48.4	11.1	<0.1
	91	20.9	4.6	44.9	26.6	<0.1

ODM was rapidly degraded in both systems. One day after application the parent compound accounted for 48.7% of the applied radioactivity in IJzendoorn and 37.6% in Lienden. After incubation for 7 days these values decreased to 11.4 and 9.7% respectively. The degradation of oxydemeton-methyl in the water/sediment systems was accompanied by the continuously increasing formation of carbon dioxide. Comparable mineralisation rates were observed in the two systems. After incubation for 91 days $^{14}CO_2$ accounted for 22% of the ^{14}C at IJzendoorn and 27% at Lienden. The identities and distribution of the components of the residue are shown in Table14 and proposed degradation pathways are shown in Figure 4.

Table 14. Distribution of ODM and its degradation products after incubation of [*ethylene*-1-^{14}C]oxydemeton-methyl in water/sediment systems at Ijzendoorn and Lienden.

Compound	Sample	% of applied ^{14}C at Ijzendoorn/Lienden after interval, days (mean of duplicates)				
		1	7	20	41	91
ODM	Surface water	46/36	11/9.3	0.2/0.7	0.4/0.4	<0.1/1.4
	Sediment	3.2/2.1	0.7/0.4	Trace/0.2	0.2/0.2	<0.1/0.1
M 01	Surface water	0.8/nd	0.3/0.6	0.2/0.5	0.4/0.3	Trace/0.7
	Sediment	nd/0.1	nd/nd	nd/0.1	nd/0.2	nd/nd
M 02	Surface water	0.7/0.4	2.6/1.3	Trace/nd	0.2/<0.1	nd/<0.1
	Sediment	3.3/0.3	0.7/0.1	0.1/nd	<0.1/nd	nd/nd
M 07	Surface water	7.2\4.9	3.1/10	3.3/11	0.3/4.5	Trace/9.0
	Sediment	0.2/nd	Nd/Trace	Nd/Nd	Nd/0.8	Nd/<0.1
M 09 + M 06	Surface water	2.3/2.4	6.5/6.5	7.3/8.6	0.8/0.2	Trace/0.5
	Sediment	0.4/0.9	1.6/0.7	0.8/0.2	0.4/0.4	0.2/0.2
M 10	Surface water	1.6/2.2	3.4/1.4	1.8/2.0	<0.1/0.3	Trace/0.9
	Sediment	1.5/trace	1.5/1.5	1.1/1.7	0.4/0.1	0.4/1.0

Compound	Sample	% of applied ^{14}C at Ijzendoorn/Lienden after interval, days (mean of duplicates)				
		1	7	20	41	91
M 11	Surface water	7.4/20	2.5/6.7	1.7/1.0	Trace/0.3	Nd/Trace
	Sediment	1.2/1.2	Nd/Nd	Nd/Nd	Nd/Nd	Nd/Nd
M 15	Surface water	Nd/1.4	Nd/Nd	Nd/Nd	Nd/<0.1	/trace
	Sediment	Nd/Nd	Nd/Nd	Nd/Nd	Nd/Nd	Nd/Nd
M 23	Surface water	1.2/4.9	1.1/3.1	Nd/0.1	Nd/<0.1	Nd/<0.1
	Sediment	Nd/Nd	Nd/Nd	Nd/Nd	Nd/Nd	Nd/Nd
Unknown	Surface water	3.7/4,7	2.1/3.5	3.1/2.2	1.2/0.5	Nd/0.5
	Sediment	Trace/0.1	1.0/0.5	2.1/0.2	0.3/0.1	0.4/0.5

M01 ODM
M02 demeton-S-methyl
M06 demethyl-ODM
M07 demethyl—ODMsulfone
M09 2-(ethylsufinylethanesulfonic acid
M10 2-(ethylsufonyl)ethanesulfonic acid
M11 bis[2-(ethylsufinyl)ethyl]disulfide
M15 bis[2-(ethylsufonyl)ethyl]disulfide
M23 2-(ethylsufinylethyl) 2-(ethylsufonylethyl disulfide
Nd = not detected

In a supplementary experiment Schmidt and Anderson (1993) applied [*ethylene*-1-^{14}C]oxydemeton-methyl to a pond sediment flooded with pond water to maintain anaerobic conditions at a nominal concentration of 2.55 µg/ml in the dark at 25 ± 1°C. Samples were collected after 0, 1, 3, 7, 14 and 21 days and 1, 2, 3, 4, 6, 9 and 12 months.

Residue levels in the water decreased from 96.1% of the applied radioactivity at day 0 to 26.1% at 12 months. The total extractable residues in the sediment changed little during the study, ranging from 3.5 to 8.5% of the applied radioactivity. Unextractable residues increased from 0.4% of the applied radioactivity at day 0 to 27% at 2 months, then decreased to 18% at 12 months. Volatile residues increased to 8.7% of the applied radioactivity at 12 months with measurable amounts of radioactivity in both the ethylene glycol and potassium hydroxide traps. The total recovery decreased from 96% at 1 day , to 81% at 1 month and 59% at 12 months.

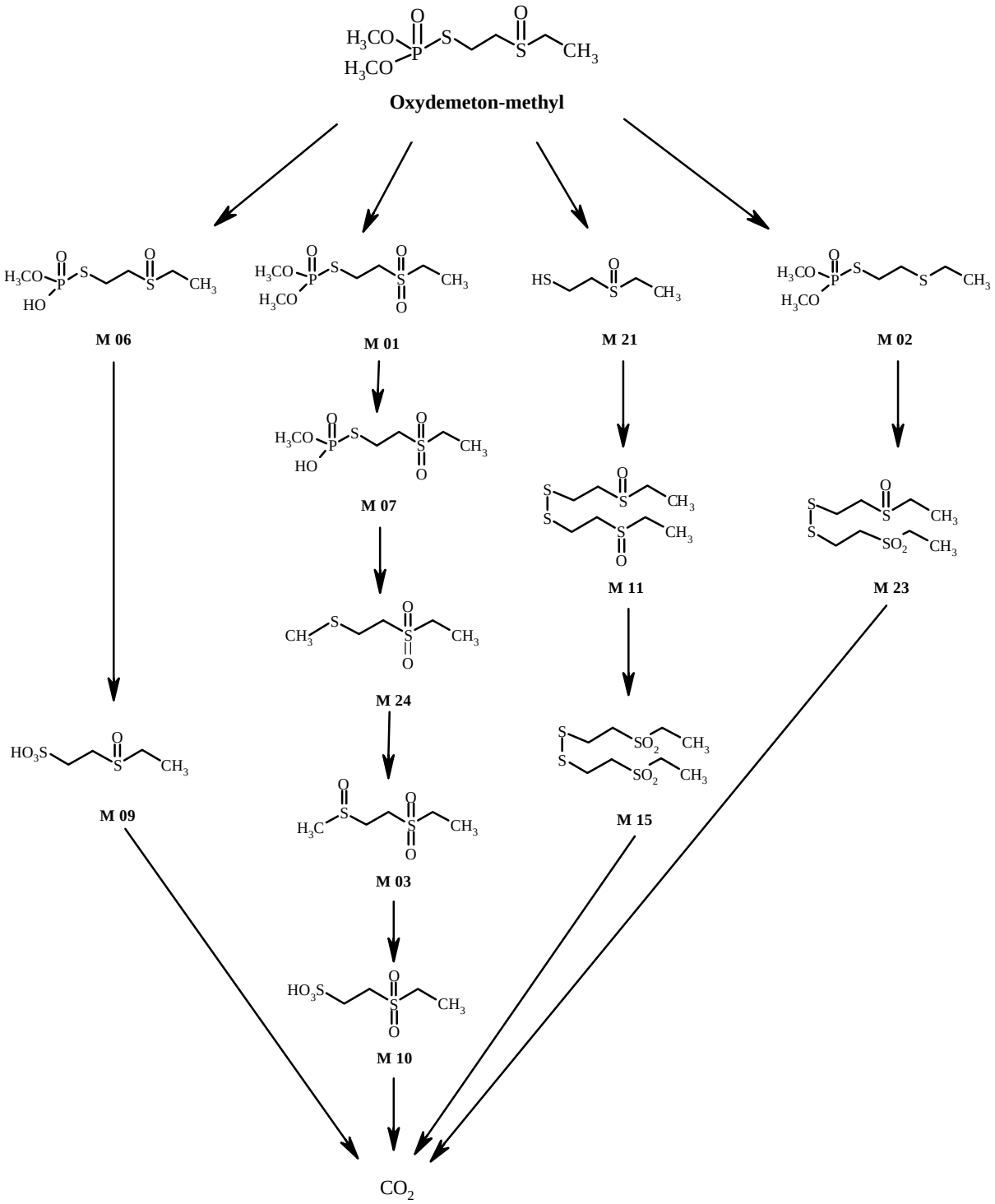
ODM was rapidly degraded. The main products were demeton-S-methyl (M 02) formed by reduction and 1-(ethylsulfinyl)-2-(methylsulfinyl)ethane (M 03) formed by oxidation to the sulfone and cleavage of the P-S linkage. Significant levels of M 03 did not appear until about one month into the incubation. The distribution of the residues is shown in Table 15.

Table 15. Distribution of ODM and its degradation products after incubation of [*ethylene*-1-^{14}C]oxydemeton-methyl in a water/sediment system under anaerobic conditions.

Com-pound	Fraction	% of applied ^{14}C after												
		Days						Months						
		0	1	3	7	14	21	1	2	3	4	6	9	12
ODM	surface water	93.3	60.6	44.7	20.4	2.7	1.8	2.7	5.3	5.9	2.0	0.7	nd	nd
	sediment	3.4	6.7	2.0	2.6	0.2	0.2	0.1	0.2	0.4	0.4	Nd	nd	nd
	acidic extract	--	---	---	nd	nd	nd	nd	nd	nd	nd	Nd	nd	nd
M 01	surface water	nd	0.2	0.6	0.8	0.4	0.6	4.1	3.7	0.4	nd	Nd	0.8	0.4
	sediment	nd	nd	nd	nd	0.2	nd	nd	0.2	nd	nd	Nd	nd	nd
	acidic extract	---	---	---	nd	nd	nd	nd	nd	nd	nd	Nd	nd	nd
M 02	surface water	0.1	21.2	36.5	53.9	43.9	46.1	23.0	2.4	0.1	0.2	Nd	nd	nd
	sediment	0.1	nd	4.7	nd	2.7	3.3	2.5	nd	nd	nd	Nd	nd	nd
	acidic extract	---	---	---	nd	nd	0.4	0.4	0.2	nd	nd	Nd	nd	nd
M 03	surface water	0.1	nd	nd	nd	0.8	1.2	1.3	2.7	7.5	8.6	14.9	17.6	12.9
	sediment	nd	nd	nd	nd	0.2	nd	nd	0.4	1.2	0.6	1.3	0.6	0.7
	acidic extract	---	---	---	nd	0.6	0.6	nd	nd	nd	nd	0.3	0.6	Nd
M 09	surface water	nd	nd	0.4	0.6	1.6	1.8	4.2	5.1	5.9	6.9	6.1	5.7	8.8
	sediment	nd	nd	nd	0.2	0.2	nd	0.1	0.2	0.3	0.4	1.0	nd	0.3
	acidic extract	---	---	---	nd	0.2	0.2	0.1	0.2	0.1	0.4	0.4	0.2	0.8
M 10	surface water	nd	0.2	0.6	0.6	2.0	0.8	2.6	4.1	2.9	2.4	4.4	4.3	4.2
	sediment	nd	nd	nd	0.2	nd	nd	nd	nd	0.4	nd	0.3	nd	0.1
	acidic extract	---	---	---	nd	nd	nd	nd	0.2	0.1	0.4	Nd	0.2	0.4
M 22	surface water	1.7	nd	nd	nd	0.4	0.4	2.0	2.6	7.1	5.5	2.0	nd	Nd
	sediment	nd	nd	nd	0.6	0.2	nd	0.1	0.2	nd	0.2	Nd	nd	Nd
	acidic extract	---	---	---	nd	nd	nd	nd	0.2	nd	nd	0.3	nd	Nd
M 24	surface water	0.3	nd	0.2	1.8	2.0	0.6	1.2	1.0	0.7	nd	Nd	0.2	Nd
	sediment	nd	0.4	nd	nd	nd	nd	nd	nd	nd	nd	Nd	nd	Nd
	acidic extract	---	---	---	nd	0.2	nd	nd	0.2	nd	nd	Nd	nd	Nd
Un-knowns	surface water	0.4	4.4	4.8	3.4	14.8	7.7	9.4	3.1	1.1	0.6	Nd	0.4	0.4
	sediment	nd	nd	nd	3.5	2.4	1.0	1.8	2.6	0.1	0.6	Nd	2.0	1.4
	acidic extract	---	---	---	1.2	0.6	0.8	1.1	2.2	1.8	2.0	2.1	1.4	2.8

M 01 = oxydemeton-methyl sulfone
M 02 = demeton-S-methyl
M 03 = 1-(ethylsulfinyl)-2-(methylsulfinyl)ethane
M 09 = 2-(ethylsulfinyl)ethanesulfonic acid
M 10 = 2-(ethylsulfonyl)ethanesulfonic acid
M 22 = 2-(ethylthio)ethanesulfonic acid
M 24 = 1-(ethylsulfonyl)-2-(methylthio) ethane

Figure 4. Proposed degradation pathways of oxydemeton-methyl in the aquatic environment.



METHODS OF RESIDUE ANALYSIS

Analytical methods

The Netherlands reported a multi-residue method for the determination of pesticides amenable to GLC, including ODM and demeton-S-methyl (Netherlands, 1996). ODM is oxidized to the sulfone and determined as demeton-S-methylsulphon. The same procedure is used for demeton-S-methyl. Foodstuffs are extracted and analysed without clean-up on a gas chromatograph with an ion trap detector (ITD). The limit of determination is estimated to be 0.01–0.05 mg/kg. Recoveries were demonstrated for demeton-S-methyl (various substrates, n = 10, mean recovery 79% at 0.29 mg/kg) and for demeton-S-methylsulphon (lettuce, n = 10, mean recovery = 107% at 0.29 mg/kg). The Netherlands defines the residue as the sum of ODM and demeton-S-methylsulphon, expressed as demeton-S-methyl.

Bayer AG reported both enforcement methods of the Deutsche Forshungsgesellshaft and methods used with various field trials. The enforcement method combines DFG Method S19, a multi-residue method for the extraction of numerous lipoid- and water-soluble pesticides, and DFG Method S16 (Hild and Their, 1979) a multi-residue GLC analytical method Method M012, a modification of S19 (Specht, 1990; Specht and Tillkes, 1982).

In Method S19 plant material is extracted with acetone and water is added to give an acetone/water ratio of 1/1. This is saturated with sodium chloride and partitioned with methylene chloride. The methylene chloride extract is concentrated and cleaned up by gel permeation chromatography on Bio Beads S-X3 with cyclohexane and ethyl acetate as eluants. The residue-containing fractions are concentrated, cleaned up on a silica gel minicolumn if necessary (1 g deactivated silica gel; elution with cyclohexane/ethyl acetate) and analysed by DFG method S16.

Method S16 specifies oxidation with potassium permanganate, which converts demeton-S-methyl and ODM to the sulfone. The mixture is diluted with water and extracted with methylene chloride. The solvent is replaced with acetone and the extract analysed on a gas chromatograph equipped with a flame-photometric detector. The nominal limit of quantification is 0.01 mg/kg. The only validation provided was the analysis of a single sample of sunflower seed fortified at 0.01 mg/kg, with a 99% recovery (Specht, 1990).

Bayer AG also reported its Method 00246 for the enforcement determination of ODM in plant, animal and soil samples (Thornton *et al.*, 1997). Plant samples (100 g) are homogenized and extracted with acetone (200 ml) in a blender, diluted with water and filtered. The filtrate is washed with hexane (150 ml) and extracted with chloroform (1 x 200 ml, 1 x 50 ml). Oily substrates (50 g) are extracted directly with chloroform (300 ml). The chloroform is evaporated and the residue dissolved in hexane. The hexane is partitioned with water and the water with chloroform. The final chloroform extract is evaporated to dryness.

Soil samples (50 g) are extracted in a Soxhlet apparatus for 4 hr using 300 ml of a 1/1 chloroform/methanol mixture. The extract is evaporated to dryness.

Animal tissues except fat, milk and eggs (50 g) are blended with anhydrous sodium sulfate (50 g), Hyflo Super-Cel (10 g) and acetonitrile (200 ml). The mixture is filtered and the cake is extracted with hexane (300 ml). The filtrates are combined and shaken and the acetonitrile layer is retained and evaporated. The residue is dissolved in hexane and extracted with water. The water fraction is extracted with chloroform and the chloroform extract evaporated to dryness. Fat (50 g) is extracted directly with hexane and the filter cake is extracted with acetonitrile. The acetonitrile and hexane fractions are combined and processed as above. Milk (100 g) is extracted in the same way as animal tissues, but the

sodium sulfate is omitted. Single whole eggs are blended with acetone and filtered. The cake is washed with chloroform and the combined chloroform and acetone fractions are allowed to separate. The organic layer is evaporated to dryness, taken up in hexane and extracted with acetonitrile (3 x 50 ml). The combined acetonitrile extracts are evaporated to dryness.

The evaporated residue is dissolved in acetone (2 ml) and oxidized with potassium permanganate (25 ml of 0.1 M). The reaction is allowed to proceed for 30 minutes at room temperature. The mixture is extracted with chloroform (3 x 25 ml) and the combined extracts are evaporated to dryness, dissolved in acetone and analysed on a gas chromatograph equipped with a alkali-flame detector and a 1 m packed column of 10% DC 200 and 1.5% QF-1, run isothermally at 210°C. Calibration is with external standards taken through the oxidation step, or ODM sulfone may be used as the standard. The reported recovers are shown in Table16.

Table 16: Recovery of ODM and demeton-S-methyl from various samples by Bayer Method 00246.

Sample	Fortification, mg/kg (ODM and demeton-S-methyl at same level)	ODM		Demeton-S-methyl	
		Number	Recovery, %	Number	Recovery, %
Apples	0.05-0.10	8	108±10	6	94±6.6
Grapes	0.05-0.10	3	103±5.2	3	85±2.9
Lettuce	0.05-0.50	10	93±7.8	12	99±11
Nut meat	0.05-0.10	6	100±13	5	102±9.1
Animal tissue	0.05-0.10	17	94±7.8	13	92±8.4
Animal fat	0.05-0.10	5	93±4.2	5	94±3.7
Bovine milk	0.005-0.01	6	93±6.5	6	96±13

Bayer AG reported several similar methods for the determination of ODM in field trial samples. All involve solvent extraction, clean-up of the extract, oxidation of the residue with permanganate, post-oxidation clean-up and gas chromatography. The differences are in the extraction solvents, the types of clean-up and the detector. The newer methods use flame photometric detectors are used instead of alkali FIDs. All the methods determine the combined residue of demeton-S-methyl, its sulfoxide (ODM) and its sulfone as the sulfone.

In Method I47 (Thornton and Olson, 1967, revised 1971), the plant sample (100 g) is chopped and extracted with acetone (200 ml) and water. The filtrate is mixed with skellysolve B and the acetone phase is extracted with chloroform (200 + 50 ml). The solvent is changed to acetone and the extract oxidized with permanganate. The mixture is extracted with chloroform (3 x 20 ml). The combined extracts are redissolved in acetone and analysed by GLC as in Method 00246. Calibration is by external standard taken through the oxidation step. The LOD is estimated to be 0.05 mg/kg. Recoveries at 0.1 and 0.4 mg/kg (5 replicates at each level) were 68-104% for ODM and 77–102% for ODM sulfone from lettuce, 70-104% for ODM and 81-116% for ODM sulfone from sugar beet roots, and 76-110% for ODM and 90-108% for ODM sulfone in sugar beet tops.

Method RA-133/74 (Wagner, 1974) is a modification of Method I47. Only the extraction procedure varies. The sample (100 g) is macerated with acetone (200 ml) and water (to 300 ml total volume) and an aliquot of the filtrate (150 ml) is partitioned with chloroform (5 x 100 ml). The solvent is changed to acetone and the residues oxidized with 0.5 N potassium permanganate solution (30 minutes at room temperature). Recoveries from various plant materials fortified at 0.1 mg/kg were reported to be 67-96%, but no details were provided. The nominal limit of quantification was 0.01 or 0.05 mg/kg.

Bayer Method 148 (Olson, 1967, revised 1971) was for crops with a high oil content, such as cotton seed, or dry crops such as walnuts. The sample (100 g) is blended with chloroform (300–500 ml). After filtration, the chloroform is stripped and the residue dissolved in skellysolve B (200 ml). This is extracted with water (2 x 50 ml) and the combined water extracts are partitioned with chloroform (300 ml, 2 x 100 ml). The residue is oxidized with permanganate and the final solution is analysed by gas chromatography with a flame ionization detector. The recoveries at 0.1 mg/kg were 101% for ODM and 103% for ODM sulfone from cotton seed (single samples) and 106% and 117% for ODM and 104% for ODM sulfone from walnuts. The limit of quantification is estimated to be 0.01 mg/kg.

Bayer Method 00009 and its variants are the most commonly used with field trials (Wagner and Thornton, 1977). Plant samples are macerated with acetone and filtered. The macerate is extracted 3 times with chloroform and the solvent changed to acetone. The solution is oxidized with potassium permanganate and the mixture extracted 3 times with chloroform. The organic fraction is dried with sodium sulfate, re-dissolved in acetone, and determined as ODM sulfone by gas chromatography (flame ionization detector). Recoveries are shown in Table 17.

Several variations of 00009 exist. M 003 uses methylene chloride in the initial extraction of the macerate. The limit of quantification is about 0.05 mg/kg (Blass, 1990). In M 004 the proportions of solvents are changed, and toluene is substituted for acetone as the final (GLC) solvent¸ and an FPD is used. The limit of quantification is about 0.01 mg/kg.

In modification M 002 (Ohs, 1988) the oxidation mixture is on an “Extrelut” column and the sulfone is eluted with methylene chloride. A flame photometric detector replaces the thermionic detector. M 007 (Seym, 1993) is a further modification of M 002. The methylene chloride extract from the “Extrelut” column is dissolved in cyclohexane and cleaned up on a Mega Bond silica gel cartridge (SPE), which is rinsed 3 times with cyclohexane/ethyl acetate and eluted with ethyl acetate and acetonitrile. Recoveries are shown in Table 17.

Method 00015/M 009 is used specifically for the determination of “Enduro”, a mixture of ODM and cyfluthrin. The procedure for ODM is similar to method 00009 with modification M 002 and electron capture detection. The limit of quantification is 0.04–0.05 mg/kg.

Method 00255 (Ohs, 1992) is also used for the determination of ODM and cyfluthrin. The plant samples are extracted with an acetone/water mixture and the filtered extract is partitioned with methylene chloride. Oily samples are taken up again in acetonitrile and partitioned with n-hexane. The solvent is changed to acetone and the residue oxidized with potassium permanganate. The product mixture is cleaned up on a Chem-Elut column eluted with methylene chloride. The chromatograph is equipped with

a 30 m x 0.53 mm megabore column (HP 1) and the oven is programmed from 205°C to 280°C at 20°/min. The residues re determined as in 00009/M 002. Recoveries are shown in Table 17.

Table 17. Recoveries of ODM from various crops by Method 00009 and its variants (single analyses).

Crop	Commodity	Fortification, mg/kg	Recovery, %		
			Demeton-S-methyl	ODM	ODM sulfone
Method 00009					
Apples		0.01	100	108	
		0.1	95	72	
		0.5		75	97
		1.0	100		97
Potatoes		0.01	100	99	100
		0.1	89		100
		0.5		86	98 (0.4 mg/kg)
		1.0	95		
Lettuce		0.01		96	
		0.1	90		
		0.2		78	
		0.6		85	
		1.0	91		
Grapes		0.01	95		
		0.1		82	98
		0.5		91	
		1.0			91
	wine	0.1			100
		0.2		114	
Wheat	grain	0.01	81	88	
		0.1	91		
		0.2		87	
		0.4		88	
		1.0	100		
	straw	0.1	84		
		1.0	90	96	
Sugar beet	root	0.01	100	81	
		0.05			86
		0.5		76	98

Crop	Commodity	Fortification, mg/kg	Recovery, %		
			Demeton-S-methyl	ODM	ODM sulfone
		1.0		81	
	tops	0.05			96
		0.5			100
		1.0		85	
Bush beans		0.1		72	
		0.6		67	
Strawberries		0.2		72	
		0.5		80	101
Currants		0.05		90	
		0.1			100
		0.5		98	
		1.0		90	100
Potatoes		0.01		99	100
		0.05			102
		0.1			100
		0.2			101
		0.4			98
		0.5		86	
Kohlrabi		0.1		85	
		1.0		72	
Carrots		0.01		91	100
		0.05			102
		0.1		77	
		0.4			102
Grape must		0.05		88	
		0.5			94
Peaches		0.05		80	
		0.5		94	
Plums		0.05		98	
		0.1			97
		0.5		80	
		1.0			96
Spinach		0.1		72	
		0.6		83	
Tomatoes		0.1		81	

Crop	Commodity	Fortification, mg/kg	Recovery, %		
			Demeton-S-methyl	ODM	ODM sulfone
Cabbage (Savoy)		0.5		82, 76	
Modification M 007					
Lettuce	head	0.02		91, 96	
		0.50		76, 77	
Kale		0.02		65, 75	
		0.50		71, 83	
Almonds	kernels	0.02		83, 85	
		0.50		93, 94	
Modification M 002					
Fodder beet	leaves	0.02		80	
		0.05		92	
		0.2		73	
		1.0		92	
		2.0		84	
	roots	0.02		88	
		0.2		83	
Modification M 003					
Cabbage	head	0.05		74, 76	
		1.0		77, 88	
	cooked head	0.05		75, 81	
		1.0		65, 65	
Modification M 004					
Orange	pulp	0.1		75, 80	
	peel	0.1		75, 80	
Cauliflower	head	0.1		94, 94	
Kale	head	0.1		89, 94	
Peaches	fruit	0.1		94, 94	
Cabbage (Savoy)	head	0.1		99, 103	
Sugar beet	leaves	0.01		94, 94	
	roots	0.01		94, 94	
Modification M 009					
Wheat	forage	0.05		90	
		2.0		86	
	grain	0.05		96	
		2.0		116	

Crop	Commodity	Fortification, mg/kg	Recovery, %		
			Demeton-S-methyl	ODM	ODM sulfone
	straw	0.05		77	
		2.0		93	
Barley	forage	0.04		92, 97, 90, 95	
		2.0		110	
	grain	0.04		100, 100, 108, 121	
		2.0		116	
	straw	0.04		129, 129, 77, 81	
		2.0		98	
Oats	forage	0.04		97	
		2.0		99	
	grain	0.04		97	
		2.0		116	
	straw	0.04		89	
		2.0		95	
Method 00255					
Peas	forage	0.01		85, 101	
		0.05		74, 77, 93	
	vines (green)	0.01		81, 83	
		0.1		84, 90, 98	
	seeds	0.01		78, 98, 108, 123	
		0.1		84, 90, 98	
Field pea	vines (green)	0.01		92, 101	
		0.1		81, 87	
	vines (dry)	0.04		73, 86	
	seeds	0.01		112, 115	
		0.1		91, 102	
Barley	forage	0.04		94, 96	
		0.08		93	
		0.4		83, 97	
		0.8		92	
	grain	0.04		76, 99	
		0.4		88	
	straw	0.04		74, 76, 111	
		0.4		79, 72	
Oats	forage	0.04		102, 102	

Crop	Commodity	Fortification, mg/kg	Recovery, %		
			Demeton-S-methyl	ODM	ODM sulfone
	grain	0.04		87, 96, 98	
		0.4		79, 85	
	straw	0.04		99, 102	
		0.4		77, 79, 91	
Potatoes	tubers	0.01		93, 94, 88	
		0.1		73, 86, 89	
Wheat	forage	0.04		64, 74, 84, 88, 111, 121	
s		2.0		85, 101	
	grain	0.04		93, 100, 114, 118	
		0.4		104, 106	
	straw	0.04		76, 91, 94, 96	
		0.4		74	
		2.0		94	
Sugar beet	roots	0.01		90, 92, 96	
		0.1		61, 71, 73, 75, 80, 85, 89	
	leaves	0.04		92, 93	
		0.4		65, 68, 69, 70, 73, 75, 79, 79	
		2.0	79; 94		

Stability of pesticide residues in stored analytical samples

Bayer AG reported a study of the storage stability of ODM in cabbage (Lenz and Smyser, 1989) and summary information on its stability in lettuce, papaya and maize (Morris, 1980a,b; Anon., 1985). The cabbage trial was part of a study of metabolism. Cabbages treated with [^{14}C]ODM were analysed, stored frozen at –10°C, then re-analysed for ODM and ODM sulfone after 5 days and 4, 10 and 115 weeks of frozen storage. The samples were extracted with acetone (97% efficiency), partitioned into chloroform and spotted on TLC plates. Radioactive areas were defined by autoradiography, scraped and quantified by LSC. The methods used for maize, lettuce and papaya were I47 and I48.

The results are shown in Table 18.

Table 18. Stability of ODM and ODM sulfone in frozen plant samples.

Sample	Storage, days	Storage temperature, °C	ODM recovery, %	Sulfone recovery, %
Cabbage	28	-10	89[1]	133[1]
	49		108[1]	116[1]
	805		115[1]	123[1]
Maize forage (green)	14	-18 to -23	91	94
	43		101	65
	62		74	97
	157		59	91
Maize kernels	15		106	109
	43		108	111
	93		-	146
Maize cob	14		102	84
	43		69	60
Maize husk	15		85	103
	43		91	98
	93		127	98
Lettuce	51	-18 to –23	89	
	183		98 (69; 128)	
Papaya	9	-18 to –23	118[1]	
	10		131	
	13		134	

[1] Relative to the radioactive components at 5 days. No day 0 samples analysed

Definition of the residue

On the basis of the metabolism of oxydemeton-methyl (ODM) by plants and animals, and the residues determined by the available analytical methods, the residue should be defined as the sum of demeton-S-methyl, ODM and demeton-S-methylsulphon, expressed as ODM, both for compliance with the MRLs and for the estimation of dietary intake.

USE PATTERN

Bayer AG submitted labels and extensive information on GAP. The labels from Finland, France, Germany, Morocco, Sweden, Portugal and Austria were not however translated into English and the information could not be adequately verified in those cases. New and presumably unapproved labels were provided for Austria, Greece and Spain, but only the label for Spain had an adequate translation. The Netherlands stated that neither demeton-S-methyl nor ODM were approved for use. Germany submitted information on GAP. Bayer AG emphasized that the labels were for their formulations only. The information is shown in Table 19.

Table 19. Registered uses of ODM on crops.

Crop	Country	Form	Application				PHI, days	Comments
			Rate, kg ai/ha & l water/ha	Spray conc., kg ai/hl	No.	Method		
Almonds	Spain	EC 250 g/l	0.25 1000	0.025	2	Individual tree spray	30	
Anise	Turkey	EC 265 g/l	0.26 600	0.044	1	Broadcast spray	21	
Apple	Austria	EC 250 g/l	0.38 1500	0.025	3	Row spraying	35	
		SL 100 g/l	0.25 1500		2	Row spraying	90	
	Finland	EC 250 g/l		0.025	2	Broadcast spray		
	France	EC 250 g/l		0.020		Broadcast spray	60	
	Germany	EC 250 g/l	0.38 1500	0.025	1	Row spray	~60	Before or directly after flowering
		SL 100 g/l	0.38 1500	0.025	3	Row spray	28	
	India	EC 250 g/l	1.8 2500	0.07	2	Individual tree spray	21	
	Ireland	EC 250 g/l		0.0075 high volume (1500 l water max /ha) 0.081 low volume (200 l water/ha)	2	Foliar	~90	Apply before and/or immediately after flowering
	Italy	SL 189 g/l	0.34 1200	0.028	1	Broadcast spray	30	
	Mexico	EC 250 g/l	0.75 l/ha 1500 l water/ha	-	1 or 2	Broadcast spray	30	
	Morocco	EC 250 g/l	0.38 1500	-	4	Broadcast spray	21	
	Peru	EC 250 g/l	0.2 800	-	2	Broadcast spray	30	
	Portugal	EC 250 g/l	0.37 1000 (calculated)	0.037	2	Broadcast spray	56	
	South Africa	EC 250 g/l	0.88 3500	0.025	1	Individual plant spray	21	
	Spain	EC 250 g/l	0.25 1000	0.025	2	Individual plant spray	30	`
	Turkey	EC 250 g/l	0.53	0.026	1	Individual tree spray	21	
Apricot	Germany	EC 250 g/l	0.38 1500	0.025	1	Row spray	28	
	Germany	SL 100 g/l	0.38 1500	0.025	3	Row spray	28	
	South Africa	EC 250 g/l	0.88 3500	0.025	1	Individual tree spray	21	
	Spain	EC 250 g/l	0.25 1000	0.025	2	Individual tree spray	30	
Banana	India	EC 250 g/l	0.25 500	0.05	1	Broadcast spray	21	
Barley	Austria	EC; SL 250 g/l;	0.12 400	0.031	1	Broadcast spray	21	

Crop	Country	Form	Application				PHI, days	Comments
			Rate, kg ai/ha & l water/ha	Spray conc., kg ai/hl	No.	Method		
		100 g/l						
	Germany	EC 250 g/l 375 g/l	0.12 400	0.031	2	Broadcast spray	21	
	Ireland	EC 250 g/l	0.12 (200 l water/ha)		1	broadcast	21	
	Kenya	EC 250 g/l	0.12 800	0.016	2	Broadcast spray	-	
	Peru	EC 250 g/l	0.2 ?	-	1	-	14	
	South Africa	EC	0.12 300	0.042	2	Broadcast spray	33	
Bean	Italy	SL 189 g/l	0.17 600	0.028	1	Broadcast spray	21	
	Kenya	EC 250 g/l	0.15 800	0.019	2	Broadcast spray	-	
	Mexico	EC 250 g/l	0.25 400	0.062	1 or 2	Broadcast spray	21	
	South Africa	EC 250 g/l	500	0.02	2	Broadcast spray	14	
Bean, Field	Germany	EC 250 g/l	0.15 0.22	-	2	Broadcast spray	28	Under 50 cm uses lower rate.
	Ireland	EC 250 g/l	0.15 0.22 (200 l water/ha)	-	2	Broadcast spray	28	Lower rate for plants under 50 cm.
	Sweden	EC 250 g/l	400	-	1	Individual leaf spray	21	
Bean, French	Germany	EC 250 g/l 375 g/l	0.17–0.33	-	3	Broadcast spray	7	0.17 if <50 cm 0.25 if 50-125 cm
		SL 100 g/l	0.23	-	2	Row spray	7	
Bean, mung	India	EC 250 g/l	0.12 500	0.025	1	Row spray	14	
Beet, beta	France	EC 250 g/l	0.38 300	0.12	3	Broadcast spray	-	
Beet, fodder	Germany	EC 250 g/l 375 g/l 590 g/l	0.24 400	0.06	4	Broadcast spray	28	
Broccoli	Germany	EC 375 g/l	0.12	-	1	Broadcast spray	21	
	Mexico	EC 250 g/l	0.25 400	-	1 or 2	Broadcast spray	7	
	South Africa	EC 250 g/l	0.1 500	0.02	2	Row spray	10	
Brussels sprouts	Austria	EC 250 g/l	0.25 1000	-	1	Row spray	21	
	Germany	EC 375 g/l	0.12 or 0.19	-	2	Broadcast spray	14	Higher rate >50 cm
	Mexico	EC 250 g/l	0.25 400	-	1 or 2	Broadcast spray	7	
	South Africa	EC 250 g/l	0.1 500	0.02	2	Row spray	14	

Crop	Country	Form	Application				PHI, days	Comments
			Rate, kg ai/ha & l water/ha	Spray conc., kg ai/hl	No.	Method		
Cabbage	Austria	EC 250 g/l SL 100 g/l	0.25 1000	-	1	Row spray	21	Savoy and head
	Germany	EC 375 g/l	0.12	-	2	Broadcast spray	21	Head, red, Savoy
		EC 250 g/l SL 100 g/l	0.15		1	Broadcast spray	21	Head, red, Savoy. Under 50 cm
	Ireland	EC 250 g/l	0.15		1	Broadcast spray	21	Under 50 cm
	Italy	SL 189 g/l	0.28 1000	0.028	1	Broadcast spray	-	Wild
	Mexico	EC 250 g/l	0.25 400	-	1 or 2	Broadcast spray	21	Wild
	South Africa	EC 250 g/l	0.1 500	0.02	2	Row spray	10	Wild
Cauli-flower	Austria	EC 250 g/l	0.25 1000	-	1	Row spray	21	
		SL 100 g/l	0.22 1000	-	1	Row spray	21	
	Germany	EC 375 g/l	0.12	-	1 or 2	Broadcast spray	14	
		EC 250 g/l	0.15	-	1	Broadcast spray	21	Under 50 cm
	Ireland	EC 250 g/l	0.15	-	1	Broadcast spray	21	Under 50 cm
	Mexico	EC 250 g/l	0.25 400	-	1 or 2	Broadcast spray	7	
	South Africa	EC 250 g/l	0.1 500	0.02	2	Row spray	10	
Cereals	France	EC 250 g/l	0.10			Foliar	21[1]	
Cherry	Austria	EC 48 g/l	0.36 1500	-	3	Row spray	35	Dwarf and sweet
	Spain	EC 250 g/l	0.25 1000	0.025	2	Individual tree spray	30	Sweet
Chilli	Sri Lanka	EC 250 g/l	0.25 665	0.038	6–8	Broadcast spray	21	
Citrus	India	EC 250 g/l	1.25 2500	0.05	1	Individual tree spray	21	
	Kenya	EC 250 g/l	0.25 1000	0.025	3	Broadcast spray	-	
	Portugal	EC 25 g/l	0.1 2000	0.005	1	Row spray	35	
	Portugal	EC 250 g/l	0.75 calc	0.050	2	Foliar	84	
	South Africa	EC 250 g/l	0.1 500	0.02	1 or 2	Broadcast spray	-	
Coconut	Sri Lanka	EC 250 g/l	0.6 1	60	1	Trunk inject	21	
Coffee	India	EC 250 g/l	0.62 1000	0.062	1	Individual tree spray	21	
Cotton	India	EC 250 g/l	0.25 500	0.05	2	Broadcast spray	21	

Crop	Country	Form	Application				PHI, days	Comments
			Rate, kg ai/ha & l water/ha	Spray conc., kg ai/hl	No.	Method		
	Kenya	EC 250 g/l	0.38 800	0.047	2	Broadcast spray	-	
	Mexico	EC 250 g/l	0.38 400	-	1 or 2	Broadcast spray	14	
	Morocco	EC 250 g/l	0.25 1000	-	2	Row spray	21	
	Peru	EC 250 g/l	0.25 100	-	3	Broadcast spray	14	
	South Africa	EC 250 g/l	0.12 300	0.042	2	Broadcast spray	21	
	USA	EC 250 g/l	0.84		3	Broadcast spray	14	
	Turkey	EC 265 g/l	0.26 600	0.044	1	Row spray	21	
Cucum-ber	Germany	EC 250 g/l	0.3	-	3	Broadcast spray	4	0.17 if <50 cm
	Italy	SL 189 g/l	0.23 800	0.028	1	Broadcast spray	21	
	Mexico	EC 2509 g/l	0.75 400	-	1 or 2	Broadcast spray	-	
Cucur-bits	Peru	EC 250 g/l	0.2 800	-	2	Broadcast spray	14	
Currant	Austria	EC 48 g/l	0.36 1500	-	3	Row spray	35	Red
Egg plant (aubergi ne)	India	EC	0.25 l/ha 500 l water/ha	0.05	2	Broadcast spray	14	
	Mexico	EC	0.5 l/ha 400 l water/ha	-	1 or 2	Broadcast spray	7	
	South Africa	EC	0.1 l/ha 500 l water/ha	0.02	2	Row spray	14	
Endive	Germany	EC 375 g/l 250 g/l	0.12 0.15	-	2 ?	Broadcast spray	14	winter
Fodder peas	France	EC 250 g/l	0.10			Broadcast spray	-	
Garlic	India	EC 250 g/l	0.12 500	0.025	2	Broadcast spray	14	
Gourd	Mexico	EC 250 g/l	0.75 400	-	1 or 2	Broadcast spray	14	
	Peru	EC 250 g/l	0.4	-	2	-	14	
Grapes	Austria	SL 100 g/l	0.2 1000	0.02	1	Row spray	-	European
	Germany	EC 250 g/l	0.5 2000	0.025	1	Row spray	-	European. Applied from 2 leaf stage to inflorescence
	India	EC 250 g/l	0.19 500	0.038	2	Broadcast spray	21	European
	Italy	SL 189 g/l	0.23 800	0.028	1	Broadcast spray	40	European
	Mexico	EC 250 g/l	0.5 600	0.083	1 or 2	Broadcast spray	90	European
	Morocco	EC	0.02	-	1	Row spray	21	European

Crop	Country	Form	Application				PHI, days	Comments
			Rate, kg ai/ha & l water/ha	Spray conc., kg ai/hl	No.	Method		
		250 g/l	800					
Grape-fruit	Mexico	EC 250 g/l	0.75 1500	-	1 or 2	Broadcast spray	7	
Ground-nut	India	EC 250 g/l	0.25 500	0.038	2	Broadcast spray	14	
	South Africa	EC 250 g/l	0.12 500	0.025	2	Broadcast spray	21	
Kale	Austria	SL 100 g/l	0.22 1000	-	1	Row spray	21	Including curly. turnip
	Germany	EC 250 g/l	0.22	-	2	Broadcast spray	14	Curly only
		SL 100 g/l	0.15	-	2	Broadcast spray	14	Including curly. Turnip
		EC 250 g/l	0.15	-	1	Broadcast spray	21	Under 50 cm
	Ireland	EC 250 g/l	0.15	-	1	Broadcast spray	21	Under 50 cm.
		EC 375 g/l	0.12	-	2	Broadcast spray	14	Turnip
Kohlrabi	Germany	EC 214 g/l	0.13 400	0.021	2	Broadcast spray	14	
		EC 250 g/l	0.15		1	Broadcast spray	21	Under 50 cm
Leek	Italy	SL 189 g/l	0.17 600	0.028	1	Broadcast spray	-	Common
Lemon	Mexico	EC 250 g/l	0.75 1500	-	1 or 2	Broadcast spray	7	
Lettuce	Austria	EC 250 g/l SL 100 g/l	0.15 600	0.025	1	Row spray	21	Cutting
	Germany	EC 375 g/l	0.12	-	2	Broadcast spray	14	Cutting, head
		EC 250 g/l	0.16	-	1	Broadcast spray	21	Cutting, head
	Ireland	EC 250 g/l	0.15 (200 l water/ha)	-	1	Broadcast spray	21	
		SL 100 g/l	0.15	-	2	Broadcast spray	14	Head
	Mexico	EC 250 g/l	0.5 400	-	1	Broadcast spray	21	
Maize	India	EC 250 g/l	-	-	-	-	14	
	Kenya	EC 250 g/l	0.12 800	0.016	2	Broadcast spray	-	
	Mexico	EC 250 g/l	0.25 400	-	1	Broadcast spray	7	
	South Africa	EC 250 g/l	0.12 300	0.042	1	Broadcast spray	21	
Mango	India	EC 250 g/l	2.5 2500	0.1	2	Individual tree spray	21	
Melon	Mexico	EC 250 g/l	0.75 400	-	1	Broadcast spray	14	
	Portugal	EC 25 g/l	0.025 1000	0.0025	1	Row spray	35	
Mustard	India	EC	0.19	0.038	1	Broadcast	14	Black

Crop	Country	Form	Application				PHI, days	Comments
			Rate, kg ai/ha & l water/ha	Spray conc., kg ai/hl	No.	Method		
		250 g/l	500			spray		
Oats	Austria	EC 250 g/l	0.12 400	0.031	1	Row spray	21	
Okra	India	EC 250 g/l	0.25 500	0.05	2	Broadcast spray	7	
Oil seed	France	EC 250 g/l	0.15			Broadcast	-	
Olive	South Africa	EC 250 g/l	0.25 1000	0.025	2	Individual tree spray	90	
Onion	India	EC 250 g/l	0.19 500	0.038	2	Broadcast spray	14	
	Mexico	EC 250 g/l	0.25 400	-	1	Broadcast spray	30	
	South Africa	EC 250 g/l	0.075 1000	0.0075	2	Broadcast spray	21	
Orange	Mexico	EC 250 g/l	0.75 1500	-	1 or 2	Broadcast spray	7	
	Spain	EC 250 g/l	0.75 3000	0.025	2	Individual plant spray	30	Sweet. Mandarin.
Paprika	India	EC 250 g/l	0.25 500	0.05	2	Broadcast spray	14	
Pea	Germany	EC 375 g/l	0.18	-	2	Broadcast spray	7	Garden
	India	EC 250 g/l	0.19 500	0.038	1	Broadcast spray	14	Garden
	Italy	SL 189 g/l	0.23 800	0.0283	1	Broadcast spray	21	Outdoor and greenhouse. Garden.
	Mexico	EC 250 g/l	0.25 400	0.062	1	Broadcast spray	21	
	South Africa	EC 250 g/l	0.12 500	0.025	21	Broadcast spray	21	
	Sweden	EC 100 g/l	0.2 400	-	1	Individual leaf spray	21	Garden
Peach	Austria	EC 48 g/l	0.36 1500	-	3	Row spray	35	
	Germany	EC 250 g/l	0.38 1500	0.025	1	Broadcast spray	28	
		SL 100 g/l	0.38 1500	0.025	3	Row spray	28	
	India	EC 250 g/l	0.62 2500	0.025	1	Individual tree spray	21	
	Italy	SL 189 g/l	0.28 1000	0.028	1	Broadcast spray	30	
	Portugal	EC 25 g?l	0.05 1000	0.005	1	Row spray	35	
	South Africa	EC 250 g/l	0.88 3500	0.025	1	Individual tree spray	21	
	Turkey	EC 265 g/l	0.53 2000	0.0265	1	Individual tree spray	21	
Pears	France	EC 250 g/l		0.02		Broadcast spray	-	
	Germany	EC 250 g/l SL 100 g/l	0.38 1500	0.025	1	Broadcast spray (EC) Row spray (SL)	~60	For EC, apply before or directly after flowering
	Ireland	EC 250 g/l	0.32 calculated at	0.0075 high volume	2	Foliar	~90	Apply before and/or directly after

Crop	Country	Form	Application				PHI, days	Comments
			Rate, kg ai/ha & l water/ha	Spray conc., kg ai/hl	No.	Method		
			low volume	0.081 low volume (200 l water/ha)				flowering
	Italy	SL 189 g/l	0.34 1200	0.028	1	Broadcast spray	30	
	Mexico	EC 250 g/l	0.75 1500	-	1	Broadcast spray	30	
	Portugal	EC 250 g/l	0.38 1000 (cal-culated)	0.038	2	Row spray	56	
	South Africa	EC 250 g/l	0.88 3500	0.025	1	Individual plant spray	21	
	Spain	EC 250 g/l	0.25 1000	0.025	2	Individual tree spray	30	
	Turkey	EC 265 g/l	0.53 2000	0.026	1	Individual tree spray	21	
Pepper, Sweet	Mexico	EC 250 g/l	0.5 400	-	1	Broadcast spray	-	
	South Africa	EC 250 g/l	0.1 500	0.02	2	Broadcast spray	14	
Pistachio	Turkey	EC 265 g/l	0.80 2000	0.040	1	Individual tree spray	21	
Plum	Austria	EC 48 g/l	0.37 1500	-	3	Row spray	35	
	Germany	EC 250 g/l SL 100 g/l	0.38 1500	0.025	1	Row spray	~60	Including Syrian plum. Before or directly after flowering.
	India	EC 250 g/l	0.62 2500	0.025	1	Individual Plant spray	21	
	Ireland	EC 250 g/l		0.022 high volume 0.19 low volume (200 l water/ha)	1	Foliar	~90	Apply before cot-split stage.
	Mexico	EC 250 g/l	0.88 1500	-	1	Broadcast spray	35	
	South Africa	EC 250 g/l	0.88 3500	0.025	1	Individual tree spray	21	
	Spain	EC 250 g/l	0.25 1000	0.025	2	Individual tree spray	30	
Pome fruit	Germany	EC 276 g/l	0.41 1500	0.027	3	Broadcast spray	28	Status of this formulation is unknown.
	Germany	EC 250 g/l	0.40	0.026	1	Foliar	60	
	France	EC 250 g/l		0.020		Foliar	60	
Potato	Austria	EC 250 g/l SL 100 g/l	0.25 400	0.0625	3	Broadcast spray	42	
	Germany	EC 375 g/l	0.3 400 600 pending	0.075	3	Broadcast spray	21 28 pending	
	India	EC	0.25	0.05	1	Broadcast	14	

Crop	Country	Form	Application				PHI, days	Comments
			Rate, kg ai/ha & l water/ha	Spray conc., kg ai/hl	No.	Method		
		250 g/l	500			spray		
	Ireland	EC 250 g/l	0.15 0.22 (200 l water/ha)		2-4	Broadcast spray	28	Lower rate under 50 cm.
	Italy	SL 189 g/l	0.23 800	0.028	1	Broadcast spray	21	
	Mexico	EC 250 g/l	0.38 400	-	1	Broadcast spray	7	
	Peru	EC 250 g/l	0.3 800	-	2	Broadcast spray	21	
	South Africa	EC 250 g/l	0.25 500	0.05	4	Broadcast spray	21	
	Spain	EC 250 g/l	0.3 600	-	3	Individual plant spray	30	
Quince	France	EC 250 g/l	0.25 1000	0.025	2	Broadcast spray	-	
Radish	India	EC 250 g/l	0.19 500	0.038	1	Broadcast spray	21	
Rape	France	EC 250 g/l	0.12 400	0.031		Broadcast spray	-	
Rice	India	EC 250 g/l	0.25 500	0.05	1	Broadcast spray	14	Planted (paddy)
Rye	Austria	EC 250 g/l SL 100 g/l	0.12 400	0.031	1	Broadcast spray	21	
	Germany	EC 375 g/l	0.12 400	0.03	2	Broadcast spray	21	
	Ireland	EC 250 g/l	0.12 (200 l water/ha)		1	Broadcast spray	21	
Safflow-er	India	EC 250 g/l	0.15 500	0.03	1	Broadcast spray	14	
	Mexico	EC 250 g/l	0.25 400	0.062	1	Broadcast spray	7	
Sesame	India	EC 250 g/l	0.15 500	0.03	1	Broadcast spray	14	
Sorghu m	India	EC 250 g/l	-	-	-	-	14	Grain
	Mexico	EC 250 g/l	0.25 400	-	1	Broadcast spray	45	Grain
	South Africa	EC 250 g/l	0.12 200	0.062	2	Broadcast spray	57	Grain
Soya bean	India	EC 250 g/l	0.19 500	0.038	1	Broadcast spray	14	
Spinach	Germany	EC 375 g/l	0.12	0.022	2	Broadcast spray	14	
Stone fruit (except cherry)	Germany	EC 276 g/l	0.41 1500	0.027	2	Broadcast spray	28	
Straw-berry	Germany	EC 250 g/l	0.5 2000	0.025	1	Broadcast spray	-	
	Ireland	EC 250 g/l		0.022 high volume 0.25 low	1	Broadcast	Post harv est	

Crop	Country	Form	Application				PHI, days	Comments
			Rate, kg ai/ha & l water/ha	Spray conc., kg ai/hl	No.	Method		
				volume (200 l water/ha)				
	Mexico	EC 250 g/l	0.25 400	-	1	Broadcast spray	3	
	Portugal	EC 250 g/l	0.025 1000	0.0025	1	Row spray	-	
Sugar beet	Austria	EC 250 g/l SL 100 g/l	0.2 400	-	2	Broadcast spray	28	
		EC 48 g/l	0.1 400	0.024	2	Broadcast spray	35	
	France	EC 258 g/l	0.15 400	0.038		Broadcast spray	28	
		EC 250 g/l	0.38 300	0.12	3	Broadcast spray	-	
	Germany	EC 590 g/l	0.24 400	0.06	4	Broadcast spray	28	
		EC 375 g/l	0.2 400	0.05	2	Broadcast spray	28	
		EC 250 g/l	0.38		1	Broadcast spray	28	
	Italy	SL 189 g/l	0.14 500	0.028	1	Broadcast spray	30	
	Morocco	EC 250 g/l	0.25 600	-	1	Row spray	21	
	Spain	EC 250 g/l	0.38 600	-	3	?	30	
	Sweden	EC 100 g/l	0.2 400	-	1	Individual leaf spray	21	
Sun-flower	France	EC 258 g/l	0.1 400	0.025	1	Broadcast spray	-	
	France	EC 250 g/l	0.10			Broadcast spray	-	
Tea	South Africa	EC 250 g/l	0.12 500	0.025	1	Individual plant spray	21	
Tomato	Germany	EC 250 g/l	0.33 1200	0.028	3	Broadcast spray		0.17 if <50 cm
	India	EC 250 g/l	0.25 500	0.05	2	Broadcast spray	14	
	Italy	SL 189 g/l	0.23 800	0.028	1	Broadcast spray	21	Outdoors and green-house
	Portugal	EC 25 g/l	0.025 1000	0.0025	1	Row spray	35	
	South Africa	EC 250 g/l	0.1 500	0.02	2	Row spray	14	
Triticale	France	EC 258 g/l	0.1 400	0.025	3	Broadcast spray	-	See wheat
Turmeric	India	EC 250 g/l	0.25 500	0.05	2	Broadcast spray	14	
Walnut	Mexico	EC 250 g/l	0.88 1500	-	1	Broadcast spray	30	
Water-melon	Peru	EC 250 g/l	0.4	-	2	-	14	
Wheat	Austria	SL 100 g/l EC	0.12 400	0.031	1	Broadcast spray	21	

Crop	Country	Form	Application				PHI, days	Comments
			Rate, kg ai/ha & l water/ha	Spray conc., kg ai/hl	No.	Method		
		250 g/l						
	Germany	EC 375 g/l	0.12 400	0.03	2	Broadcast spray	21	
		EC 250 g/l	0.14 400	0.03	1	Broadcast spray	21	
	India	EC 250g/l	0.12 500	0.025	1	Broadcast spray		Soft
	Ireland	EC 250 g/l	0.12 (200 l water/ha)		1	Broadcast spray	21	Includes triticale
	Italy	SL 189 g/l	0.17 600	0.028	1	Broadcast spray	30	Soft
	Kenya	EC 250 g/l	0.12 800	0.016	2	Broadcast spray	-	Soft
	Peru	EC 250 g/l	0.2 600	-	2	Broadcast spray	14	Soft
	Portugal	EC 250 g/l	0.12		1	Broadcast spray	21	Winter
	South Africa	EC 250 g/l	0.12 300	0.042	2	Broadcast spray	48	soft

[1] or unspecified

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of the supervised residue trials are shown in Tables 20–30. The trials were reported in sufficient detail, including acceptable information on sample storage and analysis, unless otherwise noted.

The trials are reviewed in the sequence of the Codex Alimentarius Classification of Foods and Feeds.

Citrus fruits

Trials were reported on the spray application of ODM to oranges and lemons in Spain, Italy and Portugal (Seym, 1996; Seym and Heinemann, 1996). GAP for oranges in Spain is 2 x 0.75 kg ai/ha, 30-day PHI (90 days proposed), and for citrus fruit in Portugal 2 x 0.050 kg ai/hl (0.75 kg ai/ha), 84-day PHI. GAP for Italy was not available and is assumed to be that of Portugal.

Table 20. Residues of ODM + ODM sulfone following application of ODM EC formulation to lemons and oranges in Spain, Italy and Portugal.

Location, year	Application			PHI, days	ODM + ODM sulfone, mg/kg[1]	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment, (days), Growth stage at final application			
Orange						
Pobla Llarga, Spain 1994	0.75	3000	2 15 early fruit setting	0 21 35 64 pulp 92 64 peel 92	0.33 0.03 0.01 <0.01 ≤0.01 0.01 0.01	Method 00009/ M 004 Recovery 83–101% at 0.01 and 0.1 mg/kg. Up to 11 months from sampling to extraction
Vinaroz, Spain 1994	0.75	3000	2 15 30% final size	0 21 35 62 pulp 90 62 peel 90	0.83 0.04 0.01 ≤0.01 <0.01 ≤0.01 <0.01	
Pobla Llarga, Spain 1994	0.75	3000	2 19 early fruit setting	0 92 pulp 92 peel	0.22 ≤0.01 0.01	
Riudoms, Spain 1995	0.75	3000	2 30 start of ripening	0 89 pulp 89 peel	0.26 0.02 0.13	Method 00009/ M 007. Recovery 71–098% at 0.01 and 0.1 mg/kg from pulp and 79–108% from peel (n = 10)
Chamusca, Portugal 1995	0.75	3000	2 31 start of ripening	0 18 35 pulp 35 peel 62 pulp 62 peel	0.28 0.10 0.03 0.21 0.02 0.09	
Raval de Jesus, Spain 1995	0.75	3000	2 28 start of ripening	0 90 pulp 90 peel	0.26 0.04 0.13	
Sta. Barbara, Spain 1995	0.75	3000	2 29 Begin of ripening	0 90 pulp 90 peel	0.17 0.01 0.06	
Lemons						
Alhama de Murcia, Spain 1995	0.75	3000	2 29 Bloom to fruit growing	0 fruit 21 fruit 35 pulp 35 peel 63 pulp 63 peel 90 pulp 90 peel	0.56 0.03 <0.01 0.02 <0.01 <0.01 ≤0.01 ≤0.01	Method 00009/ M 007. Recovery 68–79% at 0.01 and 0.1 mg/kg from pulp and 75–83% from peel (n = 4).
Avola, Italy 1995	0.75	2500 3000	2 30 20% fruit size	0 fruit 90 pulp 90 peel	0.95 ≤0.01 <0.01	

Location, year	Application			PHI, days	ODM + ODM sulfone, mg/kg[1]	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment, (days), Growth stage at final application			
Siracusa, Italy 1995	0.75	2500 3000	2 30 bloom to fruit growing	0 fruit 89 pulp 89 peel	0.86 <0.01 <0.01	
Orihuela, Spain 1995	0.75	3000	2 30 40% fruit size	0 fruit 21 fruit 35 pulp 35 peel 63 pulp 63 peel 90 pulp 90 peel	0.39 0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01	

[1]In whole fruit unless otherwise stated

Pome fruits

Supervised field trials on apples and pears in various European countries were reported (Seym, 1993, 1996a,b; Anon., 1991). GAP for apples and pears in France is 0.020 kg ai/hl, 60-day PHI, and in Germany 1 x 0.026 kg ai/hl (0.40 kg ai/ha calculated for 1500 l water/ha), applied before or directly after flowering, with an estimated PHI of 60 days. GAP for pears in Portugal, applicable to Spain and Italy, is 0.025 kg ai/hl with a 56-day PHI. GAP for Belgium was not reported and was assumed to be that of Germany. The conditions and results of the field trials are shown in Table 21.

Table 21. Residues of ODM + ODM sulfone following application of ODM EC formulation to apples and pears in France, Belgium and Germany.

Location, year	Application			PHI, days	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment, (days), Growth stage at final application			
Apples						
Versuchsgut Hofchen (NE Cologne), Germany, 1995	0.25 0.38	1000 1500	2 41 20 mm fruit	90	<0.01	Method 0009/ M 0007. Recovery 65–89% at 0.01 and 0.1 mg/kg, n = 8. Samples stored 3 or 5 months frozen before analysis.
Versuchsgut Laacherhof (S Dusseldorf), Germany 1995	0.25 0.38	1000 1500	2 49 20 mm fruit	90	<0.01	
St. Etienne du Gres, France 1995	0.25 0.38	1000 1500	2 25 2nd fruit fall	30 45 60 75 92	0.08 0.05 0.03 0.01 0.01	Method 00009/ M 007
Pernes les Fontaines, France 1995	0.25 0.38	1000 1500	2 26 2nd fruit fall	30 92	0.10 <0.01	Method 00009/ M 003

Location, year	Application			PHI, days	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment, (days), Growth stage at final application			
Melkwezer, Belgium 1991	0.25	300	1 end of flowering	94 108 122	<0.04 <0.04 <0.04	Method 0009/ M 003
Ezemaal, Belgium 1991	0.25	300	1 after flowering	100–128	<0.01	Method 00009/ M 003
St. Paterne Racan, France, 1991	0.25	1000	1 50 mm fruit	29, 58	<0.04	Method 00009/ M 003
Hofchen, Germany 1990	0.38	1500	1 5 cm fruit	0 14 21 29 29 sauce 29 juice	0.26 0.15 0.12 0.09 <0.05 0.08	Method 00009/ M 003
Laacherhof, Germany 1990	0.38	1500	1 advanced ripening	0 14 20 28 35 28 sauce 28 juice	0.33 0.43 0.41 0.39 0.26 0.13 0.38	Method 00009/ M 003
Pears						
Versuchsgut Hofchen (NE Cologne), Germany 1995	0.25 0.38	1000 1500	2 56 20 mm fruit	44 77 105	<0.01 <0.01 <0.01	Method 00009/ M 0007. Recovery 59-115% at 0.01 and 0.1 mg/kg, n =14 (mean 84% ± 19%).
Versuchsgut Laacherhof (S Dusseldorf) , Germany 1995	0.25 0.38	1000 1500	2 58 2nd fruit fall	44 120	<0.01 <0.01	
Pogio Renatico, Italy 1995	0.25 0.38	1000 1500	2 4 10-20 mm fruit	45 60 75 90 115	<0.01 <0.01 <0.01 <0.01 <0.01	Method 00009/ M 007. Recovery 63-115% at 0.01 and 0.1 mg/kg, n = 14.
Dugliolo, Italy 1995	0.25 0.38	1000	2 8	45, 86	<0.01	
Ezemaal, Belgium 1991	0.25	300	1 end of flowering	109–137	<0.04	Method 00009/ M 003. Samples stored frozen up to 6 months before analysis
Rivarennes, France 1991	0.25	1000	1 fruit development	0 14-52	0.21 <0.04	Method 00009/ M 003. Samples stored frozen for 5 months before analysis.

Stone fruits

Supervised field trials on plums in Germany were reported (Seym, 1996). GAP for stone fruit in Germany is 1 x 0.026 kg ai/ha (0.38 kg ai/ha calculated), with application before or directly after flowering. This gives a PHI of about 60 days. The results of the trials are shown in Table 22.

Table 22. Residues of ODM + ODM sulfone following application of ODM EC formulation to plums in Germany, 1995.

Location	Application			PHI, days	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment, (days), Growth stage at final application			
Plums						
Hofchen Burscheid, Germany	0.38	1500	1 fruit fall after flowering	61 107	0.040 0.011	Method 00009/ M 007. Recovery 66-114% at 0.01 and 0.1 mg/kg, n = 9. Samples stored frozen for 7 months before analysis.
Laacherhof Monheim, Germany	0.38	1500	1 sepals falling	60 118	0.014 <0.01	
Obstbaubetrieb Tackheide Tonisvorst, Germany	0.38	1500	1 sepals falling	60 120	0.044 <0.01	
Obsthof Schick Freinsheim, Germany	0.38	1500	1 sepals falling	60 120	0.028 <0.01	

Berries and other small fruits

Supervised field trials on grapes in Germany and Italy were reported (Seym, 1993a,b). GAP for use on grapes in Germany is 1 x 0.025 kg ai/hl, applied for 2 leaves to inflorescence development, PHI not specified, and in Italy 1 x 0.23 kg ai/ha, 40-day PHI. The results of the trials are shown in Table 23. The report was a summary only and did not include details of sampling, sample storage or analysis.

Table 23. Residues of ODM + ODM sulfone following application of ODM EC formulation to grapes in Germany and Italy.

Location/ Year	Application			PHI, days	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Grapes						
Bickensohl, Germany 1991	0.2	800	1	115	<0.04	Method 00009/ M 003. Samples stored about 4 months before analysis.
Albig, Germany 1991	0.2	800	1	94	<0.04	
Diesesfeld, Germany 1991	0.2	800	1	109	<0.04	
Ravenna, Italy 1991	0.28	1000	1 fruit setting 70%	0 40 60 40 must 40 wine	0.37 <0.04 <0.04 <0.04 <0.04	Method 00009/ M 003. Two trials were on different varieties. Samples stored at –20°C for about 4-6 months before analysis.
Ravenna, Italy 1991	0.28	1000	1 fruit setting 30%	0 40 60 40 must 40 wine	0.30 0.06 <0.04 <0.04 <0.04	

Brassica vegetables

Supervised field trials were carried out in Germany on cabbage (Anon., 1973-1986; Schmidt, 1992), curly kale (Seym and Heinemann, 1996) and kohlrabi (Anon., 1974-1980). The results are given in Table 24. The reports of the cabbage and kohlrabi trials were summaries only. For example details of the sampling, sample storage and analysis including validation and chromatograms were not provided. The report of the curly kale trials was complete. Although 21 trials on cabbages were reported, 5 of the 9 trials in 1976 were apparently replicates of others, so only 4 results from that year were evaluated separately. GAP for cabbage, kale and kohlrabi in Germany is 1 x 0.15 kg ai/ha at a plant height under 50 cm and a PHI of 21 days.

Table 24. Residues of ODM + ODM sulfone in or on brassica vegetables after foliar application of ODM EC formulation. Germany.

Location, year	Application			PHI, days	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Cabbage						
Monheim Laacherhof, 1976	0.15	600	2	0 7-14	0.08 <0.01	Method 00009
Monheim, Laacherhof, 1976	0.15	600	2	0 7-14	0.21 <0.01	Method 00009
Monheim, Laacherhof, 1976	0.15	600	2	0 7 14	0.21 0.01 <0.01	Method 00009
Monheim Laacherhof, 1979	0.15	600	2 flower diameter 10 cm	0–28	<0.03	Method 00009
Klein-Niedesheim, 1979	0.15	600	2 start of head development	0–28	<0.05	Method 00009
Worms-Heppenheim, 1986	0.15	600	2 start of head development	0 3 7	0.4 0.18 <0.01	Method 00009
Monheim, Laacherhof, 1986	0.15	600	2 start of flower development	0 3 7 14	0.15 0.06 0.04 <0.01	Method 00009
Monheim, Laacherhof, 1976	0.12	600	2	0–21	<0.06	Method 00009
Monheim, Laacherhof, 1976	0.12	600	2	0–21	<0.06	Method 00009
Monheim, Laacherhof, 1976	0.12	600	2	0–21	<0.06	Method 00009
Burscheid, 1978	0.18	600	2 head formation	0 3 7 14 21 28	0.75 0.27 0.31 0.25 0.02 0.02	Method 00009
Klein-niedersheim, 1978	0.18	600	2 head formation	0 4–28	1.2 <0.05	Method 00009
Monheim, Laacherhof, 1973	0.12	600	2	22	<0.01	Method 00009. Trials with 3 varieties.
Klein Niedesheim, 1986	0.12	600	3 start of head	0 3-21	1 <0.1	Method 00009

Location, year	Application			PHI, days	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
			development			
Monheim Laacherhof, 1986	0.12	600	3 flower formation	0 3-21	0.1 <0.1	Method 00009
Monheim, Laacherhof, 1979	0.15	600	2 start of head development	0 7-28	0.7 <0.04	Method 00009
Burscheid, 1990	0.15	300	1 33% final head size	0 7 14 14 cooked head 14 cooking water	0.70 0.13 <0.05 <0.05 <0.05	Method 00009
Monheim, Laacherhof, 1990	0.15	600	1 66% final head size	0 7 14 14 cooked head 14 cooking water	0.40 <0.05 <0.05 <0.05 <0.05	<Method 00009
Leichlingen, 1976	0.12	600	2	0 4 7 14-21	0.31 0.05 0.11 <0.03	Method 00009
Langenfeld-Reusrath, 1976	0.12	600	2	0 4 14-21	0.72 0.11 <0.03	Method 00009
Leichlingen, 1976	0.12	600	2	0 4-21	0.06 <0.03	Method 00009
Kale						
Klein- Niedesheim, Germany 1994	0.15	600	1 plant development	0 5 6 14-28	2.7 0.28 0.13 <0.01	Method 00009. Samples stored 6.5 months before analysis. Recovery 74-86%, mean 80%, fortified at 0.01 and 0.1 mg/kg n = 5, for all kale trials
Worms-Heppenheim, 1994	0.15	600	1 plant development	0 5 7 14-28	2.6 0.11 0.05 <0.01	Method 00009. Samples stored 7 mos. before analysis. See first kale entry for recovery.
Burscheid Hofchen, 1994	0.15	600	1 plant development	0 plant (aerial) 5 7 14 21 leaf 21 leaf cooked 21 leaf cooking water	1.2 0.17 0.12 0.02 <0.01 <0.01 <0.01	Method 00009. Samples stored 7 months before analysis
Monheim Laacherhof, 1994	0.15	600	1 plant development	0 plant (aerial) 4	3.2 0.89	Method 00009. Samples stored 8 months before

Location, year	Application			PHI, days	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
				7 14 21 leaf 21 leaf cooked 21 leaf cooking water	0.42 0.01 <0.01 <0.01 <0.01	analysis.
Kohlrabi						
Monheim, Laacherhof	0.15	600	2 walnut size	0 leaf 7 14 21 0–28 root	3.59 0.62 0.22 <0.01 <0.01	Method 00009
Klein Niedesheim, 1979	0.15	600	2 50% final diameter	0 leaf 7–28 0–28 root	0.48 <0.06 <0.06	Method 00009
Dicksander-koog, 1975	0.15	300	3	0 root 14-35 root	<0.01; 0.02; 0.02 <0.01	Method RA133/74. Three trials
Monheim, Laacherhof, 1974	0.12	600	2 mature	0 7 14 21 28	0.06 0.05 0.05 0.03 0.01	Method I11 (unknown)

Leafy Vegetables

Supervised field trials were reported from Germany on lettuce (Anon., 1975a,b; Seym and Nusslein, 1995). Only the 1995 report was detailed, the 1975 reports being only summaries. GAP for the use of ODM on lettuce in Germany is 1 x 0.16 kg ai/ha of an EC formulation, PHI 21 days. The results are given in Table 25. There were only three independent trials, with triplicate plots at Monheim in 1975 and duplicates at Monheim and Burscheid in 1993.

Table 25. Residues of ODM + ODM sulfone in or on lettuce after foliar application of ODM EC formulation in Germany

Location, year	Application			PHI, days	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Monheim, Laacherhof 1975	0.12	600	2 before harvest	0 8 14 21-28	2.5 0.04 0.04 <0.01	Method I 47 modified
Monheim, Laacherhof 1975	0.12	600	2	0 8 14 21-28	4.91 0.21 0.05 <0.01 <0.01	Method I47 modified
Monheim, Laacherhof 1975	0.15	600	2	0 8 15 21 28	5.29,5.32,5.21 0.76,0.77,0.79 0.29,0.16,0.17 0.02,0.02,0.03 0.01,0.01,0.01	Method I 47 modified. Results represent trials with 3 varieties
Burscheid Hofchen 1993	0.15	600	1 80% final size	0 7 10 14	1.5 0.39 0.18 0.13	Method 00009, M 07. Samples stored frozen 5–6 months before analysis. Head were fortified at 0.02, 0.20 and 0.50 mg/kg with ODM. Recovery ranged from 71–96%, mean 88%.
Monheim Laacherhof 1993	0.15	600	1 80% final size	0 7 10 14	2.5 0.72 0.31 0.20	
Burscheid Hofchen 1993	0.15	600	1 80% final size	0 7 10 14	1.1 0.29 0.09 0.04	
Monheim Laacherhof 1993	0.15	600	1 harvest	0 7 10 14	0.55 0.09 0.09 <0.02	

Pulses

Supervised field trials were conducted in Germany and France on field peas (Anon., 1991; Seym, 1996)., and in Germany on field beans (Anon., 1975, 1979). The results are shown in Table 26. GAP for beans in Germany is 2 x 0.15 kg ai/ha (under 50 cm), 0.25 kg ai/ha (over 50 cm), with a 28-day PHI. GAP for peas was not reported for Germany or France for the 250 kg ai/l EC formulation. GAP for Italy is 1 x 0.23 kg ai/ha, 21-day PHI.

Table 26. Residues of ODM + ODM sulfone in or on dried field peas and field beans after foliar application of ODM EC formulation.

Location, year	Application			PHI, days, Sample	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Field peas						
Worms-Heppenheim, Germany 1995	0.1	600	2 pods 10% length	0 pea with pod 28 seed, dry 28 straw	0.22 ≤0.01 <0.02	Method 00009, M 007. ODM recoveries at 0.01 and 0.1 mg/kg, 67, 71, 89, 76, 79% from pod with seed, 69, 77, 87, 76, 78% from seed. ODM recoveries at 0.01, 0.02, 0.1 mg/kg from straw 67, 75, 85, 70, 82%
Burscheid Hofchen, Germany 1995	0.1	600	2 pods typical size	0 pea with pod 13 seed, dry 13 straw 28 straw	<0.01 ≤0.01 <0.02 0.15	
Monheim Laacherhof, Germany 1995	0.1	600	2 10% pods ripe	0 pea with pod 28 seeds, dry 28 straw	0.19 ≤0.01 <0.02	
Prey, France 1991	0.1	280	2 10 pod development	0 hull, green 11 hull, green 23 hull, dry 23 seed	0.33 0.02 <0.04 ≤0.01	Method 00255. Summary translation only.
Les Essarts, Bretagnolles, France 1991	0.1	280	2 10 pod development	0 hull, green 11 hull, green 23 hull, dry 23 seed	0.19 <0.01 <0.04 ≤0.01	Method 00255. ODM recoveries 90% at 0.01 mg/kg. Summary translation only.
Field beans						
Monheim, Laacherhof, Germany 1975	0.15	600	3 19 26	0 bean 7 14 21 28 0 pod 7 14 21 28 0 straw 7 14-28	<0.01 0.02 0.05 <0.01 <0.01 0.3 0.04 0.02 0.0-4 <0.01 2.9 0.1 <0.01	Method I47 modified. Samples analysed within 1 month
Monheim, Laacherhof, Germany 1975	0.15	600	3 19 26	0 bean 7 14 21 28 0 pod 7 14 21 28 0 straw 7 14 21 28	0.05 0.02 <0.01 <0.01 <0.01 0.42 0.08 0.04 0.04 <0.01 13. 0.35 0.06 <0.01 <0.01	Method I 47 modified. Samples stored up to 2 months before analysis.

Location, year	Application			PHI, days, Sample	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Monheim, Laacherhof, Germany 1975	0.15	600	3 19 26	0 bean 7 14 21 28 0 pod 7-28 0 straw 76 14 21 28	0.05 0.05 0.05 0.05 0.05 0.04 <0.01 1.8 0.1 0.04 0.04 0.04	Method 00009. Samples stored up to 2 months before analysis.
Monheim Laacherhof, Germany 1979	0.22	900	3 14 14	0-28 bean 0 pod 7-28 pod 0 straw 7 straw 14-28 straw	0.05 0.04 <0.01 1.8 0.1 0.04	Method 00009. Samples stored 6 months before analysis.
Klein niedesheim, Germany 1979	0.22	900	3 14 14 start of pod development	0 bean 7 14 21 28 0 pod 7-28 0 straw 7 14 21 28	<0.02 <0.02 <0.04 <0.04 <0.04 0.06 <0.04 2.1 0.76 0.24 0.04 <0.03	Method 00009. Samples stored 8 months before analysis.

Root and tuber vegetables

The Netherlands provided summary information on a field trial with potatoes in 1971 (Olthof and Meyer, 1973), and Bayer AG reported supervised field trials in Germany, France and the UK (Anon., 1977; Seym, 1993a,b, 1996; Heinemann and Seym, 1998; Schmidt, 1992).

Bayer AG also reported supervised field trials on sugar beet (Anon., 1973, 1991; Ohs, 1993; Schmidt, 1989, 1992).

GAP for the use of ODM on potatoes in Germany and Austria is 3 x 0.3 kg ai/ha with a 21-day PHI (28-day pending) and 3 x 0.25 kg ai/ha with a 42-day PHI respectively. No information was supplied for the UK or France. GAP for Ireland is 0.15 kg ai/ha (under 50 cm), 0.22 kg ai/ha (over 50 cm), 200 l water/ha, 28-day PHI. GAP for sugar beet (fodder beet) in Germany and France is 4 x 0.24 kg ai/ha and 1 x 0.15 kg ai/ha respectively, with a 28-day PHI. No information was supplied for the UK or The Netherlands.

The results are shown in Table 27. Two of the German trials in 1993 were replicates of others and therefore not included in the evaluation.

Table 27. Residues of ODM + ODM sulfone in or on root and tuber vegetables after foliar application of ODM EC formulation.

Location/Year	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application	PHI, day, Sample	ODM + ODM sulfone, mg/kg	Comments
Potato						
Klein Niedersheim, Germany 1993	0.33 0.28 0.22	600	3 10 10 tubers 30%	0–63	≤0.02	Method 00009, M 003. Samples stored 6-8 months before analysis. ODM recoveries at 0.02 mg/kg 49-93%, n=11; at 0.2 mg/kg 44-64%, n=7; at 0.5 mg/kg 67, 68%. Example chromatograms provided.
Burscheid Hofchen, Germany 1993	0.33 0.28 0.22	600	3 13 37 tubers 70%	0–63	≤0.02	
Worms Heppenheim, Germany 1993	0.33 0.28 0.22	600	3 10 11 tubers 30%	0–63	≤0.02	
Monheim Laacherhof, Germany 1993	0.33 0.28 0.22	600	3 12 15 tubers 70%	0–63	≤0.02	
Burscheid Hofchen, Germany 1993	0.33 0.28 0.22	600	3 13 37 tubers 70%	0–63	<0.02	
Monheim Laacherhof, Germany 1993	0.33 0.28 0.22	600	3 12 15 tubers 70%	0–63	<0.02	
Haltern Hullern, Germany 1991	0.3	300	2 6 pre-ripening	0–42	≤0.02	Method 00009, M 003. Samples stored frozen for up to 8 months before analysis.
Burscheid, Germany 1991	0.3	300	2	0–42	≤0.02	Method 00009, M 003
Burscheid, Germany 1990	0.3 0.25 0.2	300	3 15 68	0 foliage 14–21 tuber 14 cooked tuber 14 peel 14 cooking water	3.8 ≤0.05 <0.05 <0.05 <0.05	Method 00009, M 003. Summary translation.
Monheim Laacherhof, Germany 1990	0.3	300	3	0 foliage 14-21 tuber 14 peel 14 cooked tuber 14 cooking water	11 ≤0.05 <0.05 <0.05 <0.05	Method 00009, M 003
Monheim Laacherhof, Germany 1977	0.3 0.24 0.2	600	3 12 14	6-36 tuber	≤0.1	Method 00009. Limited summary only.
Dohnson, Germany 1977	0.3 0.24 0.2	400	3 10 11-14	30-76 tuber	≤0.1	Method 00009. Limited summary only.

Location/Year	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application	PHI, day, Sample	ODM + ODM sulfone, mg/kg	Comments
Elm Farm Development Station, UK 1991	0.24	200	2 15 flowering	0–20	<0.02	Method 00009, M 003. Samples stored frozen for 6 months before analysis.
Deal, Kent, UK 1991	0.26 0.24	200	2 13 late flowering	0–21	<0.02	
Burscheid Hofchen, Germany 1996	0.25	300	3 8 8 tuber 70%	0-28	<0.02	Method 00255. Samples stored frozen 7-10 months before analysis. Recovery of sulfone at 0.1 mg/kg 77%.
Monheim Laacherhof, Germany 1996	0.25	300	3 8 8 tuber 100%	0-27 tuber	<0.01	
Thurston, UK 1996	0.25	400	3 9 7 tuber 60%	0-28 tuber	<0.01	
Criquebeuf-sur-Seine, France 1996	0.25	400	3 8 8 tuber 30%	0-28 tuber	<0.01	
Udenhout, The Netherlands 1971	0.25	500	1	35 tuber	<0.01	Similar to Method 00009
Blaaksedijk, The Netherlands 1971	0.25	500	1	31 tuber	<0.01	Similar to Method 00009
Sugar beet						
Sibiville, France 1991	0.38	280	2 15 before maturity	0 leaf 29 0-61 root	1.90 <0.04 <0.04	Method 00009, M 003. Samples stored 6 months before analysis.
Domart en Ponthieu, France 1991	0.38	280	2 15 before maturity	0 leaf 29-61 0-61 root	0.80 <0.04 <0.04	Method 00009, M 003. Samples stored 6 months before analysis.
Monheim Laacherhof, Germany 1973	0.2	600	2 25	21 root 21 leaf	<0.01, <0.01, <0.01 <0.01, 0.01, 0.03. avg 0.02	Method I47. 3 variants. Information incomplete.
Monheim Laacherhof, Germany 1991	0.2	300	4 12 7 9 root 80%	0-35 root 0 leaf 7 leaf 14 leaf 28-35 leaf	<0.01 3.0 0.38 0.08 <0.04	Method 00255 See fodder beet Germany 1991 for recoveries.
Albig, Germany 1991	0.2	300	4 9 10 14 root 80%	0-35 root 0 leaf 7 leaf 14 leaf 28-35 leaf	<0.01 5.7 1.7 0.54 <0.04	

Location/Year	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application	PHI, day, Sample	ODM + ODM sulfone, mg/kg	Comments
Burscheid Hofchen, Germany 1990	0.19	300	4 13 14 18 4-6 wk after crop covering (51)	0-35 root 0 leaf 7 leaf 14 leaf 28-35 leaf	≤0.04 1.9 0.66 0.09 ≤0.04	Method 00255, M 009. About 9 months frozen storage before analysis. Concurrent recoveries 94, 88%, at 0.04 mg/kg demeton-S-methylsulphon
Monheim Laacherhof, Germany 1990	0.19	300	4 13 14 18 near maturity	0-35 root 0 leaf 7 leaf 14-35 leaf	≤0.04 3.2 0.31 ≤0.04	
Klein Niedesheim, Germany 1990	0.19	300	4 13 14 18 harvest size	0-35 root 0 leaf 7 leaf 14 leaf 28-35 leaf	≤0.04 2.9 0.07 0.05 ≤0.04	
Worms Hepppen-heim , Germany 1990	0.19	300	4 13 14 18 harvest size	0-35 root 0 leaf 7 leaf 14-35 leaf	≤0.04 6.3 0.05 ≤0.04	
Burscheid, Germany 1988	4.2	600	3 14 15 6-8 week after crop cover	0 root 30 root 0 leaf 30 leaf 30 chips 30 mud 30 thin juice 30 thick juice 30 molasses 30 white sugar 30 refined sugar	0.40 <0.04 9.4 0.05 <0.04 <0.04 <0.04 <0.04 <0.04 <0.04 <0.04	Method 00009, M 002. Chromatograms included. Processing described. ODM recoveries at 0.04 and 1.0 mg/kg 60-105% from root, 78-105% from leaves, 75-102% from pulp, 92-99% from juice, 87-99% from molasses, 93-94% from sugar.
Burscheid, Germany 1988	0.83	600	3 14 15 6-8 weeks after crop cover	0 root 30 root 0 leaf 30 leaf	0.06 <0.04 3.7 <0.04	
Fodder beet (animal feed)						
Monheim, Germany 1991	0.19	300	4 12 7 9 root 80%	0-35 root 0 leaf 7 leaf 14 leaf 28-35 leaf	≤0.01 2.9 0.72 0.13 <0.04	Method 00255. ODM recovery from leaf 92, 93% at 0.04 mg/kg; from root 92, 90, 96% at 0.01 mg/kg.
Kothel, Germany 1991	0.19	300	4 10 11 11 harvest (100%)	0-35 root 0 leaf 7 leaf 14-35 leaf	≤0.04 4.1 0.69 ≤0.04	Method 00255. Root residues corrected for mean recovery of 66%.

Cereal grains, fodders and straws

Supervised trials were reported for the use of ODM on wheat, oats and barley in Europe (Schmidt, 1992a,b; Seym, 1993a,b). GAP for wheat and barley is 1 x 0.14 kg ai/ha, 21-day PHI, in Germany and 1 x 0.12 kg ai/ha, 21-day PHI in Austria. GAP for cereals in France is 3 x 0.1 kg ai/ha, PHI 21 days or not

specified. No GAP was reported for the UK, but GAP for Ireland is 0.12 kg ai/ha, 21-day PHI. The field trial conditions and results are shown in Table 28.

Table 28. Residues of ODM + ODM sulfone in or on cereals after foliar application of ODM EC formulation.

Location/Year	Application			PHI, days, Sample	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Wheat						
Borstorf, Germany 1990	0.12	300	1 start of ripening (80)	0 forage 7 14 29 grain 35 29 straw 35 29 wholemeal flour 29 white flour 29 wholemeal bread 29 white bread	2.3 0.36 0.17 <0.05 <0.05 <0.10 <0.10 <0.05 <0.05 <0.05 <0.05	Method 00009, M 003. Samples stored at –20ºC for 8–9 months before analysis.
Neuberg/ Rudigheim, Germany 1990	0.12	300	1 watery ripe (71)	0 forage 7 14 ear 14 straw 21 35 21 grain 35 21 wholemeal flour 21 white flour 21 wholemeal bread 21 white bread	2.4 2.2 1.1 1.2 1.2 0.75 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05	
Monheim, Germany 1991	0.12	300	2 54 dough stage	0 forage 7–28 grain 7 straw 14–28 straw	3.6 <0.04 0.14 <0.04	Method 00255. Method 00015 for straw. ODM recovery at 0.04 and 2.0 mg/kg for forage, 64-101%, n=6; for grain 104-118%, n=4; at 0.04, 0.4, 2.0 mg/kg for straw, 74-94%, n=4.
Worms Heppenheim, Germany 1991	0.12	300	2 19 end of flowering	0 forage 7 14 21–28 grain 21 straw 28	2.6 0.37 0.17 <0.04 0.12 0.14	
Monheim Laacherhof, Germany 1990	0.12	300	2 14 end of heading	0 forage 5 14 21-51 straw 51 grain 21 ear	0.19 0.10 <0.05 <0.05 <0.05 <0.05	Method 00015, M 009.
Worms Heppenheim, Germany 1990	0.12	300	2 47 grain development	0 forage 7 14 21-28 grain 21 straw 28 straw	3.2 0.99 1.9 <0.05 1.3 0.82	Method 00015, M 009. Samples stored frozen for 8 months before analysis.

Location/Year	Application			PHI, days, Sample	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Datteln, Germany 1991	0.12	300	1 grain development	0 forage 7 14 21 ear 21 straw 28 28 grain	1.8 0.69 0.27 0.09 0.18 0.06 ≤0.04	Method 00009, M 003. Samples stored frozen for 6 months before analysis.
Burscheid, Germany 1991	0.12	300	1 milky ripe	0 forage 7 15 21 straw 29 21 ear 29 grain	2.2 0.25 0.05 ≤0.04 <0.04 <0.04 <0.04	Method 00009, M 003. Samples stored frozen for 6 months before analysis.
Elm Farm Development Station, UK 1991	0.12	200	1 soft dough	0 forage 14 28 grain 28 straw	1.4 0.06 ≤0.04 ≤0.04	Method 00009, M 003
Barley						
Burscheid, Germany 1990	0.12	300	2 18 end of heading	0 forage 7–14 21 ear 21 straw 45 straw 45 grain	3.6 <0.04 <0.04 <0.04 0.05 <0.04	Method 00015, M 009. Samples stored frozen for 10 months before analysis.
Burscheid, Germany 1991	0.12	300	2 42 milky ripe	0 forage 7 15 21–28 grain 21–28 straw	2.4 0.09 <0.04 ≤0.04 ≤0.04	Method 00255. ODM recoveries at 0.04 and 0.4 mg/kg, n=4, 83-97% for forage; 99, 76, 88% for grain; 111, 74, 79% for straw.
Datteln, Germany 1991	0.12	300	1 grain development (caryopsis watery)	0 forage 7 14 21 ear 21 straw 28 28 grain	0.98 0.18 <0.04 <0.04 0.06 0.05 ≤0.04	Method 00009, M 003. Samples stored frozen for 8 months before analysis.
Elm Farm Development Station, UK 1991	0.13	212	1 start of ripening	0 forage 14 27 grain 27 straw	1.1 0.06 ≤0.05 ≤0.05	Method 00009, M 003
Oats						
Heppenheim, Germany 1990	0.12	300	2 44 caryopsis watery	0 forage 7 14 21 grain 28 21 straw 28	2.8 0.30 0.14 0.05 <0.04 0.11 0.04	Method 00009, M 003

Location/Year	Application			PHI, days, Sample	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Worms-Heppenheim, Germany 1991	0.12	300	2 21 end of flowering	0 forage 7 14 21 grain 28 21 straw 28	0.14 0.10 0.10 <0.01 <0.01 0.14 0.21	Method 00255. ODM recoveries at 0.04 and 0.4 mg/kg 94, 102, 102% in forage; 87, 98, 79% in grain; 102, 99, 77% in straw

Tree nuts

Supervised field trials were reported on almonds in Spain, where GAP is 2 x 0.25 kg ai/ha with a 30-day PHI (Seym, 1996; Seym and Nusslein, 1995). The results are shown in Table 29.

Table 29. Residues of ODM + ODM sulfone in or on almonds after foliar application of ODM EC formulation in Spain

Location, year	Application			PHI, days, sample	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Jorba-Sant Genis 1995 Variety Ferraduel.	0.25	800	2 31 7-8 cm fruit	27 fruit 42 61 nut with shell 75 91 91 kernel	0.35 0.19 <0.01 <0.01 <0.01 <0.01	Method 00009, M 007. Samples stored frozen about 5 months before analysis.
Jorba-Sant Genis 1995 Variety Ferragnes.	0.25	800	2 29 7-8 cm fruit[1]	29 fruit 44 63 nut with shell 77 93 93 kernel	0.28 0.18 0.02 0.02 0.01 <0.01	Method 00009, M 007. Samples stored frozen about 5 months before analysis.
Les Gunyoles, Spain 1995	0.25	800	2 31 8-9 cm fruit	33 fruit 46 55 77 nut with shell 82 82 kernel	1.1 0.85 0.58 0.05 <0.01 <0.01	Method 00009, M 007. Samples stored frozen about 5 months before analysis
Eis Garidells, Spain 1995	0.25	800	2 31 8-9 cm fruit	33 fruit 46 55 77 nut with shell 82 82 kernel	0.55 0.31 0.12 0.04 0.01 <0.01	Method 00009, M 007. Samples stored frozen about 5 months before analysis. Recoveries of ODM at 0.01 and 0.1 mg/kg from kernels 72-86%, n = 5; from fruit 64-89%, n=7.

Location, year	Application			PHI, days, sample	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Les Gunyoles, Spain 1993	0.18	710	2 28 70% final size (77)	90 nut	<0.02	Method 00009, M 007 ODM recoveries from nut fortified at 0.02 and 0.2 mg/kg, 70-99%, n=5.
Castellri de la Marca, Spain 1993	0.19	710	2 32 70% final size (77)	87 nut	<0.02	

[1]Immature nut with shell

Oilseed

Bayer AG reported supervised field trial for rape (Anon., 1988, 1989, 1990, 1991, 1996a,b,c,d; DeMonte, 1996, Hanlon, 1996; Leslie, 1989; Seym and Nusslein, 1995).

GAP in France for the use of ODM on rape (oil seed) is 1 x 0.12 kg ai/ha, PHI not specified, and on sunflower 1X 0.1 kg ai/ha, PHI not specified. GAP for ODM on cotton in Brazil and Australia was not reported, but GAP for Peru is 3 x 0.25 kg ai/ha and for the USA is 3 x 0.84 kg ai/ha, both with PHIs of 14 days.

Table 30. Residues of ODM + ODM sulfone in or on oilseed crops after foliar application of ODM EC formulation.

Location, year	Application			PHI, days, sample	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Rape						
St. Valery en Caux, France 1991	0.12	280	1 pod development	0 forage 79 seed 79 oil 79 pomace	1.5 <0.05 <0.05 <0.05	Method 00009, M 003. Samples stored 11-13 months before analysis.
Cany Barville, France 1991	0.12	280	1 pod development	0 forage 79 seed 79 oil 79 pomace	1.1 <0.05 <0.05 <0.05	Method 00009, M 003. Samples analysed within 2 months
Jouaville, France 1991	0.12	300	1	0 forage 63 seed 63 oil 63 pomace	1.4 <0.05 <0.05 <0.05	Method 00009, M 003. Samples stored 5-12 months before analysis.
Sunflower						
Laudun, France 1993	0.12	280	1 inflorescence	0 forage 29 head 83 seed	2.9; 2.4 <0.04; <0.04 <0.01; <0.01	Method 00255. Duplicate plots. ODM recoveries at 0.04-0.4 mg/kg 67-97% from forage (n=6), 74-82% (n=4) from heads; at 0.01 and 0.1 mg/kg 72-108% (n=4) from seed.

Location, year	Application			PHI, days, sample	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Drache, France 1989	0.1	300	1 6 leaf stage	87 seed	<0.01	Method 00086, M 012. Limited summary translation.
Maille, France 1989	0.1	300	1 10 leaf stage	87 seed	<0.01	Method 00086, M 012. Sample stored 9 months before analysis.
Cotton						
Narrabri, NSW, Australia 1993	0.075	110	1	0-21 seed	<0.01	Method 00246 ODM recoveries (not concurrent) from seed at 0.01-0.11 mg/kg 64-89% (n=4). Sulfone recovery from seed at 0.01-0.05 mg/kg 77, 85, 86%.
Narrabri, NSW, Australia 1993	0.15	110	1	0-21 seed	<0.01	
Narrabri, NSW, Australia 1995	0.075	140	1 late boll fill	0-21 seed	<0.01	Method 00246. Duplicate plots. Average recoveries for ODM (0.01-0.06 mg/kg) 82%.
Narrabri, NSW, Australia 1995	0.15	140	1 late boll fill	0-21 seed	<0.01	
Boggabilla via Goondiwindi, NSW, Australia 1996	0.075	110	2 12 6 days before defoliation	7-21 seed 7 trash 14 trash 21 trash	<0.01 0.68 0.07 0.12	Method 00246 ODM recoveries at 0.01-0.02 mg/kg from seed 74-85%, n=3; at 0.14 and 2.8 mg/kg from trash, 93 and 109%. Sulfone recoveries at 0.02 mg/kg from seed, 85%; at 0.10 and 0.60 mg/kg from trash 104 and 100%.
Boggabilla via Goondiwindi, NSW, Australia 1996	0.15	110	2 12 6 days before defoliation	7-21 seed 7 trash 14 trash 21 trash	<0.01 3.5 0.45 0.33	
Tipton via Dalby, QL, Australia 1996	0.075	77	2 9 15 days before defoliation	7-20 seed 7 trash 14 trash 20 trash	<0.01 1.5 1.6 0.86	Method 00246. Recoveries as Boggabilla, 1996.
Tipton via Dalby, QL, Australia 1996	0.15	77	2 9 15 days before defoliation	7-20 seed 7 trash 14 trash 20 trash	<0.01 4.4 2.2 0.62	
Bellata, NSW, Australia 1994	0.075	110	1 late boll fill	0-21 seed	<0.01	Method 00246. Recoveries as Narrabri 1993.
Bellata, NSW, Australia 1994	0.15	110	1 late boll fill	0-21 seed	<0.01	
Rolandia, Brazil 1988	0.2	300	4 18, 13, 14 bolls opening	0 boll 4 seed 7 seed 10 seed 14 seed	2.6 0.05 0.04 0.04 0.03	Method 00009. Samples stored 5-6 months before analysis.
Rolandia, Brazil 1988	0.4	300	4 18 13 14 bolls opening	14 seed	0.05	Method 00009. Sample stored 5 months before analysis.

Location, year	Application			PHI, days, sample	ODM + ODM sulfone, mg/kg	Comments
	Rate, kg ai/ha	Spray, l/ha	No., Retreatment (days), Growth stage at final application			
Municipio de Terenos, Brazil 1989	0.2	300	4 22 15 24 maturity	0 boll 4 seed 7 seed 11 seed 15 seed	1.8 0.04 0.04 0.03 0.02	Method 00009. Samples stored 9 months before analysis.
Municipio de Terenos, Brazil 1989	0.4	300	4 22 13 24 maturity	15 seed	0.03	Method 00009. Samples stored 9 months before analysis.
Lubbock, Texas, US 1988	0.56	190	2 open bolls	7 seed 14 21	0.03 0.01 0.02	Method 00246
Yuma, Arizona, US 1988	0.56	190	2 mature	7 seed 14	0.04 0.01	Method 00246
Calipatria, California, USA 1988	0.56	58	2 open bolls	7 seed 14	0.03 0.01	Method 00246
Benoit, Mississippi, USA 1988	0.56	61	2 mature	0 seed 4 seed 14-21 seed	0.07 0.02 ≤0.01	Method 00246
Benoit, Mississippi, USA 1988	0.56	47	2 mature	0 seed 4 14 21	<0.01 0.02 0.02 <0.01	Method 00246
Adams Gardens, Texas, US 1988	0.56	200	2 open bolls	0 seed 7-21 seed	0.38 ≤0.01	Method 00246
Adams Gardens, Texas, US 1988	2.8	200	2 open bolls	14 seed 14 hull 14 meal 14 oil 14 soapstock	0.11 <0.02 0.06 <0.02 <0.02	Method 00246

Animal feeding studies

Residues of ODM and ODM sulfone were determined in the milk and tissues of lactating dairy cows fed a diet containing ODM (Smyser and Halpin, 1987). Nine cows were divided into three groups of three each and a tenth cow was used as a control. The treated animals were fed ODM by bolus for 28 consecutive days at levels equivalent to 10, 30 or 100 ppm in the diet, or 0.3, 0.9 or 3.0 mg/kg bw. The high-dose group was removed from the study because of organophosphorus poisoning. The feed concentrations are only approximate as the actual feed consumption was not measured; it was assumed to be 3% of the body weight, or about 15 kg feed, per day. Milk was collected twice daily and the samples within each group were mixed. A 500 ml sample from each group was frozen. Within 14 hours of the last dose the cows were slaughtered and appropriate tissues were homogenized and stored frozen. The combined residue of ODM and ODM sulfone in the milk at all intervals and in liver, kidney, muscle and fat was <0.01 mg/kg. Details of the study were not provided, e.g. no analytical method was described or referenced.

A feeding study was reported on poultry (Lee and Wood, 1987). Thirty laying hens were divided into groups of 10 and fed rations containing 0.65, 1.95, or 6.50 ppm ODM for 28 days. Ten birds were

maintained as a control. Water and feed were provided *ad lib* throughout the study. The actual feed consumption was not determined. Eggs were collected each morning, stored in a refrigerator, and pooled within groups by day for analysis. The hens were asphyxiated at the end of the 28 days and liver, kidney, heart, gizzard, composite thigh and breast muscle and composite fat were taken from each hen. The samples were stored frozen, and analysed within five weeks of collection for ODM plus ODM sulfone by a method equivalent to Method 00246. The combined residue was reported as <0.01 mg/kg in all samples. Only tissues from the 6.50 ppm feed group were analysed. The recoveries from control samples fortified at 0.1 mg/kg with ODM sulfone were muscle 68%, liver 68%, gizzard 106%, skin 88%, fat 80%, heart 106%, kidney 98%, eggs 82, 85, 79, 93, 80 and 80%, and chicken feed 87, 104, 96 and 106%.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

In a processing study on apples in Germany in 1990 (Schmidt, 1992) trees (Cox's Orange) were sprayed twice at 0.38 kg ai/ha, with about 60 days between applications. The apples were harvested 29 days after treatment and processed into juice and sauce. Details of the process were provided in German. Samples were analysed by Method 00009/ M 003. The fruit contained 0.086–0.097 mg/kg, the sauce <0.05 mg/kg, and the juice 0.071–0.091 mg/kg sulfone equivalents. In a separate trial, Delicious apple trees were sprayed twice at 0.38 kg ai/ha with an ODM EC formulation, with about 5 months between treatments. Apples were harvested 28 days after the final treatment and processed into juice and sauce. Residues on the apples were 0.335 to 0.438 mg/kg, in the juice 0.315 to 0.447 mg/kg and in the sauce 0.124 to 0.139 mg/kg. The processing factors from the two trials were about 1 for juice and 0.5 for sauce.

In a cotton seed processing study in Texas in 1988 (Leslie, 1989) cotton was treated twice at 2.8 kg ai/ha (190 l/ha) or about 3 times the US GAP rate (3 x 0.84 kg ai/ha, 14-day PHI). The cotton bolls were harvested 14 days after the second application and immediately ginned. The ginned seed was treated by a simulated industrial process within 4 months. The seed was hulled and the kernels extracted with solvent. The process was not described in detail. The raw and processed commodities were analysed by Method 00246. Several modifications were made to the method, including the use of a 13 m x 0.32 mm i.d. capillary column (DB-5) and the addition of a silica gel column clean-up after chloroform extraction of the oxidized mixture. The longest frozen storage period before analysis was 290 days. The results are shown in Table 31. Acceptable recoveries were claimed for control analyses at 0.02 mg/kg, but no details were provided.

Table 31. Effects of processing cotton seed on ODM residues.

Sample	Residue, mg/kg	Processing factor	Control analyses	
			Fortification, mg/kg	Recovery, %
Delinted cotton seed	0.11		0.05 0.50	100 114
Hulls	<0.02	0.2	-	-
Meal	0.06	0.6	0.10	81; 80
Crude oil	<0.02	0.2	0.10	100
Refined oil	<0.02	0.2	0.10	107
Soapstock	<0.02	0.2	0.10	95

Limited information on processing was included with reports of supervised field trials on sugar beet in Germany, grapes in Italy (must and wine), curly kale in Germany (cooked leaves and cooking water), potatoes in Germany (peel, cooked potatoes, cooking water), rape in France (pomace, crude oil, refined oil) and wheat in Germany (flour and bread). In all cases both the raw agricultural commodities and the processed products lacked quantifiable residues, so processing factors could not be estimated.

Residues in the edible portion of food commodities

The analyses of pulp and peel in the supervised field trials on oranges in Spain and Portugal (1995) indicated a mean transfer factor from whole fruit to pulp of 0.4, range 0.33 to 0.6.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The Netherlands submitted the summary information on the monitoring of foods in commerce for the period 1994–1996 shown in Table 32.

Table 32. Residues of demeton-S-methylsulphon in food in commerce in The Netherland1994-1996.[1]

Commodity	No. analysed	No. <0.05 mg/kg	No. with residues <MRL	No. with residues >MRL	Mean, mg/kg	MRL, mg/kg
Cherries	252	251		1	0.05	0.5
Onions	97	97			<0.05	0.5
Peppers	1525	1524	1		<0.05	0.5
Cauliflower	348	346	2		<0.05	0.5
Leafy cabbage	99	99			<0.05	0.5
Head cabbage	62	62			<0.05	0.5
Head lettuce	471	469		2	0.07	0.5
Endive	1137	1136	1		<0.05	0.5
Beans (fresh; with pod)	617	616	1		<0.05	0.5
Other arable products	699	698		1	<0.05	0.05

[1] The method determines all compounds oxidized to demeton-S-methylsulphon

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported by Bayer AG.

Country/ Commodity	**MRL mg/kg**
Argentina	
Alfalfa forage	0.2
Carrot	0.2
Cereals	0.2
Citrus fruit	0.5
Cotton seed	0.1
Melon	0.5
Other vegetables	0.5
Pome fruit	0.7
Potato	0.2
Stone fruit	0.7
Sweet potato	0.2

Austria
Sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, expressed as demeton-S-methyl

Beet, sugar	0.4
Cereals	0.2
Fruit	0.4
Other plant commodities	0.05
Potato	0.2
Vegetables except carrots	0.4

Belgium
Sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, expressed as demeton-S-methyl

Cereals	0.2
Fruit	0.4
Other plant commodities	0 [1]
Vegetables except carrots	0.4

Canada

Asparagus	0.10 [2]
Barley	0.10 [2]
Bean	0.10 [2]
Beet, sugar	0.10 [2]
Cabbage	0.10 [2]
Cranberry	0.10 [2]
Cucumber	0.10 [2]
Gourd	0.10 [2]
Maize/Corn	0.10 [2]
Melon	0.10 [2]
Oats	0.10 [2]
Pea, Garden	0.10 [2]
Potato	0.10 [2]
Pumpkin	0.10 [2]
Strawberry	0.10 [2]
Turnip, edible	0.10 [2]
Wheat	0.10 [2]

Denmark
Sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, expressed as demeton-S-methyl

Berries and small fruit	0.5
Brussels sprouts	0.5
Cabbage	0.5
Carrot	0.2
Cauliflower	0.5
Citrus fruit	0.5
Fruiting vegetables	0.5
Leafy vegetables	0.5
Legume vegetables	0.5
Pome fruit	0.5
Potato	0.2
Root vegetables exc. carrots	0.5
Stem vegetables	0.5
Stone fruit	0.5
Tropical fruit	0.5

European Community
Demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, singly or combined

Carrot	0 [3]

Sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon,
expressed as demeton-S-methylsulphon

Other plant commodities	0.4

Finland
Sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, expressed as demeton-S-methyl

Carrot	0.05
Fruit	0.4
Other vegetables	0.4
Potato	0.05

France

Sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, expressed as demeton-S-methyl

Almond	0.4
Apple	0.4
Barley	0.05
Beets (Beta vulgaris)	0.4
Buckwheat, common	0.05
Chestnut	0.4
Fig	0.4
Hazel nut	0.4
Nuts	0.4
Oats	0.05
Other fruit	0.4
Pea	0.02 T
Pea preserve	0.02 T
Plum	0.4
Rape	0.05 T
Rye	0.05
Triticale	0.05
Vegetables except carrots	0.4
Wheat	0.05

Germany

Sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, Expressed as demeton-s-methyl

Beet, Sugar	0.1
Cereals	0.2
Currant, Black	2
Currant, Red	2
Grape	2
Other fruit	0.5
Other plant commodities	0.05
Peach	1
Plum	1
Pome fruit	1
Potato	0.2
Vegetables except carrots	0.5

Greece

Carrot	0 [4]
Other plant commodities	0.4

Israel

Sum of demeton-S-methyl and demeton-S-methylsulphon, expressed as demeton-S-methyl

Aubergine	0.5
Bean	0.5
Beet, sugar	0.1
Brassica vegetables	0.1
Citrus fruit	0.5
Cotton seed	0.1
Cucurbits	0.5
Forage crops	0.5
Grape	0.2
Pepper, sweet	0.2
Pome fruit	0.2

Potato	0.2
Squash, summer	0.5
Stone fruit	0.2
Tomato	0.5

Italy

Sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, expressed as demeton-S-methylsulphon

Beet, sugar	0.1
Carrot	0[4]
Fruit	0.4
Other vegetables	0.4
Potato	0.1
Tobacco	0.1
Wheat	0.1

Luxembourg

Oxydemeton-methyl, demeton-S-methyl and demeton-S-methylsulfon, separately calculated or summed up to demeton-S-methyl

Carrot	0.05
Cereals	0.2
Fruit	0.4
Vegetables except carrots	0.4

Mexico

Alfalfa	5
Apple	1
Aubergine	1
Bean green	0.5
Broccoli	1
Brussels sprouts	1
Cabbage	1
Cauliflower	1
Cotton	0.1
Cucumber	1
Grape	0.1
Grapefruit	1
Lemon	1
Lettuce	2
Maize/Corn fodder	0.5
Maize/Corn grain	0.5
Melon	0.3
Onion	05
Orange	1
Pea, garden	0.3
Pea, Chick-	0.3
Pear	1
Pepper, sweet	0.75
Plum	1
Potato	0.1
Pumpkin	1
Quince	1
Safflower	1
Sorghum fodder	0.75
Sorghum grain	0.75
Strawberry	2
Walnut	0.3
Zucchini	1.0

Netherlands (Same information also reported by government of The Netherlands)

Sum of oxydemeton-methyl and demeton-S-methylsulphon, expressed as demeton-S-methylsulphon

Carrot	0.05 [4]
Cereals	0.1

Fruit	0.5
Other plant commodities	0 [1]
Other vegetables	0.5
Potato	0 [4]

Portugal

Sum of oxydemeton-methyl and demeton-S-methylsulphon, expressed as demeton-S-methylsulphon

Carrot	0.05
Fruit	0.4
Other plant commodities	0.4
Vegetables	0.4

South Africa

Sum of oxydemeton-methyl and its sulfone, expressed as oxydemeton-methyl

Apple	0.4
Apple	0.4 E
Apricot	0.4
Apricot	0.4 E
Aubergine	0.2
Bean	0.2
Citrus fruit	0.5
Cotton	0.1
Cruciferae	0.2
Cucurbits	0.4
Maize/Corn green	0.2
Nectarine	0.4
Nectarine	0.4 E
Olive	0.1
Onion	0.1
Pea, garden	0.2
Peach	0.4
Peach	0.4 E
Peanut	0.2
Plum	0.4
Plum	0.4 E
Potato	0.2
Rooibos tea	0.1
Sorghum grain	0.02
Tomato	0.2

Spain

Sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, expressed as demeton-S-methylsulphon

Apple	1
Beet, sugar	0.1
Berries and small fruit	0.4
Brassica vegetables	0.4
Bulb vegetables	0.4
Cacao	0.05
Carrot	0.05
Cereals	0.05
Citrus fruit	0.4
Coffee	0.05
Cola	0.05
Forage crops and straw	0.05
Fruit and vegetables, dried	0.05
Fruiting vegetables	0.4
Herbs	0.4
Hops	1
Leafy vegetables	0.4
Legume vegetables	0.05
Mushroom	0.4
Nectarine	1

Nuts	0.4
Oil plants seed	0.05
Other pome fruit	0.4
Other root vegetables	0.4
Other stone fruit	0.4
Peach	1.0
Potato	0.05
Pulses	0.05
Spices	0.05
Stem vegetables	0.4
Sugarcane	0.05
Tea	0.05
Tobacco	0.05
Trop. and subtrop. fruit	0.4

Sri Lanka

Aubergine	0.2
Bean	0.2
Bean, mung	0.2
Cowpea	0.2
Other vegetables	0.2
Pepper, Cayenne-	1
Soya	0.2

Sweden

Sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, expressed as demeton-S-methyl

Cereals	0.2 [5]
Cereals flakes	0.1 [5]
Cereals flour	0.1 [5]
Cereals grain, hulled	0.1 [5]
Fruit	0.5
Potato	0.05 [5]
Vegetables	0.5

Switzerland

Single or combined with demeton-S-methylsulphon and oxydemeton-methyl, expressed as demeton-S-methylsulphon

Beet, sugar	0.4
Fruit	0.4
Vegetables except carrots	0.4

USA

Oxydemeton-methyl and cholinesterase-inhibiting metabolites

Alfalfa	5
Alfalfa chaff	11
Alfalfa hay	11
Alfalfa seed	11
Apple	1
Apricot	0.5 R Idaho
Aubergine	1
Bean, Kidney	0.5
Bean, Kidney forage	2
Bean, Lima	0.5
Bean, Lima forage	2
Beet, sugar	0.3
Beet, sugar top or leaves	0.5
Blackberry	2
Broccoli	1
Brussels sprouts	1
Cabbage	1
Capsicum (Peppers/Chilli)	0.75
Cattle fat	0.01
Cattle meat	0.01

Cattle meat by-products	0.01
Cauliflower	1
Clover green	5
Clover hay	11
Clover seed	11
Corn, sweet corn-on-the-cob	0.5
Corn, sweet fresh	0.5
Cotton seed	0.1
Cucumber	1
Goat fat	0.01
Goat meat	0.01
Goat meat by-products	0.01
Grape	0.1
Grapefruit	1
Hazel nut	0.05
Horse fat	0.01
Horse meat	0.01
Horse meat by-products	0.01
Lemon	1
Lettuce, head	2
Maize/Corn fodder	3
Maize/Corn forage	3
Maize/Corn fresh	0.5
Maize/Corn grain	0.5
Melon	0.3
Milk	0.01
Mint, pepper hay	12.5
Onion dry bulb	0.05
Orange	1
Pea, garden	0.3
Pea, garden forage	2
Pea, garden hay	8
Pear	0.3
Pig fat	0.01
Pig meat	0.01
Pig meat by-products	0.01
Plum	1
Potato	0.1
Pumpkin	0.3
Raspberry, American red	2
Safflower	1
Sheep fat	0.01
Sheep meat	0.01
Sheep meat by-products	0.01
Sorghum forage	2
Sorghum grain	0.75
Sorghum milled fractions except flour	2 F
Squash, summer	1
Squash, winter	0.3
Strawberry	2
Turnip, edible	0.3
Turnip, edible top or leaves	2
Walnut	0.3

[1] Below the limit of determination (0.05 mg/kg)
[2] Negligible residue tolerance
[3] Lower limit of analytical determination
[4] Below the limit of determination
[5] Level at or about the limit of determination

T = temporary
R = regional tolerance
E = export tolerance
F = food-additive tolerance

APPRAISAL

Oxydemeton-methyl (ODM), *S*-2-ethylsulfinylethyl *O,O*-dimethyl phosphorothioate, is a systemic and contact insecticide and is a metabolite (sulfoxide) of the insecticide demeton-S-methyl, *S*-2-ethylthioethyl *O,O*-dimethyl phosphorothioate. The 1992 JMPR carried out a complete re-evaluation of oxydemeton-methyl. The residue is currently defined as the sum of oxydemeton-methyl, demeton-S-methyl, and demeton-S-methylsulphon, expressed as oxydemeton-methyl.

The present evaluation is part of the Periodic Review Programme of the CCPR.

Extensive data and information were submitted for oxydemeton-methyl. No information was provided on demeton-S-methyl, except on its metabolism by wheat.

Animal metabolism

Metabolism studies were submitted on rats, poultry, and goats. Rats treated orally or intravenously with a single dose of [*ethylene*-^{14}C]ODM (20 mg/kg bw) eliminated at least 89% of the dose in the urine within 72 hours. In a composite 0–24 hour urine sample ODM accounted for about 50% of the administered radioactivity. The identified metabolites were 1-(ethylsulfinyl)-2-(methylsulfinyl)ethane and 1-(ethylsulfonyl)-2-(methylsulfinyl)ethane, each 16%, demethyl-ODM and demethyl-ODM sulfone, each 2–3%.

Lactating goats were dosed orally with [*ethylene*-^{14}C]ODM for three consecutive days at a rate of 7 mg ODM per kg body weight. Urine and milk were collected daily, the goats were slaughtered 2 hours after the final dose, and tissues were collected. Water extracted virtually all of the radioactive residues from all samples except fat, from which about 85% was extracted. Milk was centrifuged, and the supernatant was eluted from C-18 solid phase extraction cartridges. The eluate contained about 80% of the original ^{14}C in the milk. The total radioactive residue (TRR) concentrations, expressed as ODM, were kidneys 13 mg/kg, liver 4.2 mg/kg, muscle 4.0 mg/kg, fat 0.62 mg/kg, and milk 3.8 mg/kg. The only compounds identified were ODM and its sulfone, with the parent constituting 23–61% of the TRR and the sulfone 0.8–23%.

Laying hens dosed with [*ethylene*-^{14}C]ODM at 6.9 mg/kg body weight for three consecutive days were killed within four hours of the final dosing, and appropriate tissues were collected and analysed. The total radioactive residues as ODM were breast 0.51 mg/kg, thigh 0.43 mg/kg, liver 0.60 mg/kg, kidney 1.4 mg/kg, skin 0.41 mg/kg, and eggs (day 3) 0.36 mg/kg. A mixture of acetone and methylene chloride extracted >80% of the TRR from all samples except eggs (70% extraction). Demethyl-ODM sulfone was the main compound in the breast (70% of the ^{14}C), thigh (80%), liver (48%), skin (100%) and eggs (100%). The main residue in the kidneys was a mixture of 2-(ethylsulfinyl)ethanesulfonic acid and 2-(ethylsulfonyl)ethanesulfonic acid (84%). These compounds also constituted a high proportion (42%) of the residue in the liver.

The results of the three metabolism studies indicate oxidation to the sulfone and cleavage of the P-S linkage. The Meeting concluded that the animal metabolism studies were adequate.

Plant metabolism

The metabolism of [*ethylene*-^{14}C]ODM in cabbage and sugar beet, of [*ethylene*-^{14}C]demeton-S-methyl in wheat , and of demeton-S-methylsulphon in apples were reported. The radioactive residues in cabbage were characterized only as highly polar and water-soluble. The radioactive residues in the foliage and roots of sugar beet were extracted and some of the major metabolites were identified by MS. ODM was a

minor component on the foliage (2% of the TRR). The main metabolites were demethyl-ODM 14%, bis(2-ethylsulfinylethyl) disulfide 12%, 2-hydroxy-3-(2-ethylsulfinylethylthio)propionic acid 14%, 2-hydroxy-3-(2-ethylsulfonylethylthio)propionic acid 10%, and 2-hydroxy-3-(2-ethylsulfonylethylsulfinyl)propionic acid 11%. All except demethyl-ODM involve cleavage of the P-S bond.

The metabolism of [*ethylene*-^{14}C]demeton-*S*-methyl by wheat grown in a greenhouse again revealed cleavage of the P-S bond with the formation of sulfonic acids, disulfides, and ethanol derivatives: 2-(ethylsulfonyl)ethanesulfonic acid 8% of the TRR, 1-(ethylsulfinyl)-2-(methylsulfinyl)ethane 9%, 1-(ethylsulfinyl)-2-(methythio)ethane 4%, 2-ethylsulfinylethanol, 5%. ODM and ODM sulfone constituted 20% of the radioactive residue.

The metabolism of [*ethylene*-^{14}C]-demeton-S-methylsulphon by apples produced compounds formed by P-S bond cleavage, as well as demethyl- and didemethyl-demeton-S-methylsulphon (5-6% of the TRR). At day 27, demeton-S-methylsulphon (the test material) accounted for 24% of the applied radioactivity in both peel and pulp. The main metabolites were *S*-2-ethylsulfonylethyl *O*-methyl *O*-hydrogen phosphorothioate (demethylated parent) 3% in both pulp and peel, *S*-2-ethylsulfonylethyl *O*-*O*-dihydrogen phosphorothioate (didemethylated parent), 1% in pulp and 3% in peel, 2-ethylsulfonylethanesulfonic acid 3%, and 2-ethylsulfonylethanol 3% in pulp. The total of the identified compounds at 27 days accounted for less than 40% of the applied radioactivity.

The Meeting concluded that the plant metabolism studies were marginally acceptable. The details and raw data of the studies were not provided and therefore some results, particularly the quantitative results, could not be verified. Isolated metabolites were positively identified by mass spectrometry and comparison with authentic standards. The four studies indicate a common mechanism involving oxidation to the sulfone, formation of the demethyl and didemethyl derivatives, and cleavage of the P-S linkage.

Environmental fate

The Meeting received reports of studies on uptake by rotational crops, dissipation under field conditions, photolysis on soil, adsorption and desorption on four types of soil, leaching from clay, aerobic and anaerobic degradation on soil, and aerobic and anaerobic degradation in water/sediment systems.

The degradation of [*ethylene*-^{14}C]ODM on sandy loam soil was studied over a 12-month period. Volatile compounds accounted for only 9% of the applied radioactivity after 12 months. The major products were 2-ethylsulfinylethanesulfonic acid and 2-ethylsulfonylethanesulfonic acid, 20–30% of the applied radioactivity. The half-life of ODM, assuming first order kinetics, was 3.2 days. A similar degradation of ODM was observed under anaerobic conditions, but the data were not adequate to calculate a half-life. The Meeting concluded that ODM is degraded at a moderate rate under aerobic conditions in soil, with formation of the sulfonic acid after cleavage of the P-S bond.

For the rotational crop study, kale, wheat, and beetroot were planted in soil that had been treated with [*ethylene*-^{14}C]ODM at 3.4 kg ai/ha in Kansas, USA. The crops were planted at intervals of about 30, 180, and 300 days after treatment of the soil and harvested at normal maturity. Beet roots, beet tops and kale contained no residues after any planting interval. Immature wheat (boot stage) showed radioactivity equivalent to 0.02 mg/kg ODM from the 34-day planting. Wheat grain, straw and chaff contained low levels of radioactivity, 0.01–0.06 mg/kg, from the 34-day and 184-day plantings. These levels represent the sum of ODM and its metabolites, so ODM and demeton-S-methylsulphon are not expected to be quantifiable in crops planted at the intervals studied. The Meeting concluded that inadvertent residues in rotational crops were not a significant source of dietary exposure and need not be considered in estimating maximum residue levels.

[*Ethylene*-^{14}C]ODM applied to sandy loam soil was exposed to natural sunlight for 30 days. The rate of degradation was no more than in a dark control sample. A similar result was found for ODM in sterile buffer solution at pH 5 exposed to natural sunlight for 30 days. The Meeting concluded that photolysis was not a significant degradation pathway for ODM.

The adsorption and desorption of ODM was measured by a batch equilibrium procedure in four types of soil. ODM was not bound substantially to any of the soils.

The leaching of [*ethylene*-^{14}C]ODM through a sandy clay loam soil was studied. Aerobic ageing of the soil for 30 days before leaching caused a 50% loss of radioactivity as CO_2. Water (1.25 cm of simulated rainfall) was applied each day for 45 days to the aged soil. Over 80% of the radioactivity remained in the top 2.5 cm of the soil. A soil dissipation study under field conditions in California, USA, showed a half-life of ODM of about 2 days, with no tendency to migrate below 15 cm. The Meeting concluded that ODM is not leached through soil.

The degradation of [*ethylene*-^{14}C]ODM was studied in sterile buffer solution at 25ºC. The half-life decreased dramatically with increasing pH, from 94 days at pH 5 to 2.5 days at pH 9. The identified products were demethyl-ODM and 2-ethylsulfinylethanethiol (34 and 13% respectively after 35 days at pH 7).

Water and sediment from an orchard drainage ditch and from a fish pond were treated in separate experiments with [*ethylene*-^{14}C]ODM at 0.5 mg ai/l. Samples were taken on days 1, 7, 20, 41, and 91. Volatile compounds accounted for about 25% of the applied radioactivity after 91 days. After 7 days, ODM accounted for about 10% of the applied ^{14}C in the waters and <1% in the sediments. The main products were demethyl-ODM, 2-ethylsulfinylethanesulfonic acid, 2-ethylsulfonylethanesulfonic acid, demethyl-ODM sulfone, and bis(2-ethylsulfinylethyl) disulfide. ODM sulfone accounted for <1% of the applied ^{14}C at all intervals in all fractions.

A water/sediment degradation study was also conducted under anaerobic conditions for a period of 12 months. [*Ethylene*-^{14}C]ODM represented only 3% of the applied radioactivity within 14 days. The main products were 1-(ethylsulfinyl)-2-(methylsulfinyl)ethane (18% of the applied ^{14}C in the surface water), 2-ethylsulfinylethanesulfonic acid (9% in the surface water), and 2-ethylsulfonylethanesulfonic acid (4% in the surface water).

The Meeting concluded that ODM is degraded rapidly in soil and in water via cleavage of the P-S bond.

Methods of residue analysis

Numerous similar methods were presented for enforcement and data collection. All determine the combined residue of demeton-S-methyl, oxydemeton methyl, and demeton-S-methylsulphon. The analyte measured is the sulfone. The crop sample is extracted with solvent, typically acetone/water, the extract is cleaned up (optionally) by gel permeation chromatography (GPC), oxidized with permanganate, cleaned up if necessary by solid-phase extraction (SPE), and analysed on a gas chromatograph equipped with a flame photometric detector. The oxidation step converts demeton-S-methyl and ODM to the sulfone. Extensive recovery data were presented. Typical lower limits of determination are 0.01 and 0.05 mg/kg as ODM.

The Meeting concluded that adequate methods exist for the determination of demeton-S-methyl and ODM in plant and animal commodities.

Stability of residues in stored analytical samples

Storage stability studies were reported for cabbage, maize forage, maize kernels, maize husks, lettuce, and papaya. ODM and demeton-S-methylsulphon were stable on cabbage stored frozen for 800 days. Demeton-S-methylsulphon was stable on maize forage stored frozen for 160 days, but ODM showed significant loss after 60 days. ODM was stable on lettuce and papaya stored frozen for 50 days and 13 days respectively. (The Meeting did not accept the apparent recovery from lettuce of 98% after 180 days as valid because it was the mean of 69% and 128%).

The Meeting concluded that the data were generally inadequate and contradictory, and that additional studies were highly desirable.

Definition of the residue

The residue is currently defined as the sum of oxydemeton-methyl, demeton-S-methyl and demeton-S-methylsulphon, expressed as oxydemeton-methyl. The analytical methods determine the combined residue as the sulfone. The pesticide demeton-S-methyl is metabolized to its sulfoxide, ODM. The Meeting confirmed the current definition, both for compliance with MRLs and for the estimation of dietary intake.

Residues resulting from supervised trials

Supervised field trials were reported for oranges, lemons, apples, pears, plums, grapes, cabbage, kale, kohlrabi, lettuce, peas, beans, potatoes, sugar beet, wheat, oats, barley, almonds, rape, sunflower, and cotton seed.

The Meeting was informed that instruction labels were being revised in Europe for some crops to include conditions aimed at yielding lower residues, such as reduced application rates and extended PHIs. Some labels may be awaiting approval by national governments. The Meeting based its recommendations on the available labels and did not consider pending or possible changes.

Oranges and lemons. Supervised field trials were conducted on oranges in Spain (6 trials, GAP for oranges 2 x 0.75 kg ai/ha, 30-day PHI) and Portugal (1 trial; GAP for citrus fruit 2 x 0.050 kg ai/hl (calculated 0.75 kg ai/ha), 84-day PHI). All the trials complied with GAP for Portugal and two of them with GAP for Spain, but the peel and pulp were analysed separately and their relative weights were not reported. The higher residues in the peel were used to estimate maximum residue levels, and the residues in the pulp to estimate STMRs. Two field trials on lemons in Spain and two in Italy complied with Portuguese GAP, and the Spanish trials also with Spanish GAP for oranges. The 11 trials on oranges and lemons may be combined for the estimation of maximum residue levels and STMRs to give rank orders of residues in the pulp of <0.01 (7), 0.01, 0.02 (2) and 0.04 mg/kg, and in the peel of <0.01 (5), 0.01 (2), 0.06, 0.09 and 0.13 (2) mg/kg. The Meeting estimated maximum residue levels of 0.2 mg/kg and STMRs of 0.01 mg/kg for oranges and lemons.

Apples and pears. Supervised field trials on apples in Germany (4 trials, GAP 1 x 0.025 kg ai/hl (0.40 kg ai/ha, 1500 l water/ha) before or directly after flowering, PHI about 60 days), Belgium (2 trials, no GAP reported), and France (3 trials, GAP 0.020 kg ai/hl, 60-day PHI) were reported. The trials in Belgium were at the higher rate of 0.083 kg ai/hl and did not comply with French or German GAP, and in two of the German trials application was apparently at a later growth stage. Two trials in Germany and three in France were according to GAP.

Field trials were also reported on pears: 2 in Germany, same GAP as apple; 1 in France, same GAP as apple, 2 in Italy according to Portuguese GAP (0.038 kg ai/hl, 56-day PHI) and 1 in Belgium, GAP not reported. All the trials were according to GAP except the Belgian trial with a longer PHI (100 days) than the 60 days of German GAP.

The five apple and five pear trials may be evaluated together: GAP for the two fruits is very similar and the residues are in one population. The residues in rank order were <0.01 (7), 0.03 and <0.04 (2) mg/kg. The Meeting estimated maximum residue levels of 0.05 mg/kg and STMRs of 0.01 mg/kg for apples and pears.

Plums. Four supervised field trials in Germany were according to GAP (1 x 0.025 kg ai./hl, before or directly after flowering, PHI about 60 days). The residues were 0.040, 0.014, 0.044 and 0.028 mg/kg). The Meeting concluded that 4 trials were insufficient for the estimation of a maximum residue level or an STMR and recommended withdrawal of the draft MRL.

Grapes. Supervised field trials were reported from Italy (2 trials, GAP 1 x 0.23 kg ai/ha, 40-day PHI) and Germany (3 trials, GAP 1 x 0.025 kg ai/hl applied from 2 leaves to developed inflorescences, BBCH Code 57). The residues were <0.04 (4) and 0.06 mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg and an STMR of 0.04 mg/kg.

Cabbages (head). Sixteen supervised field trials in Germany were according to GAP (1 x 0.15 kg ai/ha (height under 50 cm), 21-day PHI). The residues in rank order were <0.01 (6), 0.02, <0.03 (3), <0.04, <0.05 (4) and <0.06 mg/kg. The Meeting estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.03 mg/kg for head cabbages, and recommended withdrawal of the draft MRL for Savoy cabbage.

Kale. Four trials in Germany were according to GAP (the same as for cabbages). All the residues were <0.01 mg/kg. The Meeting considered the four trials an adequate database for kale and estimated a maximum residue level of 0.01* mg/kg and an STMR of 0.01 mg/kg.

Kohlrabi. Four supervised field trials in Germany complied with GAP for kohlrabi (the same as for cabbages). The residues were <0.01 (2), 0.03 and <0.06 mg/kg. The Meeting estimated a maximum residue level of 0.05 mg/kg and an STMR of 0.02 mg/kg .

Lettuce. Seven reported trials in Germany comprised one trial in triplicate (same location, time, and application) which complied with GAP (1 x 0.16 kg ai/ha, 21-day PHI) and two duplicate trials in which the PHIs were more than 33% below the GAP PHI and which displayed quantifiable residues. The Meeting concluded that one trial was not adequate for the estimation of a maximum residue level or STMR and recommended the withdrawal of the draft MRL for leaf lettuce.

Field peas and beans (dry). Three of five trials on field beans in Germany accorded with GAP (2 x 0.15 kg ai/ha (height under 50 cm) or 0.25 kg ai/ha (over 50 cm), 28-day PHI). The other two trials were apparently replicates of one of these. Three trials on field peas were conducted in Germany (GAP only for garden peas) and two in France (no GAP). GAP for Italy is 1 x 0.23 kg ai/ha, 21-day PHI, but the trials were at less than half this rate. All residues in the shelled dry peas were <0.01 mg/kg. The Meeting decided that the three trials on field beans, supplemented by the 5 trials on field peas whose rates and PHIs approximated GAP for field beans, provided an adequate data base for the estimation of a maximum residue level and STMR for beans but not peas. The residues in rank order were <0.01 (5), <0.04, 0.05 and 0.05 mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg and an STMR of 0.01 mg/kg for common bean (dry), and recommended withdrawal of the draft MRLs for beans (dry) and peas (dry).

Potatoes. Supervised trials were reported from Germany (14 trials, GAP 3 x 0.3 kg ai/ha, 21-day PHI), France (1 trial; no GAP reported), the UK (3 trials, no GAP reported), and The Netherlands (2 trials, no GAP reported). GAP for Ireland is 2-4 x 0.15 kg ai/ha (height under 50 cm) or 0.22 kg ai/ha (over 50 cm), 200 l water/ha, PHI 28 days. All the trials approximated German or Irish GAP but two German trials were discounted because they were replicates and not independent trials. In the 18 independent trials the residues in rank order were <0.01 (7), <0.02 (9) and <0.05 (2) mg/kg. The Meeting estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.02 mg/kg.

Sugar beet (root). Supervised field trials were reported from Germany (9 trials + 2 on fodder beet, GAP 4 x 0.24 kg ai/ha, 28-day PHI) and France (2 trials, GAP 0.15 kg ai/ha, 28-day PHI). The two trials in France and two of the German trials were at excessive application rates. Seven trials on sugar beet and the two trials with fodder beat in Germany complied with GAP for sugar beet. The residues in rank order in the sugar and fodder beets were <0.01 (4) and <0.04 (5) mg/kg. The residues in the four trials at excessive rates were all <0.04 mg/kg. The Meeting estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.04 mg/kg.

Sugar beet (tops). The residues in the leaves of the sugar and fodder beets treated according to GAP were 0.02 and <0.04 (8) mg/kg. The residues from the two German trials at excessive rates were also <0.04 mg/kg. The Meeting estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.04 mg/kg for sugar beet leaves or tops.

Wheat, barley and rye. Supervised field trials on wheat were reported from Germany (8 trials, GAP 2 x 0.12 kg ai/ha, 21-day PHI) and the UK (1 trial; no GAP reported; Irish GAP for wheat, rye and barley: 0.12 kg ai/ha, 200 l water/ha, 21-day PHI). Six trials in Germany were according to maximum GAP conditions and complied with Irish GAP. Three trials on barley were reported from Germany and one from the UK. Two German trials and the UK trial (according to Irish GAP) were at the maximum GAP conditions and gave residues of <0.04 (2) and <0.05 mg/kg in the grain. Two supervised field trials on oats (grain residues <0.01 and 0.05 mg/kg) were submitted from Germany, but no current GAP was available.

A total of 10 trials on wheat and barley complied with GAP. The results may be combined for the evaluation of these crops and rye. The residues in the grain in rank order were <0.04 (6), <0.05 (2) and 0.05 mg/kg. The Meeting estimated maximum residue levels of 0.05* mg/kg and STMRs of 0.04 mg/kg for wheat, barley and rye.

Wheat, barley and rye straw and fodder. The 10 trials according to GAP for wheat and barley described above yielded residues in or on the straw of <0.04 (4), <0.05, 0.06, 0.12, 0.18, 1.2 and 1.3 mg/kg. The Meeting estimated maximum residue levels of 2 mg/kg and STMRs of 0.06 mg/kg for the fodders and straws of wheat, barley and rye.

Almonds. In six supervised field trials on almonds in Spain (GAP 2 x 0.25 kg ai/ha, 30-day PHI) all the PHIs were 90 days. The Meeting concluded that there were no results from trials according to GAP and that no maximum residue level or STMR could be estimated.

Rape seed. Three supervised field trials in France (GAP 0.12 kg ai/ha, unspecified PHI) yielded residues in the seed of <0.05 mg/kg after application at 0.12 kg ai/ha and a 63- or 79-day PHI. The Meeting concluded that 3 trials were insufficient to estimate a maximum residue level or STMR.

Sunflower seed. Three trials in France (GAP 1 x 0.1 kg ai/ha, PHI unspecified) gave residues in the seeds of <0.01 mg/kg after a foliar treatment at 0.1 kg ai/ha and an 83–87-day PHI. The Meeting concluded that 3 field trials were inadequate for the estimation of a maximum residue level or STMR.

Cotton seed. Ten trials in Australia (no GAP reported), 4 in Brazil (Peruvian GAP 3 x 0.25 kg ai/ha, 14-day PHI), and 7 in the USA (GAP 3 x 0.84 kg ai/ha, 14-day PHI) were reported. Two of the trials in Brazil with residues of 0.03 and 0.02 mg/kg complied with GAP and six US trials approximated GAP. The status of the remaining trials could not be ascertained from the information provided. The residues in rank order were <0.01 (2), 0.01 (3), 0.02 and 0.03 mg/kg. The Meeting estimated a maximum residue level of 0.05 mg/kg and an STMR of 0.01 mg/kg.

Feeding studies

Animal feeding studies on lactating dairy cows and laying hens were reported. The cows received daily doses of ODM for 28 days at levels equivalent to 10, 30, or 100 ppm in the feed. The combined residue of ODM and ODM sulfone was <0.01 mg/kg in all milk samples and in the liver, kidneys, muscle and fat. The demonstrated lower limit of quantification was 0.01 mg/kg.

Three groups of ten hens each were fed ODM in the daily diet for 28 days at rates of 0.65, 1.95, or 6.5 ppm in the feed. The combined residue was <0.01 in all egg samples and in the tissues of the 6.5 ppm group. Tissues from the other groups were not analysed.

The potential animal feed items containing ODM and the relevant maximum residue levels are as follows: potato culls and processed waste (potatoes 0.05 mg/kg), sugar beet tops, pulp, and molasses (sugar beet 0.05 mg/kg), wheat and barley grain (0.05 mg/kg) and straw (2 mg/kg), cotton seed and cotton seed oil, meal and hulls (cotton seed 0.05 mg/kg). A dietary burden for dairy cattle can be calculated as follows: barley straw (2 mg/kg/0.89 dry matter) x 60% of the diet + cotton seed (0.05 mg/kg/0.88 dry matter) x 20% of the diet + sugar beet tops (0.05 mg/kg/0.23 dry matter) x 20% of the diet = 1.5 ppm. The dietary burden for poultry would be cotton seed meal (0.05 mg/kg/0.89 dry matter x 20% of the diet) + grain (0.05 mg/kg/0.88 dry matter x 50% of the diet) = 0.04 ppm. The cattle and hen feeding studies at maximum rates represent approximately 66 times (100/1.5) and 160 times (6.5/0.04) these levels respectively, and no residues were found. The Meeting concluded that quantifiable residues of demeton-S-methyl, ODM, and/or demeton-S-methylsulphon in commodities of animal origin (meat, milk, poultry and eggs) are unlikely and that MRLs could be set at the practical limits of quantification of 0.05* mg/kg for all commodities except milk and at 0.01* mg/kg for milk. The Meeting recommended these levels as MRLs, estimated STMRs of 0 mg/kg for all the commodities, and recommended withdrawal of the draft MRL for derived milk products.

Processing studies

Processing studies on apples and cotton seed were reported. The processing factor for apple juice was 1 and for sauce 0.5. The processing factor for refined cotton seed oil was 0.2, for meal 0.6, and for hulls 0.2. Limited information on processing was provided for sugar beet, kale, potatoes, rape, and wheat, but in all cases the raw agricultural commodity lacked quantifiable residues.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

All recommendations are based on the use of oxydemeton-methyl. No data were supplied for the use of demeton-S-methyl or demeton-S-methylsulphon. The residues will be the sum of oxydemeton-methyl and demeton-S-methylsulphon. Any inadvertent demeton-S-methyl would also be included.

Definition of the residue for compliance with MRLs and for the estimation dietary intake: sum of demeton-S-methyl, oxydemeton-methyl, and demeton-S-methylsulphon, expressed as oxydemeton-methyl.

Commodity		Recommendations, mg/kg		
CCN	Name	MRL		STMR
		New	Previous	
AL 1020	Alfalfa fodder	W	5	
FP 0226	Apple	0.05	1	0.01
JF 0226	Apple juice	-	-	0.005
	Apple sauce			0.01
GC 0640	Barley	0.05*	0.2	0.04
AS 0640	Barley straw and fodder, dry	2	-	0.055
VD 0071	Beans (dry)	W	0.01*	
VB 0400	Broccoli	W	1	
VB 0402	Brussels sprouts	W	1	
VB 0403	Cabbage, Savoy	W	0.01*	
VB 0041	Cabbages, Head	0.05*	1	0.03
MF 0812	Cattle fat	0.05*	0.05*	0
VB 0404	Cauliflower	W	0.01*	
FS 0013	Cherries	W	1	
AL 1031	Clover hay or fodder	W	5	
VD 0526	Common bean (dry)	0.1	-	0.01
VP 0526	Common bean (pods and/or immature seeds)	W	0.2	
SO 0691	Cotton seed	0.05	0.05	0.01
OR 0691	Cotton seed oil, edible	-	-	0.002
	Cotton seed meal			0.006
	Cotton seed, hulls			0.002
VC 0424	Cucumber	W	0.5	
LD 0106	Derived milk products	W	0.05	
VO 0440	Egg plant	W	0.2	
PE 0112	Eggs	0.05*	0.05*	0
VP 0528	Garden pea (young pods)	W	0.1	
FC 0203	Grapefruit	W	0.1	
FB 0269	Grapes	0.1	0.5	0.04
VL 0480	Kale	0.01*	0.05	0.01
VB 0405	Kohlrabi	0.05	0.01*	0.02
FC 0204	Lemon	0.2	1	0.01
VL 0483	Lettuce, Leaf	W	2	
VP 0534	Lima bean (young pods and/or immature beans)	W	0.2	
GC 0645	Maize	W	0.2	
AS 0645	Maize fodder	W	5	
FC 0206	Mandarin	W	0.5	
MM 0097	Meat of cattle, pigs and sheep	0.05*	0.05*	0
ML 0106	Milks	0.01*	0.01*	0
HH 0738	Mints	W	20	
GC 0647	Oats	W	0.2	
VA 0385	Onion, Bulb	W	0.05	
FC 0004	Oranges, Sweet, Sour	0.2	0.5	0.01
FS 0247	Peach	W	1	
FP 0230	Pear	0.05	0.5	0.01
VD 0072	Peas (dry)	W	0.01*	
VO 0051	Peppers	W	1	
MF 0818	Pig fat	0.05*	0.05*	0
FS 0014	Plums (including Prunes)	W	0.5	

Commodity		Recommendations, mg/kg		
CCN	Name	MRL		STMR
		New	Previous	
VR 0589	Potato	0.05*	0.2	0.02
PF 0111	Poultry fats	0.05*	0.05*	0
PM 0110	Poultry meat	0.05*	0.05*	0
VC 0429	Pumpkins	W	0.1*	
GC 0650	Rye	0.05*	-	0.04
AS 0650	Rye straw and fodder, dry	2	-	0.055
SO 0699	Safflower seed	W	1	
MF 0822	Sheep fat	0.05*	0.05*	0
GC 0651	Sorghum	W	0.5	
AF 0651	Sorghum forage (green)	W	1	
AS 0651	Sorghum straw and fodder, dry	W	3	
VC 0431	Squash, Summer	W	0.1*	
FB 0275	Strawberry	W	0.5	
VR 0596	Sugar beet	0.05*	0.05*	0.04
AV 0596	Sugar beet leaves or tops	0.05*	0.5	0.04
VO 0447	Sweet corn (corn-on-the-cob)	W	0.05	
VO 1275	Sweet corn (kernels)	W	0.05	
VO 0448	Tomato	W	0.5	
TN 0085	Tree nuts	W	0.05*	
VR 0506	Turnip, Garden	W	0.1*	
AV 0506	Turnip leaves or tops	W	5 fresh wt	
VC 0432	Watermelon	W	0.2	
GC 0654	Wheat	0.05*	0.2	0.04
AS 0654	Wheat straw and fodder, dry	2	-	0.055
VC 0433	Winter squash	W	0.1*	

FURTHER WORK OR INFORMATION

Desirable

Data on the stability of stored analytical samples of raw agricultural commodities containing quantifiable residues of oxydemeton-methyl are highly desirable. The available information was not representative of the various crop groups, did not cover extended storage intervals, and suggested variable storage stability.

DIETARY RISK ASSESSMENT

STMRs have been estimated for oxydemeton-methyl in 30 commodities, of which five are processed commodities and seven are products of animal origin. Where consumption data were available, these STMRs were used in the estimate of dietary risk. No MRLs were used.

The International Estimated Daily Intakes for the five GEMS/Food regional diets ranged from 10 to 90% of the ADI. The Meeting concluded that the intake of residues of oxydemeton-methyl resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

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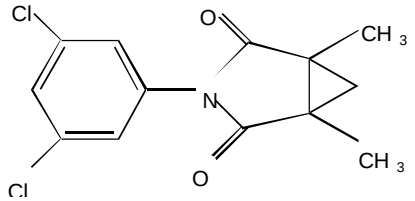
PROCYMIDONE (136)

EXPLANATION

Procymidone was reviewed by the JMPR in 1981, 1989, 1990 and 1993. Recommendations from the 1993 review included the withdrawal of draft MRLs for apples, currants (black, red and white), egg plant, kiwifruit, melons, except watermelon, potatoes and rice (polished and husked). These recommendations were confirmed by the CCPR at the 27th (1995) Session.

At the 1996 CCPR, MRLs for nectarines and peaches were withdrawn in the absence of new data (ALINORM 97/24). The Committee was informed by the manufacturer that new data on kiwifruit, peaches, plums, peas and brassica vegetables would be available for evaluation in 1998 (ALINORM 95/24A, para 131, 132, 133 and 134). In addition, residue data for pears have been reported. Information on analytical methods and monitoring was provided by The Netherlands.



Structure of procymidone

METHODS OF RESIDUE ANALYSIS

Analytical methods

Validated methods for the quantification of procymidone in pears, peaches, plums, cabbages and peas were provided (Provot, 1996a,b,c, 1997, 1998). All analytical reports were validations of Method No. BA-70-0020 (Sumitomo Reference No. BA-70-0220). Various methods were reported in the 1981 monograph and reviewed by Ambrus *et al.* (1991). Validation of the methods used for the determination of procymidone in kiwifruit was not provided, and recoveries in all kiwifruit trials were either not or inadequately reported.

The validated methods are all similar. The sample is homogenized with acetone and filtered through celite and the extraction with acetone is repeated with the filter cake. The combined filtrates are washed with 10% aqueous NaCl solution and hexane. The hexane layer is collected, dried and evaporated to near-dryness. The remaining residues are transferred to a Florisil column, eluted with 10:1 hexane/ethyl acetate and evaporated to dryness. The remaining procymidone residues are re-dissolved in hexane for quantification by GLC with a thermionic nitrogen detector (NPD). The limit of determination in all crops is 0.02 mg/kg; recoveries were 70-110%, as shown in Table 1.

Table 1. Recoveries of procymidone from in pears, peaches, plums, cabbages and peas.

Sample	Fortification levels, mg/kg [1]	Recovery range, %	Mean % ± SD
Pears	0.02, 0.2, 2.0	78-109	88 ± 11.6
Peaches	0.02, 0.2, 2.0, 3.0, 4.0	70-108	90 ± 13.2
Plums	0.02, 0.2, 2.0	80-110	95 ± 8.7
Cabbages	0.02, 0.2, 10	75-109	94 ± 12
Peas, seeds	0.02, 0.2, 2.0	83-110	100 ± 8
Empty pods	0.02, 0.2, 2.0	73-102	88 ± 10
Whole plants (early harvest)	0.2, 10, 30	72-115	93 ± 16
Whole plants (late harvest)	0.2, 10, 30	78-110	94 ± 12

[1] Triplicate samples at each concentration.

A multi-residue method was provided by The Netherlands government (1996). Residues in fruits and vegetables may be extracted by homogenising the commodity with ethyl acetate and sodium sulfate, followed by gravity filtration, or by extraction with acetone followed by CH_2Cl_2 and petroleum ether and separation of the organic phases. The extracts are cleaned on an alumina column, eluted with hexane and ethyl acetate (9:1) and the residue determined by GLC with an ECD, NPD or ion trap detector. The limits of determination ranged from 0.001 to 0.1 mg/kg with recoveries above 80%. Recoveries from lettuce were 98-111% at fortification concentrations from 0.12 to 1.0 mg/kg.

Stability of residues in stored analytical samples

Negligible degradation of residues was found in strawberry samples which were fortified with procymidone at concentrations of 0.05 and 0.5 mg/kg, stored at -26°C and analysed after 0, 6 and 12 months. Recoveries ranged from 77 to 110% at 0.05 mg/kg and from 81 to 96% at 0.5 mg/kg over the 12-month period (Halasz-Laky, 1992).

Procymidone residues were stable in field-treated and fortified cherry samples for 12 months (Kadenczki, 1993). Treated samples were collected 21 days after application of a 50 WP formulation at 0.7 kg ai/ha and stored whole. Untreated samples were pipped and homogenised, then fortified at levels of 0.05 and 0.5 mg/kg. The samples were kept in frozen storage (-20 to -25 °C) for 12 months and analysed at 0, 6, 9 and 12 months. Procymidone residues in field-treated samples ranged from 0.30 to 0.45 mg/kg at 0, 0.28 to 0.49 mg/kg at 6, and 0.37 to 0.50 mg/kg at 12 months. Recoveries from homogenised samples fortified at 0.05 mg/kg ranged from 62 to 96% and from those fortified at 0.5 mg/kg from 64 to 112% over the 12-month storage period. The average recoveries from all the samples at levels of 0.02-3 mg/kg ranged from 63 to 102%.

Procymidone was stable in homogenised lettuce fortified at concentrations of 0.1 and 1.0 mg/kg and stored at -20°C for 12 months (Gillis, 1995a). Analyses after 1, 3, 6 and 12 months gave recoveries of 93 to 104% at 0.1 mg/kg and 91 to 99% at 1.0 mg/kg over the 12-month period.

Homogenised haricot beans were fortified with procymidone at concentrations of 0.1 and 1.0 mg/kg and stored at -20°C for 12 months (Gillis, 1995b). After 0, 1, 3, 6 and 12 months of storage recoveries were 83 to 105% at 0.1 mg/kg and 87 to 99% at 1.0 mg/kg. No degradation of procymidone was detected.

USE PATTERN

Procymidone, *N*-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, is a fungicide used for the prevention and control of *Monilinia*, *Sclerotinia* and *Botrytis* species in fruits and

vegetables. It is marketed as a 25% suspension concentrate (25 SC), 500g/l suspension concentrate (500 SC), 50% wettable powder (50 WP), 50% water-dispersible granule (50 WG) and 75% water-dispersible granule (75 WG).

Information on registered use patterns in EU member countries was provided by The Netherlands government and on uses in various countries by the manufacturer. The use patterns for pears, peaches, plums, kiwifruit, peas and cabbages are shown in Table 2. Information on GAP for cabbages in Greece and peas in Germany was tabulated but registered product labels were not provided.

Table 2. Use patterns of procymidone

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Almond	France	500 g/l Liq, SC, 50 WP	High volume	0.75 0.75	0.075 0.075	– –	8 15
Almond	Italy	50 WP, 50 WG, 75 WG	High volume	1.13-1.80 1.5-2.0	0.075-0.10 0.075-0.10	–	
Almond	Lebanon	50 WP	Foliar		0.025-0.05		14
Apple	Lebanon	50 WP	Foliar		0.025-0.05		14
Apricot	France	500 g/l Liq., SC, 50 WP	High volume	0.75	0.075	–	8
Apricot	Italy	50 WP, 50 WG, 75 WG	High volume	1.13-1.80 0.75-1.35 1.5-2.0 1.0-1.5	0.075-0.1 0.05-0.075 0.075-0.1 0.05-0.075	2-3 2 2-3 2	14
Apricot	Jordan	50 WP	Foliar		0.025-0.05		14
Apricot	Lebanon	50 WP	Foliar		0.025-0.05		14
Asparagus	Italy	50 WP, 50 WG, 75 WG	Foliar	0.5-0.9	0.05-0.075		[1]
Aubergine	France	500 g/l Liq., SC, 50 WP	Foliar	0.75 0.75			7 3
Aubergine	Italy	50 WP, 50 WG, 75 WG	Foliar	0.04-0.05	0.24-0.42	3	14
Aubergine	Jordan	50 WP	Foliar		0.025-0.05		3
Aubergine	Netherlands	EC, 50 WP	Foliar	0.125-0.375	0.025	5	3
Aubergine	Poland	SC	Foliar	0.5-0.75	0.05	2-3	3
Beans[2]	Australia	500 g/l Liq.	Foliar	0.75	0.075	2	–
			Post-harvest dip	50 g ai/100 l solution			–
Beans	France	500 g/l Liq, SC, 50 WP	Foliar spray	0.75		1-2	14-15
Beans	Germany	500 g/kg WG	Foliar[3]	0.38	0.063	3	7
Beans	Italy	50 WP, 50 WG, 75 WG	Foliar	0.3-0.6	0.05-0.075		14
Beans	Jordan	50 WP	Foliar		0.025-0.05		21
Beans	Lebanon	50 WP	Foliar		0.025-0.05		3
Beans	New Zealand	25 FL	Foliar	0.5	0.05	2	3
Beans	Poland	SC	Foliar	0.51	0.083	2	3
Beans	Romania	50 WP	Foliar	0.5	0.05		14
Beans	South Africa	250 g/l SC	Foliar	0.375	0.075	2-3	14
Blackberry	Switzerland	50 WG	Foliar	0.75-1.0			14
Broad beans	Netherlands	EC, 50 WP	Foliar	0.5		2	14

[1] Treatment of vegetation post-harvest.
[2] Same use pattern for green beans and navy beans.
[3] At beginning, middle and end of flowering.

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Cabbages	France	500 g/l Liq, SC, 50 WP	Foliar spray	0.75		–	21
Cabbage	Jordan	50 WP	Foliar		0.025-0.05		14
Celery	Jordan	50 WP	Foliar		0.025-0.05		14
Cherry	Italy	50 WP, 50 WG, 75 WG	High volume	1.125-1.80 1.5-2.0	0.075-0.10 0.075-0.10	2-3[4]	21
Cherry	Jordan	50 WP	Foliar		0.025-0.05		14
Cherry	Lebanon	50 WP	Foliar		0.025-0.05		14
Colza	Italy	50 WG, 75 WG	Foliar	0.50-0.75		1	
Colza	France	500 g/l Liq.	Foliar	0.75			
Courgette	France	500 g/l Liq., SC, 50 WP	Foliar	0.75			7 3
Courgette	Netherlands	EC, 50 WP	Foliar	0.125-0.375	0.025	5	3
Cucumber	Italy	50 WP, 50 WG, 75 WG	Foliar	0.3 –0.6	0.05-0.075		14
Cucumber	Netherlands	EC, 50 WP	Foliar	0.125-0.375	0.025	5	3
Cucumber	Jordan	50 WP	Foliar		0.025-0.05		3
Cucumber	Poland	SC	Foliar	0.5-0.75	0.05	2-3	3
Cucumber	Romania	50 WP	Foliar	0.5	0.05		14
Currants	Poland	SC	High volume	0.75	0.038-0.075	2-3	14
Faba beans	Australia	500 g/l Liq.	Foliar	0.25			
Garlic	Australia	500 g/l Liq.	Pre-plant treatment	5 g ai/kg cloves			
Garlic	France	500 g/l Liq., SC, 50 WP	Bulb Foliar	150 g ai/100 kg of bulbs[5] 0.75			21
Garlic	Italy	50 WP, 50 WG, 75 WG	Bulb Foliar	15 g ai/100 kg 0.3-0.8	0.05-0.1[6]		
Garlic	Uruguay	50 WP	Bulb	500 g ai/100 kg cloves			
Gherkin	France	500 g/l Liq., SC, 50 WP	Foliar	0.75			7 3
Gherkin	Netherlands	EC, 50 WP	Foliar	0.125-0.375	0.025	5	3
Grapes	Australia	500 g/l	Foliar	0.5	0.038	4	5
Grapes (vines)	France	500 g/l Liq. SC, 50 WP	High volume	0.75 0.75	0.075	1[7]	14
Grapes (vines)	Italy	25 SC, 50 WP, 50 WG, 75 WG	Foliar	0.4-0.75	0.050-0.075 0.04-0.075 0.038-0.075	3-4 2-4 2-4	21
Grapes	New Zealand	25 FL	High volume	0.75	0.05	2	
Grapes	Romania	50 WP	Foliar	0.5-0.75			14
Grapes (table)	South Africa	250 g/l SC	Foliar		0.05	4	28
(wine)					0.05	3	7
Grapes	Switzerland	50 WG	Foliar	1.0	0.05	4	[8]
Grapes	Uruguay	50 WP	Foliar	0.5-0.75	0.0375-0.05		28
Green beet	Italy	50 WP, 50 WG, 75 WG	Foliar	0.3-0.4	0.05 0.0525		2
Green peppers	France	SC, 50 WP	Foliar	0.75			3
Green peppers	Italy	50 WP, 50 WG, 50 WG	Foliar	0.24-0.40 0.225-0.42	0.04 –0.05 0.038-0.053	1	14
Green peppers	Netherlands	EC, 50 WP	Foliar	0.125-0.375	0.025	5	3
Green peppers	Poland	SC	Foliar	0.5-0.75	0.05	1-2	3
Hazel nut	France	500 g/l Liq., SC, 50 WP	High volume	0.75	0.075	–	8

[4] No more than 3 sprays per season.
[5] Bulb treatment before planting.
[6] Bulb treatment against *Botrytis* and *Sclerotinia*; not indicated as pre-planting, so presumably storage.
[7] At veraison.
[8] Last spray end of August.

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Hazelnut	Italy	50 WG, 75 WG			0.038-0.053		
Kiwifruit	France	500 g/l Liq, SC, 50 WP	High volume	0.75	0.075	–	8[9]
Kiwifruit	Italy[10]	25 SC	Foliar	–	0.075-0.100	5	14
		50 WP, 75 WG		0.56-0.95	0.038-0.053	2-3	
		50 WG		0.75-1.0	0.038-0.050	2-3	
		50 WP, 50 WG	Post-harvest dip	6 g ai/100 l solution		1	60[11]
Lentils	France	500 g/l Liq, SC, 50 WP	Foliar	0.75		1-2	14-15
Lettuce	Australia	500 g/l Liq.	Foliar	0.28-0.6	0.038-0.05		
			Drench	2.5 g ai/L/800 seedlings in a tray			2
			Soil surface spray	1.0	0.1		2
Lettuce[12]	France	500 g/l Liq. SC, 50 WP	Soil, storage	30 g ai/hl[13] 1.5 g ai/m^2 [14]			21
			Foliar	0.75			
Lettuce	Italy	50 WP, 50 WG, 75 WG	Foliar	0.75-1.0 0.5-0.75		2	14
Lettuce	Jordan	50 WP	Foliar		0.025-0.05		–
Lettuce	Lebanon	50 WP	Foliar		0.025-0.05		3
Lettuce[12]	Netherlands	EC, 50 WP	Foliar[15]	0.75 2.0		3 1	
Lettuce	Uruguay	50 WP		0.05			7
Melon	France	500 g/l Liq., SC, 50 WP	Foliar	0.75			7 3
Melon	Netherlands	EC, 50 WP	Foliar	0.125-0.375	0.025	5	3
Melon	Poland	SC	Foliar	0.5-0.75	0.05	2-3	3
Minneola	South Africa	250 g/l SC	Foliar		0.05		120
Onions	Australia	500 g/l Liq.	Seed treatment	10 g ai/kg seed			28
			In-furrow	2 kg ai/ha			28
			Soil spray	1 kg ai/ha		2	28
			Transplant dip	0.5 kg ai/100 l solution			28
Onions, shallots	France	500 g/l Liq., SC, 50 WP	Bulb Foliar, soil	150 g ai/100 kg of bulb[16](shallots) 0.75 (Botrytis, Sclerotinia)			21
Onions	Italy	50 WP, 50 WG, 75 WG	Seed treatment,	0.5 g ai/kg onion seed			
			Foliar	0.3-0.6	0.05-0.075		28
					0.053-0.075		14
Onions	Jordan	50 WP	Foliar		0.025-0.05		1
Onions Shallots	Netherlands	EC, 50 WP	Soil pre-planting	2-3		1	28
			Foliar (shallots)	0.25		1-2	28
Onions	Uruguay	50 WP	Transplanting	100 g ai/100 l solution			3
			Foliar	0.75	0.075		3
Peaches	Australia	500 g/l Liq.	Foliar		0.025 0.0375	4-6	8

[9] Reduction in PHI to 3 days has been proposed in EU submission.
[10] 3 foliar sprays plus a post-harvest dip treatment or 5 consecutive sprays.
[11] 60 days after harvest or post-harvest treatment.
[12] Lettuce includes chicory, witloof, endive and cos lettuce.
[13] Foliar spray and root treatment after planting and after harvest for storage or transport.
[14] Root treatment and soil/bed treatment at planting or transplanting.
[15] Lower rate for 3 sprays, 1st 7 days after planting and 2nd 14 days after planting; higher rate 7 days after planting only.
[16] Bulb treatment before planting.

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
			Post-harvest dip	50 g ai/100 l solution			
Peaches	France	500 g/l Liq, SC, 50 WP	High volume	0.75	0.075		8
Peaches	Italy	25 SC	Foliar spray	–	0.075-0.100	3	
				–	0.05-0.075	2[17]	
		50 WP, 75 WG	High volume	1.125-1.80	0.075-0.100	2-3	
		50 WG		1.50-2.0	0.075-0.100	2-3	14
Peaches	Jordan	50 WP	Foliar		0.025-0.05		30
Peaches	Lebanon	50 WP	Foliar		0.025-0.05		14
Peaches	Morocco	50 WP	Foliar		0.25		
Peaches	New Zealand	25 FL	High volume	0.75-1.0	0.038-0.05	3	1
Peaches	Romania	50 WP	Foliar	0.5-0.75	0.05-0.075		14
Peaches	South Africa	250 g/l SC	Foliar		0.0375	2	7
Peaches	Switzerland	50 WG	Foliar	1.0			
Peaches	Uruguay	50 WP	Foliar	0.5-0.75	0.025-0.0375		7
Pears	Italy	25 SC, 75 WP	High volume	0.75-1.35	0.050-0.075		14
		50 WG		1.0-1.5	0.050-0.075		14
Pears	Lebanon	50 WP	Foliar		0.025-0.05		3
Pears	South Africa	250 g/l SC	Foliar		0.05		
Pears	Switzerland	50 WG	Foliar	1.0	0.05		
Peas	France	500 g/l Liq, SC, 50 WP	Foliar spray	0.75		1-2	14-15
Peas (field)	Germany	500 g/kg WG	Foliar	0.5	0.125	1	14
Peas	South Africa	250 g/l SC	Foliar	0.5			21
Peppers	Jordan	50 WP	Foliar		0.025-0.05		7
Peppers	Lebanon	50 WP	Foliar		0.025-0.05		21
Pimento	France	500 g/l Liq.	Foliar	0.75			7
Plums	Italy	50 WP, 75 WG	High volume	1.125-1.80	0.075-0.100	3	21
		50 WG		1.50-2.00	0.075-0.100		
Plums	France	500 g/l Liq, SC, 50 WP		0.75	0.075	–	8
Plums	Lebanon	50 WP	Foliar		0.025-0.05		14
Potato	Australia	500 g/l Liq.	Foliar	0.25 0.5			7
Potato	Jordan	50 WP	Foliar		0.025-0.05		
Potato	Lebanon	50 WP	Foliar		0.025-0.05		45
Potato	South Africa	250 g/l SC	Foliar	0.625-0.937	0.125		35
Rape seed	France	SC					8
Rape seed	Germany	500 g/kg WG	Foliar	0.5	0.125	1[18]	56
Rape seed	Italy	50 WP	Foliar	0.5-0.75		1[19]	7
Rape seed	Poland	SC	High volume	0.75	0.19-0.38	1-2	56
Raspberry	France	500 g/l Liq., SC, 50 WP	Foliar	0.75	0.075	–	14
Raspberry	Switzerland	50 WG	Foliar	0.75-1.0			14
Strawberry	France	500 g/l Liq., SC, 50 WP	Foliar	0.75		3-4[20]	–
Strawberry	Germany	500 g/kg WG	Foliar	0.75	0.038	3[21]	7
Strawberry	Italy	25 SC, 50 WP, 50 WG, 75 WG	Foliar	0.23-0.42	0.0375-0.050 0.038-0.053	3 3	14
Strawberry	Jordan	50 WP	Foliar		0.025-0.05		
Strawberry	Netherlands	EC, 50 WP	Foliar	0.19-0.45	0.0375-0.05 0.25-0.60	3-5	14

[17] Apply 4 or 5 weeks and 2 or 3 weeks before harvest.
[18] At beginning of infection or when 50 to 60% of buds have opened.
[19] Apply at first flowering.
[20] 3 or 4 sprays from beginning of flowering.
[21] Beginning, middle and end of flowering.

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Strawberry	New Zealand	25FL	Foliar	0.5	0.05	2	
Strawberry	Poland	SC	Foliar	0.75-1.25	0.05-0.38	1-2	7
Strawberry	Romania	50 WP	Foliar	0.5-0.75	0.05-0.075		14
Strawberry	Switzerland	50 WG	Foliar	0.75-1.0			14
Strawberry	Uruguay	50 WP	Foliar	0.5-0.75	0.0475-0.05		–
Sugar beet	Poland	SC	High volume	5 g ai/ton of root*			
Sunflower	Italy	50 WP, 50 WG, 75 WG	Seed	50-100 g ai/100 kg seed (57.75-97.5)			7
			Foliar	0.3-0.4	0.05		3
				0.315-0.42	0.053	2[22]	21
Sunflower	Romania	50 WP	Seed treatment	0.5 g ai/kg seed			14
			Foliar	0.5			14
Tomato	Australia	500 g/l Liq.	Foliar	0.28-0.60	0.0375-0.05		14
Tomato	France	500 g/l Liq., SC, 50 WP	Foliar	0.75			3
Tomato	Italy	25 SC, 50 WP, 50 WG, 75 WG	Foliar	0.24-0.40 0.225-0.42	0.04-0.05 0.038-0.053	–	7
Tomato	Jordan	50 WP	Foliar		0.025-0.05		3
Tomato	Morocco	50 WP	Foliar		0.3		
Tomato	Netherlands	EC, 50 WP	Foliar	0.125-0.375	0.025	5	
Tomato	Poland	SC	High volume	0.5-0.75	0.05	2-3	3
Tomato	Romania	50 WP	Foliar	0.5	0.05		14
Tomato	South Africa	250 g/l SC	Foliar		0.025		3
Watermelon	Jordan	50 WP	Foliar		0.025-0.05		21
Watermelon	Lebanon	50 WP	Foliar		0.025-0.05		3

RESIDUES RESULTING FROM SUPERVISED TRIALS

Data from numerous supervised trials on pears, peaches, plums, kiwifruit, peas and brassica vegetables were submitted for evaluation and are shown in Tables 3-11. All the trials were in France and Italy.

Table 3 Pears, *Italy*.
Table 4 Peaches, *France and Italy*.
Table 5 Plums, *France and Italy*.
Table 6 Kiwifruit, *France and Italy*.
Table 7 Kiwifruit, *Italy*.
Table 8 Cabbage, *France*.
Table 9 Cauliflower, Brussels sprouts, broccoli, *France*.
Table 10 Peas, *France*.
Table 11 Pea plants; legume animal feeds, *France*.

Trials where residues were found in untreated control samples are indicated by *c* followed by the corresponding residues in the control. Trials unsuitable for evaluation owing to the residues found in untreated samples and/or lack of appropriate information on recoveries are shaded in the Tables. The residues in the peaches and plums were calculated from the ratio of the weight of the stone and flesh to that of the flesh alone.

Residues from trials according to GAP are underlined; those used to estimate STMRs are double underlined. In instances where more than one figure is given, the samples were taken from

[22] 2 sprays before flowering.

different replicate plots. All residues are defined as procymidone. The limit of quantification was 0.02 mg/kg, unless otherwise stated.

Pears. Five applications were made at 1.08 to 1.38 kg ai/ha (0.075 kg ai/hl) which complied with Italian GAP. Although a re-treatment interval of 7 to 10 days is specified on the labels provided, the actual intervals between sprays 4 and 5 were 14 or 15 days. In two trials, finite residues were detected in untreated control samples. The results are shown in Table 3 (Sumitomo, 1997c).

Peaches. The trials in France and Italy complied with GAP. Applications were made at rates from 0.075 to 0.1 kg ai/hl. In one of the 1993 French trials recoveries were not adequately reported since an average over a range of fortification levels was reported without indication of recoveries at individual concentrations. The results are shown in Table 4 (Benet and Massenot, 1994a, 1995a).

Plums. Trials according to GAP in France (north and south regions) and Italy were reported. Residues in prunes were reported in one French trial. Application rates ranged from 0.75 to 1.8 kg ai/ha. The results are shown in Table 5 (Benet and Massenot, 1995b; Massenot and Cohadon, 1996a, 1997a).

Kiwifruit. Trials with foliar and post-harvest treatments were reported, but GAP was reported only for post-harvest treatments. The residues were determined in fruit treated up to 4 weeks before harvest and in cold storage for up to 4 months. On registered product labels 2 to 5 consecutive foliar sprays are indicated, but only single applications were made in the trial. The results are shown in Tables 6 and 7 (Massenot and Cohadon, 1987; Maini and Boni, 1985; Gandolfi and Collina, 1989).

The residues in the whole fruit are shown, although individual figures for pulp and peel were given. After post-harvest treatment (Table 7), residues in the pulp were 0.02 mg/kg to 0.15 mg/kg from dip concentrations of 3.25 to 25 kg ai/100 l. Recoveries were not adequately reported for any of the trials nor any storage details for the 1984 Italian trial.

Brassica vegetables. GAP was reported only for head cabbages in France and Jordan, although trials on cauliflower, broccoli and Brussels sprouts were also reported. In all the trials two applications were made at the maximum rate of 0.75 kg ai/ha. The registered labels provided describe specific application to cabbages only; not to other brassica crops. The residues in cabbages are shown in Table 8 and those in cauliflower, Brussels sprouts and broccoli in Table 9 (Benet and Massenot, 1994b,c, 1995c; Massenot and Cohadon, 1996b, 1997b). Recoveries in the two 1993 trials on cabbages were not adequately reported;. an average was given over a range of fortifications.

Peas. Supervised trials in France were reported, where a maximum of 2 sprays may be applied at 0.75 kg ai/ha. The residues were determined in whole plants with pods (early harvest and late harvest), whole pods, peas, and empty pods. The residues in whole plants, which are used as animal feed, are shown in Table 11. Differences were noted between the residues in mechanically and hand-harvested pods. The highest residues were found in whole plants and empty pods.

Table 3. Supervised trials on pears in Italy (Sumitomo, 1997c).

Year, Trial ID.	Application				PHI, days	Residues, mg/kg
	Form	No.	kg ai/ha	kg ai/hl		
1995 IIQ95/IT/01/01	50 WP	5	1.376	0.075	14	0.62
1995 IIQ95/IT/01/02	50 WP	5	1.082	0.075	14	0.16

Year, Trial ID.	Application				PHI, days	Residues, mg/kg
	Form	No.	kg ai/ha	kg ai/hl		
1995 IIQ95/IT/02/A	50 WP	5	1.361	0.075	0 3 7	1.85, 2.12, 2.24, 2.38 1.32, 1.33, 1.57, 1.60 1.10
					14 21	0.58 0.25, 0.27, 0.32, 0.34
1995 IIQ95/IT/02/B	50 WP	5	1.103	0.075	0 3 7 14 21	1.40, 1.43, 1.66, 1.71 *c* 0.25 1.49 *c* 0.16 0.77 *c* 0.11 0.45 *c* 0.05 0.30 *c* 0.09
1996 IIQ96/IT/02/A	50 WP	5	1.361	0.075	0 3 7 14 21	1.45 1.02 0.97 0.43 0.37
1996 IIQ96/IT/02/B	50 WP	5	1.340	0.075	0 3 7 14 21	1.26 1.43 1.20 0.65 *c* 0.11, 0.12 0.40 *c* 0.06
1996 IIQ96/IT/01/01 IIQ96/IT/01/02	50 WP 50 WP	5 5	1.348 1.348	0.075 0.075	14 14	0.43 0.35

c Untreated control samples.

Table 4. Supervised trials on peaches.

Country, Year Trial ID.	Application				PHI, days	Residues, mg/kg Whole fruit	Reference
	Form	No.	kg ai/ha	kg ai/hl			
Italy 1995 IIQ95/IT/03A	50 WP	3	1.1	0.1	0 3 7 14 21	1.67 1.17 0.92 0.72 0.35	BR-0488
IIQ95/IT/03B	50 WP	3	0.917	0.1	0 3 7 14 21	1.63 2.23 3.25 1.33 0.51	BR-0488
France 1993 S 323.93	500 g/l SC	2	0.75	0.075	-0 1 4 8 15	0.22 0.69 0.56 0.39 0.28	BR-31-0445F (Benet and Massenot, 1994a)
S 502.93					-0 1	0.40 1.80	BR-31-0445F
					4 8 14	1.90 1.30 0.87	
France 1995 94FARSA01	500 g/l SC	2	0.73 0.75	0.079 0.084	1 8	0.41 0.19	BR-0477F (Benet and Massenot, 1995a)

Country, Year Trial ID.	Application				PHI, days	Residues, mg/kg Whole fruit	Reference
	Form	No.	kg ai/ha	kg ai/hl			
94FARSA02	SC	2	0.75	0.10	1	0.65	BR-0477F
			0.75	0.11	8	0.44	
					14	0.30	
94FARSA03	SC	2	0.73	0.093	1	1.40	BR-0477F
			0.75	0.094	8	1.40	
					14	0.72	
94FARSA04	SC	2	0.75	0.094	1	0.75	BR-0477F
			0.76	0.093	8	0.68	
					14	0.28	

Table 5. Supervised trials on plums.

Country, Year Trial ID.	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
Italy 1995	50 WDG	3	1.80	0.188	0	1.17	BR-0489
F-R-11-6011/95					7	1.21	
					14	0.83	
					21	0.74	
					28	0.52	
F-R-12-6012/95	50 WDG	3	1.80	0.178	21	1.50 *c* 0.02, 0.03	BR-0489
F-R-13-6013/95	50 WDG	3	1.80	0.191	22	1.38 *c* 0.03, 0.03	BR-0489
France 1994	500 g/l SC	2	0.75	0.188	8	0.61 plum	BR-0478F
1/94/03302					8	0.51 dried fruit *c* 0.03	(Benet and Massenot, 1995b)
					14	0.84 flesh	
1/94/0	500 g/l SC	2	0.75	0.15	7	0.48	BR-0478F
					17	0.66	
France 1995	500 g/l SC	2	0.75	0.138	0	0.22	BR-0482
95 FARSA P 01					1	0.24	(Massenot, 1996a)
					3	0.40	
					7	0.59	
95 FARSA P 02		2	0.75	0.251	0	0.75	BR-0482
				0.240	1	0.65	
					3	0.58	
95 FARSA P 03		2	0.75	0.186	0	0.66	BR-0482
				0.182	1	0.65	
					3	0.67	
					8	0.60	
95 FARSA P 04		2	0.75	0.192	0	1.16	BR-0482
				0.194	1	1.66	
					3	0.78	
					8	1.06	
95 FARSA P 05		2	0.75	0.103	0	0.48	BR-0482
				0.099	1	0.44	
					3	0.31	
					8	0.19	
France 1996	500 g/l SC	2	0.75	0.109	7	0.31	BR-0492
96 FARSA P16				0.098			(Massenot, 1997a)
96 FARSA P17		2	0.75	0.183	7	0.77	BR-0492
				0.204			
96 FARSA P18		2	0.75	0.126	7	1.20	BR-0492
				0.157			
96 FARSA P19		2	0.75	0.219	7	0.90	BR-0492
				0.216			

Country, Year Trial ID.	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
96 FARSA P20		2	0.75	0.239 0.224	0 1 3 7	0.89 0.98 1.02 0.86	BR-0492

Table 6. Supervised trials on kiwifruit, pre-harvest foliar treatment.

Country, Year Trial ID.	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
France 1986	500 g/l SC	2	1.50		2	1.60 (whole fruit) 0.14 (pulp)	BR-71-0174F (Massenot and Culoto, 1987)
Italy 1984 [1] A	50% WP	2	0.112	0.075	161	0.07	BR-51-0154 (Maini and Boni, 1985)
B [2]		1	0.100	0.050	0 7 14 21 28 28 (5)[3] 28 (35) 28 (66) 28 (107)	1.89, 2.30, 1.53, 1.69 2.16, 1.49, 1.99, 0.97 2.12, 1.29, 0 79, 1.10 1.73, 1.46, 1.49, 0.81 1.01, 0.89, 0.79, 0.73 1.48, 0.95, 1.13, 0.83 *c* 0.03 1.31, 1.18, 1.22, 1.20 *c* 0.01 1.05, 1.19, 0.99, 0.93 *c* 0.02 1.09, 0.59, 1.02, 0.89 *c* 0.10	BR-51-0154
C		1	0.100	0.050	0 7 12 12 (30)[3] 12 (61) 12 (98)	0.96 (2), 1.17, 0.87 0.52, 0.94, 1.04, 1.64 0.88, 0.92, 0.82, 1.29 *c* 0.03 0.57, 1.16, 0.87, 0.80 *c* 0.01 0.96, 0.77, 0.99, 0.83 *c* 0.02 0.78, 0.77, 0.75, 0.66 *c* 0.01	BR-51-0154
D		1	0.100	0.050	0 5 5 (30)[3] 5 (61) 5 (100)	2.23, 1.34, 2.06, 2.54 1.41, 1.93, 1.73, 1.83 *c* 0.03 2.35, 0.68, 0.72, 0.65 *c* 0.01 1.61, 1.29, 2.60, 0.78 *c* 0.02 1.84, 0.78, 1.17, 1.14 *c* 0.01	BR-51-0154

[1] The limit of determination was not stated. [2] Individual figures represent four different trial sites.
[3] Samples were analysed after the periods of storage shown in parentheses.

Table 7. Supervised trials on kiwifruit in Italy, post-harvest dip treatment.

Year Trial ID.	Application			PHI, days	Residues, mg/kg	Reference
	Form	No.	g ai/100 l[1]			
1984[2]			50	0 31 60	2.68 (0.09 pulp) 2.74 4.30	BR-51-0154 (Maini and Boni, 1985)

Year Trial ID.	Application			PHI, days	Residues, mg/kg	Reference
	Form	No.	g ai/100 l[1]			
				101	3.09	
			100	0	4.36 (0.11 pulp)	
				31	5.51	
				60	5.77	
				101	4.92	
1989	50 WP	1	3.25	0	0.45	BR-91-0254 (Gandolfi and Collina, 1989)
				30	0.51	
				57	0.40	
				90	0.48	
				117	0.31	
		1	6.5	0	1.39	
				30	1.25	
				57	0.85	
				90	0.85	
				117	0.76	
		1	12.5	0	2.63	
				30	2.51	
				57	2.16	
				90	2.00	
				117	1.45	
		1	25	0	3.31	
				30	3.58	
				57	1.99	
				90	2.21	
				117	2.33	

[1]. g ai/100 l of dipping solution.
[2] LOD not reported.

Table 8. Supervised trials on cabbages, France.

Year Trial ID	Application				PHI, days	Residues, mg/kg[1]	Reference
	Form	No.	kg ai/ha	kg ai/hl			
1993 S 203.93	500 g/l SC	2	0.75	0.25	26	0.04	BR-41-0452F (Benet and Massenot, 1994b)
1993 S 201.94	500 g/l SC	2	0.75	0.25	139	0.03	BR-41-0460F (Benet and Massenot, 1994c)
S 342.94		2	0.75	0.15	93	0.20	
1994 S 201.95	500 g/l SC	2	0.75	0.25	14	0.30	BR-0480 (Benet and Massenot, 1995c)
				0.15	21	0.30	
					28	0.09	
S 101.95		2	0.75	0.25	13	<0.02	BR-0480
					20	<0.02	
					27	<0.02	
S 605.95		2	0.75	0.25	15	0.67	BR-0480
					22	0.12	
					29	0.26	
S 341.95		2	0.75	0.15	14	1.40	BR-0480
					21	1.30	
					28	1.40	
1995 S 207.95	500 g/l SC	2	0.75	0.25	0	1.18	BR-0483 (Massenot and Cohadon, 1996b)
				0.15	9	0.31	
					14	0.03	
					21	0.03	

Year Trial ID	Application Form	No.	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg[1]	Reference
S 208.95		2	0.75	0.25	0	1.36	BR-0483
				0.15	7	0.02	
					14	0.04	
					21	<0.02	
S 209.95		2	0.75	0.25	0	1.17	BR-0483
				0.15	8	0.08	
					14	0.05	
					20	0.03	
S 606.95		2	0.75	0.25	0	0.45	BR-0483
					7	0.55	
					14	0.05	
					20	0.17	
1995	500 g/l SC	2	0.75	0.25	0	0.97	BR-0491
S 203.96				0.15	7	0.55	(Massenot 1997b)
					14	0.33	
					21	0.44	
S 501.96		2	0.75	0.25	0	4.75	BR-0491
					7	1.72	
					13	1.60	
					21	0.43	
S 340.96		2	0.75	0.15	0	1.01	BR-0491
					7	0.40	
					13	0.23	
					21	0.32	

[1] Outer wrapper leaves removed before analysis.

Table 9. Supervised trials on cauliflower, Brussels sprouts and broccoli in France.

Year Trial ID	Application Form	No.	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference
CAULIFLOWER							
1993	500 g/l SC	2	0.85	0.15	21	0.05	BR-41-0452F
S 345.93			0.75	0.15			(B. & M., 1994b)
1993	500 g/l SC	2	0.75	0.25	85	0.05	BR-41-0460F
S 202.94							(B. & M., 1994c)
S 340.93		1	0.75	0.15	30	0.03	
S 321.93		2	0.75	0.15	67	0.06	
1994	500 g/l SC	2	0.75	0.25	14	0.03	BR-0480
S 202.95				0.15	21	<0.02	(B. & M., 1995c)
					28	0.03	
S 401.95		2	0.75	0.25	15	<0.02	
					21	<0.02	
					28	0.04	
S 604.95		2	0.75	0.25	14	0.24	
					21	0.12	
					28	0.17	
S 321.95		2	0.75	0.15	14	0.49	
					21	0.56	
					28	0.65	
1995	500 g/l SC	2	0.75	0.25	0	1.33	BR-0483
S 402.95					6	0.75	(M. & C., 1996b)

Year Trial ID	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
					14	0.28	
					19	0.22	
S 608.95		2	0.75	0.25	0	1.93	
					7	1.62	
					14	0.68	
S 641.95		2	0.75	0.25	0	0.26	
					7	0.08	
					14	0.04	
					19	0.05	
S 642.95		2	0.75	0.25	0	0.06	
					7	0.08	
					14	0.06	
					19	0.05	
1995 S 204.96	500 g/l SC	2	0.75	0.25 0.125	0 7	0.03 <0.02	BR-0491 (M. & C., 1997b)
					12	<0.02	
					20	<0.02	
S 205.96		2	0.75	0.25 0.125	0 7	0.04 0.03	
					14	0.02	
					20	<0.02	
BRUSSELS SPROUTS 1995 S 607.95	500 g/l SC	2	0.75	0.25	0 6	0.29 0.21	BR-0483 (M. & C., 1996b)
					14	0.08	
					21	0.09	
1995 S 642.96	500 g/l SC	2	0.75	0.25	0 7	0.75 0.37	BR-0491 (M. & C., 1997b)
					14	0.22	
					20	0.14	
BROCCOLI 1995 S 609.95	500 g/l SC	2	0.75	0.25	0 7	2.30 1.65	BR-0483 (M. & C., 1996b)
					14	0.93	
					20	0.39	
1995	500 g/l SC	2	0.75	0.25	0	3.07	BR-0491
S 641.96					7	1.29	(M. & C., 1997b)
					14	0.40	
					19	0.23	

B. & M. = Benet and Massenot M. & C. = Massenot and Cohadon

Table 10. Supervised trials on peas in France.

Year Trial ID.	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
1992 S 322.92	500 g/l SC	2	0.75	0.25	13	0.49 whole pod 0.15 peas 1.20 empty pods	BR-21-0336F (Benet and Massenot, 1992)

Year Trial ID.	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
S 341.92		2	0.75	0.25	20	0.25 whole pod 0.07 peas 0.44 empty pods	BR-21-0336F
S 201.92		2	0.75	0.25	21	0.17 whole pod 0.03 peas 0.43 empty pods	BR-21-0336F
S 202.92		2	0.75	0.25	27	0.05 whole pod <0.02 peas 0.13 empty pods	BR-21-0336F
1994 S 203.94	500 g/l SC	2	0.75	0.25	1 7 14 21	1.8 whole pod 0.69 whole pod peas 0.16 0.36 whole pod peas 0.07 0.24 whole pod peas 0.07	BR-0476 (Benet and Massenot, 1995d)
S 406.94		2	0.75	0.25	1 7 14 21	1.7 whole pod 1.1 whole pod peas 0.32 0.66 whole pod peas 0.16 2.1 whole pod peas 0.48	BR-0476
1994 S 407.94		2	0.75	0.25	1 7 14 21	2.0 whole pod 0.96 whole pod peas 0.21 0.66 whole pod peas 0.16 1.50 whole pod peas 0.27	BR-0476
S 663.94		2	0.75	0.25	1 7 14 21	2.20 whole pod 1.10 whole pod peas 0.13 0.26 whole pod peas 0.07 0.24 whole pod peas 0.09	BR-0476
1995 S 104.95	500 g/l SC	2	0.75	0.25	0 7 10	1.05 whole pod 25.1 whole plant 0.46 whole pod 0.08 peas 0.84 empty pod 0.46 whole pod *c* 0.03	BR-0499 (Provot 1997)
						0.11 peas	
						0.98 empty pod	
					13	0.28 whole pod *c* 0.04 0.17 peas *c* 0.03 0.60 empty pod *c* 0.09	
					32 33	0.40 peas 19.6 whole plant	
S 105.95		2	0.75	0.25	0 7	2.04 whole pod *c* 0.14 23.5 whole plant *c* 0.02 0.77 whole pod	BR-0499
					  11 14	0.19 peas 1.94 empty pod 0.64 whole pod 0.20 peas 1.90 empty pods 0.83 whole pod 0.20 peas 3.23 empty pod *c* 0.02	

Year Trial ID.	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
					26	0.29 peas	
					27	14.1 whole plant	
S 106.95		2	0.75	0.25	0	3.80 whole pod *c* 0.03 16.5 whole plant *c* 0.15	BR-0499
					7	2.19 whole pod 0.70 peas 2.37 empty pod *c* 0.02	
					10	1.13 whole pod 0.11 peas 1.28 empty pod	
					15	0.46 whole pod 0.07 peas 0.57 empty pods	
					22	1.12 whole pod 0.08 peas 1.93 empty pods	
					22	0.20 peas	
					41	0.63 peas 10.3 whole plant *c* 0.19	
1995 S 661.95		2	0.75	0.25	0	1.93 whole pod 23.0 whole plant	BR-0499
					7	1.02 whole pod 0.08 peas 2.63 empty pods *c* 0.02	
					10	0.60 whole pod 0.09 peas *c* 0.02 1.47 empty pods	
					14	0.60 whole pod 0.08 peas 2.11 empty pods	
					27	0.19 peas 16.5 whole plant *c* 0.11	

Table 11: Residues in whole pea plants (leguminous animal feed), France, 1995.

Trial ID	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
S 104.95	500 g/l SC	2	0.75	0.25	0	25.1	BR-0499
					33	19.6	(Provot 1997)
S 105.95	500 g/l SC	2	0.75	0.25	0	23.5	BR-0499
					27	14.1	
S 106.95	500 g/l SC	2	0.75	0.25	0	16.5 *c* 0.15	BR-0499
					41	10.3 *c* 0.19	
S 661.95	500 g/l SC	2	0.75	0.25	0	23.0	BR-0499
					27	16.5 *c* 0.11	

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

After 117 days storage at 0°C and 90% relative humidity, procymidone residues in the pulp and peel of kiwifruit were 55% to 70% of the levels found immediately after post-harvest dip treatment at rates ranging from 3.25 to 25 g ai/100 l (Gandolfi and Collina, 1989). The residues in the peel ranged

from <0.01 to 21.62 mg/kg and in the pulp <0.01 to 0.15 mg/kg. A linear relation was observed between application rate and residues in peel.

The residues in the pulp and peel of kiwifruit after dip treatment at 6.25 g ai/100 l are shown in Table 12. This rate is close to GAP for post-harvest treatments in Italy. After 117 days of cold storage (0°C, 90% r.h.), the residues in the peel decreased slowly to 50-60% of their initial levels, and those in the pulp to 25%. Ratios of average residues in the peel to those in the pulp ranged from 0.004 to 0.01.

Table 12. Residues in kiwifruit peel and pulp after a post-harvest dip treatment at 6.25 g ai/100 l.

Storage period, days	Residues in peel, mg/kg	Residues in pulp, mg/kg	Mean ratio, pulp:peel
0	7.76, 7.94, 8.13	0.08, 0.08	0.01
30	7.08, 7.17, 7.27	0.06, 0.06	0.008
57	4.29, 4.89, 5.50	0.04, 0.04	0.008
91	4.40, 4.90, 5.40	0.04, 0.04	0.008
117	4.37, 4.47, 4.57	0.02, 0.02	0.004

Residues in kiwifruit treated with a single foliar application ranged from 67% to 78% of the levels found at harvest after cold storage for 98 to 107 days (Maini and Boni, 1985). The interval from treatment to harvest ranged from 5 to 28 days. The maximum decline of 33% of the procymidone residues is comparable to that observed from a post-harvest dip. Additional data from post-harvest dip treatments at rates of 50 and 100 g ai/100 l showed no decrease after 101 days of storage, but details of the storage conditions were not reported.

Residues in the edible portion of food commodities

Residues in the edible portion of the commodity were reported for kiwifruit and peas, where residues were determined in kiwifruit pulp, peas and empty pods.

In two trials in Italy the residues in kiwifruit pulp were approximately 2.5 and 3.3% of the levels found in the whole commodity, after dip treatments at 50 and 100 g ai/100 l solution (Table 7). After dip treatments at 3.25 to 25 g ai/100 l solution and storage up to 117 days, residues in the pulp ranged from 0.02 to 0.15 mg/kg, approximately 4-8% of those found in the whole commodity.

The residues in whole pea pods 13 to 15 days after treatment were 0.26 to 0.83 mg/kg and in peas 0.07 to 0.20 mg/kg. Overall, peas contained approximately 13-30% of the residues found in the whole pod.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

National monitoring data were reported by The Netherlands (Table 13).

Table 13. Monitoring data for procymidone in The Netherlands (1994-1996).

Commodity	Samples analysed	Samples without residues (LOD = 0.02 mg/kg)	Samples with residues <MRL	Samples with residues >MRL	Mean, mg/kg[1]	MRL, mg/kg
CITRUS FRUIT						0.02*
Grapefruit	327	321		6	<0.02	
Tangerines	632	632			<0.02	

Commodity	Samples analysed	Samples without residues (LOD = 0.02 mg/kg)	Samples with residues <MRL	Samples with residues >MRL	Mean, mg/kg[1]	MRL, mg/kg
Oranges	982	965		17	<0.02	
STONE FRUIT						0.02*
Apricots	91	90		1	<0.02	
Peaches	283	283			<0.02	
Nectarines	247	247			<0.02	
Plums	467	463	2	2	<0.02	
BERRIES AND SMALL FRUIT						
Grapes	765	653	112		0.23	5
Strawberries	2743	2650	93		0.14	5
Raspberries	269	269			<0.02	10
Currants (red, black, white)	481	479	2		<0.02	0.02*
TROPICAL FRUIT						
Kiwi	260	231	23	6	0.40	5
Mangoes	217	217			<0.02	0.02*
Passion fruit	50	49		1	<0.02	0.02*
ROOT AND TUBER VEGETABLES						
Carrots	500	490	1	10	<0.02	0.02*
Scorzonera (black salsify)	23	22		1	<0.02	0.02*
Potatoes	417	415	1	1	<0.02	0.02*
BULB VEGETABLES						
Onions (incl. Pearl, cocktail onions)	112	110	2		<0.02	0.2
Onions (small)	110	109		1	<0.02	0.2
FRUITING VEGETABLES						
Tomatoes	1242	1137	105		0.02	2
Peppers	1655	1556	99		0.02	2
Aubergines	176	174	2		<0.02	2
Cucumbers	1089	1054	35		<0.02	1
Courgettes	257	242	15		<0.02	1
Melons	455	447	8		<0.02	1
BRASSICA VEGETABLES						
Cauliflower	378	378			<0.02	0.02*
Brussels sprouts	197	197			<0.02	0.02*
Chinese cabbage	352	350		2	<0.02	0.02*
LEAFY VEGETABLES AND FRESH HERBS						
Lettuce	3834	3699	130	5	0.03	5
Iceberg lettuce	535	488	46	1	<0.02	5
Endive	1297	1265	31	1	<0.02	5
Spinach	532	531		1	<0.02	0.02*
Witloof	549	548		1	<0.02	0.02*
Other leafy vegetables	230	229		1	<0.02	0.02*
Parsley	390	389		1	<0.02	0.02*
Other herbs	224	223		1	<0.02	0.02*
LEGUME VEGETABLES						
Beans, fresh (with pod)	690	683	7		<0.02	2
Peas, fresh	66	65	1		<0.02	0.02*
STEM VEGETABLES						
Celery	300	299		1	<0.02	0.02*
Leek	459	458		1	<0.02	0.02*

Commodity	Samples analysed	Samples without residues (LOD = 0.02 mg/kg)	Samples with residues <MRL	Samples with residues >MRL	Mean, mg/kg[1]	MRL, mg/kg
Other	375	371		4	<0.02	0.02*
FUNGI Cultivated Mushrooms	460	459		1	<0.02	0.02*
Other ARABLE PRODUCTS	759	752		7	<0.02	0.02*

[*] Lower limit of determination.
[1] For samples without residues (<LOD), half the LOD is taken for the calculation of the mean.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs, mainly in EU countries, were reported.

sCountry	MRL, mg/kg	Commodity
Belgium	5	kiwifruit
EU	0.02 5	broccoli, Brussels sprouts, cabbage (head), cauliflower, peas kiwifruit
France	2 5	stone fruit kiwifruit
Germany	0.02 0.05 0.1 0.2 1	other foods of plant origin tree nuts, remaining oilseeds hops, tea, tealike products knoblauch, onions, shallots cucurbits with edible and inedible peel, peas with pods (fresh), sunflower seeds with pods, rape seed, soya beans
Germany	2 5 10	beans with pods (fresh), solanaceae grapes, kiwifruit, lettuce (and similar), strawberries raspberries
Italy	1.5	peaches, pears
Poland	0.02 0.05 0.1 0.2 1 2 5	cereal grains, citrus fruits, potato, root and tuber vegetables (except potato) eggs, meat and meat products, milks, milk products tea onion, bulb cucumber, fruits (except as otherwise listed) legume vegetables, tomato berries and other small fruit, leafy vegetables, stalk and stem vegetables
Spain	0.02 2 5	brassica vegetables, pears, peas without pods, stone fruit peas with pods kiwifruit
The Netherlands	*0.02 *0.05 *0.1 0.2 1 2 5 10	other food commodities eggs, meat, milk, nuts, other oil seeds, hops, tea garlic, onions, shallots, cucurbits with edible peel, cucurbits with inedible peel, rape seed, soya beans, sunflower seeds with cups beans (pods), solanaceae, kiwifruit, lettuce and similar, strawberries (except wild), table and wine grapes raspberries

APPRAISAL

Residue aspects of procymidone were reviewed by the JMPR in 1981, 1989, 1990 and 1993. At the 27th session of the CCPR (1995), draft MRLs for apples, currants (black, red, white), egg plant, kiwifruit, melons (except watermelon), potatoes and rice (polished and husked) were recommended for deletion. The Committee noted that residue data for peaches, plums, kiwifruit, peas and brassica

vegetables would be made available for evaluation in 1998. In addition to these commodities, data on pears were also submitted. Information on analytical methods, stability of residues in stored analytical samples and current GAP in numerous countries was provided.

Validated methods for the determination of procymidone in pears, peaches, plums, cabbage and peas were provided. The limit of determination in all these crops was 0.02 mg/kg and validated recoveries ranged from 70 to 110%. The methods are almost identical to the method reviewed in the 1981 monograph. The Netherlands government provided a multi-residue method for the determination of procymidone in fruits and vegetables. The limits of determination ranged from 0.01 to 0.1 mg/kg, with recoveries above 80%.

The storage stability of procymidone in strawberries, homogenised cherries, lettuce and haricot beans was reported. The Meeting concluded that procymidone residues were stable under frozen storage conditions for the duration of the 12 month studies in strawberries, lettuce and homogenised haricot beans, but some degradation was observed in homogenised cherry samples.

Supervised residue trials

Pears. GAP from Italy was reported, where registered use patterns indicate a maximum rate of 0.075 kg ai/hl using 25 SC, 50 WP or 75 WDG formulations. Procymidone may be applied from the end of flowering with repeated applications at intervals of 7 to 10 days depending on disease indications. A 14-day pre-harvest interval is recommended. In the reported trials 5 sprays were applied with a minimum re-treatment interval of 14 days. In two trials finite procymidone residues were found in untreated control samples; the result found in one of these was included in the estimation of the MRL and STMR as the residue in the control sample was comparable to the limit of quantification in the study.

The residues reflecting GAP ranged from 0.16 to 0.62 mg/kg 14 days after the fifth application. The residues used in the estimation of the STMR were in rank order 0.16, 0.35, 0.43, 0.43, 0.45, 0.58 and 0.62 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.43 mg/kg for procymidone in pears on the basis of GAP in Italy.

Peaches. Data from supervised trials in France and Italy were reported. Application rates were 0.075-0.11 kg ai/hl, with a maximum of 3 applications in the Italian trials. Registered labels in Italy allow a maximum of five applications. at appearance of flowering buds, when 25% of flowers have opened, at full flowering and at a lower rate at 4-5 and 2-3 weeks before harvest. In the French trials, two applications were made at the maximum rate of 0.75 kg ai/ha.

The residues resulting from treatments according to GAP in France and Italy ranged from 0.19 to 1.40 mg/kg 8–14 days after treatment. The residues in rank order were 0.19, 0.39, 0.44, 0.68, 0.72, 1.30, 1.33 and 1.40 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR of 0.70 mg/kg on the basis of GAP in France and Italy.

Plums. In France GAP allows a maximum rate of 0.75 kg ai/ha, with no indication of application timing or maximum number of sprays; a pre-harvest interval of 8 days is recommended. In Italy, 2–3 applications from the appearance of flowering buds to full flowering are recommended at rates from 1.1 to 1.8 or 1.5 to 2 kg ai/ha. A pre-harvest interval of 21 days is indicated.

Trials according to GAP were carried out in France and Italy. The residues in the French trials ranged from 0.19 to 1.20 mg/kg 7 or 8 days after 2 foliar applications at 0.75 kg ai/ha and in the 3 Italian trials were 0.74, 1.38 and 1.50 mg/kg 21 days after 3 sprays at 1.8 kg ai/ha.

The residues in rank order were 0.19, 0.31, 0.48, 0.52, 0.59, 0.60, 0.61, 0.74, 0.77, 0.86, 0.90, 1.06, 1.20, 1.38 and 1.50 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg and an STMR of 0.74 mg/kg for plums.

Kiwifruit. GAP was reported for Italy and France. The maximum label rate in France is 0.75 kg ai/ha; the labels did not indicate application timings or a maximum number of sprays. Italian labels for the 25 SC formulation indicate a maximum of 5 consecutive foliar applications at a maximum rate of 0.1 kg ai/hl, including a spray 14 days before harvest as a storage protection measure. For the 50 WP and 50 WDG formulations, 2–3 sprays are recommended followed by a post-harvest dip. A pre-harvest interval of 14 days and post-harvest storage period of 60 days are recommended.

Pre-harvest trials were reported from France and Italy, and post-harvest from Italy. The pre-harvest trials did not reflect GAP for foliar application in Italy or France. In some of them, single applications were made at various intervals before harvest and the residues were monitored for prolonged storage periods. Details of the storage conditions were not given, and analytical recoveries were not adequately reported. The post-harvest trials were in accordance with GAP and details of storage conditions were provided, but no analytical recoveries were reported. The data from post-harvest treatment and storage trials indicate that residues can decrease by as much as 50% of their initial levels, but without details of the storage conditions the results could not be evaluated.

On the basis of the minimal data provided, the Meeting could not estimate a maximum residue level in kiwifruit. Further information such as details of post-harvest storage conditions and analytical recoveries would be needed.

Cabbages. Trials on cabbages, cauliflowers, broccoli and Brussels sprouts were carried out in France, but GAP was reported only for cabbages. The application rate for cabbages in France is 0.75 kg ai/ha with a pre-harvest interval of 21 days; the maximum number of applications is not indicated on any product labels.

Procymidone residues in cabbages after two sprays at varying intervals ranged from <0.02 to 1.30 mg/kg 20 or 21 days after treatment. The results reflecting GAP were <0.02 (2), 0.03 (2), 0.17, 0.26, 0.30, 0.32, 0.43, 0.44 and 1.40 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR of 0.26 mg/kg for head cabbages.

The trials on Brussels sprouts, broccoli and cauliflower could not be evaluated in the absence of appropriate registered labels.

Peas. Data were reported from supervised trials reflecting GAP in France, where a maximum of 2 sprays are permitted at 0.75 kg ai/ha, with a re-treatment interval of 20–21 days and a pre-harvest interval of 14 days. Residues were determined in whole plants with pods, whole pods, peas and empty pods. Re-treatment intervals were typically 14 to 19 days. The highest levels of procymidone were found in whole plants with pods, with residues of 16.5–25.1 and 10.3–19.6 mg/kg at early and late harvests respectively. Residues in empty pods were 0.6 to 3.23 mg/kg 13 to 15 days after treatment. The residues in peas ranged from 0.03 to 0.48 mg/kg. It was noted that higher residues were found in peas harvested mechanically than in those which were hand-picked.

The residues in whole pods 13 to 15 days after treatment were in the range 0.26–0.83 mg/kg. In trials where the residue was higher after 21 days than after the GAP PHI the higher value was used in the estimation of the STMR. The residues at 13-21 days ranged from 0.26 to 2.1 mg/kg in whole pods and from 0.03 to 0.48 mg/kg in peas.

The residues reflecting GAP in the whole pods in rank order were 0.26, 0.28, 0.36, 0.49, 0.60, 0.83, 1.12, 1.50 and 2.1 mg/kg, and those in the shelled peas were 0.03, 0.07 (4), 0.08, 0.15, 0.17, 0.20, 0.27 and 0.48 mg/kg. The Meeting estimated a maximum residue level of 3 mg/kg and an STMR of 0.60 mg/kg for garden pea (young pods) and a maximum residue level of 1 mg/kg and an STMR of 0.08 mg/kg for garden pea (shelled).

The Meeting did not consider that the data on whole pea plants were adequate for estimating a maximum residue level for a leguminous animal feed commodity as appropriate GAP had not been reported.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting estimated the maximum levels and STMR levels listed below.

The maximum residue levels are recommended for use as MRLS

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: procymidone.

Commodity		MRL, mg/kg		STMR
CCN	Name	new	current	mg/kg
VB 0041	Cabbages, Head	2	–	0.26
VP 0529	Garden pea, shelled (succulent seeds)	1	–	0.08
VP 0528	Garden pea (young pods)	3	–	0.60
FS 0247	Peach	2	–	0.70
FP 0230	Pear	1	–	0.43
FS 0014	Plums (including Prunes)	2	–	0.74

FURTHER WORK OR INFORMATION

Desirable

Details of post-harvest storage conditions and analytical recoveries in relation to the reported supervised residue trials on kiwifruit.

DIETARY RISK ASSESSMENT

STMRs have been estimated for procymidone in six commodities. These have been used in estimating the dietary intake together with MRLs for 12 commodities. The International Estimated Daily Intakes for the five GEMS/Food regional diets were in the range 1 to 12% of the ADI. The Meeting concluded that the intake of residues of procymidone resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

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QUINTOZENE (064)

EXPLANATION

Quintozene was evaluated as a periodic review by the 1995 JMPR. That Meeting estimated a number of maximum residue levels but agreed not to recommend their use as MRLs, and recommended the withdrawal of existing MRLs, because of the lack of critical supporting data on environmental fate. Some of the processing studies could not be evaluated because of their uncertain validity.

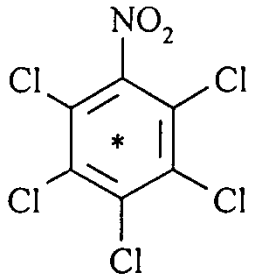
The CCPR in 1996 was informed that environmental fate studies would be made available to the JMPR (ALINORM 97/24, para 48). The compound was scheduled for evaluation by the JMPR in 1997, but rescheduled to 1998 at the request of the company.

The 1997 CCPR recommended the deletion of the CXL for banana as the use was not supported, and retained the other CXLs for 4 years according to the Periodic Review procedure. The Committee noted that data from supervised trials on head lettuce and potatoes would be submitted for evaluation by the 1998 JMPR (ALINORM 97/24A, para 54).

Data on environmental fate, residues in rotational crops, supervised trials on lettuce and the effects of processing on residues in cotton seed, peanuts and potatoes have been made available to the present Meeting by the manufacturer but no new information from supervised residue trials on potatoes was received. Information on residue analytical methods and national MRLs was provided by The Netherlands and on national MRLs by Germany and Poland.

METABOLISM AND ENVIRONMENTAL FATE

Figure 1. Structures, chemical names and abbreviation codes of quintozene and degradation products found in environmental fate studies.



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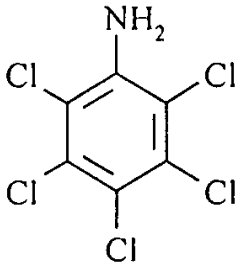
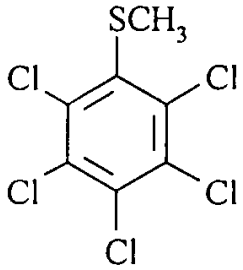
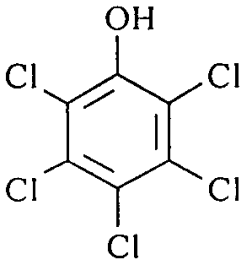
quintozene
(PCNB)



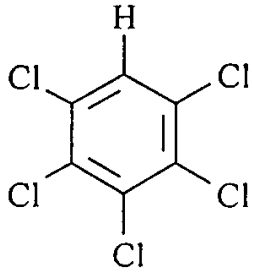
pentachloroaniline
(PCA)



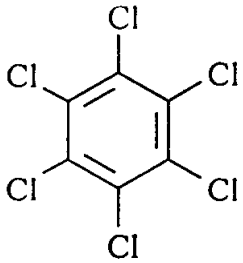
methyl pentachlorophenyl sulfide
pentachlorothioanisole
(PCTA)



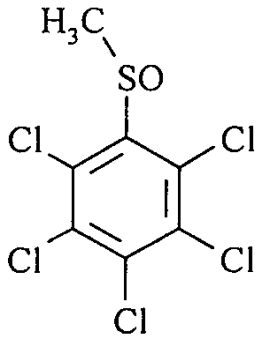
pentachlorophenol
(PCP)



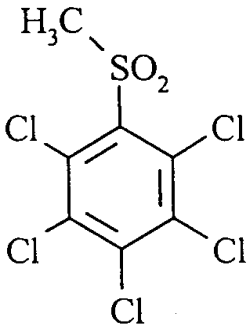
pentachlorobenzene
(PB)



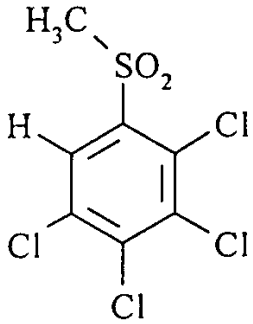
hexachlorobenzene
(HCB)



methyl pentachlorophenyl sulfoxide
pentachlorothioanisole sulfoxide
(PCTASO)



methyl pentachlorophenyl sulfone
pentachlorothioanisole sulfone
(PCTASOO)



methyl-2,3,4,5-tetrachlorophenyl sulfone
2,3,4,5-tetrachlorothioanisole sulfone
TCTASOO)

Environmental fate in soil

Photolysis

Bowman (1988a) exposed sandy loam soil treated with [^{14}C]quintozene at 10.5 :g/g to a xenon arc lamp for 30 days. Radio-analysis demonstrated a decrease in the extractable ^{14}C residues and a corresponding increase in the ^{14}C bound to the soil. The levels of [^{14}C]quintozene in the sample extracts indicated a rate constant of 0.031/day and a half-life of 22 days for the exposed samples and a rate constant of 0.002/day and half-life of 367 days for the dark control samples. It was later discovered that these samples had been exposed to the xenon source for 25 hours so the dark control

study was repeated. The repeat showed that ^{14}C was increasingly bound to the soil with time. The extractable activity was essentially all due to quintozene and no degradation products were detected. A rate constant based on the binding of ^{14}C to the soil was calculated to be 0.007 (half-life 100 days).

A corrected photolysis rate constant ($k_{exposed}$ - k_{dark}) was calculated to be 0.024/day (half-life 28.5 days based on 30 days continuous exposure of the samples). The mean total radioactivity recovered was 97.5% of that applied. After 30 days of exposure PCA accounted for 35% of the extracted ^{14}C. No other photoproducts were detected.

Misra (1993a). A 30-day photolysis study with 12 hour light/12 hour dark cycles, of uniformly ring-labelled [^{14}C]quintozene in a sandy loam soil at or near 75% field moisture capacity (FMC) was conducted at 25°C. Both PCA and PCTA were found in the irradiated and control samples but the rate of formation of PCA under irradiation was about twice that in the dark control (Table 1). The soil-bound activity in the presence of light was about twice that in the control. The half-life values in irradiated and control samples were 13 and 62 days respectively (Table 2).

Table 1. Concentrations of quintozene and its major degradation products in soil extracts (Misra, 1993a).

^{14}C residues as quintozene, mg/kg soil							
Irradiated				Control			
Time, hours	Quintozene	PCA	PCTA	Time, days	Quintozene	PCA	PCTA
0	9.6	ND	ND	0	9.4	NA	NA
13	8.1	0.38	ND	1	9.2	ND	ND
25	6.3	0.41	0.04	2	8.2	0.16	0.04
49	4.8	0.52	ND	4	8.0	ND	ND
99	5.2	0.68	0.05	8	7.4	0.04	0.05
186	3.4	0.83	0.32	15	7.7	0.37	0.22
261	2.6	0.88	0.31	22	6.9	0.44	0.36
359	1.6	0.70	0.21	30	6.4	0.42	0.30

NA: not analysed
ND: below LOD

Table 2. Results of regression analysis (Misra, 1993a).

Parameters	Irradiated	Control
Constant	2.05	2.17
R^2	0.942	0.826
No of observations	8	8
Degrees of freedom	6	6
X coefficient	-0.0044	-0.0009
Estimated half-life values	13 days	62 days

Aerobic and anaerobic degradation

Daly (1989) treated sandy loam soil with uniformly ring-labelled [^{14}C]quintozene at 25 mg/kg in the dark at a temperature of 25°C. The soils were first incubated aerobically for 30 days, then the systems were flooded with 30 ml deionized water and 0.1 g of glucose was added to each tube to facilitate microbial activity. The air supplies were changed to nitrogen to further ensure anaerobic conditions. Samples were extracted with methanol on days 0 and 1 and subsequent samples were extracted with methanol/1N acetic acid (80:20). The supernatants were analysed by LSC and TLC.

The mean balance of radioactivity was 97.8%. TLC analysis of the soil extracts and water samples revealed the presence of quintozene and three known degradation products (Tables 3 and 4). Quintozene was detected in all the soil extracts and the day 90 flood water. PCA was the main degradation product and was found in all extracts and water samples after day 1. The aerobic and anaerobic half-lives of quintozene, based on first order degradation kinetics, were calculated to be 37 days and 15 days respectively.

Table 3. Distribution of quintozene and its degradation products in soil extracts determined by TLC (Daly, 1989).

Time, days	Quintozene, % of TRR	PCTA, % of TRR	PCA, % of TRR	PCP, % of TRR
0	78.8	9.1	ND	ND
1	85.9	5.6	ND	ND
3	63.8	4.5	23.8	ND
7	72.7	6.0	6.9	ND
14	63.6	3.5	15.5	ND
30	54.5	3.2	23.4	1.6
60	4.2	ND	86.6	1.8
90	3.8	ND	84.1	2.0

ND: below LOD

Table 4. Distribution of quintozene and its degradation products in flood water determined by TLC (Daly, 1989).

Times, days	Quintozene, % of TRR	PCA, % of TRR	PCP, % of TRR
60	ND	25.2	7.5
90	4.9	28.3	6.6

Misra (1993b) conducted a year-long study of the aerobic degradation of uniformly ring-labelled [^{14}C]quintozene on a sandy loam at or near 75% FMC at 25°C in darkness. Test vessels containing 20 g dry weight equivalent of sandy loam soil were treated with a solution of [^{14}C]quintozene in acetonitrile at 10 mg/kg and placed in a stainless steel container at 25°C. At intervals, the test container was purged with carbon dioxide-free humidified air to collect volatile compounds from the container and to maintain aerobic conditions in the test systems. The soil moisture was adjusted to 75% field moisture capacity at dosing and sampling. The soil samples were extracted with 10 to 20% 1N phosphoric acid in acetonitrile. The trapping solutions, test system wipe extracts, soil extracts and test vessel washes were analysed by LSC and HPLC. GC-MSD was used as a confirmatory method of identification. The TRR recovered at each sampling was from soil extracts, soil-bound ^{14}C residues (determined by combustion and LSC), and accumulated volatile compounds collected from the test system and trapping solutions (Table 5).

Table 5. ^{14}C balance (Misra, 1993b).

Incubation time, days	Extractable ^{14}C, %	Soil bound residues, %	Volatile compounds, %	Total recovery, %
0	99.4	2.7	ND	102.1
1	98.6	4.2	0.17	103.0
3	89.7	6.1	1.4	97.2
7	85.8	8.9	3.5	98.2
14	80.0	10.8	6.2	97.0
30	74.7	11.1	9.5	95.3
60	69.4	10.8	12.6	92.8
90	67.1	13.5	15.7	96.3
120	69.5	10.1	19.3	98.9
180	64.1	12.2	23.0	99.3
270	56.6	14.2	28.3	98.9
365	50.5	17.1	33.7	101.2
			mean	98.4
			SD	2.9

ND: below LOD

Most of the volatile ^{14}C during the aerobic incubation was due to [^{14}C]quintozene. The other identified volatile compounds were PCA, PB and PCTA. Soil-bound ^{14}C residues increased to a maximum of 17% on day 365. The mean ^{14}C balance calculated for the duration of the study was 98.6$\pm$5.7%. The distribution of quintozene and its major degradation products in soil extracts are shown in Table 6.

Table 6. Concentration of quintozene and its major degradation products in soil extracts (Misra, 1993b).

Time, days	Residue, mg/kg				
	Quintozene	PCA	PCTA	PCTASO	$PCTASO_2$
0	9.96	ND	ND	ND	ND
1	9.8	ND	ND	ND	ND
3	8.4	0.36	0.14	ND	ND
7	7.3	0.64	0.37	0.09	ND
14	6.2	0.67	0.41	0.23	0.13
30	5.0	0.71	0.49	0.33	0.28
60	4.4	0.78	0.54	0.29	0.30
90	3.9	0.76	0.64	0.28	0.34
120	3.9	0.91	0.81	0.36	0.41
180	3.2	0.91	0.73	0.34	0.49
270	2.7	0.85	0.63	0.32	0.52
365	2.3	0.80	0.53	0.37	0.61

ND: below LOD

The half-life was calculated to be 189 days with a coefficient of determination of 0.79 using a first-order approximation and all the results. Independent first-order regression analysis of the first five and the last eight results yields half-lives of 20 and 278 days respectively with associated correlation coefficients of 0.95 and 0.92. This illustrates the non-linearity of quintozene degradation (Table 7).

Table 7. First order regression analysis, days 0 to 14 and 14 to 365, (Misra, 1993b).

Parameters	Day 0 to day 14	Day 14 to day 365
Constant	2.28	1.69
R^2	0.955	0.923
Number of observations	5	8
Degree of freedom	3	6
X coefficient(s)	-0.034	-0.0025

Figure 2 shows the proposed pathways for the aerobic degradation of quintozene in soil. PCTA was apparently formed from PCA by deamination and nucleophilic displacement at the aromatic ring. PCTASO and $PCTASO_2$ were formed as the incubation increased by oxidation, with a corresponding decrease in the concentration of their precursor PCTA. PCA reached a maximum concentration of about 9% of the applied ^{14}C and remained almost constant from day 14 to the end of the study. PCA was the major primary degradation product of quintozene.

Mobility (adsorption/desorption)

Esposito (1977) carried out laboratory leaching studies on sandy loam, silt loam, Smithdale sandy soil, and Carnasaw silt loam from the cotton-growing region of Arkansas, USA. [^{14}C]quintozene was added uniformly to the top 5 cm of a 20 cm column of untreated soil. Three column volumes of aqueous 0.01 M $CaCl_2$ were then passed through the column. ^{14}C was measured in the $CaCl_2$ effluents and in 5 cm soil sections. Leaching amounted to 2 to 17% in the 4 soils and the ^{14}C only reached the adjacent untreated soil zone. Less than 0.1% of the added ^{14}C was found in the $CaCl_2$ effluent from all the soils. Leaching experiments with two soils aged for 30 days gave similar results.

Bowman (1987a, b) equilibrated aqueous solutions of [^{14}C]quintozene and [^{14}C]PCA with four soils and determined the adsorption and desorption coefficients. Liquid scintillation counting was used to measure the ^{14}C concentrations in the aqueous phases (Tables 8 and 9).

Table 8. Adsorption/desorption of [^{14}C]quintozene by soil (Bowman, 1987a).

Soil	% Organic carbon	Adsorption K_d	Adsorption K_{OC}	Desorption K_d	Desorption K_{OC}
Silt loam	0.4	24	6030	38	9584
Sandy loam	0.8	46	5807	47	5929
Sand	1.05	31	2966	34.5	3285
Clay loam	1.3	89	6852	110	8480

The radiochemical purity of the applied [^{14}C]quintozene was 99%, and that at the end of the adsorption period approximately 95% as determined by TLC. The recovery of ^{14}C was 95.8%, 104%, 96.2% and 98.6% from the silt loam, sandy loam, sand and clay loam respectively (Bowman, 1987a).

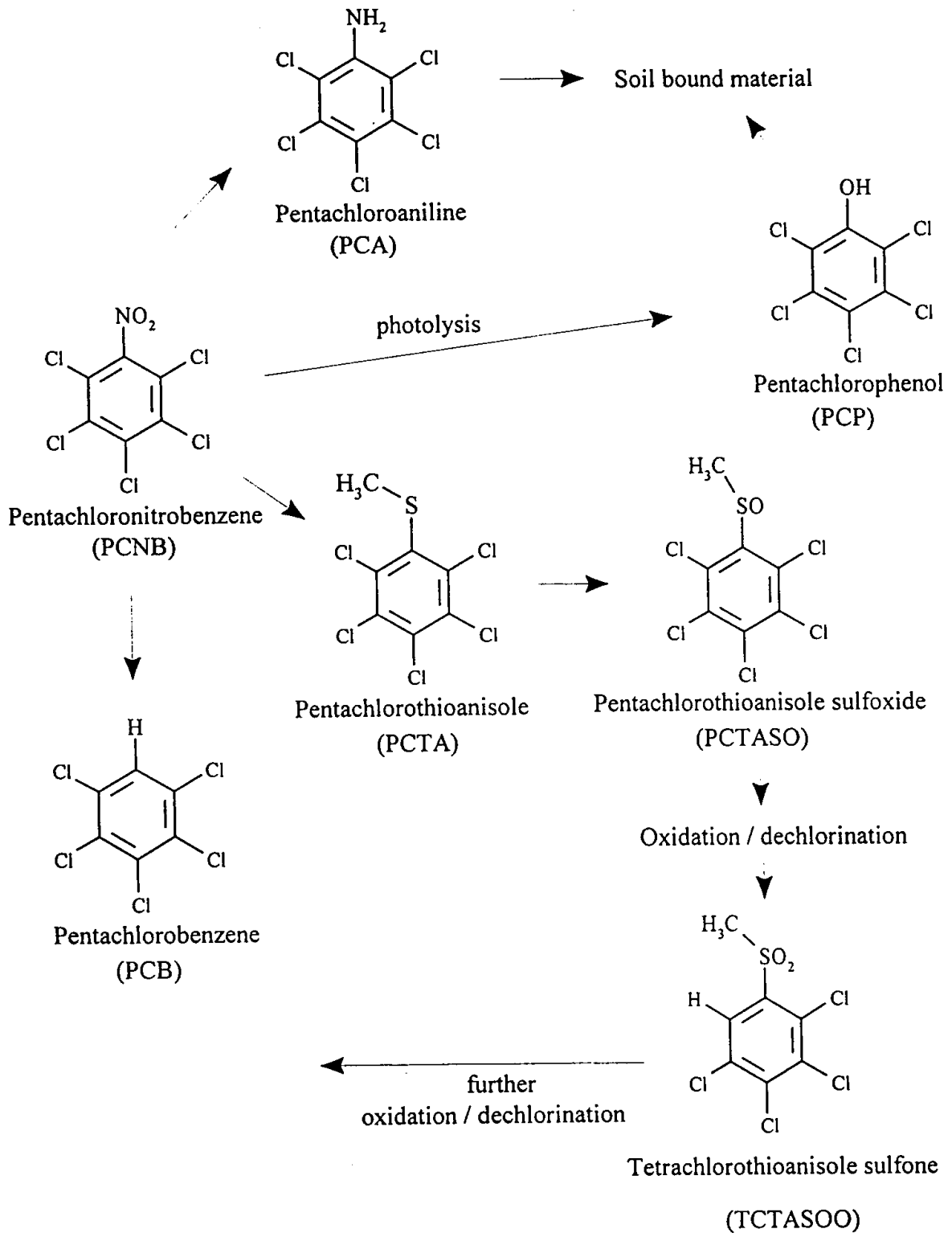
Table 9. Adsorption/desorption of [^{14}C]PCA by soil (Bowman, 1987b).

Soil	% Organic carbon	Adsorption K_d	Adsorption K_{OC}	Desorption K_d	Desorption K_{OC}
Silt loam	0.4	39	9695	33	8273
Sandy loam	0.8	80	9991	67	8367
Sand	1.05	150	14256	40	3837
Clay loam	1.3	267	20543	237	18256

The radiochemical purity of the applied [^{14}C]PCA was 98%, and that at the end of the adsorption period was approximately 91% as determined by TLC. The recovery of ^{14}C was 103%,

105%, 105% and 101% for the silt loam, sandy loam, sand and clay loam respectively (Bowman, 1987b).

Figure 2. Proposed degradation pathways of quintozene in soil (Misra, 1993b).



Quintozene is immobile to slightly mobile in soil (the Freundlich adsorption constants in silt loam, sandy loam, clay loam and sand with about 1% organic matter were 24, 46, 89 and 31 respectively).

The Freundlich constants of PCA in these soils were even higher (39, 80, 267 and 150 respectively) indicating lower mobility than the parent compound.

Terrestrial field dissipation

Several field dissipation studies (Irissarri,1988; Lengen, 1989; Rice, 1989a,b; Noon, 1990; Harned, 1993, 1997a) showed that quintozene applied to the soil surface disappeared more quickly than when applied by incorporation. When Lengen (1989) applied it to a turf surface in California the half-life was 35 days, but incorporation in soil in California and Minnesota (Rice, 1989) gave half-lives of 128-193 days. When quintozene was applied to a soil surface in Georgia (USA) at 11.2 kg ai/ha (Harned, 1993) the half-life was 13 days but when incorporated in a Texas soil before planting cotton at 2.2 kg ai/ha the half-life was 135 days (Harned, 1997a). In the recent dissipation studies by Harned the level of quintozene decreased from 17.6 mg/kg to 0.8 mg/kg by day 545, the end of the study. The main product was PCA which was present at a terminal level of 3.2 mg/kg. PB, PCTA, PCTASO and $TCTASO_2$ were formed and declined, the highest residue being 0.47 mg/kg (PCTA). The highest PCP residue was only 0.018 mg/kg. The impurity HCB ranged randomly from undetectable to 0.017 mg/kg.

It can be concluded that quintozene would not be a source of groundwater contamination and would dissipate significantly before subsequent annual applications.

Rotational crops

The uptake of [*phenyl*-U-^{14}C]quintozene by rotational crops was investigated in 1990, 1993 and 1997.

In a confined rotational crop study [^{14}C]quintozene was applied at about 34 kg ai/ha (Halls, 1990). The three most common rotational crop scenarios, replanting after crop failure (30 days), immediate recropping (120 days) and following-year recropping (365 days) were reproduced. Quintozene was applied on 11 May, 1988. Lettuce, turnips and wheat were planted after the appropriate ageing period. The results are shown in Table 10.

Table 10. ^{14}C in rotational crops, expressed as quintozene (Halls, 1990).

Sample	Days after treatment	Crop age, days	Soil residues, mg/kg	Crop residues, mg/kg
Immature lettuce				
30 day plot	75	45	8 4	3.3
120 day plot	154	34	7.2	1.4
365 day plot	404	39	5.9	5.7
Mature lettuce				
30 day plot	91	61	10	1.6
120 day plot	187	67	8.7	0.15
365 day plot	426	61	5.4	0.61
Immature turnips				
30 day plot	63	33	6.3	4.6
120 day plot	154	34	5.7	2.4
365 day plot	404	39	6.4	1.6

Sample	Days after treatment	Crop age, days	Soil residues, mg/kg	Crop residues, mg/kg
Mature turnip tops				
30 day plot	104	74	7.1	3.6
120 day plot	187	67	5.5	1.7
365 day plot	426	61	5.6	0.73
Mature turnip roots				
30 day plot	104	74	7.1	20
120 day plot	187	67	5.5	4.8
365 day plot	426	61	5.6	1.5
Immature wheat				
30 day plot	75	45	8.7	2.6
120 day plot	154	34	5.9	5.0
365 day plot	420	53	5.4	5.1
Mature wheat straw				
30 day plot	107	77	7.6	23
120 day plot	212	92	6.6	22
365 day plot	472	107	4.8	26
Mature wheat hulls				
30 day plot	107	77	7.6	11
120 day plot	212	92	6.6	6.1
365 day plot	472	107	4.8	8.0
Mature wheat grain				
30 day plot	107	77	7.6	0.33
120 day plot	212	92	6.6	0.71
365 day plot	472	107	4.8	0.38

Murty (1993) reported the uptake of quintozene by rotational wheat planted in soil that had been treated 30, 120 or 365 days previously with [^{14}C]quintozene at about 34 kg ai/ha (Table 11).

Table 11. Distribution of ^{14}C residues in rotational wheat (Murty, 1993).

Planting interval	^{14}C, mg/kg as quintozene		
	Straw	Hull	Grain
30 days	22	9.6	0.38
120 days	27	7.5	0.54
365 days	24	7.3	0.42

In the previous studies (Halls, 1990; Murty, 1993) the components of the residue were not identified. Harned (1997b) used more modern analytical techniques to isolate and identify the low levels of the residue constituents.

[^{14}C]quintozene was applied broadcast to soil and then manually incorporated. The treated soil was allowed to age for periods of 30, 120 or 365 days after which turnips, lettuce and wheat were planted. A rate of 2.2 kg ai/ha was applied to match US GAP for cotton and 11 kg ai/ha to match US GAP for peanuts. A rate of 34 kg ai/ha was applied only for rotational wheat. The results are shown in Table 12.

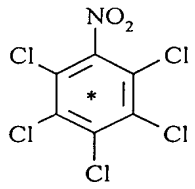
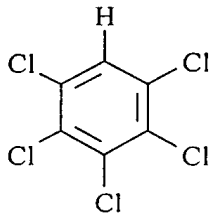
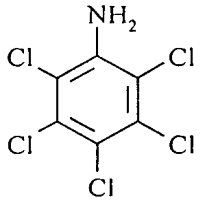
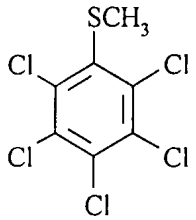
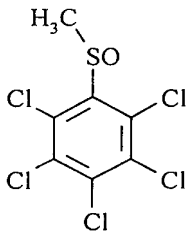
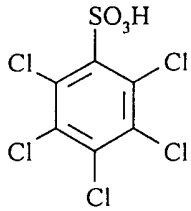
Table 12. Results of rotational crop studies (Harned, 1997b).

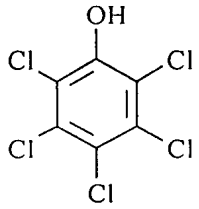
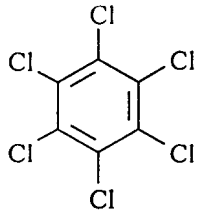
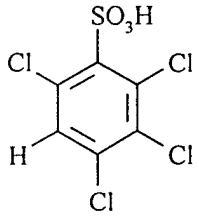
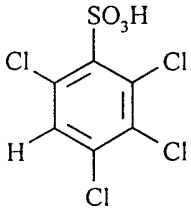
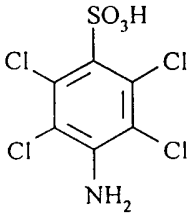
Sample	Days after treatment	Treatment, kg ai/ha	^{14}C, mg/kg as quintozene Total	Parent
Turnip top	365	2.2	0.05	ND
	365	11.2	0.12	ND
Turnip root	365	2.2	0.05	ND
	365	11.2	0.21	ND
Lettuce, mature	30	11.2	0.15	0.023
	120	11.2	0.10	0.001
	365	11.2	0.43	0.006
Lettuce, immature	30	11.2	0.18	0.032
	120	11.2	0.15	0.004
	365	11.2	0.56	0.005
Wheat forage	30	2.2	0.38	NA
	30	11.2	3.0	NA
	30	33.6	4.1	ND
	120	2.2	0.53	NA
	120	11.2	3.4	NA
	365	2.2	0.17	NA
	365	11.2	0.64	NA
Wheat grain	30	2.2	0.09	NA
	30	11.2	0.79	NA
	30	33.6	3.7	NA
	120	2.2	0.12	ND
	120	11.2	0.94	NA
	365	2.2	0.03	NA
	365	11.2	0.14	NA
Wheat straw	30	2.2	2.2	NA
	30	11.2	11	NA
	30	33.6	24	ND
	120	2.2	3.5	0.012
	120	11.2	17	NA
	365	2.2	1.3	NA
	365	11.2	4.6	NA

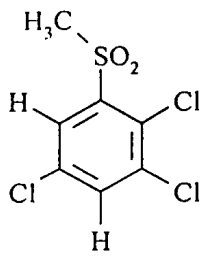
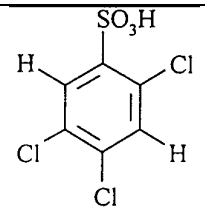
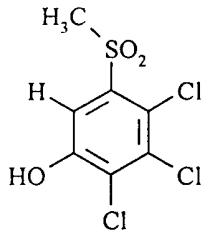
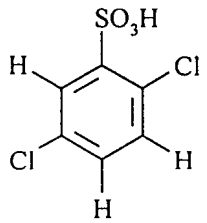
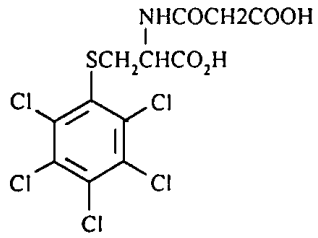
NA: not analysed
ND: not detected

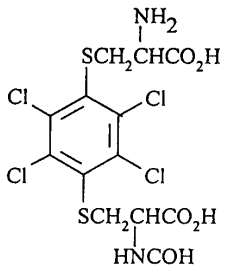
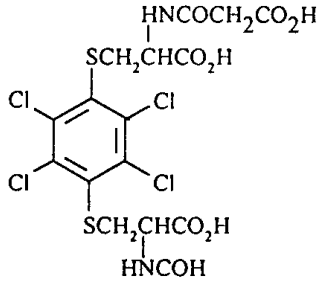
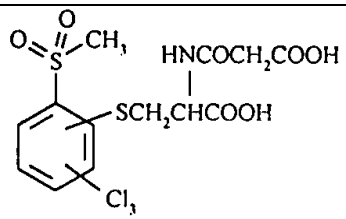
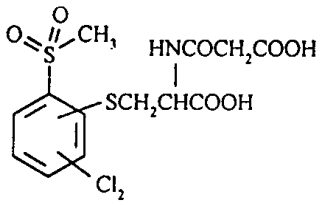
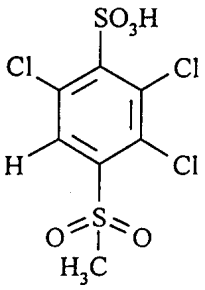
The compounds were extracted from the plant tissues and isolated by HPLC, TLC and solid-phase extraction (SPE). Identification was mainly by mass spectrometry with GLC and LC sample introduction combined with electrospray ionization and tandem quadruple MS-MS where required. Table 13 shows the compounds identified in rotational crops with their structures and abbreviation codes.

Table 13. Compounds identified in rotational turnip, lettuce and wheat (Harned, 1997b).

Compound	Structure	Source
Quintozene PCNB pentachloronitrobenzene		L immature, mature 30 DAT 10 # L immature, mature 120 DAT 10 # L immature, mature 365 DAT 10 # W straw, 120 DAT 2#
PB pentachlorobenzene		L mature 30 DAT 10 #
PCA pentachloroaniline		T top, root 365 DAT 2# T root, 365 DAT 10 # L immature, mature 30 DAT 10 # L immature, mature 120 DAT 10 # L immature, mature 365 DAT, 10 # W forage, straw 30 DAT 30 # W straw 120 DAT 2#
PCTA methyl pentachlorophenyl sulfide pentachlorothioanisole		T root, 365 DAT 2# T root, 365 DAT 10 # L immature, 30 DAT 10 # L immature, mature 120 DAT 10 # L immature, mature 365 DAT, 10 # W forage, straw 30 DAT 30 # W straw 120 DAT 2#
PCTASO methyl pentachlorophenyl sulfoxide pentachlorothioanisole sulfoxide		T top, root365 DAT 2# T top, root 365 DAT 10 #
C5SA pentachlorobenzenesulfonic acid		T top, root 365 DAT 2# T top, root 365 DAT 10 # L mature 120 DAT 10 # L immature 365 DAT 10 # W forage, straw 120 DAT 2#

Compound	Structure	Source
PCP pentachlorophenol		T top, root 365 DAT 2# T top, root 365 DAT 10 #
HCB hexachlorobenzene		W straw 120 DAT 2#
C4MS ^ TCTASOO methyl tetrachlorophenyl sulfone tetrachlorothioanisole sulfone		T top, root 365 DAT 10 # L immature, 30 DAT 10 # L immature, mature 120 DAT 10# L immature, mature, 365 DAT, 10#
C4SA ^ tetrachlorobenzenesulfonic acid		T top, root 365 DAT 2# T top, root 365 DAT 10 # L immature 365 DAT 10 # W forage, straw 120 DAT 2#
C4SANH tetrachlorosulfanilic acid		W forage 120 DAT 2#

Compound	Structure	Source
C3MS ^ methyl trichlorophenyl sulfone trichlorothioanisole sulfone		T top, root 365 DAT 2# T top, root 365 DAT 10 # L immature 30 DAT 10 # L immature, mature 120 DAT 10 # L immature, mature 365 DAT 10 # W straw 30 DAT 30 # W straw 120 DAT 2#
C3SA ^ trichlorobenzenesulfonic acid		T top, root 365 DAT 2# T top, root 365 DAT 10 # W straw 120 DAT 2#
C3MSOH ^ hydroxytrichlorophenyl methyl sulfone hydroxytrichlorothioanisole sulfone)		W straw 120 DAT 2#
C2SA ^ dichlorobenzenesulfonic acid		T top, root 365 DAT 2# T top, root 365 DAT 10 #
C5MaCy *N*-malonyl-*S*-pentachlorophenyl-*L*-cysteine		L mature 30 DAT 10 #

Compound	Structure	Source
C4CyFCy ^ *S*-(tetrachlorophenyl)-cysteine-*S'*-formylcysteine *S*-cysteinyl-*S*-[(*N*-formyl)cysteinyl]tetrachlorobenzene		L mature 30 DAT 10 # L mature 120 DAT 10 #
C4MaCyFCy ^ *S*-(tetrachlorophenyl)-*N*-malonylcysteine-*S'*-formyl-cysteine		L mature 365 DAT 10 #
C3MSMaCy ^ *S*-(*N*-carboxyacetyl)[*S*-trichloro-(methylsulfonylphenyl)]-*L*-cysteine		T top, root 365 DAT 2# T top, root 365 DAT 10 # L immature 365 DAT 10 #
C2MSMaCy ^ *N*-malonyl-*S*-dichloro-(methylsulfonophenyl)-*L*-cysteine		T top, root 365 DAT 2# T top, root 365 DAT 10 #
C3MSSA ^ methyl trichlorosulfophenyl sulfone		T top, root 365 DAT 2# T top, root 365 DAT 10 # W straw 120 DAT 2#

^position of ring substituents indeterminate; more than one isomer likely
T = turnip, L = lettuce, W = wheat, DAT = days after treatment. 2# = 2.2 kg ai/ha, 10# = 11.2 kg ai/ha, 30# = 33.6 kg ai/ha

Code key: Cn = phenyl ring with n chlorine atoms; MX = methyl sulfoxide; MS = methyl sulfone; SA = sulfonic acid; Ma = malonyl; Cy = cysteinyl; OH = hydroxy; NH = amino
F = formyl

Tables 14-17 show the quantitative results from the application of 11.2 kg ai/ha before planting lettuce. An average of 49% of the TRR was identified and quantified; the remainder of the radioactivity was either bound to plant material (about 31% of the TRR) and hydrolysed with enzymes and KOH, or was present in polar extracts (Tables 15, 16) as a complex mixture of metabolites, typically <0.03 mg/kg each. An average of 96% of the nonpolar compounds in lettuce extracts (29-50% of the TRR) were identified and quantified (Table 14). Non-proteolytic enzymes at pH 5 and pH 7 did not release significant amounts of bound material, and what was released was a complex mixture at trace levels. Most of the bound residues were associated with proteinaceous material and lignin, as evidenced by significant amounts of residues released by proteases and KOH (about 25% and 36% of the bound residues respectively). These bound residues appear to be related to PCA, which was the only compound identified in these fractions (Table 17).

Table 14. Quantification of non-polar compounds in lettuce (Harned, 1997b).

Sample	Non-polar extract				% identified
	% of TRR	:g/kg as quintozene	Compound[1]	:g/kg, as quintozene	
30 DAT immature (trial 570)	34	53	PCNB	32	112
			C3MS	3.9	
			PCA	15	
			PCTA	3.1	
			C4MS	2.5	
			Conjugate 330[2]	2.8	
30 DAT mature (trial 596)	29	31	PB	0.3	106
			PCNB	23	
			PCA	6.9	
			Conjugate 330	2.8	
120 DAT immature (trial 571)	44	60	PCNB	3.9	79
			C3MS	5.0	
			PCA	7.1	
			PCTA	2.5	
			C4MS	19	
			Conjugate 330	3.9	
			Unknowns- (3 metabolites)	6.2	
120 DAT mature (trial 597)	50	48	PCNB	0.8	91
			C3MS	5.6	
			PCA	11	
			PCTA	0.4	
			C4MS[3]	8.4	
			C4MS[3]	6.5	
			Conjugate 330	11	
365 DAT immature (trial 572)	36	206	PCNB	4.9	95
			C3MS	63	
			PCA	48	
			PCTA	4.6	
			C4MS	46	
			C4MS	15	
			Conjugate 330	15	
365 DAT mature (trial 598)	36	131	PCNB	5.6	90
			C3MS	28	
			PCA	39	
			PCTA	5.0	
			C4MS	20	
			C4MS	6.9	
			Conjugate 330	13	

[1] See Table 13 for structures [2] Conjugate 330: cysteinyl conjugate, exact structure not confirmed
[3] Two methyl tetrachlorophenyl sulfone isomers were found, substitution positions not known because insufficient material for NMR

Table 15. Polar metabolite concentrations in lettuce, trial 598, 365 DAT, mature (Harned, 1997b).

Peak RT, min	Metabolite [1]	Total peak, mg/kg as quintozene	Metabolite, mg/kg as quintozene	Total peak, % of TRR	Metabolite, mg/kg, % of TRR
37.0	C3MSMaCy	0.029	0.012	6.9	2.9
37.0	C4MaCyFCy	0.029	0.007	6.9	1.7
41.0	C4SA	0.023	0.012	5.5	2.9
55.0	C5SA	0.028	0.024	6.7	5.7

[1]See table 13 for structures
RT: retention time

Table 16. Summary of polar metabolite concentrations in lettuce, trials 596 and 597, (Harned, 1997b).

Sample	Metabolite	Fraction	mg/kg as quintozene	% of TRR
596 (30 DAT, mature)	C4CyFCy	ether	0.0019	1.8
596	C5MaCy	ether	0.0029	2.6
(30 DAT, mature)				
596 (30 DAT, mature)	C5MaCy	acidic water	0.0044	4.1
597 (120 DAT, mature)	C4CyFCy	ether	0.0027	2.8
597 (120 DAT, mature)	C5SA	acidic water	0.0021	2.2

Table 17. Pentachloroaniline (PCA) concentrations in lettuce digests and KOH hydrolysates (Harned, 1997b).

Sample	PCA, mg/kg	% of TRR
trial 570, protease digest (30 DAT, immature)	0.002	1.4
trial 572, protease digest (365 DAT, immature)	0.004	0.66
trial 598, protease digest (365 DAT, mature)	0.003	0.59
trial 570, KOH hydrolysate (30 DAT, immature)	0.008	5.3
trial 572, KOH hydrolysate (365 DAT, immature)	0.013	2.3
trial 596, KOH hydrolysate (30 DAT, mature)	0.009	8.5
trial 598, KOH hydrolysate (365 DAT, mature)	0.007	1.7

Fourteen metabolites were isolated from turnips and identified. Sulfonic acids and *N*-malonylcysteinyl conjugates were the major metabolites in the MeOH fractions of both tops and roots. The phenyl sulfoxides and sulfones were mainly in the $CHCl_3$ fractions of the tops, whereas pentachloroaniline was predominant in the $CHCl_3$ fractions of the roots. Reduction to pentachloroaniline and formation of PCTA through glutathionyl conjugation are two major metabolic pathways, followed by oxidation of the PCTA to the sulfonic acid or sulfoxide and sulfone. Tables 18 and 19 show the metabolite distribution in turnip tops and roots respectively.

Table 18. Distribution of metabolites in turnip tops (Harned, 1997b).

Fraction	HPLC RT, min	Metabolite	Sample					
			L-tops			H-tops		
			% of ^{14}C in fraction	% of TRR in tops	mg/kg as quintozene	% of ^{14}C in fraction	% of TRR in tops	mg/kg as quintozene
Me0H	4.0-5.0	Unknown	4.05	1.96	0.001	9.02	5.87	0.008
	17.5-18.5	C3MSSA & C2MSMaCy	18.5	8.91	0.004	25.1	16.3	0.024
	18.5-19.5	C2SA & C3MSMaCy	47.9	23.1	0.011	27.8	18.1	0.026
	21.0	C3SA	12.9	6.24	0.003	-	-	-
	23.0	C4SA	6.83	3.30	0.002	13.2	8.60	0.012
	24.5-25.0	C5SA	6.61	3.19	0.002	8.27	5.38	0.008
	27.0	Unknown	3.26	1.57	0.001	4.16	2.71	0.004
	29.5	Unknown	-	-	-	5.88	3.82	0.006
	32.0	Unknown	-	-	-	6.54	4.25	0.006
Subtotal			100	48.3	0.024	100	65	0.094
$CHCl_3$	17.0	C3MSSA & C2MSMaCy	12.2	3.46	0.002	-	-	-
	20.0	C3SA	7.30	2.07	0.001	-	-	-
	22.5-23.0	C4SA	13.2	3.75	0.002	8.48	1.10	0.002
	26.0-27.0	C5SA	5.47	1.55	0.001	4.90	0.64	0.001
	28.5	Unknown	-	-	-	3.94	0.51	0.001
	30.0-31.0	Unknown	4.47	1.27	0.001	5.85	0.76	0.001
	32.5	Unknown	-	-	-	6.69	0.87	0.001
	34.0-34.5	Unknown	8.85	2.51	0.001	4.66	0.60	0.001
	37.5-38.0	C3MS	28.5	8.06	0.004	39.7	5.15	0.007
	39.5-40.0	C3MS & PCTASO	14.0	3.95	0.002	16.5	2.14	0.003
	41.5	C4MS	-	-	-	5.97	0.77	0.001
	44.0	PCP	2.01	0.57	<0.001	3.35	0.43	0.001
	52.0	PCA	4.01	1.14	0.001	-	-	-
Subtotal			100.5	28.3	0.015	100	13	0.019
Water	4.5-5.0	Unknown	28.4	2.72	0.001	11.3	1.08	0.001
	18.0-19.0	C3MSSA & C2MSMaCy	32.6	3.11	0.002	39.9	3.79	0.005
	21.0	C3SA	21.6	2.06	0.001	12.6	1.19	0.002
	23.0-24.0	C4SA	10.9	1.04	0.001	17.4	1.65	0.002
	25.0	C5SA	6.58	0.63	<0.001	-	-	-
	30.0	Unknown	-	-	-	8.06	0.77	0.001
	33.0	Unknown	-	-	-	10.7	1.02	0.001
Subtotal			100.1	9.56	0.005	100	9.5	0.012
Hexane	NA			4.63	0.002		3.50	0.005
PES	NA			9.18	0.004		8.98	0.013
Total				100	0.050		99.9	0.143

NA: not analysed
L-tops: treated with 2.2 kg ai/ha, H-tops: treated with 11.2 kg ai/ha
PES: post-extraction solid fraction

Table 19. Distribution of metabolites in turnip roots (Harned, 1997b).

Fraction	HPLC RT, min	Metabolite	Sample					
			L-roots			H-roots		
			% of ^{14}C in fraction	% of TRR in roots	mg/kg as quintozene	% of ^{14}C in fraction	% of TRR in roots	mg/kg as quintozene
Me0H	3.5-4.5	Unknown	9.92	3.14	0.002	11.4	2.98	0.007
	17.5-19.0	C3MSSA & C2MSMaCy	22.0	6.96	0.004	9.35	2.45	0.006
	19.5-20.0	C2SA & C3MSMaCy	19.3	6.11	0.003	61.6	16.2	0.039
	20.5-21.5	C3SA	9.40	2.97	0.002	11.8	3.1	0.008
	22.0-23.5	C4SA	28.3	8.96	0.005	2.98	0.78	0.002
	25.0-26.5	C5SA	5.97	1.89	0.001	2.87	0.75	0.002
	31.5	Unknown	5.07	1.6	0.001		-	-
Subtotal			99.96	31.63	0.018	100	26.26	0.064
$CHCl_3$	17.0	C3MSSA & C2MSMaCy	-	-	-	3.57	1.1	0.003
	18.0	C3SA	-	-	-	3.46	1.07	0.003
	37.5	C3MS	7.93	2.72	0.002	2.79	0.86	0.002
	40.0	C3MS & PCTASO	9.02	3.09	0.002	5.8	1.79	0.004
	41.0	C4MS	-	-	-	4.35	1.34	0.003
	43.0-43.5	PCP	4.12	1.41	0.001	4.85	1.49	0.004
	52.0	PCA	76.4	26.2	0.015	71.5	22.0	0.054
	54.5	PCTA	2.48	0.85	<0.001	3.68	1.13	0.0031
Subtotal			99.95	34.25	0.02	100	30.78	0.076
Hexane-EtOAc	48.0	Unknown	-	-	-	5.35	1.36	0.003
	51.5	PCA	100	20	0.01	87.4	22.2	0.053
	54.5	PCTA	-	-	-	7.24	1.84	0.004
Subtotal			100	20	0.01	100	25.4	0.06
AQ-2	NA			1.68	0.001		5.32	0.013
AQ-3	NA			1.92	0.001		2.63	0.006
CH_2Cl_2	NA			2.32	0.001		2.34	0.006
PES	NA			8.24	0.004		7.3	0.018
Total				100.04	0.055		100.03	0.243

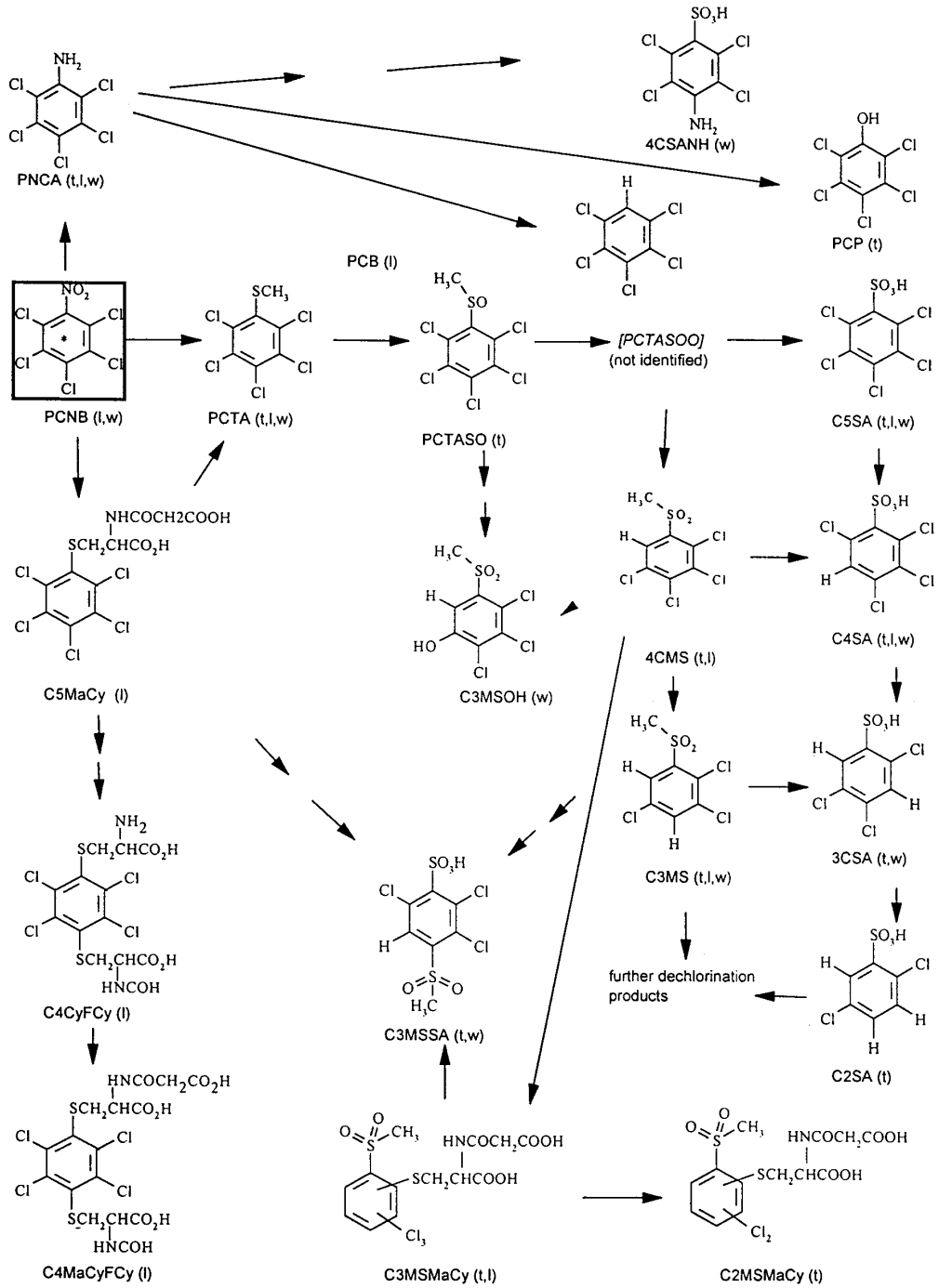
NA: not analysed
L-roots: treated with 2.2 kg ai/ha, H-roots: treated with 11.2 kg ai/ha
PES: post-extraction solid fraction

Twelve compounds were isolated from wheat: pentachlorobenzenesulfonic acid, 0.14 mg/kg in straw; three isomers of tetrachlorobenzenesulfonic acid, 0.08, 0.33 and 0.06 mg/kg in straw, 0.22 mg/kg in forage; an isomer of trichlorobenzenesulfonic acid, 0.17 mg/kg in straw; methyl trichlorosulfophenyl sulfone, 0.11 mg/kg in straw; hydroxytrichlorophenyl methyl sulfone, 0.009 mg/kg in grain; pentachloroaniline, 0.013 mg/kg in straw; pentachlorothioanisole, 0.019 mg/kg in straw, and quintozene 0.023 mg/kg in straw from the 2.2 kg ai/ha treatment planted at 120 days; tetrachlorosulfanilic acid, 0.15 mg/kg in forage from 11.2 kg/ha, 30-day planting; methyl trichlorophenyl sulfone, 0.15 mg/kg in forage from 33.6 kg ai/ha, 30-day planting.

In summary, the identification of terminal metabolites indicated that reduction and conjugation as well as dechlorination are the main metabolic pathways of quintozene in wheat. The reduction product PCA was detected in straw and forage. Oxidation of PCTA, derived from glutathione conjugates produced by plant metabolism or possibly taken up by the roots from the soil,

yielded other major metabolites, the sulfonic acids and sulfones. Proposed metabolic pathways of quintozene in rotational crops are shown in Figure 3.

Figure 3. Proposed metabolic pathways of quintozene in rotational crops (Harned, 1997b).
t: turnip, l: lettuce, w: wheat



Gaydosh (1996a,b) applied unlabelled quintozene to bare soil at the maximum GAP rate for peanuts (11 kg ai/ha), allowed the soil to age for 30, 120 or 365 days and then planted wheat, lettuce and turnips (365 days only) in two field trials in the typical peanut growing regions of Georgia and Texas. At both locations the test substance was applied in bands using common granular application equipment at a typical pegging time for peanuts and 15 or 45 days pre-harvest. The rotational crops were planted within the treated band for maximum effect. The results are shown in Tables 20 and 21.

Table 20. Residues in rotational crops planted 365 days after quintozene application (Gaydosh, 1996a).

Sample	Residue, mg/kg							
	PCNB	PCB	HCB	PCTA	PCA	TCA	TCTASOO	PCTASO
Immature wheat	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)
Mature grain	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (6) 0.0155 0.0074	<0.005 (8)	<0.005 (8)	<0.005 (8)
Mature straw	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)
Lettuce	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)
Turnip tops	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)
Turnip roots	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (4) 0.014 0.014 0.009 0.012	<0.005 (5) 0.01 0.006 0.007	<0.005 (8)	<0.005 (8)

TCA: tetrachloroaniline

Table 21. Residues in rotational crops planted 30 and 120 days after quintozene application (Gaydosh, 1996 b).

Sample	Residue, mg/kg							
	PCNB	PCB	HCB	PCTA	PCA	TCA	TCTASOO	PCTASO
30 day planting								
Immature wheat	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (7)	<0.005 (8) 0.007	<0.005 (8)	< 0.005 (8)
Mature grain	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)
Mature straw	< 0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)
Lettuce	<0.005 (4) 0.010 0.011 0.013 0.012	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)
120 day planting[1]								
Immature wheat	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)
Mature grain	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)
Mature straw	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005(6)	<0.005 (6)	<0.005 (6)	<0.005 (6)

Sample	Residue, mg/kg							
	PCNB	PCB	HCB	PCTA	PCA	TCA	TCTASOO	PCTASO
Lettuce	<0.005 (3) 0.008 0.005 0.008	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)

[1]The loss of one 120-day plot in Texas reduced the number of samples to 6
TCA: tetrachloroaniline

Environmental fate in water

No data were submitted on natural aquatic or water/sediment systems. Both the following studies relate to the stability of the purified active ingredient in buffered water.

Bowman (1988b) incubated [^{14}C]quintozene in sterile aqueous buffer containing less than 1% acetonitrile as co-solvent at 25°C and pH 5, 7 and 9 for 30 days. The half-life could not be determined experimentally as there was too little degradation. It was estimated to be more than 180 days. No hydrolysis products were detected at any pH. 96-106% of the initial radioactivity was recovered.

Horree (1992) determined the photodegradation of [^{14}C]quintozene at 25°C and pH 5 after 32 hours continuous exposure to a xenon arc lamp. The half-life was 13.4 hours (R^2=0.99). Polar photodegradation products, accounting for 50% of the applied radioactivity after 32 hours, were identified as a mixture of 8 to 10 isomeric chlorophenols and/or chloronitrophenols formed by dechlorination of the benzene ring and subsequent hydroxylation at the same position(s). Identification was by derivatization with chloroacetic anhydride and MS. Volatile photodegradation products accounted for 20% of the applied radioactivity after 32 hours, none individually exceeding 10% of the original quintozene. The recovered ^{14}C accounted for 88-96% of the applied radioactivity.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The Meeting received details of analytical methods for determining quintozene, the impurities HCB and PB and the metabolites PCA and PCTA in meat, milk and eggs (Griffith, 1975) and soil (Griffith, 1970) and a reference to the latest edition of the official methods of analysis in The Netherlands (Anon., 1996).

Griffith (1975) extracted egg whites, egg yolks, fat, liver and bile with acetonitrile, white meat and faeces with hexane, and blood with a mixture of acetone and hexane (1:10). After the addition of water, liquid-liquid partition with hexane and further clean-up the compounds were determined by GLC with an ECD. An LOD of 0.005 mg/kg with a recovery of 60% was claimed but no validation data were submitted.

Griffith (1970) in a similar method extracted soil with acetone, adding water and subsequently partitioning the compounds into hexane. The hexane extract was analysed by GLC with an ECD. An LOD of 0.005 mg/kg with 60% recovery was claimed but with no validation data.

The latest version of the official analytical method of The Netherlands for quintozene, PCA and PCTA, reported by the 1995 JMPR, was reported (Anon., 1996).

Definition of the residue

The 1995 JMPR considered that the residue definition for risk assessment purposes for plant and animal commodities should be the sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulfide, expressed as quintozene. This definition is also suitable for animal commodities for enforcement purposes since the parent quintozene is not an appropriate indicator compound for such commodities. Quintozene alone is a suitable definition of the residue for enforcement purposes for crops. The residue is fat-soluble.

The impurity hexachlorobenzene (HCB) should also taken into account for risk assessment. Before 1988, the HCB content of the technical material was approximately 0.5%. In 1988 modifications to the manufacturing process reduced the level of HCB to 0.1% or less. The ADI of 0.01 mg/kg bw was established by the 1995 JMPR for quintozene containing less than 0.1% HCB.

USE PATTERN

The Meeting received new information on use patterns in Greece, Japan and Spain (Tables 22 and 23). Registered used in other countries are listed in the 1995 evaluation.

Correction to 1995 evaluation:

In Table 9 (page 638) the rate of application for seed treatment should be shown as kg ai/100 kg seed, not ka ai/ha.

Table 22. Registered uses of quintozene for seed treatments.

Crop	Country	Form.	Application rate, kg ai/100 kg seed
Barley	Spain	ES	0.036-0.19
		WS	0.04-0.2
Cereals	Greece	WP	0.075-0.11
Cotton	Greece	WP	0.23
	Spain	ES	0.036-0.19
		WS	0.04-0.2
Maize	Spain	ES	0.036-0.19
		WS	0.04-0.2
Sugar beet	Japan	WP	0.38-0.75

Table 23. Registered uses of quintozene for soil and plant treatment.

Crop	Country	Form.	application				PHI, days F/G
			method	Rate, kg ai/ha	Spray conc., .g ai/hl	No.	
Alfalfa	Greece	WP	linear soil application surface banded pre-plant	0.75-2.3 1.9-3		1	21 F
Bean	Greece	WP	linear soil application surface banded pre-plant	0.75-2.3 1.9-3		1	21 F
	Spain	WP	irrigation water and/or soil incorporation at sowing	1.1-2.3		1	F, G
		GR	soil incorporation pre-plant row surface banded	1.2-1.6 0.1 0.23-0.26		1	21 F
Cabbage	Japan	Dust		18-40			
	Spain	WP	irrigation water and/or soil incorporation at sowing	4.5		1	F, G
Chinese cabbage	Japan	Dust		40 -50			
Cotton	Greece	WP	linear soil application surface banded pre-plant	0.75-2.3 1.9-3		1	21 F
		GR	soil incorporation pre-plant row banded, surface banded, through sowing equipment during sowing	1.2-1.6 0.1 0.23-0.26 2.3 (broad) 0.98(linear)		1	21 F
	Spain	WP	irrigation water and/or soil incorporation at sowing	1.1-2.3		1	F
Cucumber	Greece	WP	drip irrigation and soil drenching	1.2-1.6	0.12-0.36	1-2	21 F, G
Eggplant	Greece	GR	soil incorporation pre-plant	2.8		1	21 F, G
Lettuce	Japan	Dust	pre-transplanting pre-sowing	5–24 61			
Maize	Greece	GR	row banded surface banded through sowing equipment during sowing	0.1 0.23-0.26 2.3 (broad) 0.98(linear)		1	21 F
Melons	Greece	WP	drip irrigation and soil drenching	1.2-1.6	0.12-0.36	1-2	21 F, G
Mulberry	Japan	Dust	in furrow	0.02-0.04[1]			
Onions	Greece	WP	linear soil application surface banded, pre-plant	0.75-2.3 1.9-3		1	21 F
Peanuts	Greece	GR	row banded surface banded	0.1 0.23-0.26		1	21 F
Peppers	Greece	GR	soil incorporation, pre-plant	2.8		1	21 F
		WP	drip irrigation and soil drenching	1.2-1.6	0.12-0.36	1-2	21 F, G
	Spain	WP	irrigation water and/or soil incorporation at sowing	2.3		1	F, G
Potatoes	Greece	WP	linear soil application surface banded pre-plant ground application pre-plant linear application pre-plant	0.75-2.3 1.9-3	 1.9-4.5 1.4-4.5	1	21 F
		GR	soil incorporation pre-plant row banded surface banded broad application at planting linear application at planting	2.8 0.1 0.23-0.26 2.3 (broad) 0.98(linear)		1	21
Squash	Greece	WP	drip irrigation and soil drenching (grown plants)	1.2-1.6	0.12-0.36	1-2	21 F, G

Crop	Country	Form.	application				PHI, days F/G
			method	Rate, kg ai/ha	Spray conc., .g ai/hl	No.	
Sugar beet	Greece	GR	soil incorporation pre-plant row banded surface banded through sowing equipment during sowing	1.2 -1.6 0.1 0.23-0.26 2.3 (broad) 0.98(linear)		1	21 F
	Japan	WP		0.34-0.75			
Tobacco	Greece	GR	soil incorporation pre-plant row banded surface banded through sowing equipment during sowing	2.8 0.1 0.23-0.26 2.3 (broad) 0.98(linear)		1	21 F
		WP	soil drenching (seedling) soil drenching (grown plants)	2.8-3.3 1.2-1.6	0.01-0.015 0.012-0.036	1-4 1-2	21 F
Tomatoes	Greece	GR	soil incorporation pre-plant row banded surface banded	2.8 0.1 0.23-0.26		1	21 F
		WP	drip irrigation and soil drenching (grown plants)	1.2-1.6	0.12-0.36	1-2	21 F, G
	Spain	WP	irrigation water and/or soil incorporation at sowing	2.3		1	F, G
Vegetables	Greece	WP	linear soil application pre-plant surface banded pre-plant drip irrigation and soil drenching (grown plants) application before sowing or planting	0.75-2.3 1.9–3 2.8–3.3 (broad) (linear)	 0.01-0.015 1.9-4.5 1.4-4.5	1 1-4 1[2] 1[2]	21 21 F, G
		GR	soil incorporation pre-plant row banded surface banded application pre-sowing or pre-planting	2.8 0.1 0.23-0.26 2.3 (broad) 0.98(linear)		1	21 F

[1] kg ai/m
[2] Not on cucurbits
F : field, G: glasshouse

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received new supervised residue trials data only on lettuce.

Lettuce. The 1995 JMPR recommended withdrawal of the previous recommendation of 3 mg/kg because no residue data were submitted. The present Meeting received reports of two Japanese trials (1 x 60 kg ai/ha pre-transplanting, PHI 49 or 67 days) resulting in quintozene residues of 0.007 and 0.01 mg/kg (Table 24). No metabolites or impurities were determined and it was not clear whether the varieties were head or leaf lettuce.

Two further pre-planting trials in 1970 in Germany (Anon., 1997) showed quintozene residues of 0.2 and 0.27 mg/kg, but no information on rates of treatment or the analytical methods used was provided.

Table 24. Residue of quintozene in lettuce, Japan, 1989.

Variety	Application method	kg ai/ha	PHI, days	Residues, mg/kg	Reference
Universe	pre-transplanting	60	49	0.01	Mitsui Toatsu Chem., 1990
Sacrament	pre-transplanting	60	67	0.007	Mitsui Toatsu Chem., 1990

The Meeting estimated STMRs for the sum of quintozene, PCA and PCTA and for HCB of the commodities evaluated in 1995.

Animal feeding studies

No new work was reported, but the Meeting was informed that the studies on cows (Griffith *et al.*, 1969) and chickens (Griffith, 1969) evaluated by 1995 JMPR were with quintozene which contained 1.4% HCB.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

Ball (1990) determined residues of quintozene, PCA, PCTA, HCB and PB in unpeeled and peeled potatoes and the peels after one broadcast treatment at 28 kg ai/ha in Minnesota (MN) and North Dakota (ND), USA. The mean ratio of wet to dry peel weights was 7.5. The results are shown in Tables 25 and 26.

Table 25. Weights of potatoes and peels (Ball, 1990).

Location/Sample	Whole tubers, kg	Peeled tubers, kg	Peel, % of whole
MN – untreated	26.6	23.7	10.9
MN – treated	27	24.1	10.7
ND – untreated	28.3	25.3	10.6
ND – treated	27.9	25	10.4
		Average	10.65
	Wet peel, kg	Dry peel, kg	Ratio wet/dry peel
MN – untreated	2.7	0.37	7.3
MN – treated	2.7	0.36	7.5
ND – untreated	3.2	0.42	7.6
ND – treated	2.8	0.37	7.6

Table 26. Quintozene residues in potatoes and potato peels, USA, 1988 (Ball, 1990).

Location	Application kg ai/ha	PHI days	Sample	Residues, mg/kg				
				Quintozene	HCB	PCA	PB	PCTA
Hollondale, MN	28	123	whole tuber, unpeeled	0.13	0.0012	0.02	0.012	0.03
			wet peel	1.0	0.002	0.066	0.024	0.12
			dried peel	2.1	0.0028	0.27	0.15	0.20
			whole tuber, peeled	0.014	0.0007	0.0076	0.008	0.009
Northwood, ND	28	122	whole tuber, unpeeled	0.012	0.0007	0.008	0.013	0.01
			wet peel	0.067	0.0009	0.021	0.012	0.023
			dried peel	0.17	0.0015	0.091	0.031	0.051
			whole tuber, peeled	0.002	<0.0005	0.003	0.005	0.003

Gaydosh and Smudin (1996a) treated cotton at 6.7 kg ai/ha, about 3 times the US GAP rate. No residues of quintozene, PCA, PCTA or HCB above 0.0005 mg/kg, or of PB above 0.1 mg/kg were in the seed (RAC) after treatment. No residues of quintozene or its metabolites or impurities above the LOD were detected in hulls or crude or refined oil. In soapstock no residues of quintozene, PCTA or PB were detected above 0.1 mg/kg and no residues of HCB above 0.0005 mg/kg, but PCA was detected at a mean level of 064 mg/kg. From the results it cannot be concluded whether residues of quintozene are concentrated in processed products of cotton seed.

Gaydosh and Smudin (1996b) treated peanuts at 112 kg ai/ha, 10 times the US GAP rate. The maximum residues in whole peanuts of quintozene, PCA, PCTA, PB and HCB were 6.9, 1.8, 0.56, 0.34 and 0.083 mg/kg respectively. Quintozene was concentrated by a mean factor of 2.5 in the hull but not in any other fractions. PB showed slight concentration in the hulls (1.3 times), crude oil (1.3 times) and refined oil (1.7 times). HCB was concentrated in the kernels (1.7 times), soapstock (1.2 times), crude oil (3 times), and refined oil (3.9 times). PCTA was concentrated in the kernels (1.2 times), crude oil (1.6 times) and refined oil (2.1 times), and PCA in the hulls (1.2 times) and refined oil (1.2 times). The results are shown in Table 27.

Table 27. Quintozene residues in peanuts and their processed fractions, Hawkinsville, GA, USA, 1992 (Gaydosh and Smudin, 1996b).

Application, kg ai/ha	PHI, days	Sample	Residues, mg/kg				
			Quintozene	HCB	PCA	PB	PCTA
112	45	whole peanuts	1.6, 6.9 UC: 0.012	0.045, 0.083	1.5, 1.8 UC:0.015	0.26, 0.34	0.4, 0.56
		kernels	1.2, 1.3	0.1, 0.12	0.87, 1.1	0.21, 0.27	0.49, 0.61
		meal	0.045, 0.019	<0.01 (2)	<0.01, 0.01	<0.01 (2)	<0.01 (2)
		soapstock	0.58, 0.72	0.069, 0.077	0.99, 1.03	0.3, 0.36	0.32, 0.34
		crude oil	1.95, 1.7	0.18, 0.195	1.7, 1.8	0.39, 0.4	0.77, 0.79
		refined oil	2.6, 2.7	0.24, 0.26	1.8, 2.1	0.49, 0.51	0.98, 1.06
		hulls	12, 9.2 UC: 0.012	0.042, 0.037	2.2, 1.7	0.46, 0.32	0.43, 0.33

UC: residues in untreated control, validated LOD = 0.01 mg/kg for each commodity

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Table 28 shows the results of monitoring in The Netherlands during 1994-1996 (Olthof, 1998).

Table 28. Residues (expressed as quintozene) in food in commerce in The Netherlands 1994-1996 (Olthof, 1998).

Commodity	No. of samples analysed	No. of samples <LOD (0.01 mg/kg)	No of samples with residues <MRL	No of samples with residues > MRL	MRL, mg/kg
Oranges	982	982	-	1	0.01*
Carrots	500	494	-	6	0.01*
Melons	455	454	-	1	0.01*
Lettuce	3834	3833	-	1	0.01*
Endive	1297	1296	-	1	0.01*
Spinach	532	532	-	-	0.01*
Parsley	390	389	-	1	0.01*
Other herbs	224	223	-	1	0.01*
Beans, fresh (with pods)	690	689	-	1	0.01*
Other arable products	375	374	-	1	0.01*

* LOD

NATIONAL MAXIMUM RESIDUE LIMITS

New information on national MRLs in Germany (Anon., 1997), The Netherlands (Olthof, 1998) and Poland (Lzdebski, 1997) is shown below.

Country	Commodity	MRL (mg/kg)
Germany	Bananas	1
	Lettuce and similar, chicory	0.3
	Tealike products	0.1
	Oilseeds	0.03
	Brassica vegetables	0.02
	Other foods of plant origin	0.01
Netherlands	Bananas	1
	Tomatoes	0.1
	Head lettuce	3
	Broccoli	0.02
	Head cabbage	0.02
	Peanuts	2
	Cotton seed	0.03
	Beans (dry)	0.2
	Potatoes	0.2
	Other food commodities	0.01*
Poland	Banana	1
	Other food commodities of plant origin	0.01

*at LOD

APPRAISAL

Quintozene was evaluated as a periodic review by the 1995 JMPR. That Meeting estimated a number of maximum residue levels but agreed not to recommend their use as MRLs, and recommended the withdrawal of existing MRLs, because of the lack of critical supporting data on environmental fate. Some of the processing studies could not be evaluated because of their uncertain validity.

Data on environmental fate, residues in rotational crops, supervised trials on lettuce and the effects of processing on residues in cotton seed, peanuts and potatoes have been made available to the present Meeting.

Environmental fate in soil

Quintozene is unstable in soil under photolytic conditions. In sandy loam soil exposed to simulated sunlight quintozene had a half-life of 28.5 days. Pentachloroaniline (PCA) was the only significant degradation product.

Quintozene in sandy loam soil under aerobic conditions had a half-life of 189 days. The major degradation product was pentachloroaniline (PCA). A secondary product, methyl pentachlorophenyl sulfide (pentachlorothioanisole, PCTA), was formed from PCA by deamination via nucleophilic displacement at the aromatic ring. Other degradation products were methyl pentachlorophenyl sulfone ($PCTASO_2$), methyl pentachlorophenyl sulfoxide (PCTASO) and pentachlorobenzene (PB). Soil-bound products and CO_2 were formed to a limited extent.

When quintozene was subjected to anaerobic conditions in the same soil after a period of 30 days under aerobic conditions, it was degraded significantly more quickly, with a half-life of 15 days. PCA was the major residue. Minor products such as PCTA and PB were also observed.

Quintozene is immobile to slightly mobile in soil (Freundlich adsorption constants in silt loam, sandy loam, clay loam and sand with about 1% organic matter were 24, 46, 89 and 31 respectively). The mobility of the major metabolite PCA was also investigated in the same soils: its Freundlich constants were even higher, indicating less mobility than the parent compound.

Field dissipation studies showed that the half-life of quintozene applied on soil surfaces was significantly shorter than when applied by incorporation.

The uptake of [*phenyl*-^{14}C]quintozene by rotational crops was investigated. Treated soil was allowed to age for periods of 30, 120 or 365 days (DAT) before planting turnips, lettuce and wheat. The soil treatments were at a low rate of 2.2 kg ai/ha (the US GAP rate for cotton), 11 kg ai/ha (the US rate for peanuts) and 34 kg ai/ha, which was used only for rotational wheat.

After the 11 kg ai/ha treatment the total radioactive residue (TRR) expressed as quintozene in turnip tops and roots was 1.12 and 0.21 mg/kg respectively at 365 DAT, in mature lettuce 0.15, 0.10 and 0.43 mg/kg at 30, 120 and 365 DAT, in wheat forage, grain and straw 3.0, 0.79 and 11 mg/kg respectively at 30 DAT, 3.4, 0.94 and 17 mg/kg at 120 DAT, and 0.64, 0.14 and 4.6 mg/kg at 365 DAT.

Residues of the parent compound were found only in lettuce (max. 0.032 mg/kg) and wheat straw (2.2 kg ai/ha, 120 DAT, 0.012 mg/kg). PCA was found in all three crops, at the highest levels of 0.11 mg/kg in turnip roots (365 DAT, 11 kg ai/ha), 0.065 mg/kg in immature lettuce (365 DAT, 11 kg ai/ha), 0.85 mg/kg in wheat straw (30 DAT, 34 kg ai/ha) and 0.11 mg/kg in wheat forage (30 DAT, 34 kg ai/ha). PB was found only in lettuce (30 DAT, 11 kg ai/ha) at less than 0.001 mg/kg.

In another field rotational crop study unlabelled quintozene was applied to bare soil at the maximum GAP rate for peanuts (11 kg ai/ha per season) at typical times of 15 or 45 days before peanut harvest. No residues above the LOD of 0.005 mg/kg of quintozene, PB, HCB, PCTA or PCTASO were found in the leaves, roots or grain of lettuce, turnips or wheat planted 365 days after the treatment. Residues of PCA and tetrachloroaniline (TCA) were found in the turnip roots at levels

not exceeding 0.014 mg/kg, and PCA residues in two of eight mature wheat grain samples (0.007, 0.016 mg/kg).

Environmental fate in water

Quintozene is stable to hydrolysis. In buffered solutions at pH 5, 7 and 9, the half-life was longer than 180 days. However, aqueous photodegradation occurred in simulated natural sunlight (with a xenon arc lamp), with a half-life of less than two days in buffered water at pH 5.

Definition of the residue

The 1995 JMPR considered that for risk assessment purposes the residue in plant and animal commodities should be defined as the sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulfide, expressed as quintozene. This definition is also suitable for animal commodities for enforcement purposes since the parent quintozene is not an adequate indicator compound in such commodities. Quintozene alone is a suitable definition of the residue in crops for enforcement purposes. The residue is fat-soluble.

Residues of the impurity hexachlorobenzene (HCB) arising from the use of quintozene should also taken into account for risk assessment. Before 1988, the HCB content of the technical material was approximately 0.5%. In 1988 modifications to the manufacturing process reduced the level of HCB to 0.1% or less. An ADI of 0-0.01 mg/kg bw was established by the 1995 JMPR for quintozene containing less than 0.1% HCB.

New supervised residue trials

Lettuce. The 1995 JMPR recommended withdrawal of the existing CXL of 3 mg/kg because no residue data were submitted. The current Meeting received reports of two Japanese trials (1 x 60 kg ai/ha pre-transplanting, PHI 49 or 67 days) resulting in quintozene residues of 0.007 and 0.01 mg/kg. No metabolites or impurities were determined. Two German trials could not be evaluated as the application rates were not reported. The Meeting agreed that the data were insufficient to estimate a maximum residue level and confirmed the recommendation of the 1995 JMPR to withdraw the CXL of 3 mg/kg.

New processing studies

Potatoes. Potatoes treated with 1 x 28 kg ai/ha were analysed for quintozene, PCA, PCTA, HCB and PB. Analyses of whole tubers, peeled potatoes, and wet and dry peel showed that most of the residue is on the peel.

The residues of HCB were 0.0012 mg/kg in the unpeeled whole potatoes, 0.0007 mg/kg in the peeled tubers, 0.002 mg/kg in wet peel and 0.0028 mg/kg in dry peel.

Peanuts. After treatment at 112 kg ai/ha (10 times the US GAP rate) the maximum residues in whole peanuts of quintozene, PCA, PCTA, PB and HCB were 6.9, 1.8, 0.56, 0.34 and 0.083 mg/kg respectively. The mean quintozene residue was concentrated 2.5 times in the hulls but not in any other fractions. PB was concentrated 1.3 times in the hulls and crude oil and 1.7 times in the refined oil. HCB was concentrated in the kernels (x 1.7), soapstock (x 1.1), crude oil (x 3), and refined oil (x 3.9), and PCTA in the kernels (x 1.1), crude oil (x 1.6) and refined oil (x 2.1). PCA was concentrated slightly in the hulls (x 1.2) and refined oil (x 1.2).

Cotton seed. No residues of quintozene, PCA, PCTA or HCB above 0.0005 mg/kg or PB above 0.1 mg/kg were found in cotton seed after treatment at 6.7 kg ai/ha. No residues of quintozene or its metabolites or impurities were detected in crude or refined oil, or in the hulls above the LOD (0.0005 mg/kg). No residues of quintozene, PCTA or PB were detected above 0.1 mg/kg in soapstock, and no residues of HCB above 0.0005 mg/kg. Residues of PCA were detected in soapstock however (mean 0.0064 mg/kg). It cannot be concluded from the results whether quintozene or its metabolites or impurities become concentrated in the processed products of cotton seed. As quintozene is fat-soluble, it would be expected that residues in the seeds would be transferred to the oil. Since the processing procedure for the preparation of cotton seed oil is comparable to that for the preparation of peanut oil the results of the peanut processing study should be applicable to cotton seed and other oilseeds.

Recommendations for MRLs and estimation of STMR levels for commodities for which maximum residue levels were estimated by the 1995 JMPR

The evaluation of the residue data was described in the 1995 monograph and appraisal. If there were different populations of residues, the STMRs are derived from the highest population. In some commodities (sweet peppers, soya beans, soya bean forage and fodder, sugar beet, sugar beet leaves, barley straw and fodder) the residues of quintozene, PCTA and PCA were below the LOD in all the samples. The results of a rotational crop metabolism study indicated that residues could occur in succeeding crops. The main part of the total residue consisted of quintozene (about 60%), with about 30% of PCA and 10% of PCTA. The Meeting therefore estimated the STMRs for commodities with no detectable residues of quintozene, PCTA or PCA on the basis of the LOD for quintozene only.

The present Meeting recommended the maximum residue levels estimated in 1995 for use as MRLs.

No HCB residues above the LOD were found in broccoli, head cabbages, sweet peppers, tomatoes, common beans (dry), peas (dry), soya beans (dry), sugar beet (roots and leaves), barley, maize, wheat, cotton seed, pea hay (dry), maize forage, soya bean fodder or soya bean forage, and rotational crop studies did not show residues of HCB in succeeding crops. The Meeting therefore estimated an STMR of 0 for HCB in these commodities.

Broccoli. On the basis of the 1995 evaluation, the Meeting recommended an MRL of 0.05 mg/kg.

The critical use was treatment of the soil after planting the seedlings and this resulted in total residues of 0.04, 0.046, 0.057, 0.06, 0.075 and 0.098 mg/kg. The Meeting estimated an STMR of 0.0585 mg/kg for broccoli, based on the sum of quintozene, PCTA and PCA expressed as quintozene.

Head cabbages. The Meeting recommended an MRL of 0.1 mg/kg, based on the residues in samples with wrapper leaves after transplant solution treatment (the soil was treated after the seedlings were planted). The STMR estimate was based on the residues of quintozene and PCA in the samples without wrapper leaves as the PCTA residues in all the samples without wrapper leaves were below the LOD (<0.002 mg/kg). The highest residue population of the samples without wrapper leaves resulted from GR broadcast treatment, with residues of 0.0042 (6), 0.0052, 0.0053, 0.0108, 0.0119, 0.0122, 0.0152 and 0.0182 mg/kg. The Meeting estimated an STMR of 0.0052 mg/kg for head cabbages, based on the sum of quintozene and PCA expressed as quintozene.

Sweet peppers. The Meeting recommended an MRL of 0.05* mg/kg as a practical limit of determination.

The residues of quintozene, PCTA and PCA in all the samples were below the LOD. The Meeting estimated an STMR of 0.05 mg/kg.

Tomatoes. The Meeting recommended an MRL of 0.02 mg/kg. The STMR was estimated on the basis of the quintozene residues (from the WP in-furrow treatment) as the PCA and PCTA residues were all below the LOD (<0.002 mg/kg). The quintozene residues in rank order were <0.002 (7), 0.003, 0.006 and 0.012 mg/kg. The Meeting estimated an STMR of 0.002 mg/kg.

Common beans and common beans (dry). The Meeting recommended an MRL of 0.02 mg/kg for common bean (dry). The EC treatment (1 x 1.7 kg ai/ha, 1993) was identified as giving rise to the population with the highest residues.

The residues in fresh beans, as the sum of quintozene, PCA and PCTA, in rank order were <0.002 (2), 0.0327, 0.0358, 0.0795 and 0.0925 mg/kg, expressed as quintozene. The Meeting estimated an STMR of 0.0342 mg/kg for common bean (pods and/or immature seeds).

The residues in dry beans (quintozene, PCA and PCTA) were <0.002 (4), 0.0168 and 0.0297 mg/kg, expressed as quintozene. The Meeting estimated an STMR of 0.002 mg/kg for common bean (dry).

Peas (dry). The Meeting recommended an MRL of 0.01 mg/kg. The STMR was estimated on the basis of the quintozene residues as no PCA or PCTA residues exceeded the LOD (0.005 mg/kg) in any of the samples. The quintozene residues were <0.005 (6), 0.005 and 0.007 mg/kg. The Meeting estimated an STMR of 0.005 mg/kg.

Soya beans (dry). The Meeting recommended an MRL of 0.01* mg/kg as a practical limit of determination. The residues of quintozene, PCTA and PCA in all the samples were below the LOD. The Meeting estimated an STMR of 0.005 mg/kg.

Potatoes. The 1995 Meeting could not estimate a maximum residue level and recommended withdrawal of the CXL as no information on GAP was available. The present Meeting was informed that there is only a conditional time-limited registration for the use of quintozene on potatoes in the USA. The Meeting therefore confirmed the recommendation of the 1995 Meeting.

Sugar beet. The Meeting recommended an MRL of 0.01* mg/kg as a practical limit of determination. The residues of quintozene, PCTA and PCA in all the samples were below the LOD. The Meeting estimated an STMR of 0.005 mg/kg.

Barley, maize. The Meeting recommended an MRL of 0.01* mg/kg as a practical limit of determination for both commodities. The residues of quintozene, PCTA and PCA in all the samples were below the LOD. The Meeting estimated STMRs of 0.005 mg/kg for barley and maize.

Wheat. The Meeting recommended an MRL of 0.01 mg/kg. The STMR was estimated on the basis of the quintozene residues as the PCA and PCTA residues were all below the LOD (<0.005 mg/kg). The quintozene residues were <0.005 (19) and 0.0061 mg/kg. The Meeting estimated an STMR of 0.005 mg/kg.

Cotton seed. The Meeting recommended an MRL of 0.01 mg/kg. The STMR was estimated on the basis of the 1988 trials with EC and FL treatments (1995 monograph, Table 19), which gave residues of <0.016 (24), 0.0188 (2), 0.0249 and 0.0284 mg/kg for the sum of quintozene, PCTA and PCA, expressed as quintozene. The Meeting estimated an STMR of 0.016 mg/kg.

Peanuts. The Meeting recommended an MRL of 0.5 mg/kg. The STMR was estimated on the basis of the 1994 trials (EC treatment). The residues were 0.099, 0.106, 0.324, 0.382, 0.436 and 0.446 mg/kg

for the sum of quintozene, PCTA and PCA, expressed as quintozene. The Meeting estimated an STMR of 0.353 mg/kg.

The processing study showed that only PCTA moved into the oily fractions, with concentration factors exceeding 1.5 (1.6 for crude and 2.1 for refined oil). Because PCTA residues are only a third of the total, and no concentration of quintozene or PCA would be expected, no STMR was estimated for residues of quintozene or its metabolites.

On the basis of HCB residues of 0.0022, 0.0025, 0.0064, 0.008, 0.016 and 0.017 mg/kg in the 1994 trials, the Meeting estimated an STMR of 0.0072 mg/kg for HCB in peanuts.

Multiplication of the STMR by the processing factors for HCB gave derived STMRs of 0.0216 mg/kg in crude oil and 0.0281 mg/kg in refined oil.

Maize forage. The Meeting recommended an MRL of 0.01* mg/kg as a practical limit of determination. The residues of quintozene, PCTA and PCA in all the samples were below the LOD. The Meeting estimated an STMR of 0.005 mg/kg.

Cereal straws and fodders. The Meeting recommended MRLs of 0.01* mg/kg (a practical limit of determination) for barley straw and fodder, dry, 0.01 mg/kg for maize fodder and 0.03 mg/kg for wheat straw and fodder, dry.

In barley straw, the residues of quintozene, PCTA and PCA in all the samples were below the LOD. The Meeting estimated an STMR of 0.005 mg/kg for barley straw and fodder, dry.

The STMRs for maize fodder and wheat straw were calculated on the basis of the quintozene residues as the PCA and PCTA residues were all below the LOD (<0.005 mg/kg). The quintozene residues were <0.005 (12) and 0.006 mg/kg in maize fodder and <0.005 (17), 0.006, 0.007 and 0.023 mg/kg in wheat straw. The Meeting estimated STMRs of 0.005 mg/kg for maize fodder and for wheat straw and fodder, dry.

In one of 20 wheat straw samples, the HCB residue was higher than the LOD (population: <0.005 (19) and 0.014 mg/kg). Because the supervised residue trials were carried out in 1987, the HCB content of the formulation could be as high as 0.5% and the trials were therefore not applicable to the current situation.

In view of the high persistence of HCB in the soil and the results of a rotational crop metabolism study indicating that it could be taken up from the soil by cereals, the Meeting could not estimate an STMR for HCB in cereal straws and fodders, dry.

Pea hay. The Meeting recommended an MRL of 0.05 mg/kg and an STMR of 0.021 mg/kg, based on residues of 0.0156 (3), 0.0166, 0.0255, 0.0268, 0.0305 and 0.0415 mg/kg, for the sum of quintozene, PCTA and PCA expressed as quintozene, in pea hay (dry).

Soya bean fodder and forage. The Meeting recommended an MRL of 0.01* mg/kg as a practical limit of determination for both commodities. In whole green plants, the residues of quintozene, PCTA and PCA in all the samples were below the LOD. The Meeting estimated an STMR of 0.005 mg/kg for soya bean forage.

No residues of quintozene, PCTA or PCA were found above the LOD in the hay or the whole plant at harvest except one PCA residue of 0.0154 mg/kg (expressed as quintozene). The residues in rank order were <0.0055 (29) and 0.0154 mg/kg. The Meeting estimated an STMR of 0.0055 mg/kg for soya bean fodder, based on the residues of PCA expressed as quintozene.

Sugar beet leaves. No maximum residue level was estimated for sugar beet leaves in 1995 but they could be used as a feed item. The residues of quintozene, PCTA and PCA in all the samples were below the LOD. The Meeting estimated an STMR of 0.005 mg/kg for sugar beet leaves.

Animal products

Chickens. The Meeting recommended MRLs of 0.03* mg/kg for eggs and 0.1* mg/kg for chicken meat (in the fat) and edible offal as practical limits of determination.

The residues of quintozene, PCTA and PCA in all the samples from feeding levels up to the equivalent of 5 ppm in the diet were below the LODs.

Since (1) the main part of the total residue in plants is quintozene, (2) the residues in feed items for poultry will be below 1 mg/kg, (3) no quintozene occurred in meat, liver or eggs at 1 ppm in the diet or in fat at 15 ppm, and (4) the residue is fat-soluble, the Meeting estimated STMRs of 0.01 mg/kg for eggs, 0.04 mg/kg for chicken meat (in the fat) and 0.03 mg/kg for edible offal, based on the LODs for quintozene.

No STMR was estimated for HCB as the feeding study was carried out with quintozene which contained 1.4% HCB.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The estimates of maximum residue levels confirm those of the 1995 JMPR, which were not recommended as MRLs at that time owing to the lack of critical supporting studies. The maximum residue levels are now recommended for use as MRLs.

Definition of the residue

(1) For compliance with MRLs for plant commodities: quintozene.
(2) For compliance with MRLs for animal commodities: sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulfide, expressed as quintozene.
(3) For estimation of dietary intake for plant and animal commodities: sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulfide, expressed as quintozene.

The compounds are fat-soluble.

Commodity		Recommendation			
		MRL mg/kg		STMR, STMR-P mg/kg	
CCN	Name	New	Previous[1]	quintozene[1]	HCB
GC 0640	Barley	0.01*	-	0.005	0
AS 0640	Barley straw and fodder, dry	0.01*	-	0.005	
VB 0400	Broccoli	0.05	0.02	0.0585	0
VB 0041	Cabbages, Head	0.1	0.02	0.0052	0
PO 0840	Chicken, Edible offal of	0.1*	-	0.03	
PM 0840	Chicken meat	0.1* (in the fat)	-	0.04 (in the fat)	
VD 0526	Common bean (dry)	0.02	0.2	0.002	0
VP 0526	Common bean (pods and/or immature seeds)	0.1	0.01	0.0342	0
SO 0691	Cotton seed	0.01	0.03	0.016	0
PE 0112	Eggs	0.03*	-	0.01	
VL 0482	Lettuce, Head	W[2]	3		
GC 0645	Maize	0.01*	-	0.005	0
AS 0645	Maize fodder	0.01	-	0.005	
AF 0645	Maize forage	0.01*	-	0.005	0
SO 0697	Peanut	0.5	2	0.353	0.0072
OC 0697	Peanut oil, crude				0.0216
OR 0697	Peanut oil, edible				0.0281
VD 0072	Peas (dry)	0.01		0.005	0
AL 0072	Pea hay or Pea fodder (dry)	0.05		0.021	0
VO 0445	Peppers, Sweet	0.05*	0.01	0.05	0
VR 0589	Potato	W[2]	0.2		
VD 0541	Soya bean (dry)	0.01*		0.005	0
AL 0541	Soya bean fodder	0.01*		0.0055	0
AL 1265	Soya bean forage (green)	0.01*		0.005	0
VR 0596	Sugar beet	0.01*		0.005	0
AV 0596	Sugar beet leaves or tops			0.005	0
VO 0448	Tomato	0.02	0.1	0.002	0
GC 0654	Wheat	0.01		0.005	0
AS 0654	Wheat straw and fodder, dry	0.03		0.005	

[1]Withdrawal of all previous MRLs (now CXLs) was recommended by the 1995 JMPR owing to lack of supporting studies. The 29th (1997) CCPR agreed to retain them for 4 years according to the periodic review procedure

[2]This confirms the recommendation of the 1995 Meeting to withdraw the CXL.

FURTHER WORK OR INFORMATION

Desirable

Animal transfer studies on ruminants.

DIETARY RISK ASSESSMENT

The International Estimated Daily Intakes of quintozene for the five GEMS/Food regional diets were in the range of 0 to 1% of the ADI. The Meeting concluded that the intake of residues of quintozene resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

The IEDIs of hexachlorobenzene arising from the use of quintozene were estimated on the basis of the STMRs for peanuts and refined peanut oil for comparison with a Tolerable Daily Intake (TDI) of 0.00016 mg/kg bw established by WHO[1].

The IEDIs for hexachlorobenzene arising from the use of quintozene were in the range 0 to 1% of the TDI. The Meeting concluded that the intake of residues of hexachlorobenzene resulting from uses of quintozene that have been considered by the JMPR is unlikely to present a public health concern.

[1]"Hexachlorobenzene - Environmental Health Criteria 195", WHO, Geneva (1997)

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THIOPHANATE-METHYL (077)

[See also BENOMYL (069) and CARBENDAZIM (072)]

EXPLANATION

Thiophanate-methyl was first evaluated in 1973 (T,R), and the last evaluations are from 1994 (R) and 1995 (T,E). The 1994 evaluation considered desirable further information on residue in fruits and vegetables arriving from post-harvest treatment, as well as residue data on lettuce, peppers, tomatoes and sugar beets, and supporting data on crops for which CXLs are listed. The CCPR in 1994 noted that the data base for residue data was not complete (ALINORM 95/24, para 194). The periodic re-evaluation by the 1998 JMPR was confirmed by the 1997 CCPR. The main manufacture, and the government of The Netherlands and Poland (analytical method and national limits) provided data.

IDENTITY

ISO common name: thiophanate-methyl

Chemical name: dimethyl 4,4'-(*o*-phenylene)bis(3-thioallophanate) (IUPAC)
dimethyl [1,2-phenylenebis(iminocarbonothioyl)]bis[carbamate] (CAS)

CAS registry No.: 23564-05-8

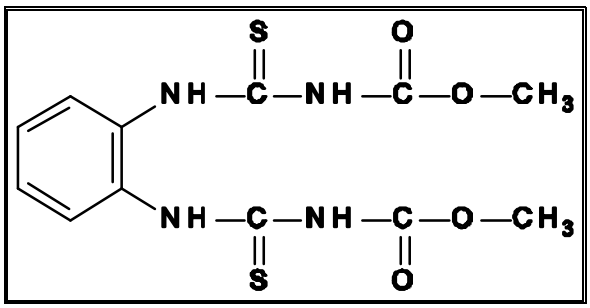
CIPAC No.: 262

Synonyms: NF-44

Molecular formula: $C_{12}H_{14}N_4O_4S_2$

Molecular weight: 342.4

Chemical structure:



Physical and chemical properties

Pure substance

Appearance: white powder

Odour: none

Vapour pressure: <1.3 x 10^{-2} mPa at 25°C(OECD No104)

Melting point: decomposition at 165.0°C(CIPAC MT-2)

Octanol/water partitition coefficient:
P_{ow} 25.3 (log P_{ow} 1.40) (Shiotani, 1992a)

Solubility: water 24.6 mg/l at 25°C
40 mg/l at 25°C

Organic solvents (g/100 ml solvent at 25°C)
acetone 2.9
methanol 0.6
acetonitrile 1.3 g/100 ml
toluene 0.04
n-Hexane 0.6 x 10^{-4}

Specific gravity: 1.45 at 20°C (CIPAC MT-3.2.1 iii)

Hydrolysis: half-life at 25°C 867 days (pH 5), 36 days (pH 7), 0.7 days (pH 9)

Dissociation constant, pKa: 7.28 at 25°C (OECD No112)

Technical grade

Melting point: decomposition 162.6 °C(CIPAC MT-2)

Stability: stable for 14 days at 54°C; for 3 years at room temperature

Formulations

Table 1 shows the formulations registered for use internationally for thiophanate-methyl. WP: wettable powder, WG: wettable granule, SC: suspension concentrate, PA: paste, OS: oily suspension, OD: oil dispersible powder, D: dustable powder

Table 1. Formulations of thiophanate-methyl.

Product	Formulation	Active ingredient	Concentration, %
ARNOS	SC	thiophanate-methyl	34.7
BOTORIRAM B	WP	Copper folpet thiophanate-methyl	10 20 10
BOTRIRAM	SC	copper folpet thiophanate-methyl	15 30 14
CASTAWAY PLUS	SC	lindane thiophanate-methyl	6 50
CERCOBIN FL	SC	thiophanate-methyl	50
CERCOBIN LIQUID	SC	thiophanate-methyl	50
CERCOBIN M	WP	thiophanate-methyl	70
COMPASS	SC	iprodione thiophanate-methyl	16.7 16.7
ENOCUPROL	D	copper thiophanate-methyl sulfur	5.0 2.5 40
ENOCUR	WP	copper thiophanate-methyl zineb	15 14 32

Product	Formulation	Active ingredient	Concentration, %
ENOCUR B	WP	copper thiophanate-methyl	23 7
ENOCUR C	WP	copper thiophanate-methyl	40 7
ENOSED TM	D	thiram thiophanate-methyl	40 40
ENOVIT F	WP	fenarimol thiophanate-methyl	4 50
ENOVIT METIL	WP	thiophanate-methyl	70
ENOVIT METIL FL	SC	thiophanate-methyl	38.3
ENOVIT METIL P	D	thiophanate-methyl	3.0
ENOVIT PZ	D	thiophanate-methyl sulfur	2.5 50
FENADOR MIX	WP	fenarimol mancozeb thiophanate-methyl	1.6 60 14
FRUMIDOR	WP	maneb thiophanate-methyl	60 14
FRUMIDOR CP	WG	clorotalonil thiophanate-methyl	50 20
FRUMIDOR-C	WP	mancozeb thiophanate-methyl	50 70
FRUMIDOR-M	WP	mancozeb thiophanate-methyl	60 14
Konker R	SC	thiophanate-methyl vinclozolin	25 25
MELPREX COMBI	WP	dodine thiophanate-methyl	32.5 35
MICEVIT P	D	maneb thiophanate-methyl zineb	3.0 2.5 2.7
MICEVIT PZ	D	maneb thiophanate-methyl sulfur	4.0 2.5 40
MILDOTHANE LIQUID	SC	thiophanate-methyl	50
NEOPTAN	WP	captan thiophanate-methyl	62 17.5
NEOTOPSIN	WP	thiophanate-methyl	70
ORGANIL 648	WP	folpet thiophanate-methyl	30 7
PELT 44 LIQUIDE	SC	thiophanate-methyl	45
PELTAR FLO	SC	maneb thiophanate-methyl	30 15
PELTIS 40	OS	thiophanate-methyl white petroleum	40 50
ROVER COMBI	SC	clorotalonil thiophanate-methyl	30 12
RUMILITE	WP	thiophanate-methyl triflumizol	45 15
RUMILITE-EX	WP	thiophanate-methyl triflumizol	45 15
SIPCAPLANT	WP	captan thiophanate-methyl	45 16
SIPCAPLANT OF	WP	captan dinocap thiophanate-methyl	32 12 10.5
SIPCASAN	WP	dodine thiophanate-methyl	35 35
SIPCASAN B	WP	dodine thiophanate-methyl	39 28

Product	Formulation	Active ingredient	Concentration, %
SIPCAVIT	SC	folpet thiophanate-methyl	45 16
SIPCAVIT Z	WP	forpet thiophanate-methyl sulfur	30 10 40
SIPCAVIT-L	SC	folpet thiophanate-methyl	40 14
SPOT	SC	cyproconazole thiophanate-methyl	5.3 30
TOCSIN	WP	thiophanate-methyl	70
TOPSIN	SC	thiophanate-methyl	45
TOPSIN COMBI	WP	mancozeb thiophanate-methyl	68 10.5
TOPSIN M PASTA	PA	thiophanate-methyl	3.0
TOPSIN M 500	SC	thiophanate-methyl	50
TOPSIN M 70	WG	thiophanate-methyl	70
Topsin M spuitpoeder	WP	thiophanate-methyl	70
Topsin M vloeibaar	SC	thiophanate-methyl	50
TOPSIN-M	WP	thiophanate-methyl	70
TOPSIN-M 70%	WP	thiophanate-methyl	70
TOPSIN-M 70%OD	OD	thiophanate-methyl	70
TOPSIN-M FL	SC	thiophanate-methyl	50
TOPSIN-M ULV	SC	thiophanate-methyl	50
TORAM	WP	thiophanate-methyl thiram	17.5 60
Valsa wax	PA	thiophanate-methyl	3.5

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Mice. An unspecified number of male dd-Y strain mice were given single doses of radiolabelled thiophanate-methyl. The mice were killed 3, 24, and 96 h after dosing, and the tissue samples analysed for the radiolabel. The faeces, urine and expired gas were analysed 3, 6, 12, 24, 48, 60, 72, 84 and 96 h after dosing, and blood samples after 3, 6, 12, 24, 48 and 72 h. The radioactivity in the blood and urine decreased steadily from peak levels within 3 h, and faecal excretion peaked at about 12 h in all cases, decreasing significantly by 48 h. The rate of excretion varied slightly between labels but the total excretion reached a plateau by about 24 h (Table 2).

Table 2. Percentage of radiolabel excreted by male dd-Y mice after 96 h.

Compound	Radiolabel excreted, % of dose			Total recovery of radiolabel by day 4, %
	Urine	Faeces	Expired gas	
[*methyl*-^{14}C]thiophanate-methyl	78	17.5	nd	95.5
[*thioureido*-^{14}C]thiophanate-methyl	66	21	nd	87
[*thioureido*-^{35}S]thiophanate-methyl	66	16	1.1	83.1
[*phenyl*-^{14}C]thiophanate-methyl	78	27	nd	105

nd = not detected

None of the labels accumulated in any organ or tissue, and they disappeared relatively rapidly within the 96-h investigation period. [*thioureido*-^{35}S] was the only label found in bone after 96 h,

suggesting that the labelled sulfur might be cleaved and hence behave differently (Fujino *et al.*, 1973).

Rats. An unspecified number of male Wistar rats were given single doses of ^{14}C-labelled thiophanate-methyl by gavage. 84% of the total administered radiolabel was excreted within 24 h, 56% in the faeces and 28% in urine, and 89% by 72 h. Table 3 shows the 24-h faecal and urinary compounds identified. Of 56% of the administered radiolabel detected in the faeces, 1% in the water-soluble phase was uncharacterized and >4% remained in the residue; of 28% of the radiolabel in the urine, 14% was not characterized because it was not extractable.

Table 3. Identified ^{14}C compounds in rat urine and faeces 24h after administration of ^{14}C-labelled thiophanate-methyl (Fujino *et al.*, 1973).

Compound	Recovery of administered ^{14}C, %	
	Faeces	Urine
Thiophanate-methyl	38	1
4-hydroxy-thiophanate-methyl (4-OH-TM)	6	3
5-hydroxy-carbendazim (5-HBC)	2	6
dimethyl 4,4´-(4-hydroxy-1,2-phenylene)bisallophanate (4-OH FH-432)	1	2
dimethyl 4,4´-(o-phenylene)bisallophanate (FH-432)	1	2
Carbendazim	1	1

Fifteen female Wistar rats were treated with [*phenyl*-U-^{14}C]thiophanate-methyl by gavage for 20 days at a dose level equivalent to 45 ppm in a daily diet of 10 g. After the last dose, the animals were fed on a normal diet for 7 days, and the faeces and urine analysed daily or every other day from the initial dose to the time of death. The rats were killed 3 h and 1, 3 and 7 days after the last dose and tissue samples analysed for the radiolabel.

An average of 89.60% of the administered radioactivity was excreted every day (urine 54.22% and faeces 35.38%). As well as the gastro-intestinal tract, some radioactivity remained temporarily in the thyroid, adrenals and liver. Table 4 shows the 24-h faecal and urinary identified metabolites.

Table 4. Recovery of ^{14}C -labelled compounds in rat urine and faeces 24h after administration of [*phenyl*-U-^{14}C]thiophanate-methyl (Kosaka *et al.*, 1975).

Compound	Recovery of administered ^{14}C, %	
	Faeces	Urine
thiophanate-methyl	2.2	0.7
4-hydroxy-thiophanate-methyl (4-OH-TM)	2.7	3.1
5-hydroxy-carbendazim (5-HBC)	11.8	28.4
dimethyl 4,4´-(4-hydroxy-1,2-phenylene)bisallophanate (4-OH FH-432)	1.6	4.6
dimethyl 4,4´-(o-phenylene)bisallophanate (FH-432)	1.1	0.6
carbendazim	1.7	3.6

Groups of five Fisher strain F344 rats of each sex were given [*phenyl*-U-^{14}C]thiophanate-methyl by gavage. Group A received single doses of 13 mg/kg bw and group B single doses of 10 mg/kg bw after 14 days of preconditioning with unradiolabelled thiophanate-methyl at 14 mg/kg bw per day; group D received single doses of 130 mg/kg bw and group C 173 mg/kg bw for males and 220 mg/kg bw for females. Blood and excreta were collected for 4 days. In all groups, >99% of the recovered radioactivity had been excreted in the urine or faeces at the time of death 4 days after treatment. Urinary excretion accounted for 52-60% of the dose in males given the low dose or preconditioned, and 31% in animals given the high dose. The average maximum concentrations of 1.7-4.2 µg/g in groups A and B were attained in blood within 1-3 h, and of 17-22 µg/g in group D within 2-4 h. The initial elimination half-lives of radioactivity in the blood were calculated to be 2.5-

2.8 h in group A, 1.6-2.2 h in group B and 2.4-4.8 h in group D. Among the tissues examined, the level of thiophanate-methyl equivalents was highest in the thyroid and liver. The 0-1 day samples of urine and faeces were combined within each group and sex for analysis. The results are shown in Table 5 (Tanoue, 1992a,b). Proposed metabolic pathways in rats are shown in Figure 1.

Table 5. Recovery of ^{14}C from rat urine and faeces 24h after administration of [*phenyl*-U-^{14}C]thiophanate-methyl.

Compound	Total recovery in faeces and urine, % of administered ^{14}C		
	group B male	group C male	group D male
thiophanate-methyl	24.2	52.4	10.0
4-hydroxy-thiophanate-methyl (4-OH-TM)	8.0	5.1	10.6
5-hydroxy-carbendazim (5-HBC)	3.3	2.0	7.0
dimethyl 4,4´-(4-hydroxy-1,2-phenylene)bisallophanate (4-OH FH-432)	0.3	0.1	0.4
dimethyl 4,4´-(*o*-phenylene)bisallophanate (FH-432)	0.1	0.1	0.1
carbendazim	2.3	1.6	2.9
5-hydroxy-carbendazim sulfate (5-HBC-S)	27.3	18.9	36.0

Dogs. An unspecified number of male beagle dogs were given single doses of [*thioureido*-^{14}C]thiophanate-methyl by capsule. Blood, urine and faeces were collected 8, 15, and 30 min and 1, 2, 3, 6, 12, 24, 35, 48, 60, 72 and 96 h after administration. The urine contained 74% of the total radiolabel and the faeces 14%. Maximal total excretion occurred after about 24 h by both routes (Fujino *et al.*, 1973).

Poultry. Thirty white leghorn laying hens were dosed daily for 10 days by capsule with the equivalent of 40–50 ppm of [*phenyl*-U-^{14}C]thiophanate-methyl. Excreta and eggs were collected daily. The hens were killed within 25 h after the last dose. No effects were observed on the vital parameters of any of the birds. Thiophanate-methyl was mainly eliminated through the excreta (up to 94%), with only a small percentage of total dose found in the tissues and eggs. The target tissues were the liver (1.66 mg/kg as thiophanate-methyl) and kidneys (1.23 mg/kg). Significant residues were also found in the egg yolks (0.54 mg/kg), and in the other tissues ranged from 0.061 to 0.145 mg/kg. The excreta contained 42.5 mg/kg at day 7.

The results indicate that thiophanate-methyl is mainly metabolized in laying hens by hydroxylation of the phenyl ring at the 3 or 4 position, followed by oxidation, cleavage and cyclization of the side chains to form 4- or 5-HBC (Figure 2). Table 6 shows the identified tissue metabolites (Wright, 1992).

Figure 1. Proposed metabolic pathways of thiophanate-methyl in rats.

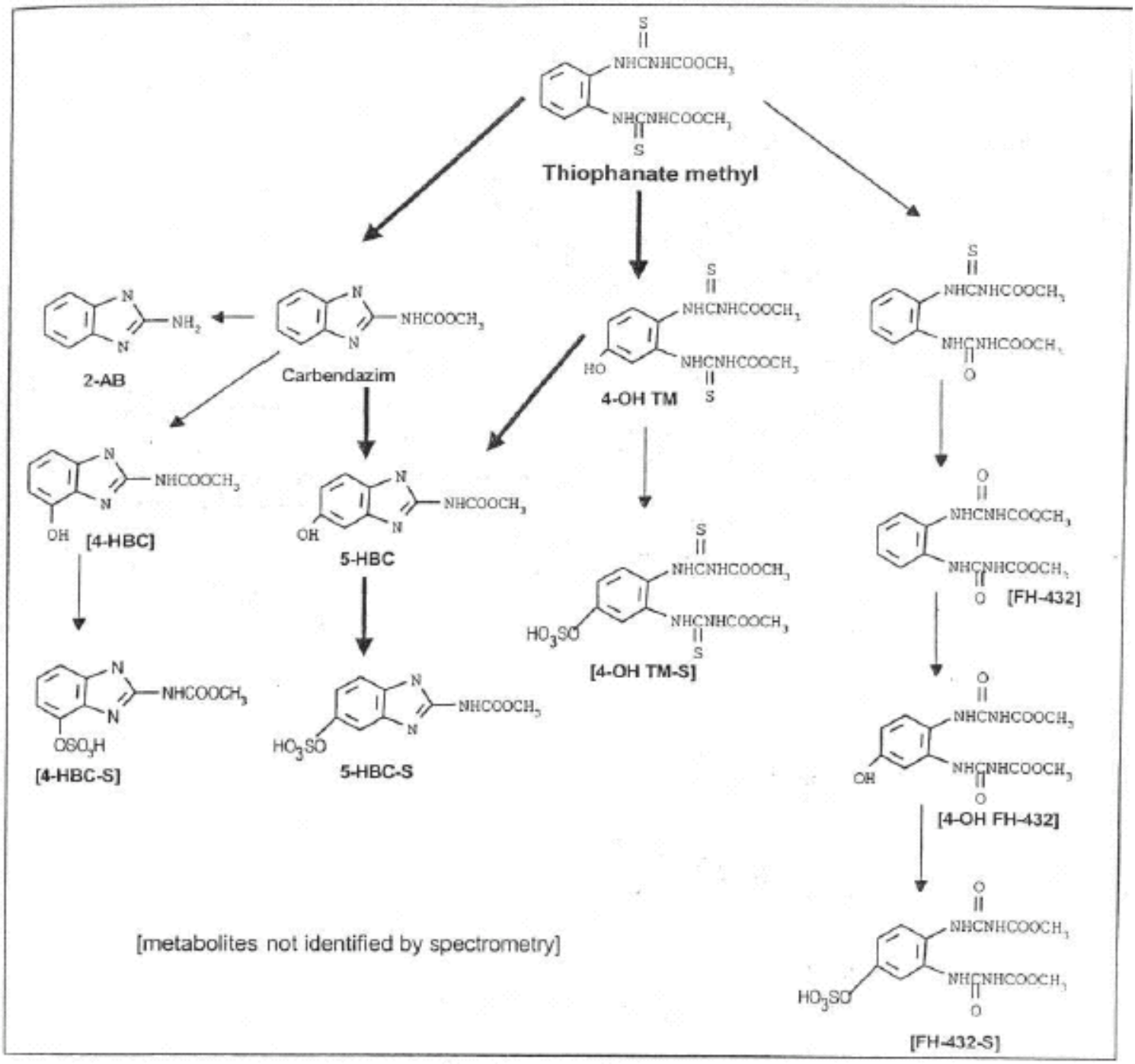


Figure 2. Proposed metabolic pathways of thiophanate-methyl in hens.

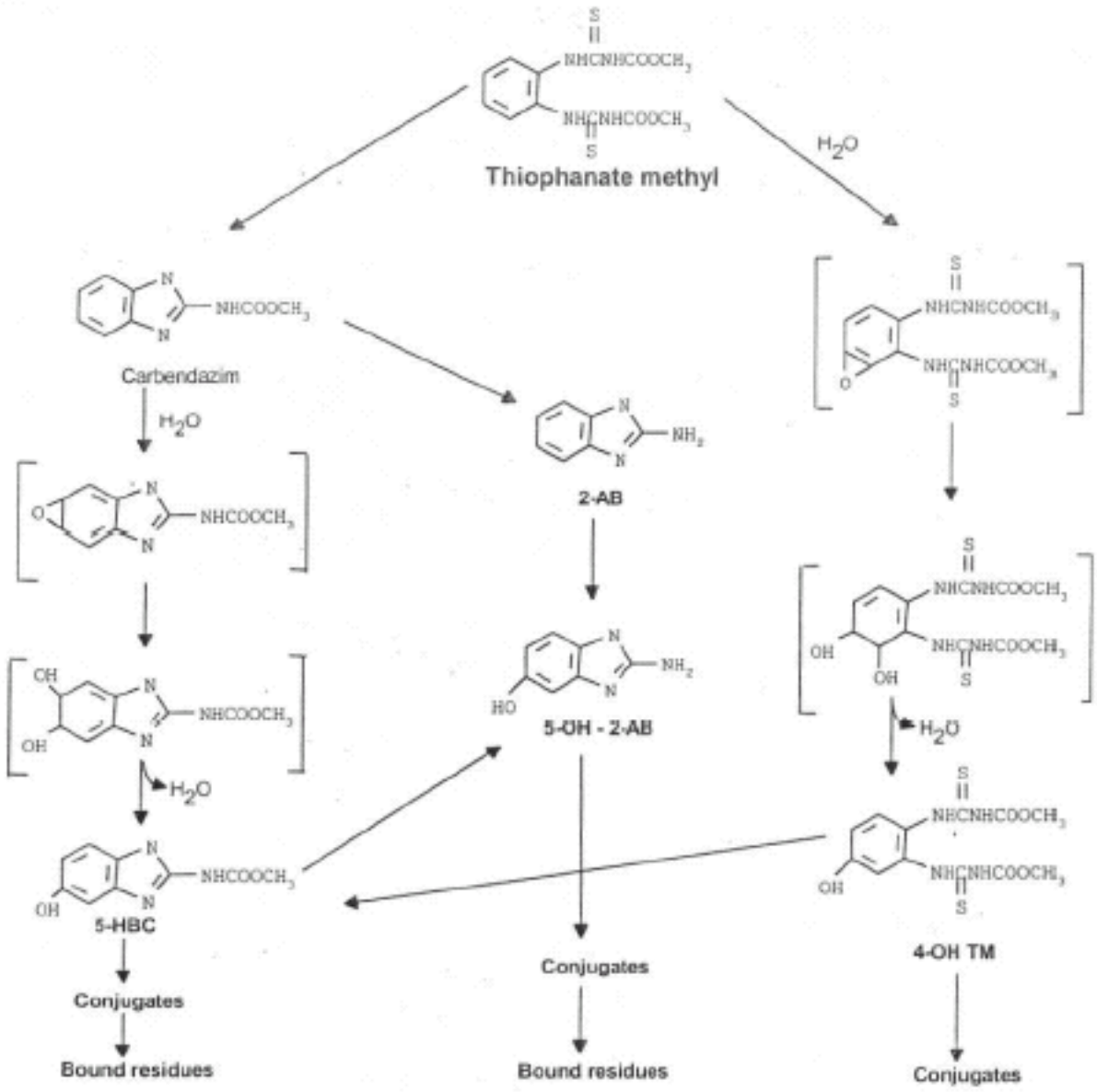


Table 6. Compounds found in hen tissues 25 h after administration of [phenyl-U-^{14}C]thiophanate-methyl.

Compound	^{14}C, mg/kg as thiophanate-methyl		
	Liver	Kidney	Egg Yolk
Total ^{14}C	1.663	1.233	0.537
Thiophanate-methyl	0.106	0.045	0.243
4-hydroxy-thiophanate-methyl (4-OH-TM)	0.026	nd	0.012
5-hydroxy-carbendazim (5-HBC)	0.105	0.179	0.056
dimethyl 4,4´-(4-hydroxy-1,2-phenylene)bisallophanate (4-OH FH-432)	nd	nd	nd
dimethyl 4,4´-(o-phenylene)bisallophanate (FH-432)	nd	nd	nd
carbendazim	0.028	0.073	0.054
5-(2-methoxycarbonylamino)benzimidazolyl sulfate (5-HBC-S)	nd	0.143	0.014
Conjugates of 4-OH-TM	0.053	0.014	nd

nd: not detected

Goats. Two lactating goats were dosed twice daily for 5 consecutive days at rates equivalent to 52.4 and 57.3 ppm of [*phenyl*-U-^{14}C]thiophanate-methyl in the diet, using a balling gun. Milk, urine and faeces were collected during the dosing period and the goats were killed approximately 14 hours after the last dose.

Thiophanate-methyl was rapidly metabolized. About 56.4% and 14.1% of the total administered dose was excreted in the urine and faeces respectively over the five days. Residues in the liver, kidney, muscle and fat constituted 2.1% of the administered dose, with maximum levels of 5.25 mg/kg, 1.3 mg/kg, 0.2 mg/kg and 0.12 mg/kg as thiophanate-methyl respectively. The milk contained 1.5% of the total dose and the residue reached 1.59 mg/kg at day 4. Table 7 shows the identified tissue metabolites (Hanlon and Norris, 1992a,b). Proposed metabolic pathways in goats are shown in Figure 3.

Table 7. Residues of thiophanate-methyl in goat tissues.

Compound	^{14}C, mg/kg as thiophanate-methyl		
	Liver	Kidney	Milk
Total ^{14}C, mean	4.72	1.21	0.847
thiophanate-methyl	0.04	0.01	0.003
4-hydroxy-thiophanate-methyl (4-OH-TM)	nd	0.04	0.008
3-hydroxy-thiophanate-methyl (3-OH-TM)	0.02	nd	nd
5-hydroxy-carbendazim (5-HBC)	0.32	0.02	0.023
4-hydroxy-carbendazim (4-HBC)	0.27	0.23	ND
carbendazim	0.19	0.27	0.085
5-hydroxy-carbendazim sulfate (5-HBC-S)	ND	0.45	0.623
UNK18’00	2.41	nd	nd

nd: not detected

On further characterization, it was concluded that UNK18’00 was the glucose conjugate of a dihydroxy-2-aminobenzimidazole (Eldeib *et al*., 1993).

Figure 3. Proposed metabolic pathways of thiophanate-methyl in goats.

Plant metabolism

Bean plants. Bean plants at the two-leaf stage were cultivated in water containing [*thioureido*-^{14}C]thiophanate-methyl or [*thioureido*-^{35}S]thiophanate-methyl for 1, 7 and 14 days. [^{14}C]thiophanate-methyl was more easily absorbed through roots than [^{35}S]thiophanate-methyl. One day after application, about 20% of the ^{14}C was detected in the roots in contrast to about 50% of the ^{35}S. However, about 40% of the applied [^{35}S]thiophanate-methyl remained in the roots, about 10% in the culture medium and a maximum of 5% in the leaves 14 days after application. About 20% of the ^{14}C radioactivity was translocated from the roots to the leaves within 14 days of application. A qualitative determination of the nature of the ^{14}C and ^{35}S radioactivity by TLC showed that thiophanate-methyl with both labels was present only in the roots and not in the leaves or stems. Carbendazim was found in all plant parts.

Other two-leaf bean plants were treated once with [*thioureido*-^{14}C]thiophanate-methyl or [*thioureido*-^{35}S]thiophanate-methyl by leaf dotting and the radiolabel was measured 14 days after application. Sixty four to 72% of the radioactivity remained in the treated leaves, but 10 to 17% was detected in the surrounding air. Translocation from the treated leaves to the roots and leaves could also be detected (2 to 9%). Four ^{14}C-labelled compounds were detected by TLC of which three were identified as thiophanate-methyl and the metabolites carbendazim and FH-432. Only two ^{35}S-labelled compounds could be detected, of which one was thiophanate-methyl and the other was not identified (Kosaka *et al.*, 1970; Noguchi *et al.*, 1971).

Five green snap bean plants with 3-4 cm pods were sprayed once with 50 mg/l of [*phenyl*-U-^{14}C]thiophanate-methyl in aqueous acetone solution and kept for 14 days in a greenhouse. Pods, leaves and stems were analysed. The total residue calculated as thiophanate-methyl was 0.47 mg/kg in pods, 23.4 mg/kg in leaves and 0.96 mg/kg in stems. About 90% of the residual radioactivity was extracted with methanol. Carbendazim (45.3% to 56.9%) and DX-105 and FH-432 (together 6.7% to 9.2%) were found in all plant parts (Nippon Soda, 1977a).

Three pairs of soya bean plants with 3.5-4.5 cm pods were sprayed once with 700 mg/l of [*phenyl*-U-^{14}C]thiophanate-methyl, one pair with a WP suspension in a greenhouse (group 1), one pair with an aqueous acetone solution outdoors (group 2), and the third pair with aqueous acetone solution in a greenhouse (group 3). The pods and leaves of all groups were analysed after 10 days. Table 8 shows the results. It is apparent that thiophanate-methyl was degraded more rapidly when sprayed as an acetone-water (1:1) solution (Nippon Soda, 1977b).

Table 8. Compounds found in soya beans 14 days after application of [*phenyl*-U-^{14}C]thiophanate-methyl.

Compound	% of TRR					
	group 1		group 2		group 3	
	pods	leaves	pods	leaves	pods	leaves
thiophanate-methyl	86.1	73.1	57.4	54.4	69.5	75.0
carbendazim	9.4	15.0	37.0	30.5	25.4	21.1
dimethyl 4,4´-(o-phenylene)bisallophanate (FH-432)	ND	3.9	5.6	8.7	3.4	3. 1
1-(3-methoxycarbonylthioureido)-2-(3-methoxycarbonylureido)-benzene (DX-105)	ND	1.0	ND	6.4	1.7	0.8

Apples. Potted young apple plants at a height of 70 cm were treated once with [*thioureido*-^{14}C]thiophanate-methyl or [*thioureido*-^{35}S]thiophanate-methyl by petiole injection and the leaves were analysed for the radiolabel 14 days after application. The metabolic pattern in apple leaves was the same as in bean leaves (Kosaka *et al*., 1970). Similar plants were also treated once with [*phenyl*-U-^{14}C]thiophanate-methyl by leaf dotting and kept in a greenhouse. Leaves were sampled after 0, 7, 14, 28, 54 and 90 days. Most of the radioactivity present was recovered by washing the leaves with chloroform, indicating that only relatively little thiophanate-methyl had penetrated into them. The identified compounds were thiophanate-methyl and the metabolites carbendazim and FH-432 (Noguchi *et al.*, 1971).

Two apple trees with mature fruit in an orchard were sprayed three times with 3.9 kg ai/ha of [*phenyl*-U-^{14}C]thiophanate-methyl at weekly intervals giving a total of 11.8 kg/ha (Alam *et al*., 1994). Samples of apples taken after one and 7 days were rinsed and separated into peel and pulp. 93.8 and 89.7% of the TRR, (the sum of the radioactive residues in the peel, pulp and rinse) were identified in the 1-day and 7-day samples respectively. Table 9 shows the results.

Table 9. Main compounds found in apples 1 and 7 days after the last application of [*phenyl*-U-^{14}C] thiophanate-methyl.

Compound	^{14}C, % of TRR and mg/kg as thiophanate-methyl			
	1 day PHI		7 day PHI	
	% of TRR	mg/kg	% of TRR	mg/kg
thiophanate-methyl	64.5	3.325	44.5	0.957
carbendazim	22.2	1.149	33.4	0.719
dimethyl 4,4´-(*o*-phenylene)bisallophanate (FH-432)	3.5	0.181	5.1	0.110
1-(3-methoxycarbonylthioureido)-2-(3-methoxycarbonylureido)-benzene (DX-105)	1.3	0.068	2.1	0.046

TRR: total radioactive residue

Grapes. Potted young vines at a height of 70 cm were treated once with [*thioureido*-^{14}C]thiophanate-methyl or [*thioureido*-^{35}S]thiophanate-methyl after 14 days (Kosaka *et al.*, 1970), or with [*phenyl*-U-^{14}C]thiophanate-methyl (Noguchi *et al.*, 1971) by leaf dotting. The leaves were analysed after 14 days (Kosaka) or after 0, 7, 14, 28, 54 and 90 days in a greenhouse (Noguchi). Most of the radioactivity present was recovered by washing the leaves with chloroform, indicating that only relatively little [^{14}C]thiophanate-methyl penetrated into them. The identified compounds were

thiophanate-methyl and the metabolites carbendazim and FH-432. FH-73 is a proposed intermediate but was not detected in the plants. Metabolism in grapes is similar to that in beans. Proposed metabolic pathways in plants are shown in Figure 4.

Figure 4. Proposed metabolic pathways of thiophanate-methyl in plants.

Environmental fate in soil

Degradation. [*Thioureido*-^{14}C]-, [*methyl*-^{14}C]- or [*thioureido*-^{35}S]-labelled thiophanate-methyl was applied to sandy loam or silty loam soils which were kept in the dark at 23°C and 33°C for 60 days. Thiophanate-methyl disappeared completely within 7 days in all cases and the main degradation product was carbendazim (Noguchi *et al.*, 1971).

[*Phenyl*-U-^{14}C]thiophanate-methyl was applied to Japanese clay loam and light clay, which were kept in the dark at 15°C and 25°C for 28 days. The half-life in light clay was about one day at both temperatures and in clay loam about 4 days at 25°C and 7 days at 15°C. The main degradation product was carbendazim, which reached maximum levels of 32% and 66% of the TRR in light clay and clay loam respectively at 25°C after 28 days. The mineralization after 28 days reached 1% at 25°C and 0.2% at 15°C in light clay and 0.2% at 25°C 0.2% at 15°C in clay loam (Nippon Soda, 1981).

Mineralization was investigated further in three Japanese soils. [*Phenyl*-U-^{14}C]thiophanate-methyl was applied to sandy loam, clay loam and light clay soils which were incubated at 22°C in the dark for 64 days. After 64 days mineralization reached 6.5%, 26.3% and 20.3% in sandy loam, clay loam and light clay respectively. The main product was carbendazim (13%, 18% and 37% respectively). No volatiles except CO_2 were detected. Thiophanate-methyl did not accumulate in the soils (Nippon Soda, 1984a).

[*Phenyl*-U-^{14}C]thiophanate-methyl was applied to sterilized Japanese sandy loam and exposed to sunlight in December (35°N latitude and 139° longitude) for 28 days. The initial half-life was calculated as 3.9 days after correcting for the dark control. The main photoproduct was carbendazim which reached 21% after 19 days exposure. Similar degradation patterns and rates were observed in both sunlight and darkness (Soeda and Shiotani, 1987a).

Solutions of thiophanate-methyl 70WP (0-5000 mg/l) were added to sandy loam or silty loam soils and kept at 30°C for 30 days. The counts of bacteria and actinomycetes were not affected. When solutions of thiophanate-methyl 50 WP (0-1000 mg/l) were percolated through sandy loam soil at 30°C for 10 days the counts of microflora were not affected. When 70 WP solutions (0-5000 mg/l) were incubated with silty loam soils at 30°C for 11 days the acceleration of respiration was proportionate to the dosage. When five strains of azotobacter were incubated at 30°C for 7 days in a medium containing thiophanate-methyl (0-500 mg/l) their growth was not affected (Kosaka *et al.*, 1972).

Adsorption

Adsorption/desorption isotherms were determined with thiophanate-methyl with the phenyl-^{14}C label.

The Freundlich constants in three Japanese soils, sandy loam, clay loam and light clay were 4.30, 5.49 and 10.2 respectively (Nippon Soda, 1984b).

Adsorption/desorption experiments were carried out with Japanese sand, silt loam, sandy loam and clay loam and one river sediment. The sandy loam was also incubated with aged residues at 22°C for 2 days. The Freundlich constant K of the parent compound was 0.3, 0.6, 3.0 and 5.7 for sand, silt loam, sandy loam and clay loam respectively and 1.5 for the aquatic sediment. The constant of the aged residues for the sandy loam was 5.5. The adsorbed thiophanate-methyl was not desorbed easily (Soeda and Shiotani, 1987b).

The Freundlich constants of thiophanate-methyl and three metabolites in four US upland soils (sand, sandy loam, loamy sand and loam) and two US paddy field soils (loam and clay loam) are shown in Table 10. Again the adsorbed thiophanate-methyl was not desorbed easily.

Table 10. Freundlich constants K of thiophanate-methyl and related compounds in upland and paddy field soils (Shiotani, 1992).

	Upland				Paddy field	
Compound	sand	sandy loam	loamy sand	loam	loam	clay loam
thiophanate-methyl	0.27	0.66	1.46	0.97	1.47	14.14
carbendazim	0.45	3.77	5.71	4.74	4.47	88.24
dimethyl 4,4´-(*o*-phenylene)bisallophanate (FH-432)	0.28	0.68	1.31	0.75	1.06	10.11
1-(3-methoxycarbonylthioureido)-2-(3-methoxycarbonylureido)-benzene (DX-105)	0.29	0.73	1.42	0.93	1.32	11.88

Mobility

The mobility of thiophanate-methyl was investigated with Japanese sandy loam, clay loam and light clay by TLC. A glass plate was coated with a water slurry of the soil at a thickness of 1 mm and [*phenyl*-U-^{14}C]thiophanate-methyl was streaked onto the soil. The plate was developed with distilled water. Simetryne and linuron were used as standard compounds. Thiophanate-methyl showed

intermediate mobility (class 3) under these conditions while simetryne and linuron were in class 2 (Nippon Soda, 1984c).

Leaching

[*Phenyl*-U-^{14}C]thiophanate-methyl was added to columns of Japanese sand, silt loam, sandy loam and clay loam. The leached radioactivity was 54.5%, 43.4%, 22.0% and 0.4% of that applied (Soeda and Shiotani, 1987c).

[*Phenyl*-U-^{14}C]thiophanate-methyl was aged for 31 days at 20°C in standard soil Speyer 2.1 and the mixture added to a column of the same soil. The recovery of ^{14}C was 1.1% in the leachate and 90% in the first 5 cm of the soil columns; 43% of the activity was from carbendazim (Bieber, 1992).

The leaching of 2-aminobenzimidazole (2-AB), a metabolite of thiophanate-methyl and carbendazim, was determined in columns of three German standard soils (two sand and one sandy loam). 2-AB was undetectable in the leachates from all three soils (Gorbach and Thier, 1989).

Environmental fate in water/sediment systems

Photodegradation in water

[*Phenyl*-U-^{14}C]thiophanate-methyl was dissolved in sterile pH 5 buffer and exposed to sunlight in December (35°N latitude and 139° longitude). The half-life was 2.17 days and the main photoproduct was carbendazim which reached 50% after 5.5 days (Soeda and Shiotani, 1987d).

Aerobic aquatic degradation.

A small amount of filtrate from a ditch bed (containing 10 or 100 µg of biomass) and 100 or 1000 µg of [*phenyl*-U-^{14}C]thiophanate-methyl was added to the oxygen-saturated water to prepare 0.1 and 1.0 mg/l test solutions at pH 7. The solutions were shaken at 20°C in the dark for 42 days and 52 days respectively. The half-life was about 15 days at 0.1 mg/l and 25 days at 1.0 mg/l. The main degradation product was carbendazim which reached 72.2% at 0.1 mg/l and 74.1% at 1.0 mg/l by the end of the experiment (Nippon Soda, 1982).

The degradation of [*phenyl*-U-^{14}C]carbendazim in two aquatic model systems under laboratory conditions was investigated during 91 days incubation. The systems consisted of river and pond water with 2% of the corresponding sediments. The initial concentration of carbendazim was 2 mg/l and its half-life 31 and 22 days in the river water and pond water respectively. The extractable radioactivity in the water of both systems decreased rapidly and could not be detected after 91 days of incubation (Ritter, 1988).

METHODS OF RESIDUE ANALYSIS

Several analytical methods used in supervised residue trials were reported. The principle is that thiophanate-methyl and carbendazim are extracted and thiophanate-methyl is converted to carbendazim by refluxing under acidic or neutral conditions. The carbendazim is determined by UV spectrophotometry, HPLC with UV detection, derivative spectrophotometry or LC-MS-MS. The detection limits are 0.02 mg/kg for UV, 0.02 mg/kg for HPLC, 0.05 mg/kg for derivative spectrophotometry and 0.003 mg/kg for LC-MS-MS (Ono, 1973; Gomyo *et al.*, 1987, 1988a; Melkebeke, 1997). The limits of determination ranged from 0.02 to 0.2 mg/kg.

In a method provided by The Netherlands government, thiophanate-methyl is partly converted to carbendazim during the analysis, which involves extraction of the compounds with

acetone/dichloromethane/petroleum ether, clean-up on diol-bonded silica SPE, and HPLC with UV-fluorescence detection. The LOD, as carbendazim, was 0.05 mg/kg and recoveries were >97.6%. Another method using ethyl acetate extraction and TLC with a spray of fungal spores, had an LOD of 0.1 mg/kg and recovery >90%.

Two methods for animal products were reported. In one method for the determination of thiophanate-methyl, DX-15, 4-OH-TM, 4-OH-FH432 and FH-432, the analytes are extracted with acetonitrile, purified by solid-phase extraction on C-18 and NH_2 cartridges and analysed by HPLC with UV or fluorescence detection. The second method was developed for the determination of carbendazim, 5-HBC, 5-HBC-S and 2-AB and involves extraction with acid acetone to hydrolyse the sulfate conjugate, ethyl acetate partition, and clean-up with an NH_2 cartridge. In both methods the limit of determination is 0.2 mg/kg (Gomyo *et al.*, 1988b).

Stability of residues in stored analytical samples

The stability of thiophanate-methyl in crops at -30°C was determined after storage for 2 years. The residue remaining at the end of the study in relation to the initial level was 98, 90, 94, 83, 78 and 71% in pears, persimmons, cabbage, soya beans and rape seed respectively. In a study with applies at 4°C, residues of thiophanate-methyl and carbendazim after 82 days were 78.8 and 100% of the initial value respectively. In another study at –20°C for 6 months, 42.3 and 68.4% of the initial thiophanate-methyl and 50 and 128% of the initial carbendazim remained at the end. In potato, thiophanate-methyl residues after 176 days at –20°C were 58.4 and 67.1% of the initial value.

USE PATTERN

Table 11 shows the registered uses of thiophanate-methyl on the crops on which supervised trials were reported as of February 1998.

Table 11. Registered uses of thiophanate-methyl

Crop	Country	Formulation	Application				PHI, days
			Number	kg ai/ha	kg ai/hl	Mode	
Citrus	Greece	WP			0.05-0.1	foliar	60
Chinese citron	Japan	WP	7		0.023-0.035	foliar	14
Orange (Unshu)	Japan	WP	7		0.023-0.07	foliar	1
Pome fruits	Greece	WP			0.06-0.12	foliar	14
	Spain	WG/WP	2	0.42-0.84	0.035-0.07	foliar	21
Apple	Belgium	SC/WP	2		0.05	foliar	14
	Denmark	SC	4	1		foliar	14
	France	SC	3-4		0.0675	foliar	
	Italy	PA	2-3		0.03-0.06	foliar	
		WP			0.035-0.105	foliar	
	Japan	WP			0.035-0.07	foliar	1
	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	14
	Portugal	WP	5-6	0.7-1.05	0.07-0.105	foliar	7
	UK	SC	12	1.1	0.05-0.33	foliar	7
		SC	1		0.05	dipping	
Pear	Belgium	SC/WP	1		0.05	foliar	14
	Denmark	SC	4	1		foliar	14
	Italy	PA	2-3		0.03-0.06	foliar	
		WP			0.035-0.105	foliar	

Crop	Country	Formulation	Application				PHI, days
			Number	kg ai/ha	kg ai/hl	Mode	
	Japan	WP			0.035-0.07	foliar	1
	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	14
	Portugal	WP	5-6	0.7	0.07	foliar	7
	UK	SC	12	1.1	0.05-0.33	foliar	7
Stone fruits	Greece	WP			0.25	foliar	14
	Italy	WP			0.042-0.049	foliar	
	Germany	SC	3	0.035	0.007	foliar	10
	Spain	WG/WP	2	0.42-0.84	0.035-0.07	foliar	21
Apricot	France	SC	3		0.0675	foliar	
	Italy	PA			0.03-0.06	foliar	
	Japan	WP	3		0.047-0.07	foliar	21
Cherry	Belgium	SC/WP	1		0.05	foliar	14
	Denmark	SC	2-3	1		foliar	14
	France	SC	3		0.0675	foliar	
	Japan	WP	3		0.047-0.07	foliar	14
Peach	France	SC	3		0.0675	foliar	
	Italy	PA			0.03-0.06	foliar	
	Japan	WP			0.047-0.07	foliar	1
Plum	Denmark	SC	2-3	1		foliar	14
	France	SC	2		0.0675	foliar	
	Italy	PA			0.03-0.06	foliar	
Blackcurrant	Denmark	SC	3-4	1		foliar	14
Gooseberry	Denmark	SC	3-4	1		foliar	14
Raspberry	Denmark	SC	3-4	1		foliar	14
Recurrent	Denmark	SC	3-4	1		foliar	14
Grapes	France	SC	1	1.35		foliar	
	France	WP	1	0.35		foliar	3 months
	Greece	WP			0.05	foliar	14
	Italy	DP 3		0.9-1.2		foliar	
	Italy	PA/SC	2-4		0.035-0.042	foliar	
	Italy	WP			0.04-0.06	foliar	
	Japan	WP	3		0.035-1.4	foliar	petal fall
	Portugal	WP	4	1.4	0.14	foliar	28
	Spain	WG /WP	3	0.5-0.7	0.05-0.1	foliar	21
Strawberry	Belgium	SC/WP		1	0.05	foliar	14
	Denmark	SC	3-4	1		foliar	14
	Greece	WP			0.07	foliar	14
	Japan	WP	3		0.14-0.233	root dipping	planting
	Spain	WG/WP	2	0.35-0.7		foliar	21
Kiwifruit	Japan	WP 70	5		0.07	foliar	1
Persimmon	Japan	WP 70			0.047-0.07	foliar	1
Onion	Japan	WP			0.07-0.14	foliar	1
	Spain	WG/WP	2	0.35-0.7		foliar	21
Onion, Welsh	Japan	WP	1		0.35-3.5	root dipping	planting
Brassica	Spain	WG/WP	2	0.35-0.7		foliar	21
Cucurbits	Greece	WP			0.05-0.07	foliar	14
Cucumber	Belgium	SC/WG/WP	1	1		foliar	3
	Japan	WP			0.035-0.047	foliar	1
	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	3
	Spain	WG/WP	2	0.35-0.7		foliar	21

Crop	Country	Formulation	Application				PHI, days
			Number	kg ai/ha	kg ai/hl	Mode	
	UK	SC	6		0.1	foliar	2
Gherkins	Belgium	SC/WG/WP	1	1		foliar	3
	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	3
Egg plant	Greece	WP	-		0.05-0.07	foliar	14
	Japan	WP			0.035-0.047	foliar	1
	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	3
	Spain	WP	2	0.35-0.7		foliar	21
Melon	Belgium	SC/WG/WP	1	1		foliar	3
	France	SC	2	0.35		foliar	
	Japan	WP	-		0.035-0.047	foliar	1
	Spain	WG/WP	2	0.35-0.7	-	foliar	21
Pepper	Belgium	SC	1	1		foliar	3
	Belgium	WG/WP	1	0.98		foliar	3
	Spain	WG/WP	2	0.35-0.7		foliar	21
Pepper, green	Japan	WP			0.035-0.047	foliar	1
Pepper, sweet	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	3
Tomato	Greece	WP			0.07	foliar	14
	Japan	WP			0.035-0.047	foliar	1
	Netherlands	SC/WP	2-3	0.34-0.42	0.042	foliar	3
	Spain	WG/WP	2	0.35-0.7		foliar	21
Lettuce	Japan	WP 70	2		0.035-0.047	foliar	7
	Spain	WG/WP	2	0.35-0.7		foliar	21
Adzuki bean	Japan	WP	4		0.07-0.1	foliar	14
Bush bean	Belgium	SC/WG/WP	1-2	0.8		foliar	6
Dwarf green bean	UK	SC	1	1	0.16-0.33	foliar	
Field bean	UK	SC	2	0.25-0.5	0.125-0.375	foliar	flowering
		SC	2	0.45-0.5	1.0-1.6	aircraft	
French bean	France	SC	2	0.75		foliar	flowering
Kidney bean	Japan	WP	4		0.07-0.1	foliar	7
Soya bean	Japan	WP	4		0.07-0.1	foliar	14
String bean	Belgium	SC/WG/WP	1-2	0.8		foliar	6
Fodder Pea	Belgium	SC		0.8		foliar	7
		WP		0.8		foliar	14
Garden pea	Japan	WP	4		0.035-0.047	foliar	7
Pea	Belgium	SC		0.8		foliar	7
	Belgium	WP		0.8		foliar	14
	France	SC	2	0.75		foliar	
	UK	SC	2	0.5	0.08-0.25	foliar	21
Sugar beet	Belgium	SC/WG/WP		0.3		foliar	-
	Greece	WP			0.05-0.07	foliar	14
	Japan	WP	5		0.023-0.035	foliar	7
	Spain	WP	2	0.21-0.28	0.03-0.04	foliar	21
Celery	Belgium	SC/WP		0.5		foliar	14
	Japan	WP	2		0.047	foliar	7
	Spain	WG/WP	2	0.35-0.7		foliar	21
Cereals	Belgium	SC/WG/WP	-	0.3-0.4		foliar	28
	Denmark	SC	1	0.4-0.5		foliar	14
	Spain	WG/WP	1	0.35-0.7	0.07-0.14	foliar	21
Barley	France	SC	1	0.75		foliar	2 months

Crop	Country	Formulation	Application				PHI, days
			Number	kg ai/ha	kg ai/hl	Mode	
	Germany	SC	1	0.5	0.125	foliar	56
	Italy	WP		0.35-0.42	0.07-0.105	foliar	
	Japan	WP	3		0.028-0.07	foliar	14
	UK	SC	1	0.5	0.17-0.25	foliar	
Rice	Japan	WP	1		0.14-2.33		
Wheat	Denmark	WP	1-2	0.21-0.263		foliar	28
	France	SC	1	0.75		foliar	1 month
	Germany	SC	1	0.5	0.125	foliar	56
	Italy	PA		1.8-2.6	0.45-0.52	foliar	
		WP			0.32-0.4	dressing	
		WP		0.35-0.42	0.07-0.105	foliar	
	Japan	WP	3		0.028-0.07	foliar	14
Wheat, winter	UK	SC	1	0.5-0.7	0.17-0.35	foliar	
Cruciferous oily crops	France	SC 150	1	0.75		foliar	1.5 months
Rape	Denmark	SC	1	0.5		foliar	14
	Germany	SC	1	0.375	0.094	foliar	56
	UK	SC	2	1	0.33-0.5	foliar	21
Rape, winter	Germany	SC	1	0.5	0.083-0.167	foliar	56
Tea	Japan	WP	2		0.035-0.047	foliar	7

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of residue trials are shown in Tables 12 to 35. Trials with the same entry in the Tables were carried out at the same site. Some trial sites were divided into sub-plots separated from each other by a sufficient distance to avoid the possibility of contamination by spray drift. Residue data from sub-plots treated with exactly the same application regime are regarded as being from a single trial. Unless otherwise indicated, all trials were conducted outdoors with foliar sprays. Underlined or double underlined residues were from trials according to GAP or maximum GAP (± 30%) respectively, and were used to estimate maximum residue levels and STMRs. Residues are the sum of thiophanate-methyl and carbendazim expressed as carbendazim.

Additional data were provided from trials carried out in the USA and Germany, but these were not evaluated because full study reports and/or labels were not supplied.

Citrus fruits. In two trials on Chinese citron in Japan at twice the GAP rate (7 x 0.023-0.035 kg ai/hl), residues 14 days PHI were 1.8 and 2.3 mg/kg in the peel and <0.02 mg/kg in the pulp. Residues in the peel decreased up to 75% from day 1 to 14, but did not change during the same period in the pulp (Table 12).

In two trials on oranges in Japan at the GAP rate (7 x 0.023-0.07.kg ai/ha), residues at 1 day PHI were 2.5 and 6.5 mg/kg in the peel, 0.06 and 0.09 mg/kg in the pulp and 0.09 and 0.14 mg/kg in the juice. The residues decreased approximately 90% in the peel after 14 or 28 days, but either increased or decreased during the same period in the pulp.

Table 12. Results from residue trials with thiophanate-methyl in Japan (1973) on oranges and Chinese citron with WP formulation

Application			PHI,	Sample	Residues,	
kg ai/ha	kg ai/hl	No.	days		mg/kg	Reference
Chinese citron						
4.2	0.07	8	1	peel	3.4	RD-9809
			1	pulp	<0.02	
			7	peel	2.33	
			7	pulp	<0.02	
			14	peel	1.8	
			14	pulp	<0.02	
4.2	0.07	8	1	peel	8.8	RD-9809
			1	pulp	<0.02	
			7	peel	7.8	
			7	pulp	<0.02	
			14	peel	2.3	
			14	pulp	<0.02	
Orange						
3.5	0.07	8	1	peel	2.5	RD-9809
			1	pulp	0.06	
			1	juice	0.09	
			7	peel	0.93	
			7	pulp	0.11	
			14	peel	0.19	
			14	pulp	0.03	
4.9	0.07	9	1	peel	6.5	RD-9809
			1	pulp	0.09	
			1	juice	0.14	
			7	peel	2.7	
			7	pulp	0.10	
			14	peel	0.89	
			14	pulp	0.16	
			28	peel	0.74	
			28	pulp	0.12	

Apples. Thirty six trials were conducted in Europe and two in Japan. In France, two trials at the GAP rate (3-4 x 0.0675 kg ai/hl) gave residues of 0.57 and 0.31 mg/kg at a PHI of 1 day. Data from 16 dipping trials at 0.02-0.07 kg ai/hl gave residues from 0.25 to 1.3 mg/kg 78 or 135 days after treatment, but no post-harvest GAP was reported to evaluate them.

In one trial in Denmark and 16 in the UK above the GAP rate (1 or 1.1 kg ai/ha) or with excessive PHIs, residues after 8 to 16 applications up to 4.2 kg ai/ha ranged from <0.2 to 2.5 mg/kg after 2 to 78 days. In one trial in the UK at twice the recommended rate for post-harvest treatment (0.05 kg ai/hl) the residues decreased from 1.2 to 0.7 mg/kg between 74 and 137 days after the treatment (Table 13).

In two trials in Japan at the GAP rate (7 x 0.07 kg ai/hl), residues at the GAP PHI of 1 day were 0.25 and 1.0 mg/kg.

Table 13. Results from residue trials with thiophanate-methyl on apples.

Country, year	Form.	Application			Days after treatment	Residues, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl			
Denmark 1974	WP	10	1.75	0.35	2 4 8 16	0.62 0.36 0.55 0.42	EN/BBP-10.3.1975
France	WP	3	0.49	0.07	1	0.57	C00146
1971	WP	3	0.49	0.07	1	0.31	
1977	WP	1	90 sec. dip	0.02	78	0.25	15.12.1977
	WP	1	90 sec. dip	0.035	78	0.42	
	WP	1	90 sec. dip	0.05	78	0.25	
	WP	1	90 sec. dip	0.07	78	0.54	
	SC	1	90 sec. dip	0.02	78	0.46	
	SC	1	90 sec. dip	0.035	78	0.38	
	SC	1	90 sec. dip	0.05	78	0.59	
	SC	1	90 sec. dip	0.07	78	0.75	
1978	WP	1	90 sec. dip	0.02	135	0.37	13.02.1978
	WP	1	90 sec. dip	0.035	135	0.58	
	WP	1	90 sec. dip	0.05	135	0.73	
	WP	1	90 sec. dip	0.07	135	0.84	
	SC	1	90 sec. dip	0.02	135	0.47	
	SC	1	90 sec. dip	0.035	135	0.73	
	SC	1	90 sec. dip	0.05	135	0.78	
	SC	1	90 sec. dip	0.07	135	1.3	
Japan 1973	WP	10	3.5	0.07	1 7 14	0.25 0.27 0.28	RD-9809
	WP	10	1.8-4.2	0.07	1 7 14	1.0 0.82 0.29	
UK [1] 1970	WP	8	2.2	-	3 14	2.1 1.5	RG/989 11
	WP	8	2.2	-	3 14 42	2.5 1.3 1.0	11A
	WP	8	2.2	-	3 14 56	2.2 0.8 0.3	13
	WP	8	2.2	-	3 14 56	0.8 1.2 <0.2	17
	WP	8	-	0.1	3	2.2	14
	WP	8	-	0.1	3	1.7	18
1971	WP	12	1.1		78	0.1	RG/1341
	WP	12	1.5		78	0.1	
	WP	16	0.56-1.1		24	0.5	
	WP	15	0.77-1.5		24	1.1	
	WP	12	0.84		70	0.1	
	WP	12	1.1		70	<0.1	
	WP	11	1.1		14	0.6	
	WP	11	1.5		14	0.4	

Country, year	Form.	Application			Days after treatment	Residues, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl			
		1	dip[1]	0.1	74 54 84 115 119 123 137	1.2 1.5 0.9 1.5 1.0 1.1 0.7	RG/1392
1972	WP	8	1.1		85	0.1	RG/1581
	WP	8	1.1		88	0.1	

[1]Results were corrected for recoveries

Pears. Two trials in Japan at the GAP rate (0.07 kg ai/hl) gave residues at 1 day of 0.54 and 0.94 mg/kg. In four trials in the UK at higher rates or longer or shorter PHIs than GAP (1.1 kg ai/ha, 7 days PHI) the residues after 3 to 60 days varied from 1.7 to <0.1 mg/kg. In two trials with post-harvest treatments at twice the recommended rate (0.05 kg ai/hl), residues were 1.2 mg/kg at day 0 and 0.9 and 1.3 mg/kg after 161 and 61 days respectively (Table 14).

Table 14. Results from residue trials with thiophanate-methyl on pears with WP formulation.

Country, year	Application			Days after treatment	Residues mg/kg	Reference
	No.	kg ai/ha	kg ai/hl			
Japan 1987	8 8 8	2.1	0.07	1 3 7	0.54 0.76 0.37	RD-9809
	8 8 8	3.5	0.07	1 3 7	0.94 0.71 0.66	RD-9809
UK[1] 1970	7	2.2		3 14 56	1.7 0.7 0.4	RG/989
	7		0.1	3	1.7	RG/989
1971	7	1.1		60	<0.1	RG/1393
	7	1.5		60	<0.1	RG/1393
1972	1	dipping	0.1	0 161	1.2 0.9	RG/1639
		dipping	0.1	0 61	1.2 1.3	

[1]Results were corrected for recoveries

Apricots. Eight trials were in Italy with 1 application of 0.76 to 2.16 kg ai/ha gave residues after 14 to 28 days of 0.07 to 0.39 mg/kg. The information on GAP was inadequate so the trials could not be evaluated (Table 15).

Table 15. Results from residue trials with thiophanate-methyl on apricots in Italy (1991-1992) with 1 application of SC formulation.

Application		PHI,	Residue,	
kg ai/ha	kg ai/hl	days	mg/kg	Reference
1.36	-	14	0.07	N.5 1993
1.45	-	21	0.09	
1.06	-	14	0.13	
0.76	-	14	0.08	
1.38	-	21	0.09	
0.99	-	21	0.11	
2.0	-	14 21 28	0.03 0.08 0.07	N.5 1994
2.16	-	14 21 28	0.39 0.35 0.19	

Cherries. Two decline trials in France below the recommended rate (3 x 0.0675 kg ai/hl) gave residues at day 0 of 2.1 and 3.6 mg/kg decreasing to 0.13 and 0.25 mg/kg after 20 days. One trial in the UK according to French GAP gave residues of 0.17 mg/kg at day 0 (Table 16).

Table 16. Results from residue trials with thiophanate-methyl on cherries.

Country year	Formulation	Application			PHI,	Residues,	
		No.	kg ai/ha	kg ai/hl	days	mg/kg	Reference
France 1988	SC	1	0.45	0.045	0 1 3 6 13 20	2.1 2.0 2.0 0.35 0.22 0.13	F90A0288/1
	SC	1	0.90	0.090	0 1 3 6 13 20	3.6 3.6 2.6 0.90 0.38 0.25	F90A0588/2
UK 1973	WP	3		0.05	0	0.17	

Peaches. In France, 3 trials at the GAP rate (3 x 0.0675 kg ai/hl) gave residues from <0.05 to 0.13 mg/kg at 12 or 19 days. Two decline trials at lower rates showed that residues decreased by about 65 to 90% from day 0 to day 21 (Table 17).

Thirteen trials, two post-harvest, were conducted in Italy. One or 2 foliar applications of 0.51 to 1.68 kg ai/ha gave residues ranging from 0.03 to 0.48 mg/kg, but the spray concentration was not reported; GAP is 0.0675 kg ai/hl. Dipping in 0.25 kg ai/hl gave residues of 0.88 to 1.3 mg/kg after 0 to 14 days. No post-harvest GAP was reported.

In two trials in Japan at the GAP rate (0.47-1.4 kg ai/ha) residues at the GAP PHI of 1 day were 19 and 21 mg/kg in the peel and 0.33 and 0.17 mg/kg in the pulp.

Table 17. Results from residue trials with thiophanate-methyl on peaches.

Country year	Formulation	Application			Days after treatment	Sample	Residues, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl				
France	SC	3	0.675		12	fruit	0.13	F23B0188
1988	SC	3	0.675		19	fruit	0.08	
	SC	3	0.675		12	fruit	<0.05	
	SC	1	0.9	0.09	0 1 3 7 14 21	fruit	3.0 4.1 3.6 1.8 0.74 1.1	F90A0488/2
	SC	1	0.45	0.045	0 1 3 7 14 21	fruit	2.6 3.2 2.9 0.92 0.29 0.28	F90A0488/1
Italy 1991	SC	1	1.68		15 22	fruit	0.06 0.09	N.5 1993
	WG	1	1.53		15 22	fruit	0.15 0.06	
	WG	1	1.09		15 22	fruit	0.13 0.12	
	SC	1	1.27		15	fruit	0.10	
	SC	1	0.85		21	fruit	0.03	
	WG	1	0.997		15	fruit	0.07	
	WG	1	0.66		21	fruit	0.35	
	WG	1	0.71		15	fruit	0.07	
	WG	1	0.51		21	fruit	0.03	
1992	SC	2	2.12		14 21 28	fruit	0.48 0.44 0.35	N.5 1994
	SC	2	2.40		14 21 28	fruit	0.44 0.28 0.47	
	SC	1	dip	0.25	0 7 14	fruit	1.2 0.88 1.1	
	SC	1	dip	0.25	0 14	fruit	1.2 1.3	
Japan 1989	WG	7	3.5	0.07	1 1 3 3 7 7	peel pulp peel pulp peel pulp	21 0.33 36 0.40 24 0.41	RD-9809 trial-1
	WG	6	3.5	0.07	1 1 3 3 7 7	peel pulp peel pulp peel pulp	19 0.17 22 0.22 12 0.18	RD-9809 trial 2

Plums. In three trials in France according to GAP (3 x 0.0675 kg ai/hl), residues varied from 0.10 to 0.19 mg/kg after 2 to 19 days. Four decline trials with fewer applications showed residues from 0.66 to 0.95 mg/kg at day 0, which decreased to <0.05 mg/kg after 14 or 21 days (Table 18).

Five studies in Italy with 1 application of 1.09 to 1.71 kg ai/ha gave residues from <0.05 to 0.33 mg/kg after 15 to 28 days, but the spray concentration was not reported; GAP is 0.0675 kg ai/hl.

Table 18. Results from residue trials with thiophanate-methyl on plums with SC formulation.

Country, year	Application			PHI, days	Residues, mg/kg	Reference
	No.	kg ai/ha	kg ai/hl			
France 1988	3	0.675		2	0.19	F23B0688
	3	0.675		19	0.10	F23B0588
	3	0.675		14	0.13	F23B0488
	1	0.459	0.09	0 1 3 7 14 21	0.95 0.70 0.26 0.22 0.12 <0.05	F90A0688/2
	1	0.229	0.045	0 1 3 7 14 21	0.66 0.75 0.30 0.10 <0.05 <0.05	F90A0688/1
	1	0.405	0.09	0 1 3 7 14 21	0.74 0.69 0.28 0.15 <0.05 <0.05	F90A0588/2
	1	0.220	0.045	0 1 3 7 13 21	0.66 0.55 0.35 0.08 <0.05 <0.05	F90A0588/1
Italy 1991	1	1.68		15 22	<0.05 0.05	N.5 1993
	1	1.53		15 22	0.06 <0.05	N.5 1993
	1	1.09		15 22	<0.05 <0.05	N.5 1993
1992	1	1.20		14 21 28	0.33 0.25 0.18	N.5 1994
	1	1.71		14 21 28	0.10 0.05 0.03	N.5 1994

Berries. Twenty one trials in the UK on berries and currants with 3 to 8 applications of 1.12 to 8.4 kg ai/ha gave residues from <0.2 to 19 mg/kg 0 to 60 days after the last treatment. No GAP was reported with which to evaluate the trials (Table 19).

Table 19. Results from residue trials with thiophanate-methyl on berries and currants in the UK with WP formulation.

Crop year	Application No.	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference
Blackberry 1973	3		0.05	0	4.6	RG/1786
Gooseberry 1972	4	1.12	0.05	0 1 3	1.5 0.8 0.9	RG/1430
	4	1.12	0.05	0	2.1	
	3	1.12	0.05	28	0.4	
	3	1.12	0.05	0 1	1.2 1.1	
	3	1.12	0.05	51	<0.2	
Raspberry 1972	8	1.12	0.05	0 1 3	7.1 7.1 7.6	RG/1439
Raspberry	7	1.12	0.05	0 1 3	3.3 2.6 1.8	RG/1439
Black currant 1971	6	3.78-6.72		1 4 7 14	4.4 6.5 4.1 2.9	RG/12883A
	6	3.78-6.72		1 4 7 14	5.6 6.2 3.3 3.3	RG/12883B
	4	6.42-8.40		1 3 7	19 15 7.2	RG/1289E
	4	6.42-8.40		1 3 7	12 11 7.2	
Black currant 1972	5	1.12	0.05	0	4.0	RG/1456
	4	1.12	0.05	53	1.3	
	4	1.12	0.05	53	1.3	
	5	1.12	0.05	0	2.1	
	4	1.12	0.05	60	0.9	
	5	1.12	0.05	0	1.3	
	4	1.12	0.05	41	1.2	
	5	1.12		37	0.3	RG/1614
	7	1.12		37	0.5	

Grapes. In twenty trials in Italy with 2 applications of 0.5 to 2.6 kg ai/ha the residues after 14 to 28 days ranged from 0.13 to 2.1 mg/kg. The information on GAP in Italy was inadequate to evaluate the trials, but four trials complied with GAP in Spain (0.5-0.7 kg ai/ha, PHI 21 days) and one with GAP in Portugal (4 x 1.4 kg ai/ha, PHI 28 days). The residues in these at PHIs of 22 or 28 days ranged from 0.21 to 1.9 mg/kg (Table 20).

Two trials in Japan at the GAP rate (3 x 0.035-1.4 kg ai/hl) gave residues of 0.27 and 0.31 mg/kg after 74 and 62 days respectively. Four trials in Portugal at GAP application rates gave residues of 1.3 and 1.1 mg/kg at 28 days and from 1.1 to 3.2 at day 7.

Table 20. Results from residue trials with thiophanate-methyl on grapes.

Country year	Formulation	Application No.	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference
Italy 1991	SC	2	2.60		15 22	0.23 0.13	N.4 1993
	WG	2	1.46		15 22	0.34 1.0	
	WG	2	1.46		15 22	0.58 1.2	
	SC	2	1.568		14 22	0.92 0.63	
	WG	2	1.02		14 22	0.96 0.80	
	WG	2	1.428		14 22	2.1 1.9	
	SC	2	1.68		15 22	0.27 0.30	
	WG	2	1.095		15 22	0.68 1.0	
	WG	2	1.53		15 22	0.94 1.5	
	SC	2	0.949- 0.988		15 22	0.905 0.57	
	WG	2	0.497- 0.553		15 22	0.62 0.36	
	WG	2	0.710- 0.800		15 22	1.3 0.87	
	SC	2	1.04		14 22	0.31 0.25	
	WG	2	0.568		14 22	0.51 0.21	
	WG	2	0.800		14 22	0.71 0.56	
	SC	2	1.90- 2.44		15 22	0.84 1.1	
	WG	2	1.292- 1.368		15 22	0.50 0.22	
	WG	2	1.742- 1.912		15 22	1.5 0.91	
1992	SC	2	1.68		14 21 28	3.1 1.5 1.9	N.5 1994
	SC	2	2.50		14 21 28	0.38 0.87 0.24	
Japan 1991	WP	3	1.75	0.07	74	0.27	RD-9809
	WP	3	2.45	0.07	62	0.31	
Portugal 1996	WP	4	1.4	0.14	0 7 14 21 28	1.9 1.1 1.1 3.2 1.3	
	WP	4	1.4	0.14	0 7 14 21 28	0.75 2.2 0.91 1.4 1.1	

Country year	Formulation	Application No.	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference
	WP	4	1.4	0.14	0 4 7	3.8 1.7 3.2	
	WP	4	1.4	0.14	0 4 7	4.8 2.1 2.9	

Strawberries. One trial in Denmark which exceeded the GAP rate (1.0 kg ai/ha) gave residues after 22 days of 0.96 mg/kg. Two trials in The Netherlands and 7 in the UK with 1 to 5 applications of 1.12 to 3.99 kg ai/ha gave residues after 3 to 31 days of <0.2 to 2.64 mg/kg (Table 21). The trials did not comply with reported GAP.

Table 21. Results from residue trials with thiophanate-methyl on strawberries with WP formulation.

Country, year	Application No.	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference
Denmark 1974	3	1.5	0.075	22 27 31	0.96 1.19 0.84	EN/BBP-10.3.1975
Netherlands 1973	5	1.5	0.1	0 8 14	2.41 2.01 0.88	R 4023
	5	1.5	0.1	0 7 15	2.17 0.81 0.65	
UK 1970	1	1.68		0 4 7	8.14 2.64 1.67	RG/1287
1971	3	2.24		1 3	2.44 1.24	RG/1287 +RG/1319
	4	2.24-2.69		1 4	1.80 1.95	
	4	2.69-3.99		1 4	2.53 2.37	
1972	4	1.12		0	<0.2	RG/1440
	3	1.12		31	<0.2	
	3	1.12		31	<0.2	
	4	1.12		0	0.3	
	3	1.12		26	0.2	

Kiwifruit. Two trials in Japan at the GAP concentration rate of 0.07 kg ai/hl gave residues of 45 and 68 mg/kg in the peel and 0.10 and 0.61 mg/kg in the pulp at the GAP PHI of 1 day, but 0.36 and 0.20 mg/kg in the pulp at 3 days. Residues in the peel increased after 7 days (Table 22).

Table 22. Results from residue trials with thiophanate-methyl on kiwifruit in Japan (1988) with 5 applications of WP formulation

Application		PHI,	Sample	Residue,	
kg ai/ha	kg ai/hl	days		mg/kg	Reference
1.75	0.07	1	peel	68	RD-9809
		1	pulp	0.61	
		3	peel	62	
		3	pulp	0.36	
		7	peel	71	
		7	pulp	0.11	
2.8	0.07	1	peel	45	
		1	pulp	0.10	
		3	peel	44	
		3	pulp	0.20	
		8	peel	61	
		8	pulp	0.06	

Persimmons. One trial in Italy in 1992 with 1 application of 1.2 kg ai/ha of SC formulation gave residues of 0.08, 0.07 and 0.07 mg/kg after 14, 21 and 28 days. No relevant GAP was reported.

Onions. Two trials in Japan with 10 applications at the GAP concentration (0.14 kg ai/hl) gave residues of <0.02 and 0.04 mg/kg at the GAP PHI of 1 day.

One trial in The Netherlands and 7 in the UK with seed dressing and/or foliar treatments gave residues from <0.03 to 12.3 mg/kg after 0 to 268 days (Table 23). No relevant GAP was reported.

Table 23. Results from residue trials with thiophanate-methyl on bulb onions with WP formulation.

Country	Application				PHI,	Residue,	
year	No.	Method	kg ai/ha	kg ai/hl	days	mg/kg	Reference
Japan 1973	10	foliar	1.4	0.14	1 7 14	<0.02 <0.02 <0.02	RD-9809
	10	foliar	2.6	0.14	1 7 14	0.04 0.03 <0.02	
Netherlands 1972	3	seed dress & foliar	0.02 kg ai/kg seed 0.75 (x2)		28 38 41	<0.03 <0.03 <0.03	R4212
UK	1	foliar	1.12		0	3.2	RG2051
1973	2	foliar	1.12		0 78 145	3.5 <0.3 <0.3	
	1	foliar	1.12		4	1.8	
	2	foliar	1.12		2 54 121	12.3 <0.3 0.3	
	1	seed dress	0.25 kg ai /kg seed		248	1.1	
	1	seed dress	0.25 kg ai /kg seed		268	0.2	
	1	seed dress	0.25 kg ai /kg seed		268	0.3	
	2	seed dress & foliar	0.25 kg ai /kg seed		143	0.2	
	1	seed dress	0.25 kg ai /kg seed		249	0.2	

Brussels sprouts. Two trials in The Netherlands (1972) with 2 applications of 1.4 kg ai/ha (0.21 kg ai/hl) of WP formulation gave residues of 3.2 and 4.3 mg/kg after 21 days. No relevant GAP was reported for northern Europe.

Cucumbers and gherkins. One trial in Denmark and 3 trials in The Netherlands below or above the GAP concentration in The Netherlands (2-3 x 0.07 kg ai/hl) gave residues at PHIs of 1-3 days ranging from <0.1 to 0.51 mg/kg. Five trials in the UK (GAP 6 x 0.1 kg ai/hl) with foliar or drench treatments gave residues after 0 to 6 days from <0.2 to 0.3 mg/kg (Table 24). The UK trials could not be related to GAP.

Table 24. Results from residue trials with thiophanate-methyl on cucumbers with WP formulation.

Country, year	Application			PHI, days	Residues, mg/kg	Reference
	No.	kg ai/ha	kg ai/hl			
Denmark 1974	1		0.07	0 1 4 7 10	0.20 0.26 0.19 0.07 0.04	EN/BBP
Japan 1973	6	0.7-1.2	0.047	1 3 7	0.27 0.18 0.06	RD-9809
	10	0.3-1.0	0.07	1 3 7	0.12 0.11 0.10	
Netherlands 1970	1		0.1	0	<0.1	R3581
	5		0.1	1	<0.1	
1972 (gherkins)	-		0.1	0 3	1.01 0.51	R4089
UK 1972	4	0.28 g ai /plant drench		0 3 9	<0.2 <0.2 <0.2	RG/1505
	4	1.12		0	0.3	
	3	0.28 g ai /plant drench		0 3 7	<0.2 <0.2 <0.2	
	4	1.12		0 1	0.2 <0.2	
	3	0.28 g ai /plant drench		0 6 10	0.3 0.3 <0.2	

Mushrooms. Ten trials in The Netherlands with 1 application of 10.1 to 73.2 kg ai/ha gave residues of 0.21 to 1.3 mg/kg after 17 to 33 days. No relevant GAP was reported (Table 25)

Table 25. Results from residue trials with thiophanate-methyl on mushrooms in The Netherlands (1972/1973) with 1 application of WP formulation

kg ai/ha	PHI, days	Residues, mg/kg	Reference
14.0	22	0.21	R 4214
14.0	23	0.17	R 4214
48.8	28	0.7	RG/1575
73.2	22	0.4	RG/1575
10.7	33	0.5	RG/1792
16.2	33	0.3	RG/1792
12.2	24	0.4	RG/1792
20.1	17	1.1	RG/1792
10.1	17	0.3	RG/1792
26.5	19	0.6	RG/1792
26.5	17	1.3	RG/1792

Tomatoes. Two trials in Italy with 2 x 1.2 kg ai/ha gave residues of <0.02 to 0.11 mg/kg after 14 to 28 days. Eight trials in the UK with drench or foliar treatments gave residues of <0.2 to 0.6 mg/kg at day 0. No relevant GAP was reported.

In four trials in Japan at the GAP rate (0.035-0.047 kg ai/hl) or higher, residues at the GAP PHI of 1 day were 0.31 to 0.73 mg/kg (Table 26).

Table 26. Results from residue trials with thiophanate-methyl on tomatoes.

Country year	Formulation	Application			PHI, days	Residue, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl			
Italy 1992	SC	1	1.20		14 21 28	<0.02 <0.02 <0.02	N.7 1994
	SC	6	1.20		14 21 28	0.113 0.085 0.025	
Japan 1973	WP	10	1.05-4.2	0.07	1 7 14	0.69 0.56 0.31	RD-9809
	WP	10	1.05	0.07	1 7 14	0.31 0.19 0.12	
1989	WP	6	1.4	0.047	1 3 7	0.73 0.49 0.61	
	WP	6	1.4	0.047	1 3 7	0.59 0.49 0.46	
UK 1972	WP	4	2.24		0 1	2.3 2.0	RG/1513
	WP	4	2.24		0 0	1.5 1.8	
	WP	3	drench	0.05	0 1 4	0.6 0.7 0.2	
	WP	4	drench	0.05	0 14	0.3 <0.2	

Country year	Formulation	Application No.	kg ai/ha	kg ai/hl	PHI, days	Residue, mg/kg	Reference
	WP	3	2.24		0 1	3.0 5.7	
	WP	3	drench	0.05	0 9	<0.2 <0.2	
	WP	5	2.24		0 1	2.2 2.3	
	WP	3	drench	0.05	0 5 9	0.2 0.2 0.1	

Other fruiting vegetables. One trial on egg plant, one on melons and two on peppers in Italy with 1.2 kg ai/ha gave residues from <0.02 to 0.11 mg/kg after 9 to 23 days. No Italian GAP was reported but one trial on melons which complied with Spanish GAP (2 x 0.35-0.7 kg ai/ha) gave residues of 0.11 mg/kg at the GAP PHI of 21 days (Table 27)

Table 27. Results from residue trials with thiophanate-methyl on fruiting vegetables in Italy (1992) with 2 applications of SC formulation.

Crop	kg ai/ha	PHI, days	Residues, mg/kg	Reference
Egg plant	1.2	14 21 28	0.04 0.03 0.02	N.8 1994
Melon	0.8	14 21 28	0.06 0.11 0.15	
	1.2	14 21 28	<0.02 <0.02 <0.02	
Pepper	1.2	9 16 23	0.08 0.06 <0.02	
	1.2	14 21	0.02 <0.02	

Lettuce. Seven trials in the UK with 1-3 applications of 0.05 kg ai/hl or 1.2 kg ai/ha gave residues from 0.7 to 7.3 mg/kg after 0 or 1 days and <0.1 to 0.9 mg/kg after 8 to 60 days. In three trials in glasshouses at 0.05 kg ai/hl, residues after 14 to 49 days ranged from 1.1 to 6.7 mg/kg (Table 28). No relevant GAP was reported

Table 28. Results from residue trials with thiophanate-methyl on lettuce in the UK.

Formulation	Application			PHI, days	Residue, mg/kg	Reference
	No.	kg ai/ha	kg ai/hl			
WP	3	1.12		1 8 15	5.7 0.4 0.2	RG 1391
WP	3	1.12		1 3 8 15	0.7 0.4 0.4 0.3	
D	3	1.12		1 8 15	4.2 0.3 0.9	
D	3	1.12		1 3 8 15	6.1 0.7 0.2 0.5	
WP	2	1.12		0	7.3	RG 1507
WP	2	glasshouse	0.05	49	1.1	RG 1713
WP	2	glasshouse	0.05	20	6.7	
WP	2	glasshouse	0.05	14	1.2	
WP	2		0.05	14	<0.1	
WP	1		0.05	60	0.1	

Beans. Two trials in Japan on kidney beans according to GAP for azuki beans (4 x 0.07-0.1kg ai/hl, 14-day PHI) gave residues of 0.09 and 0.39 mg/kg at 14 days. In four other trials on kidney and azuki beans at higher rates residues varied from 0.07 to 0.19 mg/kg at 14 days (Table 29).

Sixteen trials were conducted in the UK with several varieties of bean. In one trial with dwarf beans and one with runner beans according to GAP (1 x 1.0 kg ai/ha) the residues were 1.3 and 1.0 mg/kg at 0 days respectively. Seven other trials with higher rates and/or excessive PHIs gave residues from <0.2 to 0.4 mg/kg in beans or pods.

In six trials on field beans according to GAP (2 x 0.25-0.5 kg ai/ha) the residues in the beans varied from <0.02 to <0.2 mg/kg after 6 to 32 days. In another trial at a double rate residues were <0.2 mg/kg after 80 days (Table 29).

Table 29. Results from residue trials with thiophanate-methyl on beans.

Country year	Bean	Formulation	Application			PHI, days	Sample	Residue, mg/kg	Reference
			kg ai/ha	kg ai/hl	No.				
Japan, 1975	Kidney	WP	1.4	0.14	3	14 21	bean	0.15 0.14	RD-9809
		WP	1.4	0.14	3	14 21	bean	0.17 0.19	
1993		WP	1.5	0.10	4	7 14 21	bean	0.32 0.39 0.27	
		WP	2.0	0.10	4	7 14 21	bean	0.11 0.09 0.05	
1993	Adzuki	WP	1.5	0.14	4	14 21 28	bean	0.07 0.07 <0.03	

Country year	Bean	Formulation	Application kg ai/ha	kg ai/hl	No.	PHI, days	Sample	Residue, mg/kg	Reference
		WP	1.5	0.14	4 4 4	14 21 28	bean	0.19 0.08 0.19	
UK, 1971	Dwarf	WP	2.24		1	32	bean	<0.2	RG/1340
		WP	2.24		1	41	bean	<0.2	
		WP	2.24		1	40	bean	<0.2	
1972		WP	1.12		1	0	bean	1.3	RG/1530
	Broad	WP	2.24		1	38	bean pod	<0.2 0.4	RG/1524
		WP	2.24		1	38	bean pod	<0.2 <0.2	
	French	WP	1.12		1	30	bean	0.2	RG/1597
		WP	1.68		1	30	bean	0.3	
	Runner	WP	1.12		1	0	bean	1.0	RG/1531
1973	Field	WP	1.12		1	80	bean	<0.2	RG/1888
1986		SC	0.5		2	18	bean	0.13	D.Ag.313
		SC	0.5		2	14	bean	<0.2	
		SC	0.5		2	14	bean	0.21	
		SC	0.5		2	6	bean	<0.2	
		SC	0.5		2	14 19	bean	0.02 0.06	96-745
		SC	0.5		2	17 32	bean	0.09 0.06	

Peas. Two trials in Japan near the GAP rate (0.035-0.047 kg ai/hl) gave residues at 14 days of 0.03 mg/kg, but the GAP PHI is 7 days. Nine trials in France below the GAP rate (2 x 0.75 kg ai/ha) gave residues of <0.05 mg/kg in the peas and <0.12 or <0.13 mg/kg in the straw after 37 to 61 days. One trial gave a residue in straw of 1.6 mg/kg at 36 days. Eight trials in the UK according to GAP (2 x 0.5 kg ai/ha, 21 days PHI) gave residues at or below the LOD (0.01 mg/kg) after 14 to 35 days (Table 30).

Table 30. Results from residue trials with thiophanate-methyl on peas.

Country year	Formulation	Application kg ai/ha	kg ai/hl	No.	PHI, days	Sample	Residue, mg/kg	Reference
Japan 1990	WP	1.4	0.025	4	14 21 28	peas	0.03 0.03 <0.03	RD-9809
	WP	1.4	0.025	4	14 21 28	peas	0.03 0.03 <0.03	
France	SC	0.45	0.025	2	37	peas straw	<0.05 <0.13	F11A0192
1992	SC	0.45	0.025	2	34	peas straw	<0.05 <0.12	F11A0392
	SC	0.45	0.025	2	50	peas straw	<0.05 <0.12	F11A0492
	SC	0.45	0.025	2	36	peas straw	<0.05 1.6	F11A0592
1993	WG	0.45	0.025	2	49	peas straw	<0.05 <0.12	F11A0193
	WG	0.45	0.025	2	61	peas straw	<0.05 <0.12	F11A0293

Country year	Formulation	Application kg ai/ha	kg ai/hl	No.	PHI, days	Sample	Residue, mg/kg	Reference
	WG	0.45	0.025	2	49	peas straw	<0.05 <0.12	F11B0193
	WG	0.45	0.025	2	61	peas straw	<0.05 <0.12	F11B0293
	WG	0.45	0.025	2	48	peas straw	<0.05 <0.12	F11B0393
UK	SC	0.5		2	14	peas	<0.01	95-733
1995	SC	0.5		2	14	peas	<0.01	
	SC	0.5		2	19	peas	0.01	
	SC	0.5		2	20	peas	<0.01	
1996	SC	0.5		2	27	peas	<0.01	96-744
	SC	0.5		2	21	peas	0.01	
	SC	0.5		2	30	peas	<0.01	
	SC	0.5		2	35	peas	0.01	

Sugar beet. Two trials in Japan according to GAP (5 x 0.023-0.035 kg ai/hl) gave residues of 0.14 and 0.24 mg/kg in the tops and <0.04 mg/kg in the roots at the GAP PHI of 7 days (Table 31).

Table 31. Results from residue trials with thiophanate-methyl on sugar beet in Japan with WP formulation.

Application No.	kg ai/ha	kg ai/hl	PHI, days	Sample	Residue, mg/kg	Reference
5	0.42	0.035	1 1 7 7 15 15	top root top root top root	1.20 <0.04 0.24 ≤0.04 <0.15 <0.04	RD-9809
5	0.35	0.035	1 1 7 7 14 14	top root top root top root	0.53 <0.04 0.14 ≤0.04 <0.05 <0.04	RD-9809

Celery. Two trials in The Netherlands (1972) with 0.7 kg ai/ha of WP formulation gave residues of 0.04 or 0.20 mg/kg in the roots and 0.05 or 1.1 mg/kg in the leaves after 22 or 11 days. The results were corrected for recovery. Neither the number of applications nor information on GAP were reported.

Barley. In fourteen trials in the UK with foliar applications at higher rates than GAP (1 x 0.5 kg ai/ha), residues were below the LOD (0.1 or 0.2 mg/kg) after 72 to 121 days. In another fourteen trials with seed dressing treatments at 0.54 kg ai/hl or 0.04-0.06 kg ai/kg seed residues after 135 to 164 days were similar. No GAP for seed dressing was reported (Table 32).

Table 32. Results from residue trials with thiophanate-methyl on barley in the UK (1973-1974).[1]

Formulation	Application				PHI, days	Residue, mg/kg	Reference
	Method	No	kg ai/ha	kg ai/hl			
P	Seed dressing	1		0.54	135	<0.2	RG/2011
P	Seed dressing	1		0.54	135	<0.2	
P	Seed dressing	1		0.54	151	<0.2	
WP	Seed dressing	1		0.65	135	<0.2	
WP	Seed dressing	1		0.65	135	<0.2	
WP	Seed dressing	1		0.65	151	<0.2	
WP	foliar	1	1.25	0.7	84	<0.2	
WP	foliar	2	0.75		77	<0.1	RG/2184
WP	foliar	1	0.75		77	<0.1	
WP	foliar	1	1.4		102	<0.1	
WP	foliar	2	1.4		79	<0.1	
WP	foliar	1	1.4		79	<0.1	
WP	foliar	1	1.4		119	<0.1	
WP	foliar	2	1.4		89	<0.1	
WP	foliar	1	1.4		89	<0.1	
WP	foliar	1	1.4		121	<0.1	
WP	foliar	2	1.4		91	<0.1	
WP	foliar	1	1.4		91	<0.1	
WP	foliar	2	0.75		72	<0.1	RG/2502
WP	foliar	1	0.75		72	<0.1	
WP	Seed dressing	1		0.04 kg ai/kg seed	164	<0.2	RG/2590
WP	Seed dressing	1		0.05 kg ai/kg seed	164	<0.2	
WP	Seed dressing	1		0.06 kg ai/kg seed	164	<0.2	
WP	Seed dressing	1		0.05 kg ai/kg seed	140	<0.2	
WP	Seed dressing	1		0.06 kg ai/kg seed	140	<0.2	
WP	Seed dressing	1		0.04 kg ai/kg seed	152	<0.2	
WP	Seed dressing	1		0.05 kg ai/kg seed	152	<0.2	
WP	Seed dressing	1		0.06 kg ai/kg seed	152	<0.2	

[1]Results corrected for blanks and recoveries

Rice. Three trials in Japan with more applications (3) than the recommended GAP (1 x 0.14-2.33 kg ai/hl) gave residues in husked grain of 0.04 to 0.20 mg/kg after 15 or 30 days in dry straw and of 1.3 and 1.2 mg/kg after 15 and 30 days respectively (Table 33).

Table 33. Results from residue trials with thiophanate-methyl on rice in Japan (1988) with 3 applications of WP formulation.

Application		PHI, days	Sample	Residue, mg/kg	Reference
kg ai/ha	kg ai/hl				
1.5	0.1	15 30	grain (husked)	0.09 0.04	RD-9809
1.5	0.1	15 30	dry straw	1.26 1.16	
1.8	0.1	15 30	grain (husked)	0.20 0.05	

Wheat. In two trials in Japan at the GAP rate (3 x 0.07 kg ai/hl), residues in the grain after 14 to 30 days were <0.02 to 0.03 mg/kg. Twenty two trials in the UK at the GAP rate (1 x 0.5-0.7 kg ai/ha) or above gave residues after 46 to 111 days at or below the LOD (0.1 or 0.3 mg/kg).

In four trials in The Netherlands with 1 application of 2 to 3 kg ai/ha, residues after 34 to 73 days ranged from <0.02 to 0.05 mg/kg in the grain and from 0.07 to 0.10 mg/kg in the straw. No GAP was reported (Table 34).

Table 34. Results from residue trials with thiophanate-methyl on wheat with WP formulation.

Country year	Application			PHI,	Sample	Residue,	
	No	kg ai/ha	kg ai/hl	days		mg/kg	Reference
Japan 1988	3	0.98	0.07	14 21 30	grain	<0.02 <0.02 <0.02	RD-9809
	3	1.05	0.07	14 21 30	grain	0.03 0.03 <0.02	RD-9809
Netherlands	1	2		73	grain	<0.02	R4022
1973[1]	1	2		64	grain	<0.02	
	1	3		34	straw grain	0.10 <0.05	R4572
	1	3		35	straw grain	0.07 <0.05	
UK[1] 1973	1	0.56		46	grain	<0.1 (4)[1]	RG/2011
1974	2	0.75		70	grain	<0.3	RG/2184
	1	0.75		70	grain	<0.3	
	2	0.75		82	grain	<0.3	
	1	0.75		82	grain	<0.3	
	2	0.75		83	grain	<0.3	
	1	0.75		83	grain	<0.3	
	1	1.4		111	grain	<0.3	
	2	1.4		90	grain	<0.3	
	1	1.4		90	grain	<0.3	
	1	1.4		139	grain	<0.3	
	2	1.4		118	grain	<0.3	
	1	1.4		118	grain	<0.3	
	1	1.4		123	grain	<0.3	
	2	1.4		111	grain	<0.3	
	1	1.4		111	grain	<0.3	
	2	0.75		70	grain	0.1	RG/2502
	1	0.75		75	grain	0.1	
	2	0.75		83	grain	0.1	
	1	0.75		83	grain	<0.1	
	2	0.75		82	grain	0.1	
	1	0.75		82	grain	<0.1	

[1]Corrected for recoveries

Rape. In four trials in France with 1 or 2 applications of 0.45 kg ai/ha, residues after 65 to 87 days were < 0.05 mg/kg. No GAP was reported for France (Table 35).

Table 35. Results from residue trials with thiophanate-methyl on rape in France (1992) with SC formulation.

Application		PHI,	Residue,	
No.	kg ai/ha	days	mg/kg	Reference
2	0.45	79	<0.05	F04A0192
2	0.45	65	<0.05	F04A0292
2	0.45	87	<0.05	F04A0392
2	0.45	79	<0.05	F04A0492
1	0.45	78	<0.05	F04B0193
1	0.45	78	<0.05	F04B0293
1	0.45	81	<0.05	F04B0493
1	0.45	77	<0.05	F04B0693

Tea. Six residue trials on tea in Japan were with 1 application of 0.93 kg ai/ha (0.047 kg ai/hl) of WP formulation; GAP is 2 x 0.035-0.047 kg ai/hl. The residues were 1.8 and 1.6 mg/kg after 7 days, 1.3 and 1.4 mg/kg after 14 days, and 1.2 and 1.1 mg/kg after 21 days.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country	Commodity	MRL, mg/kg
Belgium	Potato	3
	Apple, Bush, bean Celery, Fodder Pea, Pea, Pear, Sour cherries, Strawberry, String bean	2
	Barley, Cucumber, Melon, Pepper, Gherkins	0.5
	Cereals, Leeks, Sugar beet	0.1
France	Apple Apricot Cherry Melon Plum	2
	Banana	1 for whole, 0.5 for pulp
	Peach	1
	Barley, Wheat	0.5
	Cruciferous oily crops, French bean	0.1
	Pea	0.05
Germany	Stone fruits	2
	Barley	0.5
	Rape, Rye, Wheat, Winter rape	0.1
Japan	Tea	20
	Fruits Vegetables	5
	Rice	2
	Beans and Peas, Cereals except rice, Root and Tubers, Sugar beet	1
Netherlands	Apple, Cucumber, Eggplant, Gherkins, Pear, Potato, Sweet pepper, Tomato	3
Spain	Grape, Onion, Strawberry	5
	Brassica, Celery, Cucumber, Eggplant, Green leguminosae, Lettuce, Pepper, Pome fruits, Stone fruits, Tomato	2
	Melon, Cereals, Watermelon	0.5
	Sugar beet	0.1
UK	Apple, Pear	2

Country	Commodity	MRL, mg/kg
Belgium	Potato	3
	Barley, Cucumber, Dwarf green bean, Field bean, Oilseed rape, Pea, Winter wheat	0.1
Poland	Citrus fruit	5
	Fruits, except Citrus; Mushrooms, Vegetables	1
	Cereal grains, Eggs, Meat and Meat Products, Milk, Milk Products, Potato, Tea	0.1

APPRAISAL

[See also BENOMYL (069)/CARBENDAZIM (072)]

Thiophanate-methyl was first evaluated in 1973 and the most recent evaluation of residue aspects was in 1994. The 1994 evaluation listed as desirable data from supervised trials according to currently registered uses on residues in fruits and vegetables arising from post-harvest treatments, as well as on lettuce, peppers, tomatoes and sugar beet, and on crops for which CXLs were listed. The CCPR in 1994 noted that the data on residues were not complete (ALINORM 95/24, para 194). The scheduled periodic re-evaluation by the 1998 JMPR was confirmed by the 1997 CCPR. Data on metabolism and supervised residue trials were provided by the manufacturer. Additional residue trials carried out in the USA and Germany were reported but have not been evaluated because full study reports and/or labels were not provided.

Metabolism studies were conducted in mice, rats, dogs, poultry, livestock and plants. The metabolic pathways of thiophanate-methyl in animals and plants includes hydroxylation, hydrolysis to carbendazim with subsequent metabolism, oxidation of the thiocarbonyl group, and formation of sulfate conjugates. In mice, labelled thiophanate-methyl was mainly excreted in the urine (66-78%) and faeces (17.5-27%) within 96 hours. In rats dosed daily with [^{14}C]thiophanate-methyl, an average of 89.6% of the ^{14}C was excreted every day (54.27% in the urine and 35.38% in the faeces). The main metabolites in the faeces and urine after exposure to labelled thiophanate-methyl at various doses and with various regimes were methyl 5-hydroxy-benzimidazol-2-ylcarbamate (5-HBC, 2.0-40.2%), unchanged parent compound (2.9-52.4%), 4-hydroxy-thiophanate-methyl (5.1-10.6%), dimethyl 4,4´-(4-hydroxy-1,2-phenylene)bisallophanate (0.1-6.2%) and carbendazim (2-5.3%). In one experiment the sulfate conjugate of 5-HBC accounted for 19-36% of the administered ^{14}C.

In dogs dosed once, 74% of the total radiolabel was found in the urine and 14% in the faeces after 24 hours. In goats dosed for 5 days the cumulative percentages of ^{14}C were 56% in the urine and 14% in the faeces. The residues in the edible tissues (liver, kidney, muscle and fat) constituted 2.1% of the administered dose. Milk contained 1.5% of the total dose and reached 1.59 mg/kg as thiophanate-methyl at day 4.

In poultry, thiophanate-methyl was mainly eliminated in the excreta (up to 94%), with only a small percentage of the total dose found in the tissues and eggs. In the tissues the highest residues were in the liver (1.7 mg/kg) and kidneys (1.2 mg/kg).

On average, 64% of the applied thiophanate-methyl was found unchanged in soya bean pods and apples 7 or 14 days after treatment. When bean plants were grown in water containing thiophanate-methyl labelled with ^{14}C or ^{35}S the ^{14}C label was translocated through the roots more readily than the ^{35}S. Approximately 20% of the ^{14}C was translocated from the roots to the leaves within 14 days after application. The metabolites found in the pods and leaves of soya beans 14 days after the application of [*phenyl*-U-^{14}C]thiophanate-methyl were the parent compound (54.4-86.1%), carbendazim (9.4-37%), dimethyl 4,4´-(*o*-phenylene)bisallophanate (FH-432, up to 8.7%) and 1-(3-

methoxycarbonylthioureido)-2-(3-methoxycarbonylureido)benzene (DX-105, up to 6.4%). Studies with young apple plants gave similar results.

Bean, apple and grape plants were treated by leaf dotting once with thiophanate-methyl labelled with ^{14}C or ^{35}S in the thioureido groups. After 14 days most of radioactivity remained in the treated leaves (64-72% in bean plants), and was recovered by washing in chloroform. The identified compounds were thiophanate-methyl, carbendazim and FH-432.

In studies of environmental fate [^{14}C]thioureido-, [^{14}C]methyl-, or [^{35}S]thioureido-labelled thiophanate-methyl was applied to sandy loam or silty loam soils which were kept in the dark at 23°C or 33°C for 60 days or exposed to sunlight for 28 days. Thiophanate-methyl disappeared completely within 7 days under dark conditions and had a half-life of 3.9 days in sunlight. In all cases the main degradation product was carbendazim.

When a series of thiophanate-methyl solutions (0-5000 mg/l) were incubated with sandy loam or silty loam soils at 30°C for 30 days the counts of microflora were not affected by the thiophanate-methyl.

Adsorption/desorption isotherms of labelled thiophanate-methyl and its metabolites were determined with four USA upland soils (sand, sandy loam, loamy sand and loam) and two USA paddy field soils (loam and clay loam). The Freundlich constants K ranged from 0.27 to 14.14 for thiophanate-methyl, 0.45 to 88.24 for carbendazim, 0.28 to 10.11 for FH-432 and 0.29 to 11.88 for DX-105. Sandy upland soils and clay loam paddy field soils had the lowest and highest values respectively. The adsorbed thiophanate-methyl was not easily desorbed.

In leaching studies with [*phenyl*-U-^{14}C]thiophanate-methyl in soil columns 54.5%, 43.4%, 22.0% and 0.4% of the applied ^{14}C was recovered in the leachates from sand, silt loam, sandy loam and clay loam respectively.

[*Phenyl*-U-^{14}C]thiophanate-methyl was degraded in sterile pH 5 aqueous buffer exposed to sunlight with a half-life of 2.17 days. Carbendazim was the main photoproduct and accounted for 50% of the initial ^{14}C at 5.5 days. Thiophanate-methyl in oxygen-saturated river water at pH 7, incubated under shaking and in the dark for 42 days at 0.1 mg/l and 52 days at 1.0 mg/l showed half-lives of about 15 and 25 days respectively. The major degradation product was carbendazim, which accounted for 72.2% of the initial ^{14}C at 42 days and 74.1% at 52 days.

In most residue analytical methods thiophanate-methyl and carbendazim are extracted and thiophanate-methyl is converted to carbendazim by refluxing in acidic or neutral conditions. The total carbendazim is determined by UV spectrophotometry, HPLC with UV detection, derivative spectrophotometry or LC-MS-MS. The detection limits are 0.02 mg/kg for UV, 0.02 mg/kg for HPLC, 0.05 mg/kg for derivative spectrophotometry and 0.003 mg/kg for LC-MS-MS. Limits of determination range from 0.02 to 0.2 mg/kg. In another method, thiophanate-methyl is partially converted to carbendazim during the analysis, which involves extraction of the compounds with acetone/dichloromethane/petroleum ether, clean-up by diol-bonded silica SPE and HPLC with UV-fluorescence detection. The LOD, as carbendazim, was 0.05 mg/kg and recoveries were >97.6%. In a method in which ethyl acetate extraction is followed by TLC with detection by a spray of fungal spores the reported LOD is 0.1 mg/kg with recovery >90%.

Two methods for animal products were reported. In one, which determines thiophanate-methyl, DX-15, 4-OH-TM, 4-OH-FH-432 and FH-432, the analytes are extracted with acetonitrile, cleaned up by solid-phase extraction (C-18 and NH_2) and determined by HPLC with UV or fluorescence detection. The second method was developed for the determination of carbendazim, 5-HBC, 5-HBC-S and 2-AB and involves acid extraction in acetone to hydrolyse the sulfate conjugate,

ethyl acetate partition, and clean-up on an NH_2 cartridge. In both methods the limit of determination is 0.2 mg/kg.

The stability of thiophanate-methyl and/or carbendazim in stored analytical samples was studied in many crops. Residues in pears, persimmons, cabbages, soya beans and rape seed were stable at –30°C for 2 years, with 71-98% of the initial residues remaining in the crop at the end of the study. In apples stored for 6 months at –20°C, 42.3-68.4% of the initial thiophanate-methyl and 50-128% of the carbendazim remained at the end of the study. In potatoes thiophanate-methyl residues were 58.4 and 67.1% of the initial residue after 176 days at –20°C.

The current definition of the residue is "carbendazim". The Meeting noted however that about two-thirds of the residue in crops arising from the use of thiophanate-methyl was likely to be thiophanate-methyl (which would be determined as carbendazim), and concluded that the definition for compliance with MRLs should be *sum of thiophanate-methyl and carbendazim, expressed as carbendazim*. Since the ADI of thiophanate-methyl is nearly three times that of carbendazim, the same definition would avoid under-estimating the dietary risk and would therefore be appropriate for the estimation of STMRs.

Residues resulting from supervised trials

A number of residue trials were carried out on citrus fruit, apples, pears, apricots, cherries, peaches, plums, berries, grapes, strawberries, kiwifruit, persimmons, onions, Brussels sprouts, cucumbers and gherkins, mushrooms, tomatoes, egg plants, melons, peppers, lettuces, beans, peas, sugar beet, celery, barley, rice, wheat, rape and tea. As thiophanate-methyl residues are expressed as carbendazim, which can also occur from the use of benomyl or carbendazim, residue trials with thiophanate-methyl, benomyl and carbendazim were evaluated together and are described in Section 4.3.

RECOMMENDATIONS

The maximum residue levels estimated to arise from the use of thiophanate-methyl are covered by the MRLs recommended for carbendazim listed in the carbendazim monograph. The list also includes the STMRs estimated for benomyl, carbendazim and thiophanate-methyl.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: sum of thiophanate-methyl and carbendazim, expressed as carbendazim.

DIETARY RISK ASSESSMENT

The residues of benomyl, carbendazim and thiophanate-methyl are all expressed as carbendazim, which has the lowest ADI of the three compounds. A total of 34 STMRs were estimated for benomyl, 8 for carbendazim and 5 for thiophanate-methyl. If STMRs were estimated for more than one compound in a commodity, the highest STMR was used for the calculation. No MRLs were used.

International Estimated Daily Intakes of benomyl, carbendazim and thiophanate-methyl for the five GEMS/Food regional diets were in the range of 1 to 6% of the carbendazim ADI.

The Meeting concluded that the intake of residues of benomyl, carbendazim and/or thiophanate-methyl resulting from their uses that have been considered by the JMPR is unlikely to present a public health concern.

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ANNEX I{TC "I"}

ADIs , ACUTE REFERENCE DOSES, RECOMMENDED MRLs AND MRLMs, AND STMRs RECORDED BY THE 1998 MEETING

The Table is in two parts. Part 1 includes maximum Acceptable Daily Intakes (ADIs), Acute Reference Doses (RfDs), recommendations for Maximum Residue Limits (MRLs), and Supervised Trials Median Residue (STMR) levels. In Part 2 recommendations are for Maximum Residue Limits for Monitoring (MRLMs) rather than for MRLs. MRLMs apply to compounds whose estimated dietary intakes might, on the basis of the available information, exceed their ADIs. A proposal to distinguish such compounds from those whose intakes are clearly below the corresponding ADIs was made at the 1997 Joint Meeting and its rationale is described in detail in the report (Section 2.3). It should be noted that the distinction between MRLs and MRLMs applies only to new compounds and those re-evaluated within the CCPR Periodic Review Programme.

STMR levels were introduced in 1996 in response to recommendations of a Joint FAO/WHO Consultation on Guidelines for Predicting the Dietary Intake of Pesticide Residues held in York, UK, in 1995.The 1996 JMPR report explains the reasons for their introduction and gives details of the procedures used in their calculation (Sections 2.2.1, 2.2.3, Annex IV and the introduction to Annex I).

In general, the MRLs recommended for compounds which have been reviewed previously are additional to, or amend, those recorded in the reports of earlier Meetings. If a recommended MRL is an amendment the previous value is also recorded. All recommendations for compounds re-evaluated in the CCPR periodic review programme are listed however (even if identical to existing CXLs or draft MRLs) because such re-evaluations replace the original evaluation rather than supplement it.

Some ADIs may be temporary: this is indicated by the letter T and the year in which re-evaluation is scheduled in parenthesis below the ADI. All recommended MRLs for compounds with temporary ADIs are necessarily temporary, but some recommendations are designated as temporary (TMRLs) until required information has been provided and evaluated, irrespective of the status of the ADI. Such recommendations are followed by the letter T in the table. (See also the list of qualifications and abbreviations below.)

The Table includes the Codex reference numbers of the compounds and the Codex Classification Numbers (CCNs) of the commodities, to facilitate reference to the Guide to Codex Maximum Limits for Pesticide Residues and other Codex documents. Commodities are listed in alphabetical order.

Apart from the abbreviations indicated above, the following qualifications are used in the Table.

* following recommended MRL	At or about the limit of determination
* following name of pesticide	New compound
** following name of pesticide	Compound reviewed in CCPR Periodic Review Programme

Po	The recommendation accommodates post-harvest treatment of the commodity
T	Temporary
W in place of a recommended MRL	The previous recommendation is withdrawn, or withdrawal of the recommended MRL or existing Codex or draft MRL is recommended

PART 1. ADIs, acute RfDs, recommended MRLs, and STMRs

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
Amitraz** (122)	0.01	Acute RfD 0.01 mg/kg bw Previous ADI 0-0.003 mg/kg bw Periodic review was for toxicology only				
Amitrole**	0.002	FP 0009	Pome fruits	0.05*		0
(079)		FS 0012	Stone fruits	0.05*		0
		FB 0269	Grapes	0.05		0.02
		Residue (for MRLs and STMRs): amitrole Periodic review was for residues only				
Benomyl**	0.1	Residues arising from the use of benomyl are covered by the recommendations for carbendazim				
(069)		Residue (for MRLs and STMRs): sum of benomyl and carbendazim, expressed as carbendazim Periodic review was for residues only				
Bentazone (172)	0.1	Acute RfD not considered ADI unchanged				
Bitertanol** (144)	0.01	Acute RfD unnecessary ADI unchanged Periodic review was for toxicology only				
Carbendazim**	0.03	JF 0226	Apple juice			0.147 (B)
(072)			Apple purée			0.282 (B)
			Apple sauce			0.078 (B)
		FS 0240	Apricot	W	0.1 (B)	
		VS 0621	Asparagus	W	0.1* (B)	
		FI 0326	Avocado	W	0.5 (B)	
		Fl 0327	Banana	0.2 (**B**)	1 Po (B,C,Th)	0.03 (B)
		GC 0640	Barley	0.5 (**C**)	0.1 (C,Th)	0.05 (C)
		AS 0640	Barley straw and fodder, dry	2 (**C**)	2 (B)	0.345 (C)
		VD 0071	Beans (dry)	0.5 (**Th**)	2 (B)	0.165 (Th)
		FB 0018	Berries and other small fruits	W	1 (B, Th)	
		VP 0522	Broad bean (green pods and immatu seeds)	W	2 (Th)	
		VB 0402	Brussels sprouts	0.5 (**B**)	0.5 (B)	0.065 (B)
		VR 0577	Carrot	0.2 (**B**)	-	0.04 (B)
		MM 0812	Cattle meat	0.05* (**B**)	0.1* (B)	0 (B)
		VS 0624	Celery	W	2 (B, C)	
		GC 0080	Cereal grains	W	0.5[1] (B,C,Th)	
		FS 0013	Cherries	W	2 (Th)	
		PF 0840	Chicken fat	0.05* (**B**)	0.1* (Th)	0 (B)
		SB 0716	Coffee beans	W	0.1* (C)	

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		VP 0526	Common bean (pods and/or mmature seeds)	W	2 (B, C Th)	
		VC 0424	Cucumber	0.05* (B, **C**)	0.5 (B,C,Th)	0.03 (B) 0.05 (C)
		MO 0105	Edible offal (Mammalian)	0.05* (**B**)	-	0 (B)
		VO 0440	Egg plant	W	0.5 (C)	
		PE 0112	Eggs	0.05* (**B**)	0.1* (B,Th)	0 (B)
		VP 0529	Garden pea, shelled (succulent seeds)	0.02 **(Th)**	-	0.01 (Th)
		VC 0425	Gherkin	0.05* (B,**C**)	2 (C,Th)	0.03 (B) 0.05 (C)
		FB 0269	Grapes	3 (B,**Th**)	1 (B,Th)	0.84 (B) 0.87 (Th)
		DH 1100	Hops, Dry	W	50 (C)	
		VL 0482	Lettuce, Head	W	5 (Th)	
		FI 0345	Mango	W	2 (B)	
		VC 0046	Melons, except Watermelon	W	2 Po (B,C)	
		ML 0106	Milks	0.05* (**B**)	0.1* (B)	0 (B)
			Milk cream			0 (B)
		VO 0450	Mushrooms	W	1 [2](Th)	
		FS 0245	Nectarine	W	2 (B)	
		GC 0647	Oats	W	0.1 (C)	
		VA 0385	Onion, Bulb	W	2 (C,Th)	
		FC 0004	Oranges, Sweet, Sour	1(**B**)	-	0.325 (B)
		JF 0004	Orange juice			0.13 (B)
			Orange oil			0.442 (B)
		FS 0247	Peach	2 (**B**)	2 (B)	0.255 (B)
		SO 0697	Peanut	W	0.1* (B,C)	
		AL 0697	Peanut fodder	W	5 (B,C)	
		VO 0051	Peppers	W	0.1 (Th)	
		FI 0353	Pineapple	5 (**B**)	-	0.03 (B)
		FS 0014	Plums (including Prunes)	0.5 (**B**)	0.5 (Th)	0.06 (B)
		FP 0009	Pome fruits	3 (**B,**C,Th)	2 (B,C,Th)	0.60 (B) 0.455 (C) 0.555 (Th)
		VR 0589	Potato	W	3 Po (B,C)	
		PM 0110	Poultry meat	0.05* (**B)**	0.1* (B,Th)	0 (B)
		DF 5263	Raisins			1.09 (B)
			Raisin waste			3.44 (B)
		SO 0495	Rape seed	0.05* (**C**)	0.1* (C)	0 (C)
		CM 0649	Rice, husked	2 (**B**)	-	0.05 (B)
		AS 0649	Rice straw and fodder, dry	15 **(B)**	15 (B,C,Th)	2.5 (B)
		GC 0650	Rye	W	0.1 (C,Th)	
		MM 0822	Sheep meat	W	0.1* (B)	
		VD 0541	Soya bean (dry)	W	0.2 (C)	
		AL 0541	Soya bean fodder	W	0.1* (C)	
		VC 0431	Squash, Summer	W	0.5 (B)	
		VR 0596	Sugar beet	W	0.1*(B,C,Th)	
		AV 0596	Sugar beet leaves or tops	W	5 (B,Th)	
		VR 0497	Swede	W	0.1* (C)	
		VR 0508	Sweet potato	W	1 (B)	

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		VR 0505	Taro	W	0.1* (B)	
		VO 0448	Tomato	0.5 (B,**C**)	0.1 (Th)	0.16 (C) 0.045 (B)
		JF 0448	Tomato juice			0.012 (B)
			Tomato purée			0.030 (B)
			Tomato ketchup			0.028 (B)
			Tomato pomace, wet			0.013 (B)
			Tomato pomace, dry			0.022 (B)
		TN 0085	Tree nuts	W	0.1* (B)	
		GCO 654	Wheat	0.05* (B,**Th**)	0.1 (B,C,Th)	0.03 (B) 0.01(Th)
		AS 0654	Wheat straw and fodder, dry	1 (**B,C**)	5 (B)	0.1 (B) 0.03 (C)
			Wine			0.445 (B)
		VC 0433	Winter squash	W	0.5 (B)	
		Residue (for MRLs and STMRs): carbendazim [1]To be replaced by MRLs for barley, oats, rye and wheat (1994 JMPR) [2] Group MRL for berries and other small fruits Letters in parentheses in columns 5 and 6 indicate the compounds for which sufficient data from trials Complying with GAP were provided (B=benomyl; C= carbendazim; Th= thiophanate-methyl). Bold Letters indicate the source(s) of the data on which the recommendation is based. Letters in parentheses in column 7 indicate the compound to which the STMR applies. Recommendations cover carbendazim arising from the direct use of carbendazim or (as a metabolite And/or a hydrolysis product formed during analysis) from the use of benomyl or thiophanate-methyl. Periodic review was for residues only				
2,4-D**	0.01	GC 0640	Barley	W	0.5	
020		FB 0018	Berries and other small fruits	0.1	-	
			Berries, except grapes			0.05
		FB 0264	Blackberries	W[1]	0.1	
		FC 0001	Citrus fruits	W	2	
		MO 0105	Edible offal (Mammalian)	5	-	2.745
		PE 0112	Eggs	0.01*	0.05*	0
		FC 0203	Grapefruit	0.1	2[2]	0.05
		JF 0203	Grapefruit juice			0.005
			Grapefruit molasses			0.215
			Grapefruit oil			0.05
			Grapefruit pulp, dry			0.235
			Grapefruit pulp, wet			0.044
		FB 0269	Grapes			0
			Grass forage (green)			193
		AS 0162	Hay or fodder (dry) of grasses	400	-	117.5
		GC 0645	Maize	0.05	0.05*	0.01
		CF 1255	Maize flour			0.01
		AS 0645	Maize fodder	40	-	6.4
		AF 0645	Maize forage	10	-	0.65
			Maize grits			0.01
		CF 0645	Maize meal			0.01
		MM 0095	Meat (from mammals other than marine mammals)	0.2	0.05*	0.125
			Milk products	W	0.05*	
		ML 0106	Milks	0.1	0.05*	0.043
		GC 0647	Oats	W	0.5	
		JF 0004	Orange juice			0.005
			Orange molasses			0.215
			Orange oil			0.05

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
			Orange pulp, dry			0.235
			Oranges pulp, wet			0.044
		FC 0004	Oranges, Sweet, Sour	0.1	2[2]	0.05
		FP 0009	Pome fruits	0.01*	-	0
		VR 0589	Potato	0.2	0.2	0.05
		PM 0110	Poultry meat	0.05*	-	0
		PO 0111	Poultry, Edible offal of	0.05*	-	0
		FB 0272	Raspberries, Red, Black	W[1]	0.1	
		GC 0649	Rice	W[3]	0.05*	
		CM 0649	Rice, husked	0.1	-	0.01
		AS 0649	Rice straw and fodder, dry	10	-	3.1
		GC 0650	Rye	2	0.5	0.22
		GC 0651	Sorghum	0.01*	0.05*	0.01
		AF 0651	Sorghum forage (green)	0.2	-	0.035
		VD 0541	Soya bean (dry)	0.01*	-	0
		AL 0541	Soya bean fodder	0.01*	-	0.01
		AL 1265	Soya bean forage (green)	0.01*	-	0
		FS 0012	Stone fruits	0.05*	-	0
		GS 0659	Sugar cane	0.05	-	0.01
		AV 0659	Sugar cane forage	0.2	-	0.03
		VO 0447	Sweet corn (corn-on-the-cob)	0.05*	-	0.05
		TN 0085	Tree nuts	0.2	-	0.05
		FB 0019	Vaccinium berries, including Bearberry	W[1]	0.1	
		GC 0654	Wheat	2	0.5	0.22
		CF 0654	Wheat bran, processed	-	-	0.803
		CF 1211	Wheat flour	-	-	0.024
			Wheat forage			20
		AS 0654	Wheat straw and fodder, dry	100	-	7
		Residue (for MRLs and STMRs): 2,4-D [1]Replaced by recommendation for berries and other small fruits [2]Included in MRL for Citrus fruits [3]Replaced by recommendation for Rice, husked Periodic review was for residues only				
Demeton-S-methyl**	0.0003[1]	Residues of demeton-S-methyl are covered by the recommendations for oxydemeton-methyl				
(073)		Residue: sum of demeton-S-methyl, oxydemeton-methyl, and demeton-S-methylsulphon, expressed as oxydemeton-methyl [1]For demeton-S-methyl and related compounds, alone or in combination Periodic review was for residues only				
Dicloran**	0.01	VR 0577	Carrot	15 Po	10 Po	6.11
(083)		FB 0269	Grapes	W	10 Po	
		VL 0482	Lettuce, Head	W	10	
		VA 0385	Onion, Bulb	0.2	10 Po	0.1
		FS 0247	Peach	W	15 Po	
		FS 0014	Plums (including Prunes)	W	10 Po	
		FB 0275	Strawberry	W	10	
		VO 0448	Tomato	W	0.5	
		Residue (for MRLs and STMRs): dicloran The residue is fat-soluble Acute RfD unnecessary Previous ADI 0-0.03 mg/kg bw				
Dimethoate**		See Part 2				

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
Dinocap	0.008	FP 0226	Apple	0.2	-	0.05
(087)		JF 0226	Apple juice	-	-	0.05
		VC 0045	Fruiting vegetables, Cucurbits	0.05*	-	0.05
		FB 0269	Grapes	1	-	0.105
			Grape must			0.007
		FB 0275	Strawberry	0.5	-	0.06
			Strawberry jam and preserved			0.017
		FS 0247	Peach	0.1	-	0.05
		VO 0051	Peppers	0.2	-	0.06
			Wine			0.007
		Residue (for MRLs and STMRs): sum of dinocap isomers and dinocap phenols, expressed as dinocap Acute RfD 0.008 mg/kg bw Previous ADI 0-0.001 mg/kg bw				
Diphenylamine* * (030)	0.08	Acute RfD unnecessary Previous ADI 0-0.02 mg/kg bw Periodic review was for toxicology only				
Disulfoton	0.0003	GC 0640	Barley	-	0.2	0.02
(074)		VD 0071	Beans (dry)	0.2	0.05	0.01
		VB 0400	Broccoli	-	0.1	0.025
		VB 0041	Cabbages, Head	-	0.2	0.02
		VB 0404	Cauliflower	-	0.05	0.01
		SO 0691	Cotton seed	0.1	0.1	0.03
		VP 0529	Garden pea, shelled (succulent seeds)	-	0.02*	0.01
		VL 0482	Lettuce, Head	1	1	0.05
		VL 0483	Lettuce, Leaf	1	1	0.11
		GC 0645	Maize	0.02*	0.01	0.01
		CF 1255	Maize flour			0.0025
		GC 0647	Oats	-	0.02*	0
		SO 0697	Peanut	-	0.1	0.015
		TN 0672	Pecan	-	0.1	0.01
		FI 0353	Pineapple	-	0.1	0
		VR 0589	Potato	0.5	0.5	0.08
		VR 0591	Radish, Japanese	-	0.2	0.025
		GC 0654	Wheat	-	0.2	0.02
		CM 0654	Wheat bran			0.019
		CF 1211	Wheat flour			0.004
		CF 1210	Wheat germ			0.042
		Residue (for MRLs and STMRs): sum of disulfoton, demeton-S and their sulfoxides and sulfones, expressed as disulfoton				
Endosulfan** (032)	0.006	Acute RfD 0.02 mg/kg bw ADI unchanged Periodic review was for toxicology only				
Ethoxyquin** (035)	0.005	Acute RfD unnecessary Previous ADI 0-0.06 mg/kg bw Periodic review was for toxicology only				
Folpet**	0.1	FP 0226	Apple	W [1]	10	
(041)		VC 0424	Cucumber	W	0.5	
		DF 0269	Dried grapes (= currants, raisins and	W[1]	40	

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
			sultanas)			
		FB 0269	Grapes	W[1]	10	
		VC 0046	Melons, except Watermelon	W	3	
		VR 0589	Potato	W	0.02*	
		FB 0275	Strawberry	W[1]	5	
		VO 0448	Tomato	W[1]	3	
		Residue (for MRLs and STMRs): folpet [1]The previous recommendation is withdrawn because critical supporting studies on the environmental fate of folpet were not provided for the 1998 Meeting Periodic review was for residues only				
Formothion** (042)		Formothion is metabolized by plants to dimethoate and omethoate. It is no longer used as a pesticide and no information was supplied. ADI withdrawn by 1996 JMPR				
Glufosinate-ammonium (175)	0.02	FI 0030	Assorted tropical and sub-tropical fruits - inedible peel[1]	0.05*	-	0.05
		FI 0341	Kiwifruit	W[2]	0.05*	
		TN 0085	Tree nuts	0.1	-	0.05
		AM 0660	Almond hulls	0.5	-	
		Residue (for MRLs and STMRs): Sum of glufosinate-ammonium and 3-[hydroxy(methyl)phosphinoyl]propionic acid calculated as glufosinate (free acid) [1]Except Banana [2]Replaced by recommendation for group MRL				
Hexythiazox	0.03	DH 1100	Hops, dry	2	-	0.79
(176)			Beer			0
		Residue (for MRLs and STMRs): hexythiazox				
Kresoxim-methyl*	0.4	JF 0226	Apple juice			0.02
(199)			Apple pomace, wet			0.05
		JF 0226	Apple sauce			0.02
		GC 0640	Barley	0.1		0.05
		VC 0424	Cucumber	0.05*		0.05
		DF 0269	Dried grapes (= currants, raisins and sultanas)	2		0.32
		MO 0105	Edible offal (Mammalian)	0.05*		0.01
			Grape must			0.02
			Grape pomace, wet			0.14
		FB 0269	Grapes	1		0.2
		MF 0100	Mammalian fats (except milk fats)	0.05*		0.01
		MM 0095	Meat (from mammals other than marine mammals)	0.05*		0.01
		ML 0106	Milks	0.01*		0.002
		FP 0009	Pome fruits	0.2		0.05
		PM 0110	Poultry meat	0.05*		0.01
		GC 0650	Rye	0.05*		0.05
		AS 0081	Straw and fodder (dry) of cereal grains	5		0.24
		GC 0654	Wheat	0.05*		0.05
			Wine			0.04
		Residue (for MRLs and STMRs for plant commodities): kresoxim-methyl (for MRLs and STMRs for animal commodities): α-(*p*-hydroxy-*o*-tolyloxy)-*o*-tolyl(methoxyimino)acetic acid, expressed as kresoxim-methyl Acute RfD unnecessary				
Maleic hydrazide**	0.3	VA 0381	Garlic	15	-	4.1
(102)		VA 0385	Onion, Bulb	15	15	4.1
		VR 0589	Potato	50	50	11
			Potato crisps			0.29

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
			Potato chips			38.5[1] 10.12[2]
			Potato, boiled			5.7
		VA 0388	Shallot	15	-	4.1
		Residue (for MRLs and STMRs): maleic hydrazide [1]US commercial practice [2]UK commercial practice Note changed definition of residue Periodic review was for residues only				
Methiocarb** (132)	0.02	Acute RfD 0.02 mg/kg bw Previous ADI 0-0.001 mg/kg bw Periodic review was for toxicology only				
Myclobutanil	0.03	FI 0327	Banana	2	-	0.215
(181)			Beer			0
		DH 1100	Hops, dry	2	-	0.515
		Residue (for MRLs and STMRs): myclobutanil				
Omethoate**		See Part 2				
Oxydemeton-methyl**	0.0003[1]	AL 1020	Alfalfa fodder	W	5	
(166)		FP 0226	Apple	0.05	1	0.01
		JF 0226	Apple juice	-	-	0.005
			Apple sauce			0.01
		GC 0640	Barley	0.05*	0.2	0.04
		AS 0640	Barley straw and fodder, dry	2	-	0.055
		VD 0071	Beans (dry)	W	0.01*	
		VB 0400	Broccoli	W	1	
		VB 0402	Brussels sprouts	W	1	
		VB 0403	Cabbage, Savoy	W	0.01*	
		VB 0041	Cabbages, Head	0.05*	1	0.03
		MF 0812	Cattle fat	0.05*	0.05*	0
		VB 0404	Cauliflower	W	0.01*	
		FS 0013	Cherries	W	1	
		AL 1031	Clover hay or fodder	W	5	
		VD 0526	Common bean (dry)	0.1	-	0.01
		VP 0526	Common bean (pods and/or immature seeds)	W	0.2	
		SO 0691	Cotton seed	0.05	0.05	0.01
		OR 0691	Cotton seed oil, edible	-	-	0.002
			Cotton seed meal			0.006
			Cotton seed, hulls			0.002
		VC 0424	Cucumber	W	0.5	
		LD 0106	Derived milk products	W	0.05	
		VO 0440	Egg plant	W	0.2	
		PE 0112	Eggs	0.05*	0.05*	0
		VP 0528	Garden pea (young pods)	W	0.1	
		FC 0203	Grapefruit	W	0.1	
		FB 0269	Grapes	0.1	0.5	0.04
		VL 0480	Kale	0.01*	0.05	0.01
		VB 0405	Kohlrabi	0.05	0.01*	0.02
		FC 0204	Lemon	0.2	1	0.01
		VL 0483	Lettuce, Leaf	W	2	
		VP 0534	Lima bean (young pods and/or immature beans)	W	0.2	
		GC 0645	Maize	W	0.2	

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		AS 0645	Maize fodder	W	5	
		FC 0206	Mandarin	W	0.5	
		MM 0097	Meat of cattle, pigs and sheep	0.05*	0.05*	0
		ML 0106	Milks	0.01*	0.01*	0
		HH 0738	Mints	W	20	
		GC 0647	Oats	W	0.2	
		VA 0385	Onion, Bulb	W	0.05	
		FC 0004	Oranges, Sweet, Sour	0.2	0.5	0.01
		FS 0247	Peach	W	1	
		FP 0230	Pear	0.05	0.5	0.01
		VD 0072	Peas (dry)	W	0.01*	
		VO 0051	Peppers	W	1	
		MF 0818	Pig fat	0.05*	0.05*	0
		FS 0014	Plums (including Prunes)	W	0.5	
		VR 0589	Potato	0.05*	0.2	0.02
		PF 0111	Poultry fats	0.05*	0.05*	0
		PM 0110	Poultry meat	0.05*	0.05*	0
		VC 0429	Pumpkins	W	0.1*	
		GC 0650	Rye	0.05*	-	0.04
		AS 0650	Rye straw and fodder, dry	2	-	0.055
		SO 0699	Safflower seed	W	1	
		MF 0822	Sheep fat	0.05*	0.05*	0
		GC 0651	Sorghum	W	0.5	
		AF 0651	Sorghum forage (green)	W	1	
		AS 0651	Sorghum straw and fodder, dry	W	3	
		VC 0431	Squash, Summer	W	0.1*	
		FB 0275	Strawberry	W	0.5	
		VR 0596	Sugar beet	0.05*	0.05*	0.04
		AV 0596	Sugar beet leaves or tops	0.05*	0.5	0.04
		VO 0447	Sweet corn (corn-on-the-cob)	W	0.05	
		VO 1275	Sweet corn (kernels)	W	0.05	
		VO 0448	Tomato	W	0.5	
		TN 0085	Tree nuts	W	0.05*	
		VR 0506	Turnip, Garden	W	0.1*	
		AV 0506	Turnip leaves or tops	W	5 fresh wt	
		VC 0432	Watermelon	W	0.2	
		GC 0654	Wheat	0.05*	0.2	0.04
		AS 0654	Wheat straw and fodder, dry	2	-	0.055
		VC 0433	Winter squash	W	0.1*	
		Residue (for MRLs and STMRs): sum of demeton-S-methyl, oxydemeton-methyl, and demeton-S-methylsulphon, expressed as oxydemeton-methyl [1]For demeton-S-methyl and related compounds, alone or in combination. All recommendations are based on the use of oxydemeton-methyl. No data were supplied for the use of demeton-S-methyl or demeton-S-methylsulphon. The residues will be the sum of oxydemeton-methyl and demeton-S-methylsuphon. Any inadvertent demeton-S-methyl would also be included. Previous recommendations are currently at Step 3 or Step 6 Periodic review was for residues only				
Phosmet (103)	0.01	Acute RfD 0.02 mg/kg bw ADI unchanged				
Procymidone	0.1	VB 0041	Cabbages, Head	2	–	0.26
(136)		VP 0528	Garden pea (young pods)	3	–	0.60
		VP 0529	Garden pea, shelled (succulent seeds)	1	–	0.08

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		FS 0247	Peach	2	–	0.70
		FP 0230	Pear	1	–	0.43
		FS 0014	Plums (including Prunes)	2	–	0.74
		Residue (for MRLs and STMRs): procymidone				

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg	
(Codex ref. No.)		CCN	Name	New	Previous[1]	Quintozene	HCB
Quintozene	0.01	GC 0640	Barley	0.01*	-	0.005	0
(064)		AS 0640	Barley straw and fodder, dry	0.01*	-	0.005	
		VB 0400	Broccoli	0.05	0.02	0.0585	0
		VB 0041	Cabbages, Head	0.1	0.02	0.0052	0
		PO 0840	Chicken, Edible offal of	0.1*	-	0.03	
		PM 0840	Chicken meat	0.1* (in the fat)	-	0.04 (in the fat)	
		VD 0526	Common bean (dry)	0.02	0.2	0.002	0
		VP 0526	Common bean (pods and/or immature seeds)	0.1	0.01	0.0342	0
		SO 0691	Cotton seed	0.01	0.03	0.016	0
		PE 0112	Eggs	0.03*	-	0.01	
		VL 0482	Lettuce, Head	W[2]	3		
		GC 0645	Maize	0.01*	-	0.005	0
		AS 0645	Maize fodder	0.01	-	0.005	
		AF 0645	Maize forage	0.01*	-	0.005	0
		SO 0697	Peanut	0.5	2	0.353	0.0072
		OC 0697	Peanut oil, crude				0.0216
		OR 0697	Peanut oil, edible				0.0281
		VD 0072	Peas (dry)	0.01		0.005	0
		AL 0072	Pea hay or Pea fodder (dry)	0.05		0.021	0
		VO 0445	Peppers, Sweet	0.05*	0.01	0.05	0
		VR 0589	Potato	W[2]	0.2		
		VD 0541	Soya bean (dry)	0.01*		0.005	0
		AL 0541	Soya bean fodder	0.01*		0.0055	0
		AL 1265	Soya bean forage (green)	0.01*		0.005	0
		VR 0596	Sugar beet	0.01*		0.005	0
		AV 0596	Sugar beet leaves or tops			0.005	0
		VO 0448	Tomato	0.02	0.1	0.002	0
		GC 0654	Wheat	0.01		0.005	0
		AS 0654	Wheat straw and fodder, dry	0.03		0.005	
		Residue for compliance with MRLs for plant commodities: quintozene. For compliance with MRLs for animal commodities: sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulfide, expressed as quintozene. For estimation of dietary intake for plant and animal commodities: sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulfide, expressed as quintozene. The compounds are fat-soluble. [1]Withdrawal of all previous MRLs (now CXLs) was recommended by 1995 JMPR owing to lack of supporting studies. 29th (1997) CCPR agreed to retain them for 4 years according to periodic review procedure [2]This confirms the recommendation of the 1995 Meeting to withdraw the CXL.					
Thiophanate-methyl**	0.08	Residues arising from the use of thiophanate methyl are covered by the MRLs for carbendazim.					
(077)		Residue (for MRLs and STMRs): sum of thiophanate-methyl and carbendazim, expressed as carbendazim. Acute RfD unnecessary Previous ADI 0-0.02 mg/kg bw Periodic review was for residues only					

PART 2: ADIs, recommended MRLMs and STMRs

Pesticide	ADI (mg/kg bw)	Commodity		Recommended MRLM (mg/kg)		STMR (mg/kg)
(Codex reference no.)		CCN	Name	New	Previous	
Dimethoate**	0.002[1]	FP 0226	Apple	W[2]	1	
(027)		VS 0621	Asparagus	0.05*	-	0.02
		FI 0327	Banana	W	1 Po	
		GC 0640	Barley	2	-	0.255
		AS 0640	Barley straw and fodder, dry	-	-	0.495
		VR 0574	Beetroot	W	0.2	
		VB 0402	Brussels sprouts	1	2	0.065
		VB 0041	Cabbages, Head[3]	2	2	0.46
		VB 0403	Cabbage, Savoy	0.05*	-	0.02
		VR 0577	Carrot	W	1	
		MO 0812	Cattle, Edible offal of	0.05*	-	0
		VB 0404	Cauliflower	0.5	-	0.065
		VS 0624	Celery	W	1	
		FS 0013	Cherries	2	2	0.06
		FC 0001	Citrus fruits	W	2	
		FB 0278	Currant, Black	W	2	
		PE 0112	Eggs	0.05*	-	0
		FB 0269	Grapes	2	1	0.48
		DH 1100	Hops, dry	W	3	
		VL 0480	Kale	W	0.5	
		VL 0482	Lettuce, Head	0.5	2	0.02
		MF 0100	Mammalian fats (except milk fats)	0.05*	-	0
		MM 0096	Meat of cattle, goats, horses, pigs and sheep	0.05*	-	0
		ML 0107	Milk of cattle, goats and sheep	0.05*	-	0
		OR 0305	Olive oil, refined	W	0.05*	
		FT 0305	Olives	W	1	
		DM 0305	Olives, processed	W	0.05*	
		VA 0385	Onion, Bulb	0.05*	0.2	0.02
		FS 0247	Peach	W	2	
		FP 0230	Pear	W[2]	1	
		VP 0063	Peas (pods and succulent = immature seeds)	1	0.5	0.065
		VO 0051	Peppers	W	1 Po	
		FS 0014	Plums (including Prunes)	1	0.5	0.1
		FP 0009	Pome fruits	0.5	-	0.065
		VR 0589	Potato	0.05	0.05	0.01
			Potato granules			0.002
			Potato chips			0.002
		PO 0111	Poultry, Edible offal of	0.05*	-	0
		PF 0111	Poultry fats	0.05*	-	0
		PM 0110	Poultry meat	0.05*	-	0
		MO 0822	Sheep, Edible offal of	0.05*	-	0
		GC 0651	Sorghum	0.01*	-	0.01
		AF 0651	Sorghum forage (green)	-	-	0.01
		AS 0651	Sorghum straw and fodder, dry	-	-	0.01
		VL 0502	Spinach	W	1	
		FB 0275	Strawberry	W	1	

Pesticide	ADI (mg/kg bw)	Commodity		Recommended MRLM (mg/kg)		STMR (mg/kg)
(Codex reference no.)		CCN	Name	New	Previous	
		VR 0596	Sugar beet	0.05	0.05	0.01
		AV 0596	Sugar beet leaves or tops	0.1	1 T	0.05
		VO 0448	Tomato	2	1 Po	0.21
		JF 0448	Tomato juice			0.03
			Tomato purée			0.4
			Tomato paste			0.6
			Tomato ketchup			0.4
		VR 0506	Turnip, Garden	0.1	0.5	0.1
		VL 0506	Turnip greens	1	-	0.1
		GC 0654	Wheat	0.2	-	0.09
		AS 0654	Wheat straw and fodder, dry	10	-	2.23
		VS 0469	Witloof chicory (sprouts)	W	0.5	
		Residue (for MRLMs and STMRs): dimethoate [1]For sum of dimethoate and omethoate expressed as dimethoate [2]Replaced by recommendation for Pome fruits [3]Except Savoy cabbage Periodic review was for residues only				
Omethoate**	No ADI[1]	FP 0226	Apple	W	2	
(055)		FS 0240	Apricot	W	2	
		VS 0620	Artichoke, Globe	W	0.5	
		VS 0621	Asparagus	-	-	0.02
		FI 0327	Banana	W	0.2*	
		GC 0640	Barley	-	-	0.015
		AS 0640	Barley straw and fodder, dry	-	-	0.03
		VP 0061	Beans, except broad bean and soya bean	W	0.2	
		VB 0400	Broccoli	W	0.2	
		VB 0402	Brussels sprouts	W	0.2	0.03
		VB 0403	Cabbage, Savoy	-	-	0.075
		VB 0041	Cabbages, Head	W	0.5 T	0.165
		VR 0577	Carrot	W	0.05	
		VB 0404	Cauliflower	W	0.2	0.01
		VS 0624	Celery	W	0.1	
		GC 0080	Cereal grains	W	0.05	
		FS 0013	Cherries	W	2	0.27
		FC 0001	Citrus fruits	W	2	
		VC 0424	Cucumber	W	0.2	
		FB 0278	Currant, Black	W	2	
		FB 0269	Grapes	W	2	0.11
		DH 1100	Hops, dry	W	3	
		VL 0480	Kale	W	0.2	
		VL 0482	Lettuce, Head	W	0.2	0.03
		VL 0483	Lettuce, Leaf	W	0.2	
		VA 0385	Onion, Bulb	W	0.5	0.02
		FS 0247	Peach	W	2	
		FP 0230	Pear	W	2	
		VP 0063	Peas (pods and succulent = immature seeds)	W	0.1	0.02
		VO 0051	Peppers	W	1	
		FS 0014	Plums (including Prunes)	W	1	0.05
		FP 0009	Pome fruits	-	-	0.05
		VR 0589	Potato	W	0.05	0.01
			Potato chips			0.002

Pesticide	ADI (mg/kg bw)	Commodity		Recommended MRLM (mg/kg)		STMR (mg/kg)
(Codex reference no.)		CCN	Name	New	Previous	
			Potato granules			0.002
		GC 0651	Sorghum	-	-	0.01
		AF 0651	Sorghum forage (green)	-	-	0.01
		AS 0651	Sorghum straw and fodder, dry	-	-	0.01
		VL 0502	Spinach	W	0.1	
		FB 0275	Strawberry	W	1	
		VR 0596	Sugar beet	W	0.05	0.01
		AV 0596	Sugar beet leaves or tops	W	1T	0.05
		VO 0448	Tomato	W	0.5	0.05
		JF 0448	Tomato juice	-	-	0.009
			Tomato purée			0.05
			Tomato paste			0.07
			Tomato ketchup			0.05
		VR 0506	Turnip, Garden	W	0.2	0.1
		VL 0506	Turnip greens	-	-	0.1
		GC 0654	Wheat	-	-	0.01
		AS 0654	Wheat straw and fodder, dry	-	-	0.08
		VS 0469	Witloof chicory (sprouts)	W	0.5	
		Residue (for STMRs): omethoate [1]ADI was withdrawn in 1996 because the Meeting was informed that the primary manufacturer was no longer producing omethoate Periodic review was for residues only				

ANNEX II

PREVIOUS FAO AND WHO DOCUMENTS

1. FAO/WHO. 1962 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.

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CORRECTION TO RESIDUE EVALUATIONS OF THE 1997 JMPR

Carbosulfan, p. 223, Definition of the residue

The final sentence should read "The Meeting therefore concluded that residues of carbosulfan should be defined as **carbosulfan**."