FLUOPICOLIDE (235)

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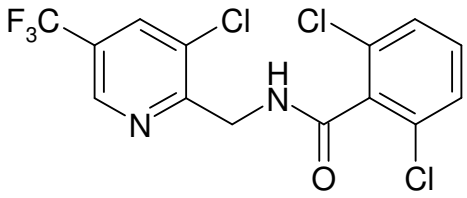
EXPLANATION

Fluopicolide belongs to the benzamide and pyridine class of fungicide. It is active against a wide range of Oomycete (Phycomycete) diseases including downy mildews (Plasmopara, Pseudoperonospora, Peronospora and Bremia), late blight (Phytophthora), and some Pythium species. The compound was listed at the 40th session of the CCPR (2008) for review by the 2009 JMPR for both residue and toxicological aspects. ADIs for fluopicolide and 2,6-dichlorobenzamide of 0–0.08 and 0–0.02 mg/kg bw respectively. For fluopicolide the ARfD is 0.6 mg/kg bw for women of child-bearing age with an ARfD not necessary for other groups of the population.

The Meeting set an ARfD for 2,6-dichlorobenzamide of 0.6 mg/kg bw for the general population. The Meeting received information on fluopicolide metabolism and environmental fate, methods of residue analysis, freezer storage stability, national registered use patterns, supervised residue trials, farm animal feeding studies and fates of residues in processing.

IDENTITY

Common name	Fluopicolide
Chemical name	
IUPAC:	2,6-dichloro-N-{[3-chloro-5-(trifluoromethyl)-2-pyridinyl]methyl}benzamide
CAS:	benzamide, 2,6-dichloro-N-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]methyl]
CAS number:	239110-15-7
Manufacturer's code numbers:	fluopicolide
Molecular formula:	$C_{14}H_8Cl_3F_3N_2O$
Molecular mass:	383.59 g/mol
Structural formula:	



Formulations	Active ingredient content
SC 687.5	62.5 g/L fluopicolide
WG 71.1	4.44 g/kg fluopicolide
WP 72.7	6 g/kg fluopicolide
SC 480	480 g/L fluopicolide

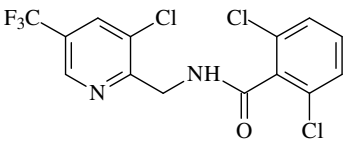
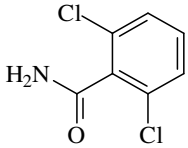
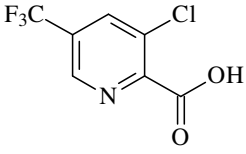
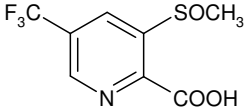
Physical and chemical properties

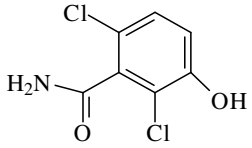
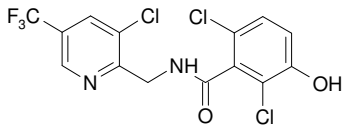
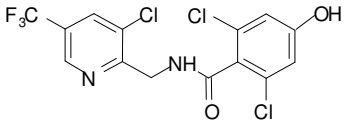
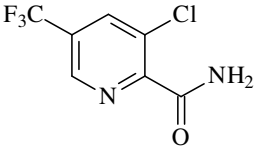
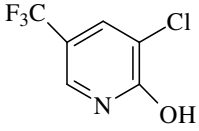
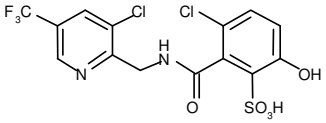
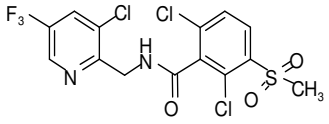
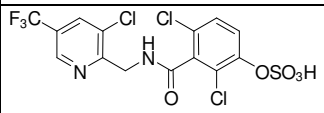
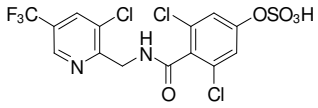
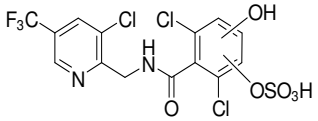
Property	Results	Reference
Appearance	Pure analytical grade: Fine crystalline beige powder Technical grade: Beige powder	Mühlberger, Eyrich, 2003 Edition no.: M-230262-01-1 and M-230264-01-1
Odour	Pure analytical grade: Weakly phenol-like odour Technical grade: No characteristic odour	Mühlberger, Eyrich, 2003 Edition no.: M-230262-01-1 and M-230264-01-1
Melting point	Pure analytical grade: 150 °C	Smeykal, 2003, Edition no. M-234480-01-1
Boiling point	Pure analytical grade: decomposes at 320 °C	Smeykal, 2003 Edition no.: M-234482-01-1
Relative density	Pure analytical grade: 1.65 (compared to water at 4 °C)	Smeykal, 2003 Edition no.: M-234484-01-1
Vapour pressure	Pure analytical grade: The vapour pressure was determined over the temperature range 93.5 to 128 °C by a gas saturation method. Clausius Clapeyron analysis gave the parameter values a = 18.73 and b = 7401.6 and the vapour pressure, by extrapolation, was found to be : 3.03×10^{-7} Pa at 20 °C 8.03×10^{-7} Pa at 25 °C	Bright, 2000 Edition no.: M-197457-01-1
Volatility	Henry's law constant at 20 °C (calculated) 4.15×10^{-5} Pa.m^3.mole^{-1}	Renaud, 2003 Edition no.: M-223275-01-1
Solubility in water including effect of pH	Unbuffered distilled water mg/L 2.86 mg/L at 20 °C at pH 4 2.80 mg/L at 20 °C at pH 7 2.80 mg/L at 20 °C at pH 9	Mühlberger, 2003 Edition no.: M-234496-01-1
Solubility in organic solvents (at 20 °C)	n-hexane : 0.2 g/L acetone : 74.7 g/L ethanol : 19.2 g/L dichloromethane : 126.0 g/L toluene : 20.5 g/L dimethylsulfoxide : 183.0 g/L ethylacetate : 37.7 g/L	Mühlberger, Eyrich, 2003 Edition no.: M-229073-01-1
Partition coefficient n-octanol/water (at 20 °C)	pH 4.0, 7.3 and 9.1: log P_{ow} = 2.9 (P_{ow} = 794)	Mühlberger, 2003 Edition no.: M-231643-01-1
Hydrolysis	The hydrolysis of [^{14}C]benzoyl labelled fluopicolide was investigated at 50 °C at pH 4, 7 and 9 over a 5 day period and at 25 °C at pH 5, 7 and 9 over a 30 day period, in the dark, under sterile conditions. Fluopicolide did not degrade significantly in any of the sterile buffer solutions after 5 days at 50 °C or 30 days at 25 °C, indicating that fluopicolide is hydrolytically stable. A degradation product, M-01 was detected in small amounts throughout the 50 °C and 25 °C tests. It reached a maximum of 3% of applied radioactivity in the 50 °C test at pH 9 after 5 days and 4% of applied radioactivity in the 25 °C test at pH 7 after 30 days.	Shepler, Runes, 2002 Edition no.: M-241162-01-1
Photolysis	[^{14}C]fluopicolide was exposed to artificial light in a sterile aqueous pH 7 buffer solution for up to 31 days of irradiation in 12 hour of light and dark cycles, at an application rate of 0.65 ppm. Light exposed and dark control samples were maintained at 25 °C. Fluopicolide exhibited slow degradation in light exposed samples and represented up to 83.6% of the dose after 31 days.	Runes, Shepler, 2003 Edition no.: M-241161-01-1

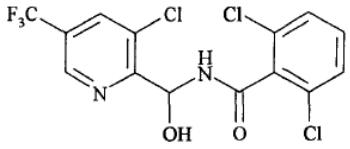
Property	Results	Reference
UV absorption	Molar extinction coefficients (ε) of the UV/VIS absorption maxima and for the wavelength with the highest absorption above 290 nm of neutral, acidic and alkaline solutions were also determined. Solvent wavelength (nm) ε (L*mol⁻1*cm) Methanol : 203 44159 271 3601 291 -23 Methanol/HCl 202 45553 90/10 v/v 270 3853 291 103 Methanol/NaOH 219 18793 90/10 v/v 271 3741 291 -0.6	Mühlberger, 2003 Edition no.: M-234474-01-1
Quantum yield	The quantum yield of fluopicolide was calculated to be 3.50 × 10^{-2} based on a concurrently irradiated [PNAP]/[PYR] actinometer. The quantum yield and average solar irradiance values at latitudes of 30º to 50 ºN were used to predict half-life (DT_{50}) at different seasons. The predicted DT_{50} values for fluopicolide at 30º, 40º and 50 ºN latitude during summer seasons were 77, 81 and 88 days respectively	Runes, Shepler, 2003 Edition no.: M-241161-01-1
Dissociation constant	There was no evidence for ionisation of fluopicolide in the pH range 1.9 to 9.8.	Bright, 2000 Edition no.: M-197456-01-

METABOLISM AND ENVIRONMENTAL FATE

Metabolites are given various abbreviations and code numbers in the studies. Structures and abbreviations and codes are shown below.

	Other identifiers	Structure	Formula	Presence in metabolism studies
fluopicolide	(parent)		2,6-dichloro-N-{[3-chloro-5-(trifluoromethyl)-2-pyridinyl]methyl}benzamide $C_{14}H_8Cl_3F_3N_2O$ MW = 383.59	
M-01 (AE C653711)	BAM		2,6-dichlorobenzamide $C_7H_5Cl_2NO$ MW = 190.0	rat liver, laying hen, crop, soil, rotational crop
M-02 (AE C657188)	PCA UMET/2		3-chloro-5-trifluoromethyl-pyridine-2-carboxylic acid $C_7H_3ClF_3NO_2$ MW = 225.6	rat, crop, rotational crop, soil, water
M-05 (AE 1344122)	P1x RPA433497		3-methylsulfinyl-5-trifluoro-methylpyridine-2-carboxylic acid $C_8H_6F_3NO_3S$ MW = 253	rotational crop

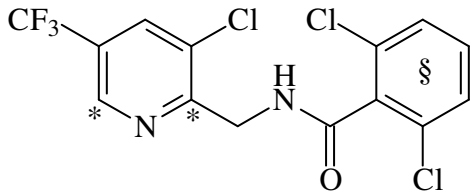
	Other identifiers	Structure	Formula	Presence in metabolism studies
M-04 (AE C657378)	3-hydroxy BAM		2,6-dichloro-3-hydroxy-benzamide $C_7H_5Cl_2NO_2$ MW = 206	rotational crop rat (BAM ADME study)
M-06 (AE C643890)	3-OH 206 MET IV MET.F/16 FMET/38 UMET/51 FMET/8 UMET/44 UMET/53 FMET/33		2,6-dichloro-N-[(3-chloro-5-trifluoromethylpyridin-2-yl) methyl]-3-hydroxybenzamide $C_{14}H_8Cl_3F_3N_2O_2$ MW = 399	laying hen, lactating cow crop, confined rotational crop, rat
M-07 (AE 0712556)	4-OH 206 UMET/54 UMET/26		2,6-dichloro-N-[(3-chloro-5-trifluoromethylpyridin-2-yl) methyl]-4-hydroxybenzamide $C_{14}H_8Cl_3F_3N_2O_2$ MW = 399	laying hen, lactating cow rat
M-08 (AE C653598)			3-chloro-5-trifluoromethyl pyridine-2-carboxamide $C_7H_4ClF_3N_2O$ MW = 224.57	confined rotational crop
M-09 (AE B102859)			3-chloro-2-hydroxy-5-trifluoromethylpyridine $C_6H_3ClF_3NO$ MW = 197.54	confined rotational crop
M-16	P9 UMET/40 FMET/23		3-chloro-2-[({3-chloro-5-trifluoromethylpyridine-2-ylmethyl}amino) carbonyl]-6-hydroxybenzene sulfonic acid $C_{14}H_9Cl_2F_3N_2O_5S$ MW = 444	rat
M-17	Metabolite 1		2,6-dichloro-N-{[3-chloro-5-(trifluoromethyl)pyridin-2-yl]methyl}-3-(methylsulfonyl)benzamide $C_{15}H_{10}Cl_3F_3N_2O_3S$ MW = 462	laying hen
M-18	HS (hydroxy sulphate of fluopicolide) UMET/45 UMET/47	 or 	2,4-dichloro-3-[({[3-chloro-5-(trifluoromethyl)pyridin-2-yl]methyl}amino)carbonyl] phenyl hydrogen sulfate or 3,5-dichloro-4-[({[3-chloro-5-(trifluoromethyl)pyridin-2-yl]methyl}amino)carbonyl] phenyl hydrogen sulfate $C_{14}H_7Cl_3F_3N_2O_5S$ MW = 477	laying hen lactating cow rat
M-19	DHS (dihydroxy sulphate of fluopicolide) UMET/23 UMET/39		3,5-dichloro-4-[({[3-chloro-5-(trifluoromethyl)pyridin-2-yl]methyl}amino)carbonyl] hydroxyphenyl hydrogen sulfate $C_{14}H_7Cl_3F_3N_2O_6S$ MW = 493	laying hen lactating cow rat

	Other identifiers	Structure	Formula	Presence in metabolism studies
	UMET/46 UMET/49			
AE 0608000	RPA 427967 (hydroxy)		2,6-dichloro-N-[(3-chloro-5-trifluoromethyl-2-pyridyl)(hydroxy)methyl]benzamide $C_{14}H_8Cl_3F_3N_2O_2$ MW = 400	

Animal Metabolism

The Meeting received studies on the metabolism of fluopicolide in rats, lactating cows and laying hens. The metabolism of fluopicolide in plants and animals was investigated using [pyridyl-2,6-^{14}C]-labelled and [phenyl-U-^{14}C]-labelled fluopicolide. In addition, rat studies were conducted with two metabolites of fluopicolide, using [phenyl-U-^{14}C]-labelled M-01 and [pyridyl-2,6-^{14}C]-labelled M-02. The studies on rats were evaluated by the WHO Core Assessment Group.

*Fluopicolide: * and § indicate positions of ^{14}C-labels*



* = [2,6-14C-pyridyl]-fluopicolide (pyridyl-label)

§ = [U-14C-phenyl]-fluopicolide (phenyl-label)

Lactating cow

Lactating cows were orally dosed with [^{14}C]fluopicolide, labelled in either the phenyl or pyridyl ring, at the equivalent of 1 or 10 ppm in the diet for 7 days. The dose was administered in two portions each day. For the phenyl-label experiment (Needham & Hardwick 2003, amended 2008, 2014/040-D1145), Holstein Friesian cows (ca 6.5 years/564–588 kg) were dosed at the equivalent of 1.1 or 10.6 ppm in the feed. During the study average milk yield was 12.4 and 13.3 kg/day respectively for the low and high dose cows while respective feed consumptions were 12.5 and 15.1 kg/day. The lower dose animal experienced bloat during the course of the experiment and the amount of feed offered was modified accordingly. For the pyridyl-label experiment (Gedik & McCombe 2003, amended 2009, 21582), Holstein Friesian cows (ca 3–7 years/554–676 kg) were dosed at the equivalent of 1 and 10 ppm (feed intakes were not reported though it was stated dosing was based on the assumption that each animal consumed 20 kg dry matter/day). Milk yields were 20 and 16 L/day for the low and high dose animals.

The cows were milked twice daily (am and pm) prior to dose administration. Urine, faeces and cage wash were collected at 24 h intervals until sacrifice. At approximately 23.5 h after administration of the last dose, samples of tissues were collected: muscle (hind and forequarter), fat (renal and omental), liver and kidneys. Excreta, milk and tissues were extracted by various methods including solvent extraction, protease hydrolysis and acid hydrolysis and the extracts were analysed by two HPLC systems for metabolite quantification. Identification work was performed with LC-MS and by comparison with authentic standards. All analysis of samples which lead to quantification of identified residues was completed within 6 months, with the exception of muscle for the phenyl label and liver and kidney for the pyridyl label. Adequate stability of fluopicolide in muscle samples was established for 194 days and liver and kidney extracts for 250 days when stored frozen (–20 ºC) by comparison of profiles from extracts analysed after 4 to 250 days storage.

Overall, the recovery of radioactivity in urine, faeces, milk, cage wash and tissues was 76–84% of the administered dose. The major route of excretion was via the faeces accounting for 55–69% of the total administered dose. Excretion in urine accounted for a further 11–19% of the dose. Levels of radioactivity in milk were low (≤ 0.002 mg equiv/kg for the low doses) reaching 0.019 mg equiv/kg for the high dose level with the phenyl-label. Distribution of radioactivity within the tissues was broadly similar for both labels and dose levels with the exception of liver for which residues were somewhat higher for the phenyl label. For both labels the highest tissue residue levels were found in the liver, kidney, renal fat, whole blood and plasma, with low residue levels found in omental fat and muscle.

Table 1 Percentage of administered doses

Sample	Phenyl label		Pyridyl label	
	1 ppm	10 ppm	1 ppm	10 ppm
Urine	17	19	14	11
Faeces	57	55	69	67
Cage wash	0.87	1.0	1.2	2.1
Final cage wash	0.05	0.06	NA	NA
Milk	0.14	0.13	0.09	0.08
Tissues	0.78	0.54	0.39	0.29
Total	76	76	84	80

NA = not applicable as value was included in cage wash result.

Table 2 Total radioactive residues in milk, plasma, blood and tissues (mg equivalents/kg)

Time point	Phenyl label		Pyridyl label	
	1 ppm	10 ppm	1 ppm	10 ppm
Milk				
Day 1	0.0004	0.008	0.001	0.007
Day 2	0.001	0.014	0.001	0.010
Day 3	0.001	0.017	0.001	0.009
Day 4	0.002	0.018	0.001	0.010
Day 5	0.002	0.019	0.001	0.010
Day 6	0.002	0.018	0.001	0.010
Day 7	0.002	0.018	0.001	0.010
Day 8	0.001	0.014	0.001	0.010
Liver	0.090	0.644	0.058	0.449
Kidney	0.026	0.30	0.033	0.196
Fat renal	0.006	0.040	0.005	0.042
Fat omental	0.005	0.043	0.005	0.039
Muscle h'qtr	< LOQ	0.023	0.001[a]	0.012[a]
Muscle f'qtr	< LOQ	0.025	–	–
Blood	0.011	0.088	0.010	0.074
Plasma	0.013	0.100	0.011	0.082

[a] Mixture of forequarter, hindquarter and loin muscle.

Low levels of radioactivity in tissues and milk hampered identification of metabolites. For the phenyl label, fluopicolide was the major component of the radioactive residues extracted by organic solvents in milk (37%) and fat (78%). Fluopicolide was detected at lower levels in muscle (5.1%), liver (0.9%) and kidney (0.7%). Other metabolites in milk, fat and muscle were unable to be identified or were associated with polar material and were individually present at levels < 0.008 mg equiv/kg. A large number of metabolites were present in kidney and liver, principally M-06 and M-07 with other metabolites present at low levels and unable to be identified.

Enzyme hydrolysis of residues that were not solvent extracted from liver and kidney indicated the radioactivity was not associated with glucuronide conjugates. Protease hydrolysis yielded polar material that was not able to be identified while cellular fractionation revealed the radioactivity was mainly associated with low molecular weight proteins, amino acids and peptides (33% TRR kidney and 17% liver), lipids (12% kidney and 15% liver), sulphurated glycosaminoglycans (14% kidney and 15% liver) with low levels associated with carbohydrates, RNA and DNA.

Acetonitrile and aqueous methanol extraction of tissue and milk samples from phenyl-dosed cows resulted in extraction efficiencies of 28% (muscle), 85% (fat), 86% (milk), 38% (liver) and 40% (kidney) TRR.

Table 3 Characterization/identification of total radioactive residues in milk and tissues after oral dosing of lactating cows with [^{14}C]fluopicolide (phenyl label) at levels equivalent to 10 ppm in feed

	Milk [a]	Fat	Muscle	Liver	Kidney
TRR (mg/kg as fluopicolide)	0.019	0.041	0.024	0.64	0.30
		%TRR			
Extracted with CH3CN	86	85	28	38	40
fluopicolide	37	78	5.1	0.9	0.7
M-06	–	–	–	1.6	6.8
M-07	–	–	–	1.2	3.3
M-01	3.9[c]	–	–	–	–
Liberated on hydrolysis of PES[b]	–	–	–	52	52
Unextracted	14	17	74	11	7.6

[a] Composite of milk from days 1–7.

[b] Liberated by pepsin hydrolysis, protease digestion, acid hydrolysis

[c] The presence of this metabolite could not be confirmed in a second system or by HPLC/MS.

For the pyridyl label experiment, fluopicolide was the major component of the radioactive residues in fat (64–73%) and was detected at lower levels in liver (2.9%) and kidney (1.8%). M-06, M-07 and a range of hydroxyl conjugates (HG, M-18, DHG, M-18/M-19) were detected in liver and kidney. As with the phenyl-label, other metabolites were unable to be identified or were associated with polar material. Enzyme hydrolysis of residues that were not solvent extracted from liver and kidney indicated the radioactivity was not associated with glucuronide conjugates. At least 14 components ranging in concentration from 0.004 to 0.039 mg equiv/kg were present in the liver hydrolysate when subject to chromatography using a column for separation of peptides. M-08 was identified in kidney at 5.1% TRR. Protease hydrolysis yielded polar material that was not able to be identified.

Table 4 Characterization/identification of total radioactive residues in milk and tissues after oral dosing of lactating cows at the equivalent of 1 ppm with of [^{14}C]fluopicolide (pyridyl label)

	Liver	Kidney	Renal Fat
TRR (mg/kg as fluopicolide)	0.058	0.033	0.005
	%TRR		

	Liver	Kidney	Renal Fat
Extracted with methanol	14	30	78
Fluopicolide [a]	–	–	64
PES	86	70	22
Pepsin and protease	44	6.8	
HCl	18	12	

[a] Assigned by co-chromatography with a reference standard

Table 5 Characterization/identification of total radioactive residues in milk and tissues after oral dosing of lactating cows with [^{14}C]fluopicolide (pyridyl label) equivalent to 10 ppm in feed

	Milk [a]	Fat	Muscle	Liver	Kidney
TRR (mg/kg as fluopicolide)	0.01	0.041	0.012	0.45	0.20
		%TRR			
Extracted with methanol	83	88	36	18	34
fluopicolide		73	–	2.9	1.8
M-06/M-07		–		4.0	2.6
HG				4.9	4.7
M-18				2.4	–
DHG				–	10
M-18/M-19				–	5.2
PES	17	12	64	82	66
Pepsin and protease				45	52
6N HCl				5	40

[a] Composite of milk from 175 h after the start of dosing.

DHG = dihydroxy glucuronide of fluopicolide; HG = hydroxy glucuronide of fluopicolide; M-18 = hydroxy sulphate of fluopicolide; M-19 = dihydroxy sulphate of fluopicolide

Methanol and aqueous methanol extraction of tissue and milk samples from pyridyl-dosed cows resulted in extraction efficiencies of 36% (muscle), 88% (renal and omental fat), 83–89% (milk), 18% (liver) and 34% (kidney) TRR.

A proposed metabolic pathway for fluopicolide in lactating cows is presented in Figure 1.

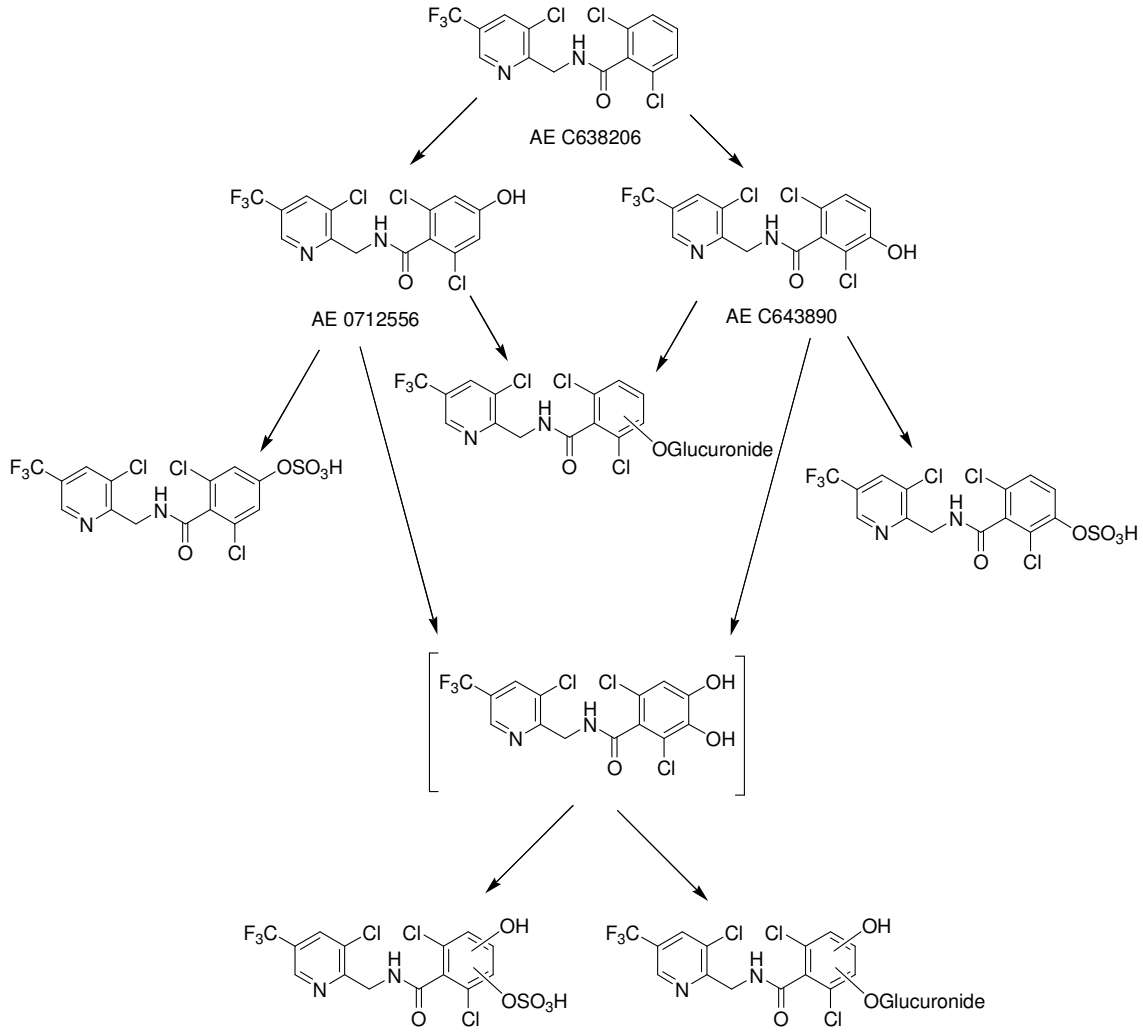


Figure 1 Proposed fluopicolide metabolic pathway in lactating cows

Laying hen

Laying hens were capsule dosed with phenyl- (Needham & Hardwick 2003, amended 2009, 2014/004-D1145) or pyridyl-labelled (Gedik & McCombe 2003, amended 2009, 21552) [^{14}C]fluopicolide at the equivalent of 1 and 10 ppm in the diet for 14 days. In the case of phenyl-label experiment Hisex hens 19–22 weeks old and weighing 1.5 to 1.8 kg were used. For dosing with the pyridyl-label, hens (breed unspecified) were 25 weeks old and weighed 1.5 to 2.2 kg. Doses were prepared by dissolving appropriate amounts of radio-labelled and non-radio-labelled fluopicolide in acetonitrile or acetone which was pipetted into gelatine capsules and the solvent allowed to evaporate at room temperature prior to the capsules being sealed. Actual doses were equivalent to 1.2 and 10.7 ppm for the phenyl-label and 1.1 and 13 ppm for the pyridyl-label. Laying efficiency was 37 and 46% during the dosing period for the phenyl-label and close to 100% for the pyridyl-label.

Eggs were collected afternoon and morning following dose administration, and excreta was collected at 24 h intervals until sacrifice, approximately 23 h to 24 h after the last dose administration. At each collection of excreta, cage debris were removed and pooled by bird over the study period.

Eggs were separated into white and yolk and pooled, by animal over 24 h periods. Tissues were homogenised in the presence of dry ice prior to storage.

Radioactivity was measured using liquid scintillation counting. Excreta, eggs and tissues were extracted by various methods including solvent extraction, protease hydrolysis and acid hydrolysis and the extracts were analysed by two HPLC systems for metabolite quantification. Identification work was performed with LC-MS and comparison with authentic standards. All metabolic profiles used for identification and quantification were completed within 6 months, with one exception. Samples of liver were extracted and analysed after up to 16 months of storage. Adequate stability of the two major identified metabolites was established in liver samples for 475 days storage under frozen conditions.

Following repeated oral administration of [^{14}C]fluopicolide with a nominal dose equivalent to 1 or 10 ppm in the diet for 14 days with either the phenyl or the pyridyl radiolabel, the overall mean recoveries of radioactivity ranged from 83–96%.

The majority of the administered radioactivity was recovered in the excreta; 82–95%. The levels of radioactivity in the tissues of the phenyl radiolabel groups were consistently higher than those for the pyridyl radiolabel groups. Presumably metabolites containing the pyridyl ring are more readily excreted.

Table 6 Percentage of administered dose

Sample	Phenyl label		Pyridyl label	
	1 ppm	10 ppm	1 ppm	10 ppm
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Excreta	82 ± 7.1	95 ± 2.9	93 ± 2.5	92 ± 3.2
Egg White	0.04 ± 0.03	0.04 ± 0.02	0.04 ± 0.01	0.02 ± 0.01
Egg Yolk	0.04 ± 0.04	0.05 ±0.03	0.09 ± 0.01	0.06 ± 0.01
Cage wash	0.46 ± 0.38	0.43 ±0.14	2.8 ± 1.2	2.3 ± 0.46
Final cage wash	0.28 ± 0.23	0.21 ±0.06	NA	NA
Tissues	0.24 ± 0.07	0.23 ±0.06	0.09 ± 0.02	0.06 ± 0.01
Total	83 ± 7.1	96 ±2.9	96 ± 1.6	94 ± 3.0

NA = not applicable as value was included in cage wash result.

SD = standard deviation

Table 7 Total radioactive residues in eggs, plasma, blood and tissues (mg equivalents/kg)

Sample	Time-point	Phenyl label		Pyridyl label	
		1 ppm	10 ppm	1 ppm	10 ppm
Egg Yolk	24 h	< LOQ	< LOQ	0.002	0.003
	48 h	0.001	0.009	0.001	0.008
	72 h	0.005	0.034	0.003	0.022
	96 h	0.007	0.064	0.009	0.043
	120 h	0.010	0.024	0.008	0.058
	144 h	0.014	0.099	0.008	0.066
	168 h	0.012	0.156	0.010	0.077
	192 h	0.014	0.156	0.011	0.085
	216 h	0.015	0.159	0.011	0.079
	240 h	0.019	0.154	0.011	0.077
	264 h	0.023	0.178	0.011	0.089
	288 h	0.019	0.198	0.014	0.085
	312 h	0.020	0.134	0.013	0.087
	335 h	0.020	0.180	0.013	0.084

Sample	Time-point	Phenyl label		Pyridyl label	
		1 ppm	10 ppm	1 ppm	10 ppm
Egg White	24 h	< LOQ	0.001	0.001	0.003
	48 h	0.004	0.022	0.001	0.009
	72 h	0.004	0.034	0.002	0.011
	96 h	0.005	0.027	0.002	0.013
	120 h	0.005	0.005	0.002	0.010
	144 h	0.007	0.054	0.002	0.013
	168 h	0.011	0.030	0.001	0.010
	192 h	0.003	0.049	0.002	0.012
	216 h	0.003	0.047	0.002	0.011
	240 h	0.004	0.037	0.001	0.011
	264 h	0.005	0.034	0.001	0.011
	288 h	0.007	0.066	0.003	0.009
	312 h	0.006	0.054	0.002	0.013
	335 h	0.004	0.043	0.002	0.013
Liver		0.126 ± 0.057	0.976 ± 0.416	0.041 ± 0.008	0.275 ± 0.049
Skin with fat		0.008 ± 0.003	0.069 ± 0.011	0.003 ± 0.001	0.022 ± 0.011
Muscle		0.004 ± 0.001	0.039 ± 0.006	0.002 ± 0.000	0.011 ± 0.003
Fat		0.006 ± 0.001	0.061 ± 0.023	0.003 ± 0.001	0.026 ± 0.014
Blood		0.018 ± 0.006	0.192 ± 0.059	0.020 ± 0.004	0.125 ± 0.021
Plasma		0.003 ± 0.001	0.042 ± 0.015	0.002 ± 0.001	0.016 ± 0.005

For the phenyl label the majority of the radioactivity present in egg yolk, egg white, skin, fat, and muscle was extracted using acetonitrile (56–98% TRR). Protease hydrolysis of liver followed by acetonitrile and methanol/water extraction recovered the majority of the radioactivity in this tissue (78% TRR). Unextracted residues accounted for ≤ 0.05 mg equiv/kg in egg white, egg yolk, skin, fat, and muscle, and 22% TRR in liver.

Characterisation of phenyl-label radioactive residues revealed low levels of fluopicolide in egg white, egg yolk, and fat (2.5–11% TRR); it was not identified in liver or skin. The major metabolite identified in egg white and fat was M17, a methyl sulfone conjugate of fluopicolide, at 51% TRR in egg white and 38% TRR in fat. M-17 was also identified in skin at 10% TRR. The major residue identified in liver was M-01 (BAM) at 37% TRR. M-06 was the major metabolite found in skin, at 15% TRR. Additionally, following enzyme hydrolysis 3.1% of liver TRR was tentatively assigned to M-06 and or AE 0608000. The remainder of the radioactivity consisted of unknowns (each present at ≤ 0.06 mg equiv/kg) and polar compounds.

Although metabolite M-01 was found in liver following enzyme hydrolysis, comparative analysis of an extract of liver with or without glucuronidase hydrolysis indicated that metabolite M-01 was not present in liver as a glucuronide conjugate. Additional characterization procedures with liver indicated that the largest portion of radioactivity after hydrolysis (≥ 90% TRR) could be extracted with water with approximately 40% TRR organosoluble. Cellular fractionation of liver indicated that the largest portions of radioactivity were associated with low molecular weight proteins, amino acids, and peptides (23% TRR), sulfurated glucosaminoglycans (29% TRR), and protein (26% TRR; released upon base hydrolysis).

Table 8 Characterization/identification of total radioactive residues in eggs and tissues after oral dosing of laying hens with of [^{14}C]fluopicolide (phenyl label) equivalent to 10 ppm in the feed

	Egg white	Egg yolk	Liver	Skin + fat	Fat	Muscle
TRR (mg/kg as fluopicolide)	0.043	0.154	0.976	0.069	0.061	0.039
			%TRR			
Total solvent extracted	98	74	78	69	76	56

	Egg white	Egg yolk	Liver	Skin + fat	Fat	Muscle
fluopicolide	2.5	11	–	–	6	–
M-06	–	–	5.4	15	–	–
M-01	–	–	37	–	–	–
M-17	51	–	–	10	38	–
Unknown	–	13	22	–	–	–
Polar	–	45	–	34	19	56
PES HCl hydrolysis	2	31 8	22	31	24	44

Egg white: Extracted with acetonitrile

Egg yolk: Sequentially extracted with acetonitrile (63%), methanol/water (11%). Total solvent extracted 74%.

M-17 assigned to a methylsulphone conjugate of fluopicolide based on LC-MS-MS analysis.

In the liver 23% of the TRR was associated with water soluble low molecular weight proteins, peptides and amino acids, 29% with sulphurated glucosaminoglycans and 26% with high molecular weight proteins.

For the pyridyl label, 62–95% of the radioactive residues were extracted from egg white, egg yolk, fat and skin using MeOH/water and 18–24% TRR from muscle and liver. A large portion of radioactivity was extracted from liver using pepsin and protease hydrolysis (51–52% TRR) and strong acid hydrolysis (10–17% TRR). Pepsin and protease hydrolysis released 29–37% TRR from egg yolk. Unextracted residues accounted for ≤ 0.01 mg equiv/kg in egg white, egg yolk, skin, fat, muscle, and liver (low-dose hens), and after extensive hydrolysis 20% TRR (0.06 mg equiv/kg) in liver from high-dose hens.

Fluopicolide was identified at low levels in egg yolk, fat, and skin (3.3–16% TRR); it was not identified in liver or egg white. The major metabolite identified in egg white, fat, and skin was M-07, at 41% TRR in egg white, 47% TRR in fat, and 30% TRR (0.007 ppm) in skin; this metabolite was also identified in egg yolk at 10–16% TRR and in liver at 6% TRR. A metabolite determined to be a dihydroxy sulfate of fluopicolide, or two metabolites that were both dihydroxy sulphates of fluopicolide, was a major portion of the residue in egg white (23% TRR) and egg yolk (15–34% TRR); it was also found in liver at 2% TRR. A hydroxy sulfate of fluopicolide was observed in egg yolk and liver at low levels (1.0–7.1% TRR), and a second hydroxy sulfate of fluopicolide was observed as a minor metabolite in liver (1.4% TRR). The remainder of the radioactivity consisted of unknowns (each present at < 0.03 mg equiv/kg). The majority of the radioactivity in liver (51–52% TRR) was released upon pepsin and protease hydrolysis, with an additional 10–17% released via strong acid hydrolysis. The hydrolysates were found to consist of several unknowns, each < 0.03 mg equiv/kg.

Table 9 Characterization/identification of total radioactive residues in eggs and tissues after oral dosing of laying hens with of [^{14}C]fluopicolide (pyridyl label) equivalent to 10 ppm in the feed

	Egg white (96 h)	Egg yolk (96 h)	Egg yolk (312 h)	Liver	Skin + fat	Fat
TRR (mg/kg as fluopicolide)	0.013	0.043	0.087	0.275	0.0229	0.026
			%TRR			
Total Extracted [a]	95	64	62	19	63	89
fluopicolide		11	3.3	–	16	16
M-07	41	9.6	16	5.9	30	47
Unknown 55		2.6		0.1	2.2	3.8
Unknown 67		0.6		0.5	8.5	7.0
M-18		3.9	7.1	2.4		
M-19	23	34	15	1.9		
Unknown 58	16			0.2		
Unknown 37				2.7		
Unknown 43				2.2		
PES	5	30	38	81	37	11

	Egg white (96 h)	Egg yolk (96 h)	Egg yolk (312 h)	Liver	Skin + fat	Fat
Pepsin		18	23	40		
Protease		11	14	11		
HCl		–	–	9.5		

[a] Extracted with methanol (2 occasions) followed by methanol:water (1:1, v/v).

In conclusion, the highest tissue concentrations were consistently observed in the liver at both dose levels and using both radiolabels. There was no evidence of any accumulation of radioactivity in eggs or edible tissues.

The identified metabolites of fluopicolide in the hen were formed by hydroxylation of the chlorophenyl ring in the meta and para positions to give metabolites M-07 and M-06, respectively. Each of these metabolites can be conjugated with sulphate or hydroxylated in a second position to give a proposed dihydroxy intermediate, which is further metabolised to a sulphate conjugate. Additionally a methyl sulphone conjugate of fluopicolide and M-01 have been observed in the liver. In the case of the pyridyl radiolabel study, the bulk of the radioactivity was associated with amino acids and peptides.

The presence of M-01 shows that a proportion of the parent molecule had been cleaved, probably by oxidative N-dealkylation, to form both M-01 containing the phenyl portion of the parent molecule and M-02 which contained the pyridyl portion of the parent. When administered to the rat [^{14}C]-M-02 was eliminated via the urine unchanged. M-01, on the other hand, underwent significant biotransformation which included conjugation with glutathione that was subsequently metabolised through to a mercapturic acid conjugate, a cysteine conjugate and a thiomethyl metabolite. The majority of the biotransformations occurred on the phenyl ring of fluopicolide as opposed to the pyridyl ring. Polar metabolites in the liver and kidney were associated with amino acids, peptides and proteins.

The proposed metabolic pathway for [^{14}C]fluopicolide in the hen following repeated administration is presented in Figure 2.

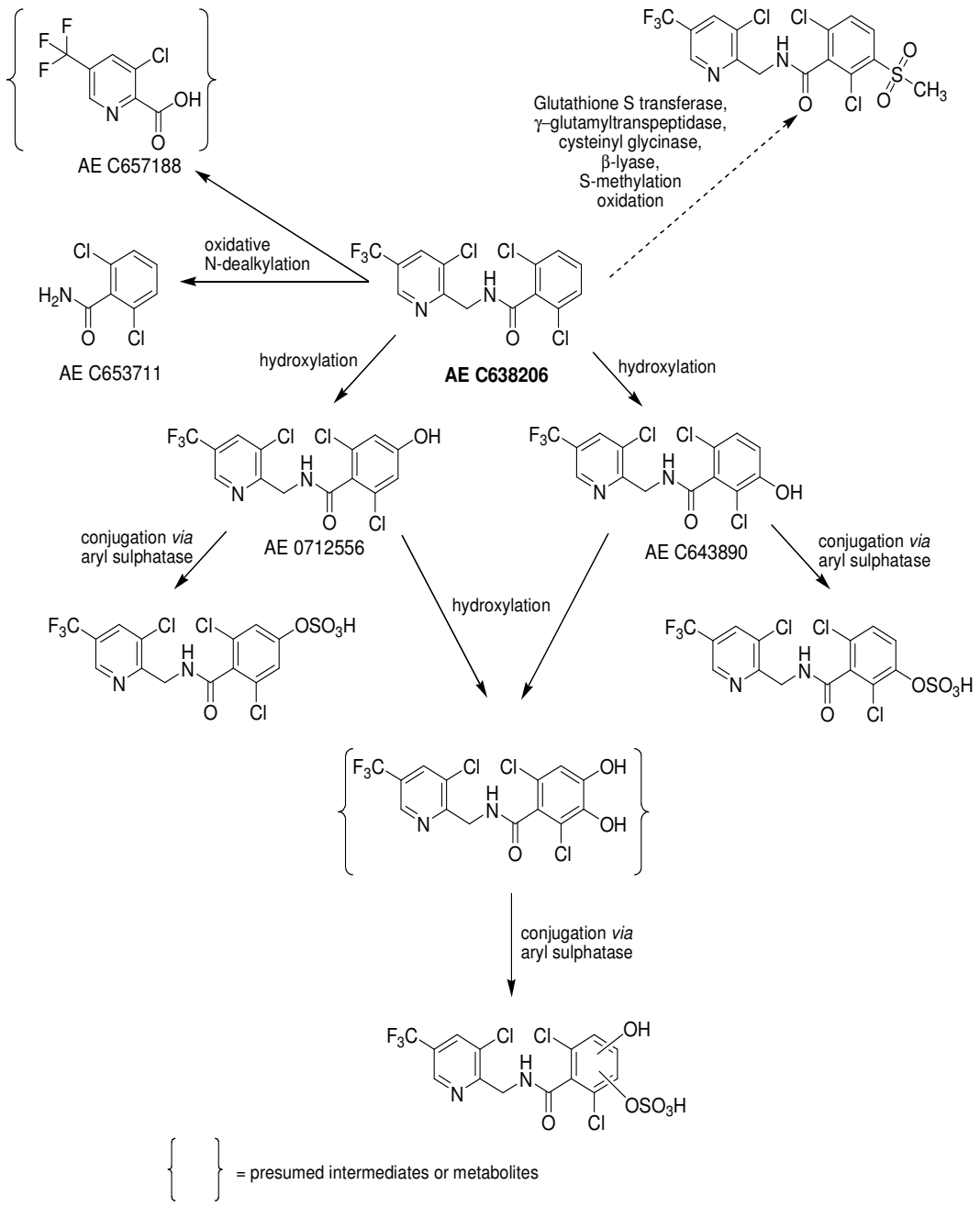


Figure 2 Proposed fluopicolide metabolic pathways in hens

Summary of metabolism of fluopicolide in animals

Radio-labelled fluopicolide separately ^{14}C-labelled at the phenyl- and pyridyl-rings, was used in the metabolism and environmental studies. The metabolism of laboratory animals was qualitatively the same as for farm animals though some species-related differences were noted. The majority of the administered radioactivity was recovered in the excreta (75–95% of dose) leaving only low levels of radioactivity in the tissues (0.06–0.78%), milk (0.08–0.14%) and eggs (0.08–0.13%). The highest tissue concentrations were consistently observed in the liver in both cow and hen at both dose levels and using both radiolabels. There was no evidence of any accumulation of radioactivity in milk, eggs or edible tissues.

The identified metabolites of fluopicolide in the cow and hen are thought to be formed by hydroxylation of the chlorophenyl ring in the meta- and para-positions to give metabolites M-07 and M-06, respectively. Each of these metabolites is conjugated with sulphate or hydroxylated in a second position to give a proposed dihydroxy intermediate, which is further metabolised to a sulphate conjugate. In the cow, conjugation with glucuronic acid was also observed. Additionally a methyl sulphone conjugate of fluopicolide and M-01 have been observed in the hen.

There was a tendency for higher tissue radioactivity concentrations to be found following dosing with phenyl radiolabel compared to the pyridyl radiolabel, presumably due to differing fates of the phenyl and pyridyl groups following cleavage of fluopicolide. Investigations into polar metabolites in the liver and kidney in the studies demonstrated that they were associated with amino acids, peptides and proteins. There was no significant association of the radioactive residues of fluopicolide with RNA or DNA.

Plant metabolism

Metabolism studies on grapes, lettuce and potato were made available to the Meeting. Each was conducted with both phenyl- and pyridyl-radio-labelled fluopicolide.

Grapes

Rupprecht (2004) studied the metabolism of phenyl- and pyridyl-labelled fluopicolide in grapevines. Grapevines (var. Sunbelt and Niagara) were grown under greenhouse conditions in pots. Grapevines were treated with an SC formulation of fluopicolide at 167 g ai/ha at the first application (BBCH 55-57, inflorescences swelling to fully developed) and at 116 g ai/ha at growth stage BBCH 71 to 73 (fruit set to groat-sized berries, bunches begin to hang) and 21 days prior to final harvest. Additional grapevines were treated at 10× the above mentioned rates. Immature grapevine samples were collected on day 0 (immediately after the 1st treatment) and days 27 and 28 (immediately prior to the second treatment) and at maturity (days 111 and 112). Grapevine foliage samples were also collected at final harvest.

All samples were immediately subjected to an acetonitrile wash on the day of sampling. Final harvest leaf and grape samples were then ground in a disk mill with dry ice after surface washing. Ground samples were returned to the freezer to allow the dry ice to sublime and stored at –15 ºC until analysis. Total radioactive residues in plant samples were determined by combustion of aliquots of the ground samples followed by liquid scintillation counting. Day 0 and immature harvest samples were further extracted two times by maceration with acetonitrile. Final harvest leaf and grape samples were extracted three times with acetonitrile. The radioactive content of extracts and concentrated extracts was determined by direct LSC and that of post-extraction residues by combustion followed by LSC. Thin layer chromatography (TLC) was used for the quantitation and identification of metabolites by comparison against authentic reference standards. Two TLC systems, one normal phase and one reverse phase were used. All extracts were stored at –15 °C or less prior to analysis. Analysis for the entire study was completed within 3 months of the final harvest.

The vast majority of the radioactive residue at all time-points was solvent extractable. Mean results of residue levels and the extraction profiles at each time-point are presented in Table 10.

Table 10 Extractability of radioactive residues in grapes (mean of duplicate values)

Time-point	Rate	TRR (mg equivs/kg)	% TRR		
			Surface Wash	Remaining [a]	
				Extracted	Unextracted
Phenyl label					
0 (Foliage)	1×	32	97	2.7	0.2
	10×	339	99	0.7	0.3
28 (Foliage)	1×	24	72	24	3.8
	10×	269	92	6.8	1.3

Time-point	Rate	TRR (mg equivs/kg)	% TRR		
			Surface Wash	Remaining [a] Extracted	Unextracted
112 (Foliage)	1×	15.5	50	43	7.6
	10×	154	70	NA	30 [a]
112 (Fruit)	1×	1.27	62	33	4.3
	10×	9.96	79	19	2.4
Pyridyl-label					
0 (Foliage)	1×	32.6	98	1.8	0.4
	10×	382	97	3.1	0.1
27 (Foliage)	1×	19.2	77	18	4.5
	10×	270	93	5.7	1.1
111 (Foliage)	1×	23.9	51	42	6.8
	10×	181	75	NA	25 [a]
111 (Fruit)	1×	1.04	46	48	6.0
	10×	10.9	73	23	3.5

[a] Residue extracted after surface wash

NA = not analysed

In grape foliage, residues declined slightly between the initial treatments and just prior to the second treatment from approcimately 32 mg equivs/kg at day 0 to approximately 19–24 mg equivs/kg at day 27–28 for the 1× rate. At final harvest, the mean residue in fruit (≈ 1 mg equivs/kg) of vines treated at the 1× rate was considerably lower than in the foliage (≈ 20 mg equivs/kg).

The majority of residue in foliage was readily removed by surface washing with > 96% of the TRR removed at day 0, 72 to 93% at day 27–28 and 50 to 75% in foliage at day 111–112. Subsequent acetonitrile extraction of the washed foliage recovered virtually all the remaining residue with < 7% of the TRR remaining.

For the phenyl and pyridyl-label treated vines, residues in grapes at final harvest were low in comparison to the foliage. Acetonitrile surface washes removed a significant amount of the radioactive residues from the fruit (46 to 79% TRR). Less than 6% of the TRR remained after surface wash and extraction of the grapes with acetonitrile extraction.

The metabolites identified in final harvest grapes are shown in Table 11. Values are quoted for combined surface wash and acetonitrile extracts.

Table 11 Identification of fluopicolide and metabolites in grapes (mean of duplicate values)

Rate	%TRR Extracted (mg equiv/kg)	%TRR				%Identified
		Fluopicolide	M-01	M-02	M-06	
Phenyl label						
1×	96 (1.21)	91	2.0	–	0.2	93
10×	98 (9.72)	95	1.3	–	0.1	97
Pyridyl label						
1×	94 (0.98)	87	–	2.3	–	90
10×	96 (10.6)	93	–	0.7	–	94

– = not detected

The principal residues in fruit were identified as fluopicolide. At the 1× rate, the metabolites M-01 (2%) and M-06 (0.2%) were identified in minor amounts in phenyl-label treated grapes. One minor metabolite, M-02 (2.3%), was identified in the pyridyl-label treated grapes. Analysis of foliage identified the majority of the residues as fluopicolide.

In conclusion, radioactive residues in grapevines treated with [^{14}C]fluopicolide were principally extractable with acetonitrile, with only small quantities remaining unextracted at final harvest. Greater than 89% of the total radioactive residue was identified in the samples at final

harvest. The majority of the residue consisted of fluopicolide, with minor amounts of M-01, M-02, and M-06. No other single metabolite comprised more than 1% of the radioactive residue.

Lettuce

Rupprecht (2004) studied the extent and nature of the metabolic breakdown of phenyl and pyridyl labelled fluopicolide in lettuce. Lettuce (var. Black Seeded Simpson) was grown outdoors under confined conditions. Lettuce was treated twice by foliar application at 200 g ai/ha with radio-labelled fluopicolide formulated as a suspension concentrate (SC) to give a seasonal rate of 400 g ai/ha. The first treatment was approximately 6 weeks after sowing, and the second treatment 14 days prior to final harvest. In additional lettuce plots the furrows between rows of lettuce plants were treated with phenyl-labelled fluopicolide at a nominal rate of 200 g ai/ha. The soil drench was applied once approximately 6 weeks after sowing.

Samples were collected on days 0 (after treatment, foliar plots only), 21 and 35. Lettuce samples collected from plots receiving foliar sprays were subjected to an acetonitrile wash on the day of sampling. Foliar and soil drench samples were homogenised and residues extracted with acetonitrile. Total radioactive residues in plant samples were determined by liquid scintillation counting (LSC). Thin layer chromatography (TLC) was used for the quantitation and identification of metabolites by comparison against authentic reference standards and using two TLC systems, one normal phase and one reverse phase. All extracts were stored at –15 °C or less prior to analysis. Analysis for the entire study was completed within 3 months of the final harvest.

The vast majority of residue (> 95% of TRR) at all time-points was extracted with the solvents used.

Table 12 Extractability of radioactive residues in lettuce samples (mean of duplicate values)

Days after 1st Application	Treatment	TRR (mg equiv/kg)	Surface Wash	%TRR Remaining [a]	
				Extracted	Unextracted
Phenyl-label					
0	Foliar	10.8	95	4.6	0.1
21	Foliar [b]	1.33	61	38	1.5
35 (Harvest PHI 14)	Foliar	13.4	85	15	0.7
21	Soil Drench	0.08	NA	97	2.9
35 (Harvest PHI 14)	Soil Drench	0.18	NA	96	4.1
Pyridyl-label					
0	Foliar	13.4	97	3.4	0.1
21	Foliar [b]	1.31	67	32	1.0
35 (Harvest PHI 14)	Foliar	14.5	84	15	1.0

[a] Residue extracted after surface wash

[b] samples collected prior to second foliar application

NA = not applicable

In immature lettuce samples residues declined significantly between the initial foliar treatment and just prior to the second foliar treatment from 11 to 13 mg equiv/kg at day 0 to ca. 1.3 mg equiv/kg at day 21. At harvest the residue in lettuce leaves resulting from the foliar treatment was 13 to 14 mg equiv/kg.

Total residues were significantly lower in lettuce treated with phenyl-label soil drench than in lettuce treated by phenyl-label foliar application. In immature lettuce leaves (day 21), the TRR for the foliar applied treated lettuce was 1.3 mg equiv/kg compared to 0.076 mg equiv/kg for the soil drench treated lettuce. At harvest the mean residue in foliar treated lettuce was 13.4 mg equiv/kg while the mean residue in the soil drench lettuce was 0.175 mg equiv/kg.

The majority of residue in lettuce treated by foliar application was readily removed by surface washing with > 95% of the TRR recovered for samples collected on day 0, approximately 64% prior to the second application at day 21 and approximately 84% in mature lettuce sampled at day 35. Subsequent acetonitrile extraction of the washed samples recovered virtually all the remaining residue. In the case of soil applied fluopicolide, acetonitrile extraction of the lettuce removed virtually all the crop radioactive residue with > 95% extracted.

The metabolic identified in lettuce samples are shown in Table 13.

Table 13 Identification of fluopicolide metabolites in lettuce (mean of replicate values)

Days after 1st Application	Application	Total %TRR	Extracted mg equiv/kg	%TRR			
				Fluopicolide	M-01	M-02	M-06
Phenyl label							
0	Foliar	99.9	10.8	98	0.1	–	–
21	Foliar[a]	98.6	1.31	92	3.9	–	1.0
35 (Harvest PHI 14)	Foliar	99.4	13.3	96	0.9	–	–
21	Soil Drench	97.2	0.07	74	16	–	–
35 (Harvest)	Soil Drench	95.9	0.17	72	20	–	2.8
Pyridyl label							
0	Foliar	99.9	13.4	96	–	–	–
21	Foliar[a]	99.1	1.29	95	–	1.5	1.4
35 (Harvest PHI 14)	Foliar	99.0	14.4	96	–	0.6	–

[a] samples collected prior to second foliar application

Following foliar applications the major residue was fluopicolide accounting for > 95% of the TRR at harvest in both phenyl- and pyridyl-label treated lettuce. The metabolite M-01 was identified in minor amounts (0.9% TRR, 0.112 mg equivs/kg) in mature lettuce treated with phenyl-label and the metabolite M-02 was identified in minor amounts (0.6% TRR, 0.078 mg equivs/kg) in mature lettuce treated with pyridyl-label. Minor amounts of the metabolite M-06 was identified in foliar treated lettuce at 1.0 and 1.4% TRR in phenyl- and pyridyl-label treated lettuce at day 21 but the metabolite was not detected at harvest.

Following phenyl-label soil drench the major residue was also identified as fluopicolide at 72% of the TRR in lettuce at harvest while M-01 was present at 19.8% of the TRR (0.034 mg equiv/kg) together with minor amounts of M-06 (2.8% TRR, 0.005 mg equivs/kg). Fluopicolide may be metabolised in soil to form M-01, which is then taken up by the lettuce plant.

In summary, radioactive residues in lettuce leaves treated with [^{14}C]fluopicolide were principally extractable with acetonitrile, with only small quantities at harvest remaining unextracted following foliar treatments (1%) and soil drench (4%). The majority of the residue in lettuce treated by foliar application consisted of fluopicolide, with minor amounts of M-01, M-02 and M-06. Following soil drench with phenyl-label, fluopicolide comprised the majority of the residue together with significant amounts of M-01 and minor amounts of M-06. No other single metabolite comprised more than 1% of the total residue in lettuce.

Potatoes

Rupprecht (2005) studied the metabolism of phenyl- and pyridyl- labelled fluopicolide in potatoes. Potatoes (var. Red Pontiac) were grown under field conditions in steel crop tanks. The soil was collected from Pikeville, North Carolina and was an acidic sandy loam soil (pH 5.7) with 0.81% organic matter. Different tanks were treated with phenyl-labelled and pyridyl-labelled fluopicolide at the 1× rate, one with phenyl label at the 10× rate. Fluopicolide (formulated as an SC) was applied to potato plants as two sprays at 200 g ai/ha for a total seasonal application rate of 400 g ai/ha. The nominal application rate for the 10× rate was two applications at 2 kg ai/ha each for a total seasonal

application rate of 4 kg ai/ha. The first treatment was at BBCH 31-33 (10–30% crop meeting between rows) and the second treatment 20 days prior to normal harvest.

Samples of foliage were collected on day 0 (post-treatment) and day 41. Potato tubers were collected at mature harvest (day 69 and day 70) together with foliage samples. All samples were surface washed twice with acetonitrile. Total radioactive residues were determined by combustion followed by liquid scintillation counting. Samples were also macerated and further extracted with acetonitrile. In the case of tubers, the extracted fibre was subjected to acid hydrolysis with 1N HCl overnight at 50 ºC. The radioactive content of extracts was determined by direct LSC and that of post-extraction solids by combustion followed by LSC. Reverse Phase Thin Layer Chromatography (RP-TLC) was used for the quantitation and identification of metabolites by comparison against authentic reference standards. A second normal phase TLC system was used for confirmation of metabolite identification. Analysis for the entire study was completed within 3 months of the final harvest.

Residues in potato foliage declined significantly between the initial spray and just prior to the second spray from 51 mg equiv/kg to 9 mg equiv/kg for the 1× rate. At harvest the mean residue in tubers (0.07 mg equiv/kg) treated at the 1× rate was considerably lower than in the foliage (11 mg equiv/kg).

The majority of residue in foliage was readily removed by surface washing with > 98% of the TRR removed from day 0 leaves, 65 to 79% from day 41 and 59 to 80% from foliage collected at day 50. Subsequent acetonitrile extraction of the macerated washed foliage removed virtually all the remaining residue.

For the phenyl and pyridyl-label treated potatoes, radioactive residues in potato tubers at harvest were low (0.081 and 0.053 mg equivs/kg, respectively at the 1× rate and 0.502 and 0.771 mg equivs/kg, respectively at the 10× rate). Acetonitrile surface washes removed a small amount of the radioactive residues (11 to 17% TRR) leaving 83 to 89% TRR in the washed tubers. Subsequent acetonitrile extraction removed an additional 72 to 79% of the TRR with 8.9 to 16% remaining unextracted. Acid hydrolysis of the post-extraction solids from the 1× treatments liberated an additional 8.7% and 5.9% of the TRR respectively for the phenyl- and pyridyl-label treated crops, leaving 6.9% and 4.9% in the fibre.

Table 14 Extractability of radioactive residues in potato samples

Time-point	Rate	TRR mg equivs/kg	%TRR		
			Surface Wash	Remaining [a] Extracted	Unextracted
Phenyl label					
0 (Foliage)	1×	47.2	98	1.9	0.1
	10×	418	99	1.3	0.1
41 (Foliage)	1×	10.2	76	20	4.4
	10×	38.9	76	22	2.5
70 (Foliage PHI 20)	1×	12.2	59	37	3.8
	10×	202	71	NA	NA
70 (Tubers PHI 20)	1×	0.08	13	72	16
	10×	0.50	11	79	10
Pyridyl label					
0 (Foliage)	1×	54.3	99	1.1	0.1
	10×	472	99	0.6	< 0.1
41 (Foliage)	1×	7.62	65	30	4.7
	10×	122	79	19	2.2
69 (Foliage PHI 20)	1×	9.63	62	34	3.9
	10×	222	80	NA	NA
69 (Tubers PHI 20)	1×	0.05	11	78	11
	10×	0.77	17	75	7.8

[a] Residue extracted after surface wash

NA = not applicable

The metabolic profiles of identified residues from potato tubers and foliage are shown in Table 15. Values are quoted for combined surface wash and acetonitrile extracts in mg equiv/kg parent equivalents and % of total radioactive residue (% TRR).

Table 15 Identification of fluopicolide metabolites in potato foliage and tubers (mean of duplicate values)

	Rate	%TRR Extracted (mg equiv/kg)	%TRR				%Identified
			Fluopicolide	M-01	M-02	M-06	
Phenyl label							
0 Foliage	1×	100 (47)	97	–		–	97
	10×	100 (418)	98	–		–	98
41 Foliage	1×	96 (9.72)	89	–		–	89
	10×	98 (38)	91	–		–	91
70 Foliage	1×	96 (12)	91	1.9		0.6	93
70 Tubers	1×	84 (0.07)	51	25		2.4	79
	10×	90 (0.45)	66	22		–	88
Pyridyl label							
0 Foliage	1×	100 (54)	98	–		–	98
	10×	100 (472)	98	–		–	98
41 Foliage	1×	95 (7.27)	89	–		–	89
	10×	98 (119)	95	–		–	95
69 Foliage	1×	96 (9.25)	90	–	0.8	0.7	91
69 Tubers	1×	89 (0.05)	70	–	12	1.7	84
	10×	91 (0.70)	57	–	26	–	83

The principal residues in potato tubers were identified as fluopicolide and the metabolite M-01 in phenyl-label treated potatoes and, fluopicolide and the metabolite M-02 in the pyridyl-label treated potatoes. Minor amounts of the metabolite M-06 was identified in both phenyl- and pyridyl-label treated potatoes. The same metabolic profile was seen in potato foliage.

In summary, radioactive residues in potatoes treated with [^{14}C]fluopicolide were principally removed by an acetonitrile surface wash and extractable with acetonitrile (84 to 89% TRR). The majority of the residue in the potato tubers consisted of the parent compound, fluopicolide, with significant amounts of M-01 and M-02 and minor amounts of M-06. No other single metabolite comprised more than 2% of the total residue in any matrix.

Summary of plant metabolism studies

Metabolism studies in grapes, lettuce and potato demonstrated that following foliar application, fluopicolide was not metabolised to any great extent. With up to three consecutive foliar applications of fluopicolide to grapes, lettuce and potato, and following a single soil drench to lettuce (1 × 200 g ai/ha), parent compound was the major component of the radioactive residues at 87–95%, 96% and 51–70% of the TRR respectively for grapes (berries), lettuce (leaves) and potato (tubers). When applied as a soil drench to lettuce, parent compound was the major component of the TRR in lettuce at harvest (72% TRR). Minor metabolites (< 0.035 mg/kg) identified in the studies were M-01 (1.3–25% TRR), M-02 (0.6–26% TRR) and M-06 (0.1–2.8% TRR) with the higher levels of metabolites resulting from uptake from soil (lettuce following a soil drench or potato tubers). Fluopicolide is predominantly a surface residue.

Environmental Fate in soil

The Meeting received information on confined rotational crops, field crop rotation and aerobic soil metabolism. The fate and behaviour of fluopicolide in soils was investigated with both phenyl- and pyridyl-radio-labelled fluopicolide. Only those data relevant to the current evaluation are reported below (FAO Manual 2002).

Confined rotational crop studies

The metabolism of fluopicolide in confined rotational crops was studied by Meyer (2003) on a sandy loam soil (sand 77%, silt 14%, clay 9.6%, bulk density 1.55, pH 6.2, CEC 1.87 meq/100g, OM% 0.81). [^{14}C]fluopicolide, labelled in either the phenyl or pyridyl ring, was applied to bare soil at a rate of 400 g ai/ha. After plant-back intervals (fallow periods) of 29 days, 133 days and 365 days crops of lettuce, radish and wheat were planted and grown to maturity. The total radioactive residues in the crops at harvest are summarised in Table 16.

Table 16 TRR (mg equiv/kg) in mature crops at harvest following planting at intervals after application of fluopicolide to bare soil (Meyer 2003)

Crop	Phenyl radiolabel			Pyridyl radiolabel		
	PBI 29	PBI 133	PBI 365	PBI 29	PBI 133	PBI 365
Lettuce	1.01	0.10	0.53	0.27	0.03	0.05
Radish Tops	6.40	0.23	1.75	1.96	0.23	0.40
Radish Roots	0.13	0.02	0.03	0.09	0.02	0.02
Immature Wheat	4.95	0.22	0.86	4.29	0.16	0.24
Wheat Grain	0.16	0.02	0.05	2.60	0.10	0.18
Wheat Straw	13.6	0.84	2.37	7.05	0.35	1.01

For PBI 29 days, harvest was 54 days after planting for lettuce, 42 for radish, 39 for immature wheat and 64 days for mature wheat for both labels

For PBI 133 days, harvest was 83 days after planting for lettuce, 63 for radish, 148 for immature wheat and 202 days for mature wheat for both phenyl label and an additional day for the pyridinyl label

For PBI 365 days, harvest was 56 days after planting for lettuce, 56 for radish, 45 for immature wheat and 84 days for mature wheat for both labels

Total radioactive residues in crops matrices generally declined with longer soil ageing. Residues in crops planted 29 days after treatment of soil ranged from 0.09 mg equiv/kg (radish root) to 13.6 mg equiv/kg (wheat straw), but declined greatly when the interval between soil application and planting was greater. The increase in residues at harvest for crops planted after 265 compared to those planted after 133 days may be a result of flooding of the 133 day plot prior to planting crops and or seasonal variation as the 133 day plots were planted in October and the crops developed through the winter when formation of soil metabolites from the degradation of parent would be slowest. The PBI 29 and 365 day plots were planted in spring and developed through the summer when formation of soil metabolites from the degradation of parent would be faster.

The principal compounds identified in phenyl-labelled experiments were the parent fluopicolide, M-01, and in wheat only, M-04 (3-hydroxy- M-01). M-06, which is the 3-hydroxy derivative of fluopicolide, was detected at a quantifiable level only in 29 day wheat grain and forage (13%, 0.021 mg equiv/kg and < 1.0%, < 0.049 mg equiv/kg, respectively).

Table 17 Summary of identification in confined rotational crops grown in soil treated with the phenyl-labelled fluopicolide

Plot (Day)	Crop Part	%TRR Extracted (mg equiv/kg)	%TRR			
			M-04	M-01	M-06	Fluopicolide
29	Lettuce	98 (0.99)	–	81	–	11
	Radish Tops	98 (6.6)	–	65	–	24
	Radish Roots	97 (0.14)	–	43	–	48

Plot (Day)	Crop Part	%TRR Extracted (mg equiv/kg)	%TRR			
			M-04	M-01	M-06	Fluopicolide
	Wheat Forage	95 (4.72)	33	6.3	< 1.0	37
	Wheat Grain	78 (0.13)	–	3.6	13	27
	Wheat Straw	71 (9.68)	14	3.4	–	23
133	Lettuce	96 (0.11)	–	61	–	27
	Radish Tops	98 (0.24)	–	77	–	15
	Radish Roots	97 (0.02)	–	55	–	28
	Wheat Forage	92 (0.21)	29	5.1	–	23
	Wheat Grain	65 (0.01)	23	19	–	7.0
	Wheat Straw	85 (0.71)	15	26	–	16
365	Lettuce	97 (0.60)	–	87	–	2.1
	Radish Tops	99 (1.98)	–	88	–	3.8
	Radish Roots	96 (0.04)	–	61	–	24
	Wheat Forage	93 (0.80)	59.3	15	–	4.8
	Wheat Grain	66 (0.04)	24.5	18	–	7.3
	Wheat Straw	65 (1.54)	28.0	5.1	–	7.2

The principal compounds identified in pyridyl-labelled experiments included the fluopicolide, M-02, and M-05. In addition M-06, M-08 and M-09 were detected at low levels only occasionally exceeding either 10% or 0.05 mg equiv/kg in crops used for animal fodder and not exceeding either 10% or 0.01 mg equiv/kg in commodities considered as human foods.

Table 18 Summary of identification in confined rotational crops grown in soil treated with the pyridyl-labelled fluopicolide

Plot (Day)	Crop Part	%TRR Extracted (mg equiv/kg)	%TRR					
			M-08	M-05	M-02	M-09	M-06	fluopicolide
29	Lettuce	95 (0.29)	–	13	17	5.3	–	36
	Radish Tops	99 (2.07)	–	3.3	10	4.8	–	51
	Radish Roots	98 (0.11)	–	9.6	34	–	–	41
	Wheat Forage	98 (4.18)	–	3.8	43	–	1.4	34
	Wheat Grain	93 (2.43)	–	13	70	–	–	1.8
	Wheat Straw	94 (6.62)	–	7.7	7.0	–	–	35
133	Lettuce	97 (0.03)	–	–	–	–	–	80
	Radish Tops	99 (0.24)	–	–	–	–	–	72
	Radish Roots	95 (0.02)	–	2.9	9.6	19	–	55
	Wheat Forage	97 (0.15)	–	41	5.4	10	–	26
	Wheat Grain	94 (0.09)	–	67	11	–	–	3.2
	Wheat Straw	94 (0.32)	9.4	1.2	2.1	22	–	26
365	Lettuce	90 (0.05)	9.0	7.8	12	3.7	–	42
	Radish Tops	96 (0.41)	–	5.1	27	6.0	–	25
	Radish Roots	95 (0.03)	9.5	5.3	10	–	–	56
	Wheat Forage	94 (0.23)	6.3	18	8.2	9.9	–	28
	Wheat Grain	94 (0.17)	–	65	14	–	–	2.9
	Wheat Straw	87 (0.88)	4.8	14	4.1	–	–	28

The proposed major metabolic pathway for fluopicolide in rotational crops is given in Figure 3. Three major components, fluopicolide, M-01 and M-02 were identified in all 29 day RACs. In addition, M-04 and M-05 formed significant residues in wheat crops only. M-04 was not detected at all in other crops and M-05 was generally a minor component.

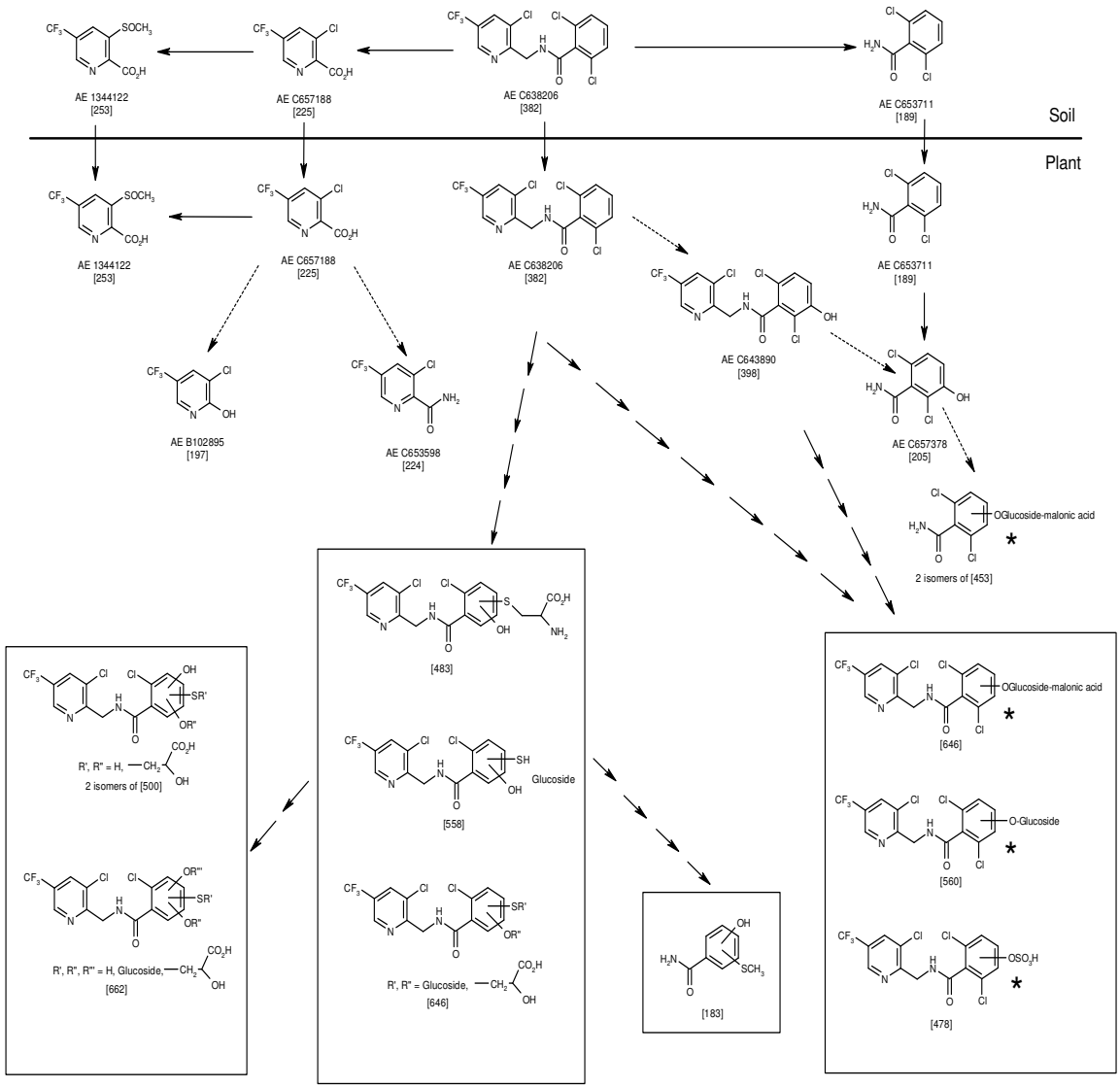


Figure 3 Proposed metabolic pathway in confined rotational crops

Field crop rotational studies

Zietz and Klimmek (2003a, b) and Shönin *et al.,* (2004) studied the uptake of soil residues by rotational crops. Fluopicolide as an SC formulation was applied to potato plants at three sites in Northern Europe and two further sites in Southern Europe. Fluopicolide was sprayed four times at 0.1 kg ai/ha. The first application was made early to mid-season to growth stage BBCH 33 with the second spray 9 to 11 days later. The third application was made later in the season at growth stage BBCH 81 with the final application between BBCH growth stages 84 and 93. The nominal PHI for the potato harvest was 25 days.

After potato harvest the plots were cultivated to enable subsequent sowing or planting of winter wheat, cabbage, field (faba) beans and spring wheat. Winter wheat was drilled 28 to 36 days after the final application of fluopicolide. Cabbage plants were transplanted 32 to 49 days after last treatment. Field beans were sown 63 to 66 days after last treatment in Southern Europe and 83 or 227 days after last treatment in Northern Europe. Spring wheat was drilled 174 to 227 days after last treatment.

Samples of the main crop potato (whole plant or tubers) and the following rotational crops were taken at appropriate occasions for residue analysis. In addition, soil core samples were taken to

provide additional information on the magnitude and nature of any residues in the soil at critical crop cultivation timings.

At one of the sites in Northern Europe (France, trial reference 00 F PT FR P03), high rainfall levels after the potato harvest meant that only winter wheat cultivation was possible.

Table 19 Residues in potato crops treated with a SC formulation of fluopicolide (M-221798-01-1)

Country, year (trial ref)	N	kg ai/ha	kg ai/hL	analysed	(days)	fluopicolide	M-01	M-02	Reference
Merville, France, 2000	4	0.100	0.040	Plant Tubers	25 25	0.30 < 0.01	0.01 < 0.01	< 0.01 < 0.01	M-221798-01-1
Dieupentale France, 2000	4	0.100	0.040	Plant Tubers	24 24	3.6 < 0.01	0.17 < 0.01	0.08 < 0.01	M-221798-01-1
Derbyshire UK, 2000	4	0.100	0.0333	Plant Tubers	27 27	3.6 0.01	0.02 < 0.01	< 0.01 < 0.01	M-221798-01-1
Champaign France, 2000	4	0.100	0.0333	Plant Tubers	25 25	1.7 < 0.01	0.15 < 0.01	0.20 < 0.01	M-221798-01-1
Hesse Germany, 2000	4	0.100	0.025	Plant Tubers	26 26	3.7 < 0.01	0.06 < 0.01	0.02 < 0.01	M-221798-01-1

Table 20 Residues in rotational crops (M-221798-01-1)

Rotational Crop	Portion analysed	DALA [a] (days)	Residue level (mg/kg)				
			fluopicolide	M-01	M-02	M-04	M-05
Merville, France, 2000							
Winter wheat	Shoots	192	0.02	< 0.01	< 0.01	0.01	0.02
	Stalks	269	0.03	< 0.01	< 0.01	0.02	0.02
	Ears	269	0.01	< 0.01	< 0.01	0.01	0.02
	Straw	303	0.05	< 0.01	< 0.01	0.03	0.03
	Grain	303	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Spring wheat	Shoots	192	0.01	< 0.01	< 0.01	0.01	0.01
	Stalks	269	0.04	< 0.01	< 0.01	0.03	< 0.01
	Ears	269	0.01	< 0.01	< 0.01	0.01	0.01
	Straw	303	0.06	< 0.01	< 0.01	0.01	< 0.01
	Grain	303	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Field (faba) beans	Shoots	178	< 0.01	< 0.01	< 0.01		
	Green pods	269	< 0.01	< 0.01	< 0.01		
	Dried pods	304	< 0.01	0.02	< 0.01		
	Dried seed	304	< 0.01	< 0.01	< 0.01		
Cabbage	Shoots	122	0.02	0.01	< 0.01		
	50% head	253	< 0.01	< 0.01	< 0.01		
	Mature head	294	< 0.01	< 0.01	< 0.01		
Dieupentale France, 2000							
Winter wheat	Shoots	18	0.03	0.01	< 0.01	0.03	0.01
	Stalks	265	0.04	< 0.01	< 0.01	0.08	0.02
	Ears	265	0.01	< 0.01	< 0.01	0.04	0.02
	Straw	299	0.07	< 0.01	< 0.01	0.06	0.03
	Grain	299	< 0.01	< 0.01	0.01	< 0.01	0.03
Spring wheat	Shoots	248	0.01	< 0.01	< 0.01	0.03	0.03
	Stalks	290	0.05	< 0.01	< 0.01	0.08	0.02
	Ears	290	0.02	< 0.01	< 0.01	0.03	0.05
	Straw	320	0.06	< 0.01	< 0.01	0.04	0.02
	Grain	320	< 0.01	< 0.01	0.02	< 0.01	0.05

Rotational Crop	Portion analysed	DALA [a] (days)	Residue level (mg/kg)				
			fluopicolide	M-01	M-02	M-04	M-05
Field (faba) beans	Shoots	174	0.03	0.06	< 0.01		
	Green pods	265	< 0.01	< 0.01	< 0.01		
	Dried pods	327	< 0.01	0.03	< 0.01		
	Dried seed	327	< 0.01	< 0.01	0.02		
Cabbage	Shoots	118	0.02	0.03	< 0.01		
	50% head	209	< 0.01	< 0.01	< 0.01		
	Mature head	249	< 0.01	< 0.01	< 0.01		
Derbyshire UK, 2000							
Winter wheat	Shoots	251	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Stalks	345	0.03	< 0.01	< 0.01	< 0.01	< 0.01
	Ears	345	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Straw	353	0.03	< 0.01	< 0.01	< 0.01	< 0.01
	Grain	353	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Spring wheat	Shoots	282	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Stalks	346	0.01	0.01	< 0.01	< 0.01	< 0.01
	Ears	346	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Straw	353	0.02	< 0.01	< 0.01	< 0.01	< 0.01
	Grain	353	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Field (faba) beans	Shoots	251	< 0.01	< 0.01	< 0.01		
	Green pods	346	< 0.01	< 0.01	< 0.01		
	Dried pods	353	< 0.01	< 0.01	< 0.01		
	Dried seed	353	< 0.01	< 0.01	< 0.01		
Cabbage	Shoots	251	< 0.01	< 0.01	< 0.01		
	50% head	282	< 0.01	< 0.01	< 0.01		
	Mature head	289	< 0.01	< 0.01	< 0.01		
Champaign France, 2000							
Winter wheat	Shoots	219	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Stalks	330	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Ears	330	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Straw	344	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Grain	344	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Hesse Germany, 2000							
Winter wheat	Shoots	227	0.04	< 0.01	< 0.01	0.02	0.03
	Stalks	289	0.02	0.01	< 0.01	0.05	0.01
	Ears	289	< 0.01	0.01	< 0.01	< 0.01	0.03
	Straw	329	0.09	0.01	< 0.01	0.07	0.03
	Grain	329	< 0.01	< 0.01	< 0.01	< 0.01	0.04
Spring wheat	Shoots	283	0.04	< 0.01	< 0.01	0.06	0.02
	Stalks	317	0.06	0.02	< 0.01	0.07	0.03
	Ears	317	0.01	0.06	< 0.01	0.03	0.01
	Straw	365	0.12	0.03	< 0.01	0.06	0.04
	Grain	365	< 0.01	< 0.01	0.02	< 0.01	0.05
Field (faba) beans	Shoots	283	< 0.01	0.10	< 0.01		
	Green pods	318	< 0.01	0.02	< 0.01		
	Dried pods	365	< 0.01	0.07	0.01		
	Dried seed	365	< 0.01	< 0.01	0.01		
Cabbage	Shoots	227	0.01	0.02	< 0.01		
	50% head	289	< 0.01	< 0.01	< 0.01		
	Mature head	318	< 0.01	< 0.01	< 0.01		

[a] DALA = days after last application

Soil samples taken at appropriate cultivation times were also analysed for the same compounds. Residues of fluopicolide in oil samples (0–10 or 0–15 cm) post final application to potato

plants ranged from 0.08 to 0.16 mg/kg. Corresponding residues of M-01 or M-02 were < 0.005 mg/kg with one value of 0.01 mg/kg M-01.

At the cultivation timing of pre-sowing (or pre-planting) of rotational crops, residues of fluopicolide ranged from < 0.005 to 0.14 mg/kg in either top soil (0–10 or 0–15 cm) or in lower depths (10–30 or 15–30 cm). At harvest of rotational crops, residues of fluopicolide also ranged from < 0.005 to 0.14 mg/kg in either top soil (0–10 or 0–15 cm) or in lower depths (10–30 or 15–30 cm). Corresponding residues of M-01 or M-02 from both of these cultivation events were mostly between < 0.005 and 0.02 mg/kg with a maximum value of 0.10 mg/kg M-01 pre-sowing of winter wheat from one trial in Southern France.

The potato tubers harvested from the primary crop 24 to 27 days after the final application gave residues of fluopicolide at or below the LOQ of 0.01 mg/kg. The metabolite residues of M-01 and M-02 were also all below their respective LOQs of 0.01 mg/kg.

Metabolite residues of M-01 or M-02 above the LOQ (0.01 or 0.02 mg/kg) were seen in green field bean pods and dried field bean seeds but were below 0.05 mg/kg. Fluopicolide and M-01 residues above the LOQ were measured in straw and forage commodities, with maximum residues of 0.12 mg/kg fluopicolide and 0.03 mg/kg M-01. In wheat grain, three out of the eight data points contained residues of M-02 at or above the LOQ with a maximum value of 0.02 mg/kg.

An SE formulation of fluopicolide was applied to potato plants at four sites in Northern Europe at 0.1 kg ai/ha. The first application was made early to mid-season to growth stage BBCH 33 with the second spray 9 to 11 days later. The third application was made later in the season to growth stage BBCH 81 with the final application between BBCH growth stages 85 and 91. The nominal PHI for the potato harvest was 25 days with actual PHIs between 23 and 31 days.

After potato harvest the plots were cultivated to enable subsequent sowing or planting of winter wheat, cabbage, field (faba) beans and spring wheat. Winter wheat was drilled 31 to 39 days after the final application of fluopicolide. Cabbage plants were transplanted 35 to 44 days after last treatment. Field beans were sown 57 to 97 days after last treatment. Spring wheat was drilled 191 to 223 days after last treatment. The cultivation timings are representative of normal agricultural practice.

Samples of the main crop potato (whole plant or tubers) and the rotational crops were taken at appropriate occasions for residue analysis. In addition, soil core samples were taken to provide additional information on the magnitude and nature of any residues in the soil at critical crop cultivation timings.

Table 21 Residues in potato crops treated with a SE formulation of fluopicolide (M-224665-01-1)

Location	N	kg ai/ha	kg ai/hL	analysed	PHI (days)	fluopicolide	M-01	M-02	reference
Derbyshire UK, 2001	4	0.100	0.0333	Plant Tubers	23 23	1.4 0.01	0.04 < 0.01	< 0.01 < 0.01	M-224665-01-1
Nottinghamshire UK, 2001	4	0.100	0.0333	Plant Tubers	23 23	1.4 < 0.01	0.04 < 0.01	< 0.01 < 0.01	M-224665-01-1
Hesse Germany, 2001	4	0.100	0.0250	Plant Tubers	31 31	13 0.01	0.16 < 0.01	0.06 < 0.01	M-224665-01-1
Schleswig-Holstein Germany, 2001	4	0.100	0.0250	Plant Tubers	31 31	10 < 0.01	0.16 < 0.01	0.05 < 0.01	M-224665-01-1

Table 22 Residues in rotational crops (M-224665-01-1)

Rotational Crop	Portion analysed	DALA [a] (days)	Residue level (mg/kg) [b]					Report reference
			fluopicolide	M-01	M-02	M-04	M-05	
Derbyshire	UK, 2001							
Winter wheat	Shoots	255	0.01	< 0.01	< 0.01	< 0.01	< 0.01	M-224665-01-1
	Stalks	351	0.06	< 0.01	< 0.01	0.01	0.01	
	Ears	351	< 0.01	< 0.01	< 0.01	< 0.01	0.01	
	Straw	358	0.08	< 0.01	< 0.01	0.02	< 0.01	
	Grain	358	< 0.01	< 0.01	< 0.01	< 0.01	0.01	
Spring wheat	Shoots	297	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	M-224665-01-1
	Stalks	351	0.03	< 0.01	< 0.01	0.02	< 0.01	
	Ears	351	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
	Straw	358	0.07	< 0.01	< 0.01	0.03	< 0.01	
	Grain	358	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Field (faba) beans	Shoots	255	< 0.01	0.01	< 0.01	–	–	M-224665-01-1
	Green pods	358	< 0.01	< 0.01	< 0.01	–	–	
	Dried pods	365	< 0.01	< 0.01	< 0.01	–	–	
	Dried seed	365	< 0.01	< 0.01	< 0.01	–	–	
Cabbage	Shoots	196	0.02	< 0.01	< 0.01	–	–	M-224665-01-1
	50% head	248	< 0.01	< 0.01	< 0.01	–	–	
	Mature head	255	< 0.01	< 0.01	< 0.01	–	–	
Nottinghamshire	UK, 2001							
Winter wheat	Shoots	257	0.02	< 0.01	< 0.01	0.03	0.05	M-224665-01-1
	Stalks	349	0.07	< 0.01	< 0.01	0.05	0.05	
	Ears	349	< 0.01	< 0.01	< 0.01	< 0.01	0.04	
	Straw	358	0.06	< 0.01	< 0.01	0.06	0.02	
	Grain	358	< 0.01	< 0.01	< 0.01	< 0.01	0.05	
Spring wheat	Shoots	296	0.02	0.02	< 0.01	0.02	0.05	M-224665-01-1
	Stalks	349	0.03	< 0.01	< 0.01	0.03	0.03	
	Ears	349	< 0.01	< 0.01	< 0.01	0.02	0.05	
	Straw	358	0.07	0.01	< 0.01	0.08	< 0.01	
	Grain	358	< 0.01	< 0.01	< 0.01	< 0.01	0.08	
Field (faba) beans	Shoots	257	< 0.01	0.03	< 0.01	–	–	M-224665-01-1
	Green pods	358	< 0.01	0.01	< 0.01	–	–	
	Dried pods	364	< 0.01	0.03	< 0.01	–	–	
	Dried seed	364	< 0.01	< 0.01	< 0.01	–	–	
Cabbage	Shoots	223	0.02	0.02	< 0.01	–	–	M-224665-01-1
	50% head	251	0.01	0.02	< 0.01	–	–	
	Mature head	257	< 0.01	0.02	< 0.01	–	–	
Hesse	Germany 2001							
Winter wheat	Shoots	245	0.02	< 0.01	< 0.01	< 0.01	0.03	M-224665-01-1
	Stalks	299	0.05	< 0.01	< 0.01	0.02	0.03	
	Ears	299	< 0.01	< 0.01	< 0.01	0.05	< 0.01	
	Straw	355	0.05	< 0.01	< 0.01	0.02	0.07	
	Grain	355	< 0.01	< 0.01	< 0.01	< 0.01	0.04	
Spring wheat	Shoots	278	0.01	0.01	< 0.01	0.02	< 0.01	M-224665-01-1
	Stalks	318	0.03	< 0.01	< 0.01	0.09	0.01	
	Ears	318	< 0.01	0.03	< 0.01	0.01	0.01	
	Straw	355	0.04	< 0.01	< 0.01	0.02	0.06	
	Grain	355	< 0.01	< 0.01	< 0.01	< 0.01	0.02	
Field (faba) beans	Shoots	243	0.02	0.06	< 0.01	–	–	M-224665-01-1
	Green pods	302	< 0.01	< 0.01	< 0.01	–	–	
	Dried pods	333	< 0.01	0.02	< 0.01	–	–	
	Dried seed	333	< 0.01	< 0.01	< 0.01	–	–	

Rotational Crop	Portion analysed	DALA [a] (days)	Residue level (mg/kg) [b]					Report reference
			fluopicolide	M-01	M-02	M-04	M-05	
Cabbage	Shoots	– [c]	–	–	–	–	–	M-224665-01-1
	50% head	280	0.03	0.05	< 0.01	–	–	
	Mature head	318	< 0.01	0.04	< 0.01	–	–	
Schleswig-Holstein	Germany, 2001							
Winter wheat	Shoots	242	0.02	< 0.01	< 0.01	< 0.01	< 0.01	M-224665-01-1
	Stalks	308	0.01	< 0.01	< 0.01	< 0.01	< 0.01	
	Ears	308	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
	Straw	350	0.02	< 0.01	< 0.01	0.01	< 0.01	
	Grain	350	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Spring wheat	Shoots	286	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	M-224665-01-1
	Stalks	319	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
	Ears	319	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
	Straw	350	0.01	< 0.01	< 0.01	0.02	< 0.01	
	Grain	350	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Field (faba) beans	Shoots	223	0.01	< 0.01	< 0.01	–	–	M-224665-01-1
	Green pods	308	< 0.01	< 0.01	< 0.01	–	–	
	Dried pods	350	< 0.01	0.01	< 0.01	–	–	
	Dried seed	350	< 0.01	< 0.01	< 0.01	–	–	
Cabbage	Shoots	242	< 0.01	< 0.01	< 0.01	–	–	M-224665-01-1
	50% head	286	< 0.01	< 0.01	< 0.01	–	–	
	Mature head	319	< 0.01	< 0.01	< 0.01	–	–	

[a] DALA = days after last application

At the cultivation timing of pre-sowing (or pre-planting) of rotational crops, residues of fluopicolide ranged from 0.01 to 0.13 mg/kg in top soil (0–30 cm). At harvest of rotational crops, residues of fluopicolide ranged from 0.02 to 0.08 mg/kg in top soil (0–30 cm). Corresponding residues of M-01 from both of these cultivation events were either < 0.005 or 0.01 mg/kg with M-02 residues all < 0.005 mg/kg at pre-sowing and harvest.

Residues of the metabolite M-01 above the LOQ were seen in mature cabbage from two trials but were below 0.05 mg/kg. Fluopicolide, M-01 and M-04 residues at or above the LOQ were found in straw and other forage commodities, with maximum residues of 0.08 mg/kg fluopicolide, 0.03 mg/kg M-01 and 0.09 mg/kg M-04.

In mature wheat grain, residues of fluopicolide, M-01, M-02 and M-04 were below the LOQ of 0.01 mg/kg. Five out of the eight mature wheat grain samples contained residues of M-05 at or above the LOQ of 0.01 mg/kg with a maximum value of 0.08 mg/kg.

The following structures show the relationship between fluopicolide and the identified metabolites in crop rotation studies (Figure 4).

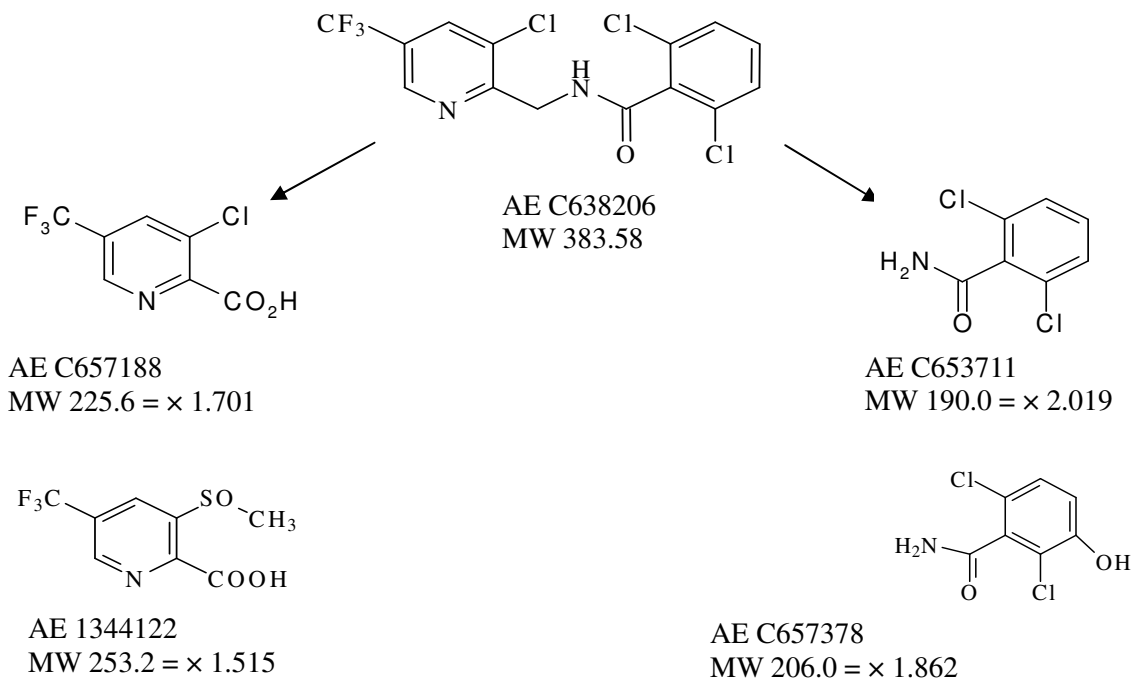


Figure 4 Fluopicolide metabolic pathways from rotational crop studies

Note: M-05 and M-04 are relevant only for cereal matrices

Aerobic soil metabolism

The route and rate of degradation of [2,6-^{14}C-pyridinyl]- and [U-^{14}C-benzoyl]-fluopicolide were studied in a sandy loam (sand 67%, silt 22%, clay 11%, pH 7.4, % OC 2.2, % OM 3.8, CEC 18 meq/100g, bulk density 1.26, microbial biomass, initial 376 µg microbial C/g soil, final 120 days 212 µg microbial C/g soil) from the United Kingdom in the dark at 20 ± 1 °C (Allan 2003). Fluopicolide was applied to flasks of soil at the equivalent of 400 g ai/ha. Both sterile and non-sterile flasks solid were used. The overall mass balance in non-sterilized samples, ranged from 93 to 100%. The majority of the applied radioactivity was able to be extracted using acetonitrile/water at ambient temperature. For both labels over 95% of the applied radioactivity was solvent extracted at day 0 declining to 78 and 85% for the pyridinyl and benzoyl labels, respectively at the end of the study (day 120). Soxhlet extraction recovered up to 5.4% of the applied radioactivity (day 98) in the pyridinyl label and 8.2% (day 56) in the benzoyl label samples. Unextracted residues increased during the course of the experiment and were 12 and 5.2% respectively for the pyridinyl and benzoyl labels at the end of the experiment. Mineralization to carbon dioxide was a minor pathway of dissipation with less than 2% of the dose recovered in the ethanolamine volatile traps.

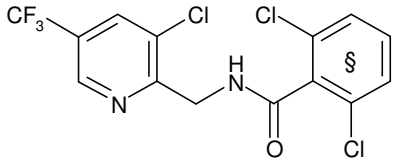
Fluopicolide degraded via oxidative cleavage to produce, 3-chloro-5-trifluoromethyl-2pyridinecarboxylic acid (M-02 or PCA) and 2,6-dichlorobenzamide (M-01 or BAM). The quantity of M-01 ranged from 4.5% (day 14), 14% (day 56) and 12% at the end of the 120 day incubation period. M-02 was generally observed at ca. 1% except on day 42 when it reached 7.3% of the applied radioactivity. Two minor metabolites (each < 3% of the applied radioactivity) were detected in the pyridinyl treated soil extracts only.

After 120 days incubation at 20 °C, fluopicolide represented approximately 77% of the radioactivity initially applied for the pyridinyl label and 80% for the benzoyl label. The DT_{50} of fluopicolide is > 200 days.

Microbial activity did not facilitate fluopicolide degradation however it did facilitate degradation of the key metabolites, M-01 and M-02. Both M-01 and M-02 accumulated in sterile samples with a maximum of 36% and 26%, respectively (day 120), which compares to M-01 and M-02 maximum in the non-sterile samples of 14% and 7.3%, respectively.

Aqueous hydrolysis

The hydrolysis of [^{14}C]-phenyl labelled fluopicolide was investigated at 50 ± 0.1 °C at pH 4, 7 and 9 and at 25 ± 1 °C at pH 5, 7 and 9, in the dark, under sterile conditions. Phenyl labelled fluopicolide was dissolved in sterile buffer at a nominal concentration of 1 mg/L.



[U-^{14}C-phenyl] labelled fluopicolide

§ = position of radiolabel.

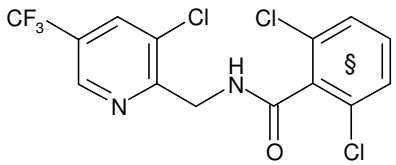
Good radiochemical balances were achieved with a mean recovery of applied radioactivity of 100% for pH 4, 97% for pH 7 and 96% for pH 9 samples incubated at 50 °C. The mean recoveries of applied radioactivity for samples incubated at 25 °C were 98% for pH 5, 100% for pH 7 and 98% for pH 9 samples. The pH values and sterility of samples was maintained throughout the study.

Fluopicolide was relatively stable to hydrolysis at all pHs and both temperatures tested. HPLC analysis confirmed that fluopicolide was the major compound detected. A degradation product, M-01 was detected in small amounts in the 50 °C and 25 °C tests reaching a maximum of 3% of applied radioactivity in the 50 °C test at pH 9 after 5 days and 4% of applied in the 25 °C test at pH 7 after 30 days.

Fluopicolide is hydrolytically stable.

Photolysis

Fluopicolide was exposed to artificial light in sterile 0.005M phosphate buffer solution at pH 7 for up to 31 days in 12 hour light and dark cycles. [^{14}C] phenyl labelled fluopicolide was dissolved in buffer at a concentration of 0.65 mg/L with 0.2% acetonitrile present as a co-solvent.



[U-^{14}C-phenyl]-fluopicolide
§ = position of radiolabel.

Good radiochemical balances were achieved with a mean recovery of applied radioactivity of 100% for light exposed samples, and 99% for dark control samples.

Fluopicolide exhibited slow degradation in light exposed samples and represented up to 83% of applied radioactivity after 31 days. Carbon dioxide was detected in potassium hydroxide traps and represented 4% of applied radioactivity by the end of the study in the irradiated samples. Virtually no organic volatiles were detected ($\leq$ 0.1%). Fluopicolide did not degrade significantly in the dark control samples and represented 95% of applied radioactivity at the end of the incubation period.

M-01 was a minor degradation product present in both light exposed and dark control samples at the time 0 sampling ($\leq$ 2.0%). It increased to a maximum 4% and 3% of applied radioactivity in light exposed and dark control samples, respectively, by the end of the experiment. These levels are comparable to those detected as a result of hydrolysis of fluopicolide.

A range of minor components represented < 3% in total in the time zero and dark control samples throughout the study. In the light exposed buffer solutions the total levels and number of heterogeneous components was greater and represented a maximum of *ca.* 16% of the radioactivity in solution (approximately 12% of applied radioactivity) by the end of the study. No single component in this background radioactivity exceeded 3.5% of applied radioactivity.

The half-life of [^{14}C]fluopicolide in light exposed samples was calculated to be 64.2 days (r^2 = 0.996), assuming single-exponential first order kinetics and based on experimental conditions of 12 hour light/dark cycles of the Suntest unit.

The results of this study indicate that aqueous photolysis is not a major mode of dissipation of [^{14}C]fluopicolide under the test conditions employed.

Methods of residue analysis

Adequate analytical methods exist for the determination of the residue as defined for both enforcement and for determination of the residues of concern for risk assessment for both plant and livestock commodities. The principle of most methods involves extraction steps using organic solvents plus varying proportions of water or water plus acid followed by different matrix dependant clean up steps. The final determination is carried out mostly by HPLC-MS/MS or GC-MSD.

For the determination of fluopicolide and/or its metabolites M-01 and M-02 the HPLC-MS/MS method no. 00782 was developed for plant matrices (LOQ for all analytes: 0.01 mg/kg in grapes, wheat grain, wheat straw and cabbage). Addition of sulphuric acid with heating converts any M-02 to its methyl ester. This derivative gave better chromatography than M-02 itself and enabled improved sensitivity for the LC/MS/MS quantification of M-02 as its methyl ester.

Multi-residue method DFG method S 19 was successfully applied to the determination of fluopicolide in matrices of plant origin (LOQ: 0.1 mg/kg in grapes; 0.02 mg/kg in wheat grain and potato tubers) (CLE 1905/082).

For animal matrices, multi-residue method testing according to DFG method S 19 for the determination of fluopicolide was performed successfully in milk, meat, egg, liver and cream. The LOQ is 0.01 mg/kg in all matrices. A confirmatory procedure (analysis by GC/MSD) is included in this multi method.

Table 23 Analytical methods for the determination of fluopicolide and/or its metabolites in plant matrices

Method name Region Report. No. Year	Substrate	Analytes	LOQ (mg/kg)	Technique
00782 EU IF-101/05424 2002	Grapes Wheat grain Wheat straw Cabbage	fluopicolide M-01 M-02	0.01 mg/kg for all matrices	HPLC-MS/MS

Method name Region Report. No. Year	Substrate	Analytes	LOQ (mg/kg)	Technique
00782/M001 EU MR-336/02 2002	Grapes Potato tuber Potato plant	fluopicolide M-01 M-02	0.01 mg/kg for all matrices	HPLC-MS/MS
00782/M002 EU MR-071/03 2003	Wheat grain Wheat straw Wheat green plant	fluopicolide M-01 M-02 M-05	0.01 mg/kg for all matrices	HPLC-MS/MS
00782/M003 EU MR-148/03 2003	Wheat grain Wheat straw Wheat green plant	M-04	0.01 mg/kg for all matrices	HPLC-MS/MS
CLE 1905/082 EU 2003 (DFG S19)	Grapes Wheat grain Potato tuber	fluopicolide	0.1 mg/kg for grapes; 0.02 mg/kg for wheat grain and potato	GC/MSD
SYN/0273 EU 2004	Apple Oil seed rape	fluopicolide	0.02 mg/kg for all matrices	GC-MSD
G06-0150 EU 2006	Grapes Wheat grain Potato tuber	fluopicolide	0.1 mg/kg for grapes; 0.02 mg/kg for wheat grain and potato	GC-MSD
METH1611-00.02 US 2002	Bulb onion Green onion (stalk) Head Cabbage Broccoli Spinach Carrot Radish Celery	fluopicolide M-01 M-02	0.01 mg/kg for all matrices and all analytes	HPLC-MS/MS

Table 24 Analytical methods for the determination of fluopicolide and/or its metabolites in animal matrices

Method name Region Report. No. Year	Substrate	Analytes	LOQ (mg/kg)	Technique
BAY-0518V EU 2005	Milk Meat Egg Liver Cream	fluopicolide	0.01 mg/kg for all matrices	GC/MSD
P 963 G EU 2005 ILV	Milk Meat Egg Liver Cream	fluopicolide	0.01 mg/kg for all matrices	GC/MSD

Table 25 Analytical methods for the determination of fluopicolide and/or its metabolites in soil

Method name Region Report. No. Year	Substrate	Analytes	LOQ (mg/kg)	Technique
AR 265-01	Soil	fluopicolide M-01 M-02 AE 0608000	0.05 mg/kg	HPLC-MS/MS

Method 00782

Zietz and Billian (2002) described an LC/MS/MS for the determination of fluopicolide and metabolites M-01 and M-02 in miscellaneous crops (grapes, wheat straw and grain and cabbage). These crops covered high acid, cereal/dry crops and high water types of matrices. The parent compound and two plant metabolites are extracted from plant samples by homogenisation with a mixture of acidified water and acetone (1:3 pH < 2 with H_2SO_4). Acetone is removed from an aliquot of the extraction mixture before partitioning into tertiary butyl methyl ether (MTBE). The solvent is allowed to evaporate from an aliquot of the MTBE extract prior to re-dissolving the extract in a water/acetonitrile mixture before direct LC/MS/MS quantification of fluopicolide and M-01. A separate aliquot of the MTBE extract was evaporated to dryness before re-dissolving the extract in methanol. Addition of sulphuric acid with heating converts any M-02 to its methyl ester for the LC/MS/MS quantification of M-02 as its methyl ester detected by their daughter ions using electrospray interface and positive mode. A Silica Uptisphere 120A ODB, 3 um, 150 × 2 mm–Interchim /Laubscher Labs column was used with a guard column (Silica Uptisphere 120A ODB, 3 um, 10 × 2 mm–Interchim /Laubscher Labs) with a gradient elution program (Eluent A: 0.01% formic acid, Eluent B: acetonitrile).The ions monitored were: fluopicolide 382.9 m/z (parent), 172.8 m/z (daughter); M-01 189.9 m/z (parent) 172.8 m/z (daughter); M-02 239.90 m/z (parent) 179.80 m/z (daughter).

The method procedure was validated on representative untreated samples of grapes, wheat grain, wheat straw and cabbage taken from European residue trial sites. The LOQ was 0.01 mg/kg for fluopicolide, M-01 and M-02 in grapes, wheat grain, wheat straw and cabbage. Almost linear response in the range 0.3 to 10 ng/mL for fluopicolide, M-01 and M-02. (Note: Over the range 0.3 to 20 ng/mL best fit achieved with a non-linear curve). No interference > 10% of the LOQ was observed for the plant control samples analysed for all compounds. The technique is specific for fluopicolide, M-01 and M-02

Table 26 Validation data for fluopicolide and its metabolites M-01 and M-02 using method 00782 in various plant matrices

Compound (matrix)		Fortification level (mg/kg)	No. of repetitions	Mean across level (%)	Overall mean (%)
Recovery efficiency					
Fluopicolide	Grapes	0.01 0.10	5 5	86% 91%	89%
	Wheat grain	0.01 0.10	5 5	104% 97%	100%
	Wheat straw	0.01 0.10	5 5	76% 78%	77%
	Cabbage	0.01 0.10	5 5	80% 84%	82%

Compound (matrix)		Fortification level (mg/kg)	No. of repetitions	Mean across level (%)	Overall mean (%)
M-01	Grapes	0.01 0.10	5 5	108% 97%	103%
	Wheat grain	0.01 0.10	5 5	109% 103%	106%
	Wheat straw	0.01 0.10	5 5	93% 108%	100%
	Cabbage	0.01 0.10	5 5	99% 99%	99%
M-02	Grapes	0.01 0.10	5 5	104% 92%	98%
	Wheat grain	0.01 0.10	5 5	79% 97%	88%
	Wheat straw	0.01 0.10	5 5	106% 107%	106%
	Cabbage	0.01 0.10	5 5	98% 86%	92%
Compound (matrix)		Fortification level (mg/kg)	No. of repetitions	RSD across level (%)	Overall RSD (%)
Repeatability					
Fluopicolide	Grapes	0.01 0.10	5 5	7.5% 4.4%	6.5%
	Wheat grain	0.01 0.10	5 5	8.2% 7.9%	8.6%
	Wheat straw	0.01 0.10	5 5	9.0% 6.4%	8.3%
	Cabbage	0.01 0.10	5 5	11.8% 1.4%	7.9%
M-01	Grapes	0.01 0.10	5 5	6.2% 9.6%	9.4%
	Wheat grain	0.01 0.10	5 5	11.2% 4.0%	8.6%
	Wheat straw	0.01 0.10	5 5	14.4% 10.8%	14.1%
	Cabbage	0.01 0.10	5 5	7.8% 5.2%	6.3%
M-02	Grapes	0.01 0.10	5 5	10.5% 3.8%	10.4%
	Wheat grain	0.01 0.10	5 5	9.0% 2.5%	12.5%
	Wheat straw	0.01 0.10	5 5	11.4% 4.1%	8.1%
	Cabbage	0.01 0.10	5 5	12.0% 5.5%	11.2%

Method 00782/001

A modification of method 00782 was reported by Schöning and Billian (2003).

The parent compound and two plant metabolites are extracted from crop samples by homogenisation with a mixture of acidified water and acetone (pH < 2 with H_2SO_4). Acetone is removed from an aliquot of the extraction mixture before partitioning into tertiary butyl methyl ether (MTBE). An aliquot of the MTBE extract is evaporated to dryness prior to re-dissolving the extract in an acetonitrile/water (2:8 + 2 mL/L acetic acid) mixture before direct LC/MS/MS quantification of fluopicolide and M-01. A separate aliquot of the MTBE extract was also evaporated to dryness before re-dissolving the extract in an acetonitrile/water/ammonium acetate mixture (2:8 +2.18 mL/L acetic acid + 10 mmol ammonium acetate/L) before direct LC/MS/MS quantification of M-02.

Chromatography was under isocratic reversed phase conditions with detected by Tandem Mass Spectrometry with electrospray ionization. The column used was a Phenomenex, Luna C18 (2), 5 urn, 15 × 0.46 cm i.d. or equivalent with mobile phase A: water/acetonitrile (90:10, v/v) + 2.0 mL acetic acid/L, B: acetonitrile + 2.0 mL acetic acid/L, C: water/acetonitrile (50:50, v/v) + 0.1 mL acetic acid (isocratic). The precursor and product ions were; 383 and 173 m/z for fluopicolide, 190 and 173 m/z for M-01 and 224 and 180 m/z for M-02.

The method procedure was validated on representative untreated samples of grapes, potato tubers and potato plants. LOQ of 0.01 mg/kg for fluopicolide, M-01 and M-02 in grapes, potato tubers and potato plants. Linear response in the range of 0.1 to 100 µg/mL for fluopicolide and M-01 and 0.25 to 250 µg/mL for M-02 (in pure solvent or matrix-matched standards). No interference > 10% of the LOQ was observed for the plant control samples analysed for all compounds. The technique is specific for fluopicolide, M-01 and M-02

Table 27 Validation data for method 00782/001 for fluopicolide and metabolites in grapes and potatoes

Compound	Matrix	Fortification level (mg/kg)	No. of repetitions	Mean across level (%)	Overall mean (%)
Recovery efficiencies:					
Fluopicolide	Grapes	0.01 0.10	5 5	96% 99%	97%
	Potato tuber	0.01 0.10	5 5	97% 89%	93%
	Potato plant	0.01 0.10	5 5	85% 85%	85%
M-01	Grapes	0.01 0.10	5 5	91% 97%	94%
	Potato tuber	0.01 0.10	5 5	96% 92%	94%
	Potato plant	0.01 0.10	5 5	90% 90%	90%
M-02	Grapes	0.01 0.10	5 5	98% 103%	100%
	Potato tuber	0.01 0.10	5 5	81% 87%	84%
	Potato plant	0.01 0.10	5 5	97% 108	102%
Compound (matrix)		Fortification level (mg/kg)	No. of repetitions	RSD across level (%)	Overall RSD (%)
Repeatability:					
Fluopicolide	Grapes	0.01 0.10	5 5	5.6% 5.1%	5.3%
	Potato tuber	0.01 0.10	5 5	7.5% 5.8%	7.9%
	Potato plant	0.01 0.10	5 5	9.7% 13.0%	10.8%
M-01	Grapes	0.01 0.10	5 5	6.9% 2.9%	5.9%
	Potato tuber	0.01 0.10	5 5	2.6% 2.2%	2.0%
	Potato plant	0.01 0.10	5 5	5.7% 2.1%	4.1%
M-02	Grapes	0.01 0.10	5 5	5.0% 3.2%	4.8%
	Potato tuber	0.01 0.10	5 5	5.6% 12.8%	10.2%
	Potato plant	0.01 0.10	5 5	1.7% 0.8%	5.9%

Method 00782/03

Schöning and Billian (2003) reported a modification to method 00782 extending the method to cereal matrices from field crop rotation studies. The parent compound and three plant metabolites are extracted from crop samples by homogenisation with a mixture of acetone/water (3:1) adjusted to pH 2 with sulphuric acid and 2 mL of L-cysteine hydrochloride (250 mg/mL). Acetone is removed from an aliquot of the extraction mixture, NaCl added and the solution adjusted to pH 2 before partitioning into tertiary butyl methyl ether (MTBE). Solvent from an aliquot of the MTBE extract was evaporated off prior to re-dissolving the extract in an acetonitrile/water (2:8 v/v + 2 mL/L acetic acid), passed through a 0.2 µm PTFE membrane filter before direct injection into a LC/MS/MS for quantification of fluopicolide and M-01. A separate aliquot of the MTBE extract was evaporated to dryness before re-dissolving the extract in an acetonitrile/water (2:8 v/v + 2.18 mL/L acetic acid plus 10 mmol ammonium acetate/L) mixture before direct LC/MS/MS quantification of M-02 and M-05. Chromatography was under isocratic reversed phase conditions with detection by Tandem Mass Spectrometry using a Phenomenex, Luna C18 (2), 5 µm, 15 × 0.46 cm i.d. column. The mobile phase was: A—water/acetonitrile (90:10, v/v) + 2.0 mL acetic acid/L; B—acetonitrile + 2.0 mL acetic acid/L; C—water/acetonitrile (50:50, v/v) + 0.1 mL acetic acid (isocratic). The precursor and product ions were; 383 and 173 m/z for fluopicolide, 190 and 173 m/z for M-01 and 224 and 198 m/z for M-02 and 252 and 61 m/z for M-06.

LOQ 0.01 mg/kg for fluopicolide, M-01, M-02 and M-05 in wheat grain, straw and green plant material. Linear response in the range 0.1 to 100 µg/mL for fluopicolide and M-01 and 0.25 to 250 µg/mL for M-02 and M-05 (in pure solvent or matrix-matched standards). No interference > 10% of the LOQ was observed for the plant control samples analysed for all compounds. The technique is specific for fluopicolide, M-01, M-02 and M-05

Table 28 Validation data for Method 00782/03 for fluopicolide and its metabolites M-01 and M-02 using LC-MS/MS in wheat matrices

Compound (matrix)		Fortification level (mg/kg)	No. of repetitions	Mean across level (%)	Overall mean (%)
Recovery efficiencies:					
Fluopicolide	Wheat grain	0.01 0.10	5 5	87% 90%	89%
	Wheat straw	0.01 0.10	5 5	88% 95%	91%
	Green plant	0.01 0.10	3 3	84% 85%	84%
M-01	Wheat grain	0.01 0.10	5 5	100% 98%	99%
	Wheat straw	0.01 0.10	5 5	95% 99%	97%
	Green plant	0.01 0.10	3 3	99% 98%	99%
M-02	Wheat grain	0.01 0.10	5 5	82% 86%	84%
	Wheat straw	0.01 0.10	5 4	74% 77%	75%
	Green plant	0.01 0.10	3 3	74% 76%	72%
M-05	Wheat grain	0.01 0.10	5 5	74% 78%	76%
	Wheat straw	0.01 0.10	5 4	73% 74%	73%
	Green plant	0.01 0.10	3 3	78% 77%	77%

Compound (matrix)		Fortification level (mg/kg)	No. of repetitions	Mean across level (%)	Overall mean (%)
Compound (matrix)		Fortification level (mg/kg)	No. of repetitions	RSD across level (%)	Overall RSD (%)
Repeatability:					
fluopicolide	Wheat grain	0.01 0.10	5 5	3.1% 4.6%	4.4%
	Wheat straw	0.01 0.10	5 5	4.3% 3.8%	5.5%
	Green plant	0.01 0.10	3 3	2.4% 1.8%	1.9%
M-01	Wheat grain	0.01 0.10	5 5	3.0% 4.0%	3.5%
	Wheat straw	0.01 0.10	5 5	3.3% 2.7%	3.5%
	Green plant	0.01 0.10	3 3	3.8% 2.4%	2.9%
M-02	Wheat grain	0.01 0.10	5 5	2.5% 1.8%	3.1%
	Wheat straw	0.01 0.10	5 4	8.6% 0.8%	6.4%
	Green plant	0.01 0.10	3 3	2.1% 4.1%	4.2%
M-05	Wheat grain	0.01 0.10	5 5	3.8% 4.1%	4.9%
	Wheat straw	0.01 0.10	5 4	6.4% 1.1%	4.6%
	Green plant	0.01 0.10	3 3	1.5% 2.7%	2.1%

Schöning, R., Billian, P. 2004 reported a modification of method 00782 that included analysis of metabolite M-04. Residues of M-04 are extracted homogenized samples with a mixture of acetone:water (3:1 v/v) adjusted with sulphuric acid to pH 2. After addition of L-cysteine hydrochloride (250 mg/L) and filtration, the extract is made to volume and the solvent evaporated off. The pH of the remaining aqueous solution is adjusted to pH 2, NaCl added and partitioned twice against MTBE. Solvent was removed from an aliquot of the MTBE extract by evaporation prior to re-dissolving the extract in an acetonitrile:water mixture (2:8 v/v + 2 mL/L acetic acid) before direct LC/MS/MS quantification of M-04. The column used was a Luna C18 (2), 5 µm, 15 × 0.46 cm i.d column. The mobile phase was: A—water/acetonitrile (90:10, v/v) + 2.0 mL acetic acid/L; B—acetonitrile + 2.0 mL acetic acid/L; C—water/acetonitrile (50:50, v/v) + 0.1 mL acetic acid (isocratic). The precursor and product ions were 206 and 189 m/z respectively.

LOQ 0.01 mg/kg for M-04 in wheat grain, straw and green plant material. A linear response was observed in the range 0.1 to 100 µg/mL for M-04 (in pure solvent or matrix-matched standards). No interference > 10% of the LOQ was observed for the plant control samples analysed for M-04. The technique is specific for M-04.

Table 29 Validation data for method 00782 for fluopicolide plant metabolites M-04 using LC-MS/MS in wheat matrices

Compound (matrix)		Fortification level (mg/kg)	N	Mean across level (%)	Overall mean (%)
Recovery efficiencies:					
M-04	Wheat grain	0.01 0.10	5 5	106% 93%	99%
	Wheat straw	0.01 0.10	5 5	88% 86%	87%
	Green plant	0.01	5	95%	93%

Compound (matrix)		Fortification level (mg/kg)	N	Mean across level (%)	Overall mean (%)
		0.10	5	90%	
Compound (matrix)		Fortification level (mg/kg)	N	RSD across level (%)	Overall RSD (%)
Repeatability:					
M-04	Wheat grain	0.01 0.10	5 5	6.3% 7.2%	9.3%
	Wheat straw	0.01 0.10	5 5	4.1% 3.0%	3.7%
	Green plant	0.01 0.10	5 5	7.2% 3.6%	6.1%

Enforcement methods

Peatman (2003) evaluated the published multi-residue analytical procedure DFG S19 for the determination of fluopicolide in grapes, potatoes and cereal (wheat) grain. The version of the method used was L 00.00-34, which uses an ethyl acetate cyclohexane mixture for solvent partition instead of dichloromethane. The modules relevant to the crop types tested were followed with only minor modifications to adapt the procedure to the equipment available. Clean-up of extracts was achieved using gel-permeation chromatography (GPC) after an initial profiling of the conditions required. Determination was performed by gas chromatography with mass selective detection (GC/MSD). Samples of potato extracts required the use of matrix-matched calibration standards to overcome matrix effects on the chromatography. LOQ 0.10 mg/kg for fluopicolide in grapes, 0.02 mg/kg for fluopicolide in potato tubers and wheat grain. Linear response in the range 0.01 to 1.0 µg/mL for fluopicolide. Standards were prepared in control matrix for the determination of potato extracts. No interference > 30% of the LOQ was observed for the control samples analysed for fluopicolide. The technique is specific for fluopicolide. Use of GC/MSD with three ions of m/z > 100 (347, 209, 173 m/z) enables confirmation of any residue and confirms selectivity of the analytical procedure for fluopicolide.

Table 30 Validation data for fluopicolide using DFG S19 and GC/MSD

Compound (matrix)		Fortification level (mg/kg)	N	Mean across level (%)	Overall mean (%)
Recovery efficiencies:					
Fluopicolide	Grapes	0.10 1.0	5 5	92% 108%	100%
	Wheat grain	0.02 0.20	5 5	89% 104%	97%
	Potatoes	0.02 0.20	5 5	93% 91%	92%
Compound (matrix)		Fortification level (mg/kg)	N	RSD across level (%)	Overall RSD (%)
Repeatability:					
fluopicolide	Grapes	0.10 1.0	5 5	7.5% 5.8%	10.6%
	Wheat grain	0.02 0.20	5 5	12.8% 12.9%	14.6%
	Potatoes	0.02 0.20	5 5	12.3% 5.7%	9.2%

Inter-laboratory validation of DFG S19 for the determination of fluopicolide in grapes, potatoes and cereal (wheat) grain was reported by Taylor (2004). The procedure was independently validated on grapes and potatoes using the reported conditions used from version L 00.00-34 of the

DFG S19 multi residue approach. In addition this study also evaluated the same version of the DFG S19 multi-residue method for the determination of fluopicolide in apples and oilseed rape grain. The modules relevant to the crop types tested were followed with only minor modifications to adapt the procedures to the independent laboratory. Clean-up of extracts was achieved using gel-permeation chromatography (GPC) after an initial profiling of the conditions required. Determination was performed by gas chromatography with mass selective detection (GC/MSD). LOQ 0.10 mg/kg for fluopicolide in grapes, 0.02 mg/kg for fluopicolide in potato tubers, apples and oilseed rape grain. Linear response in the range 0.008 to 1.0 µg/mL for fluopicolide. Standards were prepared in control matrix for the determination of potato extracts. No interference > 10% of the LOQ was observed for the control samples analysed for fluopicolide (except apples where interference was a maximum of < 20% of the LOQ). The technique is specific for fluopicolide. Use of GC/MSD with three ions 347 209 and 173 m/z enables confirmation of any residue and confirms selectivity of the analytical procedure for fluopicolide.

Table 31 Validation data for fluopicolide using DFG S19 and GC/MSD

Compound (matrix)		Fortification level (mg/kg)	N	Mean (%)	Overall mean (%)
Recovery efficiencies					
fluopicolide	Grapes	0.10 1.0 2.0	5 5 2	74% 75% 77%	75%
	Potatoes	0.02 0.20	5 5	85% 77%	81%
	Apples	0.02 0.20	5 5	77% 82%	80%
	OSR grain	0.02 0.20	5 5	81% 83%	82%
Compound (matrix)		Fortification level (mg/kg)	No. of repetitions	RSD across level (%)	Overall RSD (%)
Repeatability:					
fluopicolide	Grapes	0.10 1.0 2.0	5 5 2	4.0% 3.5% –	3.4%
	Potatoes	0.02 0.20	5 5	6.1% 4.5%	7.3%
	Apples	0.02 0.20	5 5	6.1% 15.7%	12.0%
	OSR grain	0.02 0.20	5 5	16.1% 13.7%	14.1%

Independent Laboratory Validation (ILV) of the method 1905/082 was extended by Rzepka, (2006) for the determination of fluopicolide in grapes, potato (tuber) and wheat (grain).

A series of recovery experiments were performed by fortifying control (untreated) specimens of the matrices grapes, potatoes and wheat grain. The ILV followed the procedures as described in the original validation report 1905/082. Fluopicolide was extracted from grapes, potato (tuber) and wheat (grain) specimens with acetone / water (2/1, v/v). Thereafter ethyl acetate/cyclohexane (1/1, v/v) and sodium chloride were added for liquid-liquid partition. An aliquot of the organic phase was evaporated to dryness. For all matrices the evaporated extract was cleaned up by Gel Permeation Chromatography (GPC) on Bio Beads S-X3 polystyrene gel using a mixture of ethyl acetate/cyclohexane (1/1, v/v) as eluant. All the final extracts were analysed for residues of fluopicolide by gas chromatography using mass selective detection (GC/MSD, 347, 209 and 173 m/z). Control specimens were analysed in duplicate and fortified specimens were analysed five times for each fortification level.

For fluopicolide in potato (tuber) and wheat (grain) the LOQ was 0.02 mg/kg with a limit of detection of 0.007 mg/kg. For fluopicolide in grapes the LOQ) was 0.10 mg/kg with a limit LOD of 0.03 mg/kg. The linearity of the detector response was confirmed by injecting six external solvent-matched standard solutions in the range between of 0.0033 to 2.0 µg/mL of fluopicolide. Analysis of control specimens by GC/MSD indicated no residues of the test substance above the limit of detection and no background levels of the test substance were present in the test systems before the beginning of the study.

Overall mean recovery rates for all tested materials with fortifications levels 0.01 to 1 mg/kg were in a range between 105 and 110% for mass ion m/z = 347 and between 103–108 and 101–106 for the confirmatory mass ions m/z = 209 and m/z = 173. Overall RSDs were in the range of 3.5 to 6.1% for mass ion m/z = 347 and between 3.5–7.7% and 4.2 to 8.2% for the confirmatory mass ions m/z = 209 and m/z = 173.

Table 32 Validation data for Method 1905/082 for fluopicolide in grapes, potato tubers and wheat grain for the mass ions m/z = 347, 209 and 173

	Fortification level (mg/kg)	Recoveries (%) single values	mean	SD	RSD		Overall recoveries (%) mean	SD	RSD
m/z 347									
Grapes	0.10	113, 113, 109, 110, 102	109	4.0	3.7	5	110	3.8	3.5
	1.0	107, 98, 108, 103, 108	105	4.3	4.1	5			
Potato tuber	0.02	112, 111, 110, 102, 108	109	4.0	3.7	5	109	3.8	3.5
	0.20	105, 114, 114, 110, 109	110	3.8	3.5	5			
Wheat grain	0.02	107, 109, 99, 96, 103	103	5.4	5.2	5	105	6.4	6.1
	0.20	102, 103, 112, 98, 116	106	7.5	7.1	5			
m/z 209									
Grapes	0.10	109, 107, 107, 109, 112	109	2.0	1.8	5	108	3.9	3.6
	1.0	106, 98, 110, 106, 111	106	5.1	4.8	5			
Potato tuber	0.02	111, 107, 110, 107, 102	107	3.5	3.3	5	108	3.8	3.5
	0.20	103, 113, 113, 109, 107	109	4.2	3.9	5			
Wheat grain	0.02	102, 102, 107, 87, 101	100	7.5	7.5	5	103	7.9	7.7
	0.20	103, 103, 111, 96, 116	106	7.8	7.4	5			
m/z 173									
Grapes	0.10	105, 103, 105, 104, 106	105	1.1	1.0	5	106	4.5	4.2
	1.0	106, 97, 112, 111, 111	107	6.3	5.9	5			
Potato tuber	0.02	103, 109, 100, 95, 107	103	5.6	5.4	5	106	5.5	5.2
	0.20	102, 113, 112, 107, 107	108	4.4	4.1	5			
Wheat grain	0.02	94, 104, 92, 92, 99	96	5.2	5.4	5	101	8.3	8.2
	0.20	102, 101, 111, 98, 118	106	8.3	7.8	5			

Klimmek (2005) examined the applicability of the DFG Method S 19 for the determination of residues of fluopicolide. Four different major steps were examined. The applicability of various gas chromatographic systems was evaluated. For fluopicolide, acceptable gas chromatographic results were achieved on a gas chromatographic system (GC) equipped with a mass selective detector (MSD) and a DB-5 MS column as well as an electron capture detector (ECD) and a DB-1 column. On a GC system equipped with a mass selective detector (MSD), the obtained mass spectrum of fluopicolide showed ions m/z 347, 209 and 173 as suitable for single ion monitoring. The lowest concentrations of fluopicolide used in this test were 0.01 µg/mL for MSD and 0.04 µg/mL for ECD. Using a GC equipped with a nitrogen phosphorus detector (NPD) and a DB-1 column, the sensitivity of fluopicolide was not sufficient for quantitation at an anticipated LOQ of 0.01 mg/kg.

The second step was to check, if fluopicolide can be extracted within the multi residue method according to the DFG Method S 19 (extended revision). The module E1 using a mixture of acetone/water (2/1, v/v) and ethyl acetate / cyclohexane (1/1, v/v) was checked within this study. The extraction module E1 of the DFG Method S 19 was suitable for fluopicolide extraction (Recovery = 97%).

The third step was to check, if fluopicolide can be eluted within the elution profile of the gel permeation chromatography normally used for the Method DFG S 19 (85–195 mL). The specific elution volume for fluopicolide during the clean-up step by gel permeation chromatography was found with 110–150 mL

The fourth step was to check the elution properties of fluopicolide using a cleanup at a silica gel mini column. Fluopicolide was detected totally (104%) in eluate 3.

The extraction efficiency of method 00782/M003 was tested for grapes and wheat straw (Reiner 2004). Extraction efficiency was determined for fluopicolide and the metabolites are M-01 (BAM), M-04 (3-OH-BAM), M-02 (PCA) and M-05 (sulfoxide). The residue was determined as the sum of parent compound and two typical metabolites for each radiolabel. For each extraction efficiency experiment, two plant samples were extracted in parallel.

Two different matrices were used for the analysis of aged residues with the phenyl label: Grapes were available from the metabolism study following spray application with [U-^{14}C-phenyl] fluopicolide. Straw was available from a confined rotational crop study representing aged radioactive residues following root uptake of radioactivity from soil. For the analysis of aged residues with the pyridyl label, grapes were available from the metabolism study following spray application with [2,6-^{14}C-pyridinyl] fluopicolide.

The samples for the extraction efficiency testing were extracted with a mixture of acetone/water (3/1 v/v), sulphuric acid (pH < 2) and a small amount of L-cysteine hydrochloride according to the residue method.

The total radioactive residue (TRR) was determined by summation of the radioactivity in the extracts and in the solids. The assignment of fluopicolide and its metabolites was achieved by co-chromatography HPLC/TLC. The ^{14}C-radioactivity in liquid samples was determined in a liquid scintillation counter and solid samples were combusted. The CO_2 produced by combustion was absorbed and the radioactivity measured by LSC.

The extraction of aged residues using the residue method was effective for straw and grapes. The extracted radioactivity for the two samples of straw represented 69 and 72% of the total radioactive residue (TRR). For grapes, the extracted radioactivity was very high and accounted for 93–97% of the TRR considering both labels.

The extraction efficiency testing showed that 81% of the residue of interest (fluopicolide and four metabolites) was extracted from straw. The results of grapes indicated a quantitative extraction efficiency (100%) for the phenyl and (104%) pyridyl labels.

Table 33 Extraction efficiency of the residue method 00782/M003 using wheat straw (phenyl label) from the confined rotational crop study (acetonitrile:water)

wheat straw	metabolism study		residue method (sample 1)		residue method (sample 2)	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
total radioactive residue (TRR)	100	13.6	100	13.5	100	13.9
Fluopicolide	23.1	3.13	18.7	2.53	17.5	2.42
M-01 (BAM)	3.4	0.46	3.7	0.50	3.2	0.45
M-04 (3-OH-BAM)	13.6	1.84	10.6	1.44	10.5	1.46
sum of compounds of relevant compounds:	40.1	5.44	33.0	4.46	31.2	4.32
extraction efficiency (recovery of the TTR using the residue method)			82%		80%	
			mean: 81%			

Table 34 Extraction efficiency of the residue method 00782/M003 using grapes (phenyl label) from the metabolism study (acetonitrile)

Grapes	metabolism study		residue method (sample 1)		residue method (sample 2)	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
total radioactive residue (TRR)	100	1.27	100	1.27	100	1.27
Fluopicolide	91.2	1.15	92.2	1.17	91.1	1.16
M-01 (BAM)	2.0	0.026	1.9	0.025	1.7	0.021
AE 657378 (3-OH-BAM)	ND	ND	ND	ND	ND	ND
sum of compounds of relevant compounds:	93.1	1.18	94.2	1.19	92.8	1.18
extraction efficiency (recovery of the TTR using the residue method)			101%		100%	
			mean: 100%			

Table 35 Extraction efficiency of the residue method 00782/M003 using grapes (pyridyl label) from the metabolism study (acetonitrile)

Grapes	metabolism study		residue method (sample 1)		residue method (sample 2)	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
total radioactive residue (TRR)	100	1.04	100	0.72	100	0.70
Fluopicolide	87.4	0.91	90.1	0.65	89.6	0.63
M-02 (PCA)	2.3	0.024	3.5	0.026	3.3	0.023
M-05 (sulfoxide)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
sum of compounds of relevant compounds:	89.8	0.93	93.6	0.69	92.9	0.65
extraction efficiency (recovery of the TTR using the residue method)			106%[a]		103%[a]	
			mean: 104%			

[a] calculated by scaling the fluopicolide concentration by the ratio of TRR in the residue method sample to the TRR in the metabolism sample.

Kowalsky (2006) described a method used for determining fluopicolide and its metabolites M-01 and M-02 in a variety of crop matrices. Residues of fluopicolide and its metabolites M-01 and M-02 are extracted from a homogeneous sample with acetone/water (75:25, v/v), centrifuged and the supernatant brought to volume, diluted in 0.2% acetic acid, and analysed via HPLC with mass spectrometric (LC/MS/MS) detection. Both the parent and M-01 are analysed via positive electron impact while M-02 is analysed in negative mode. The limit of quantification (LOQ) was established at 0.01 mg/kg for fluopicolide and its metabolites M-01 and M-02 in all plant matrices analysed.

Detector response factor curves for fluopicolide and its metabolites M-01 and M-02 were established for standards in solvent solutions and in the presence of crop matrix extracts. The correlation coefficient for the detector response factor curves were all > 0.99, indicating that the detector response factor was linear over the range of concentration tested. Matrix interference was minimal in the control sample chromatograms ($< 20\%$ of LOQ). Well resolved peaks were obtained with all sample commodities at all fortification levels. The mean overall recoveries for samples fortified at 0.01–20 mg/kg were between 83 and 105% for fluopicolide and its metabolites M-01 and M-02, with an RSD lower than 20% thus suggesting a satisfactory repeatability of the method.

Table 36 Validation data for fluopicolide and its metabolites M-01 and M-02 using LC-MS/MS in various plant matrices

Reference, year	Matrix	compound	Fortification level (mg/kg)	Recovery (%) Single values	N	Overall mean	RSD
02CU27780 2002	Onion bulb	fluopicolide	0.01 0.1 0.5 5.0	96 98 102 102 91 95 80 85	2 2 2 2	95	6.4
		M-01	0.01 0.1 0.5	76 83 86 89 88 86	2 2 2	85	5.6
		M-02	0.01 0.1 0.5	77 86 92 91 99 93	2 2 2	90	8.3
02CU27780 2002	Green onion stalk	fluopicolide	0.01 0.1 0.5 5.0	88 88 101 95 86 109 101 90	2 2 2 2	95	8.7
		M-01	0.01 0.1 0.5	81 70 93 96 91 93	2 2 2	87	11.4
		M-02	0.01 0.1 0.5	100 108 114 108 87 100	2 2 2	103	9.2
02CU33137 2002	head cabbage	fluopicolide	0.01 0.1 0.5 5.0	119 99 94 95 98 91 98 94	2 2 2 2	99	8.8
		M-01	0.01 0.1 0.5	76 79 85 88 88 84	2 2 2	83	5.9
		M-02	0.01 0.1 0.5	101 95 80 72 75 73	2 2 2	83	14.9
02CU33136 2002	Broccoli curd	fluopicolide	0.01 0.1 0.5 5.0	98 102 88 91 93 89 86 87	2 2 2 2	92	5.9
		M-01	0.01 0.1 0.5	82 83 94 88 86 89	2 2 2	87	5.0
		M-02	0.01 0.1 0.5	110 107 95 92 90 86	2 2 2	97	10.0
02CU33135 2002	Spinach leaf	fluopicolide	0.01 0.05 0.5 10 20	73 88 86 94 101 111 102 82 96 98	2 2 2 2 2	93	11.9
		M-01	0.01 0.05 0.5	97 85 105 112 114 112	2 2 2	104	10.9
		M-02	0.01 0.05 0.5	102 115 90 114 98 84	2 2 2	101	12.5

Reference, year	Matrix	compound	Fortification level (mg/kg)	Recovery (%) Single values	N	Overall mean	RSD
02CU33130 2002	Carrot root	fluopicolide	0.01 0.1 0.5 2.0	96 100 101 102 100 99 105 103	2 2 2 2	101	2.7
		M-01	0.01 0.1 0.5	81 89 99 96 89 90	2 2 2	91	6.9
		M-02	0.01 0.1 0.5	84 87 92 94 88 95	2 2 2	90	4.8
02CU33129 2002	Radish root	fluopicolide	0.01 0.1 0.5	94 96 105 102 90 89 96 106	4 2 2	97	6.7
		M-01	0.01 0.1 0.5	85 83 79 77 87 89 91 88	4 2 2	85	5.8
		M-02	0.01 0.1 0.5	94 87 98 100 98 98	2 2 2	96	5.0
02CU33134 2002	Celery stalk	fluopicolide	0.01 0.05 0.5 10 15	114 77 92 100 87 94 103 98 85 81	2 2 2 2 2	93	12.0
		M-01	0.01 0.1 0.5	107 99 101 107 106 109	2 2 2	105	3.7
		M-02	0.01 0.1 0.5	105 91 88 95 99 84	2 2 2	94	8.1

RSD: relative standard deviation

Residue method for foodstuff of animal origin

Klimmek (2005) studied the applicability of the DFG Method S 19 (extended and revised version) for the determination of residues of fluopicolide in meat, milk, egg, liver and cream. The extraction of fluopicolide from meat, milk, egg and liver was performed according to extraction module E 1 and from cream according to E 8 followed by clean-up procedure according to module GPC with the inclusion of a mini silica gel column.

All samples were analysed by gas capillary chromatography with mass selective detection (GC-MSD) (module D 4). Control specimens were analysed in duplicate and fortified specimens were analysed five times for each analyte and matrix at each fortification level.

For fluopicolide the LOQ was 0.01 mg/kg for all matrices (meat, milk, egg, liver and cream). The limit of detection was 0.0014 mg/kg for meat, milk, egg and cream and 0.003 mg/kg for liver. The linearity of the detector responses of the GC-MSD system was confirmed by injecting eight standard solutions covering the working range of 0.005 µg/mL–1.000 µg/mL for fluopicolide. The correlation coefficient was > 0.998. Analysis of control specimens of meat, milk, egg, liver and cream by GC-MSD yielded no residues of fluopicolide above the limit of detection when using the ions with mass to charge ratios m/z 347 (quantitation), m/z 349 and m/z 209 (confirmation). All determined residues of fluopicolide were well below 30% of the LOQ level. The individual recovery rates for

fluopicolide ranged from 76 to 122% at fortification levels of 0.01 to 0.1 mg/kg (overall means: 94–110%, overall RSDs = 7.3–11.4%) for all investigated matrices (see Table 37).

Table 37 Validation data for DFG S19 for analysis of fluopicolide in meat, milk, egg, liver and cream

Matrix	Fortification level (mg/kg)	Recoveries (%)	Mean	SD	RSD	N	Overall recovery (%) Mean	SD	RSD
Meat									
Quantitation m/z 347	0.01	97 107 102 111 118	107	8.1	7.6	5	105	8.6	8.2
	0.10	88 108 101 105 113	103	9.5	9.2	5			
Confirmation m/z 349	0.01	98 107 101 107 115	106	6.5	6.1	5	104	7.8	7.5
	0.10	88 108 100 104 113	103	9.5	9.2	5			
Confirmation m/z 209	0.01	94 104 109 106 112	105	6.9	6.6	5	104	8.0	7.7
	0.10	87 107 101 105 113	103	9.7	9.4	5			
Milk									
Quantitation m/z 347	0.01	100 113 116 106 116	110	7.0	6.4	5	110	10.6	9.6
	0.10	94 132 102 106 110	109	14.3	13.1	5			
Confirmation m/z 349	0.01	101 112 115 106 114	110	5.9	5.4	5	109	9.9	9.1
	0.10	95 131 102 106 110	109	13.6	12.5	5			
Confirmation m/z 209	0.01	97 119 122 100 113	110	11.2	10.2	5	109	12.4	11.4
	0.10	93 132 100 106 108	108	14.7	13.6	5			
Egg									
Quantitation m/z 347	0.01	106 97 105 111 106	105	5.0	4.8	5	103	7.5	7.3
	0.10	90 98 106 114 95	101	9.5	9.4	5			
Confirmation m/z 349	0.01	107 95 101 107 106	103	5.2	5.0	5	102	7.7	7.5
	0.10	89 98 108 114 95	101	10.1	10.0	5			
Confirmation m/z 209	0.01	114 92 100 103 104	103	7.9	7.7	5	102	8.4	8.2
	0.10	91 97 107 115 96	101	9.7	9.6	5			
Liver									
Quantitation m/z 347	0.01	96 111 99 115 111	106	8.4	7.9	5	104	8.2	7.9
	0.10	96 103 92 112 109	102	8.4	8.2	5			
Confirmation m/z 349	0.01	93 113 96 117 111	106	10.8	10.2	5	104	9.2	8.8
	0.10	96 103 93 112 109	103	8.1	7.9	5			
Confirmation m/z 209	0.01	88 107 88 105 92	96	9.3	9.7	5	99	8.9	9.0
	0.10	96 102 91 110 110	102	8.4	8.2	5			
Cream									
Quantitation m/z 347	0.01	97 105 88 78 110	96	12.9	13.4	5	94	9.3	9.9
	0.10	97 88 87 96 97	93	5.0	5.4	5			
Confirmation m/z 349	0.01	100 105 88 76 109	96	13.5	14.1	5	94	9.7	10.3
	0.10	97 88 87 96 98	93	5.3	5.7	5			
Confirmation m/z 209	0.01	97 106 84 77 107	94	13.3	14.1	5	94	9.7	10.3
	0.10	101 89 87 96 98	94	6.0	6.4	5			

Bacher (2005) reported on the independent validation of the German multi-residue enforcement method DFG S19 for the determination of fluopicolide residues in materials of animal origin. The ILV was performed on bovine meat and liver, milk and cream, and on hens' eggs. The confirmatory properties of the GC-MS method were demonstrated by a second ion transition for both test items (second product ion/qualifier ion pair).

Two controls, five samples fortified at LOQ (0.01 mg/kg) and five samples fortified at 10 × LOQ with fluopicolide were analysed for this ILV.

Briefly, the method used extraction module E 1 for bovine meat and liver, milk, and hens' eggs. Extraction was done with water/acetone (1/2 v/v). Partition into organic phase was by addition of NaCl and ethyl acetate/cyclohexane (1/1 v/v). Extraction module E 8 was used for cream. The clean-up modules used for all matrices were gel permeation chromatography (GPC Module) with mini silica gel column (Module C1). Determination was carried out with gas chromatography with mass spectrometric detection (GC/MS: Module D 4), using 347 m/z molecular ion for quantification. For confirmatory purposes, the relative abundances of two additional mass spectrometric fragment ions

observed at 349 m/z and 209 m/z were monitored and reported. The LOQ for fluopicolide was 0.01 mg/kg for all matrices analysed.

Standard curves were obtained for fluopicolide in both solvent and in matrix. Calibration functions using matrix-matched standards ranging from 0.1 ng/mL to 10 ng/mL (whole milk) or 0.02 ng/mL to 2.0 ng/mL (bovine meat) were established by injecting calibration solutions in matrix at six different concentrations. Linear calibration functions with 1× weighting were calculated and plotted by regression analysis. The correlation coefficients were always ≥ 0.994. Matrix-matched standards were used for evaluation of specimen extracts. Primary determination with GC/MS used the intense 347 m/z fragment ion for quantification and calculation of residues and recoveries. For confirmatory purposes, two additional GC/MS fragment ions at 349 m/z and 209 m/z were monitored with their abundances relative to the primary 347 m/z ion. For the 0.10 mg/kg fortification level the relative abundance ratio ranged from 0.63–0.68 (349 m/z) and from 0.41 to 0.54 (209 m/z), respectively. The method achieves a limit of detection of < 0.003 mg/kg (< 30% of the reported LOQ) for all matrices investigated. For independent method validation (ILV), bovine meat and liver, milk and cream, and hens' eggs were fortified (5 replicates per fortification level) with fluopicolide at the LOQ of 0.01 mg/kg and at 0.10 mg/kg. Additionally 2 replicate specimens per foodstuffs of animal origin were kept untreated serving as blank controls.

For each animal material and for each of the two fortification levels, the average recoveries obtained with the primary (347 m/z) quantification ion were in the range between 71% and 102%, and the relative standard deviations (RSD) were ≤ 13%.

Table 38 Validation data DFG S19 for fluopicolide in bovine meat and liver, milk and cream, and hens' eggs with m/z 347 quantifier ion (P 963 G 2005)

		Fortification	Recovery (%)				Overall recovery		
	Matrix	level (mg/kg)	Single values	N	Mean	RSD	N	Mean	RSD
Bovine	Meat	0.01	86 82 78 77 80	5	81	4	9	87	13
		0.10	38 [a] 80 106 105 93	4	96	13			
	Liver	0.01	101 105 97 100 101	5	101	3	10	96	9
		0.10	85 104 99 92 78	5	92	11			
	Milk	0.01	94 103 91 72 91	5	90	13	10	96	11
		0.10	102 102 97 114 93	5	102	8			
	Cream	0.01	86 100 92 87 76	5	88	10	10	84	12
		0.10	78 94 89 70 71	5	80	13			
Chicken	Egg	0.01	73 70 71 72 70	5	71	2	10	72	4
		0.10	69 75 69 71 78	5	72	6			

RSD: relative standard deviation

[a] Not use for calculation of average and standard deviation (Dixon outlier)

Description of methods for analysis of soil

An analytical method was developed to enable determination of residue concentrations of fluopicolide or its soil metabolites in soils taken from field trials (Queyrel and Rosati 2001). The parent compound and its three metabolites are extracted from soil samples by mechanical shaking with a mixture of acidified water and acetonitrile. The sample is diluted and filtered prior to determination by LC/MS/MS with quantification using external standards.

Data is presented from "initial" and "modified" conditions apart from M-02. This reflects the fact that adjustments were made to the LC/MS/MS instrument conditions to improve the performance, especially with respect to AE 0608000. LOQ 0.005 mg/kg for fluopicolide, M-01, M-02 and AE 0608000. Linear in the range 0.40 to 75 µg/L for fluopicolide and AE 0608000 and in the range 0.40 to 100 µg/L for M-01 and M-02. No interference > 10% of the LOQ was observed from the control sample analysed. The technique is specific for fluopicolide, M-01, M-02 and AE 0608000.

Table 39 Validation data for determination of fluopicolide in soil

Compound	Fortification level (mg/kg)	No. of repetitions	Mean across level (%)	Overall mean (%)
Recovery efficiencies:				
fluopicolide	0.005	5	90%	91%
initial method	0.50	5	93%	
modified method	0.005	5	97%	96%
	0.50	5	94%	
M-01	0.005	5	93%	95%
initial method	0.50	5	97%	
modified method	0.005	5	102%	101%
	0.50	5	99%	
AE 0608000	0.005	5	76%	77%
initial method	0.50	5	77%	
modified method	0.005	5	97%	96%
	0.50	5	96%	
M-02	0.005	5	97%	94%
	0.50	5	90%	
Compound	Fortification level (mg/kg)	No. of repetitions	RSD across level (%)	Overall RSD (%)
Repeatability:				
fluopicolide	0.005	5	9%	6%
initial method	0.50	5	3%	
modified method	0.005	5	3%	2%
	0.50	5	1%	
M-01	0.005	5	12%	8%
initial method	0.50	5	4%	
modified method	0.005	5	5%	3%
	0.50	5	1%	
AE 0608000	0.005	5	8%	5%
initial method	0.50	5	2%	
modified method	0.005	5	3%	3%
	0.50	5	4%	
M-02	0.005	5	14%	11%
	0.50	5	6%	

Stability of Residues in Stored Analytical Samples

Zietz (2004) studied the stability of residues of fluopicolide and its metabolites M-01 and M-02 in laboratory fortified grapes, potato tubers, cabbage and wheat grain on deep freeze storage at a nominal temperature of ≤ –18 °C. The crops selected are representative of other high moisture, root, leafy vegetable and cereal crops. Homogenised aliquots of grapes, potato tubers, cabbage and wheat grain were fortified with fluopicolide (alone) or M-01 and M-02 (combined) in glass containers at a level of 0.1 mg/kg and then placed in deep freeze storage. At intervals of approximately 3, 6, 12, 18, 24 and 30 months after fortification, samples were removed for analysis of fluopicolide, M-01 and M-02 using an appropriate method. Additionally, a time 0 interval was included by analysing selected samples on the day of fortification. After 30 months storage the measured residues in stored samples ranged were greater than 75% of the nominal level (0.1 mg/kg).

Table 40 Freezer storage stability data for fluopicolide, M-01 and M-02 in wheat grain, grapes, potato tubers and cabbage commodities fortified at 0.1 mg/kg. Recorded residue levels are unadjusted for recoveries

Storage interval (months)	Storage stability					
	fluopicolide		M-01		M-02	
	Residue (mg/kg)	Procedural recoveries	Residue (mg/kg)	Procedural recoveries	Residue (mg/kg)	Procedural recoveries
Grapes						
0	0.09 0.08 0.09 0.10 0.10		0.09 0.07 0.09 0.09 0.09		0.09 0.08 0.10 0.10 0.10	
3.2	0.08 0.08	84 85	0.09 0.09	91 90	0.08 0.09	78 80
6.2	0.09 0.08	78 91	0.10 0.10	98 119	0.09 0.09	68 77
12.1	0.08 0.09	81 89	0.10 0.10	95 97	0.09 0.09	87 89
18.3	0.08 0.08	77 79	0.10 0.10	99 99	0.08 0.08	75 76
24.4	0.08 0.08	82 81	0.09 0.09	87 85	0.10 0.09	75 75
30.4	0.09 0.08	82 124	0.10 0.10	94 104	(1.0) [a] 0.08	92 84
Potato tubers						
0	0.11 0.13 0.10 0.10 0.11		0.08 0.08 0.09 0.09 0.08		0.07 0.09 0.09 0.09 0.08	
3.1	0.09 0.09	93 92	0.09 0.11	86 86	0.08 0.09	72 72
6.1	0.09 0.08	91 92	0.10 0.09	109 99	0.08 0.08	79 87
12.1	0.09 0.10	86 84	0.10 0.10	97 93	0.08 0.09	96 83
18.3	0.08 0.08	85 90	0.10 0.09	91 97	0.06 0.06	71 81
24.3	0.09 0.09	101 97	0.10 0.11	103 104	0.08 0.08	73 68
30.3	0.10 0.10	97 103	0.10 0.10	99 95	0.08 0.08	86 89
Cabbage						
0	0.10 0.10 0.09 0.09 0.10		0.09 0.09 0.09 0.08 0.09		0.09 0.09 0.10 0.10 0.10	
3.1	0.08 0.08	87 88	0.09 0.09	104 91	0.08 0.07	74 70
6.1	0.08 0.08	84 79	0.10 0.10	119 85	0.08 0.08	75 74
12.1	0.08 0.08	77 82	0.10 0.10	93 95	0.08 0.08	77 73
18.2	0.08 0.08	84 87	0.10 0.10	92 94	0.07 0.07	71 73
24.3	0.08 0.08	93 93	0.10 0.11	103 106	0.08 0.09	72 77
30.4	0.08 0.08	97 100	0.09 0.10	98 107	0.07 0.06	78 81
Wheat grain						
0	0.10 0.10 0.09 0.10 0.11		0.09 0.09 0.10 0.09 0.10		0.09 0.10 0.10 0.09 0.09	
3.2	0.09 0.08	82 82	0.09 0.10	92 90	0.08 0.08	81 78
6.2	0.07 0.08	75 77	0.10 0.09	100 101	0.08 0.08	73 80
12.1	0.09 0.08	76 81	0.10 0.12	95 100	0.09 0.11	86 83
18.3	0.09 0.08	81 86	0.10 0.10	100 101	0.08 0.08	75 77
24.4	0.11 0.10	97 100	0.10 0.10	104 102	0.08 0.08	76 74
30.4	0.09 0.10	85 87	0.10 0.10	96 114	0.08 0.07	78 75

[a] unrealistic recovery attributed to laboratory error.

The results demonstrate that all three analytes are stable when stored at –18 °C or below in all tested matrices for at least 30 months.

Billian and Schöning (2007) studied the stability of residues of fluopicolide and its metabolites M-04, AEC653711 and M-05 in laboratory fortified wheat matrices (wheat straw, grain, green material) during freezer storage for 25 months; additionally results for 41 months freezer storage of straw samples are reported in amendment 1 to the report. Homogenised aliquots were fortified with fluopicolide or M-01 (alone) or M-04 and M-05 (combined) in glass containers at a level of 0.1 mg/kg and then placed in deep freeze storage. The samples were analysed at nominal intervals of 0, 30, 90, 180, 360, 540 and 760 days. Residues of fluopicolide and its metabolites M-01,

M-04 and M-05 in/on plant material were determined by HPLC-MS/MS according to method 00782/M001, and 00782/M002 and 00782/M003 (M-04, M-05). The LOQ was 0.01 mg/kg for all compounds.

Fluopicolide and its metabolites M-04, AEC653711 and M-05 in samples of wheat straw, grain and green material were stable for at least 25 months (41 months for fluopicolide and AEC653711 in wheat straw) under deep-freezer storage conditions.

Table 41 Freezer storage stability data for fluopicolide and M-01 in wheat commodities fortified at 0.1 mg/kg. Recorded residue levels are unadjusted for recoveries

Sample Material	Storage Interval (days)	fluopicolide Residue (mg/kg)	Procedural recoveries	M-01 Residue (mg/kg)	Procedural recoveries
Wheat Straw	0	0.08 0.08 0.08 0.09 0.08		0.07 0.09 0.10 0.09 0.10	
	30	0.09 0.09 0.09	73 75	0.06 0.08 0.08	73 76
	89	0.09 0.09 0.09	91 90	0.08 0.08 0.09	91 88
	182	0.10 0.10 0.10	90 100	0.10 0.09 0.09	97 100
	363	0.09 0.08 0.08	97 95	0.10 0.09 0.10	80 90
	545	0.09, 0.10, 0.10	104 105	0.09 0.10 0.09	91 99
	777	0.10, 0.07, 0.09	85 76	0.09 0.10 0.08	90 86
	1251	0.08, 0.09, 0.09	90, 83	0.09 0.09 0.09	88, 91

Table 42 Freezer storage stability data for M-04 and M-05 in wheat commodities fortified at 0.1 mg/kg. Recorded residue levels are unadjusted for recoveries

Sample Material	Storage Interval (days)	M-04 Residue (mg/kg)	Procedural recoveries	M-05 Residue (mg/kg)	Procedural recoveries
Wheat Straw	0	0.07 0.07 0.08 0.08 0.08		0.07 0.08 0.08 0.09 0.08	
	30	0.08 0.08 0.08	75 46	0.10 0.08 0.09	80 74
	89	0.09 0.11 0.10	79 79	0.08 0.10 0.09	82 88
	182	0.09 0.09 0.10	68 72	0.07 0.07 0.07	85 87
	363	0.08 0.09 0.08	69 73	0.08 0.08 0.08	81 82
	553	0.09 0.09 0.10	81 80	0.08 0.08 0.08	105 104
	770	0.07 0.07 0.07	61 65	0.06 0.06 0.06	81 82
Wheat Grain	0	0.07 0.09 0.09 0.08 0.10		0.06 0.08 0.08 0.06 0.08	
	28	0.08 0.10 0.08	78 88	0.10 0.10 0.10	74 77
	114	0.11 0.09 0.09	89 86	0.09 0.08 0.11	85 76
	168	0.08 0.09 0.09	86 88	0.06 0.08 0.07	88 83
	349	0.09 0.10 0.10	90 88	0.08 0.09 0.09	82 85
	552	0.08 [b] 0.08 [a b]	96	0.07 0.07 [a]	75 71 68
	754	0.09 0.09 0.09	109 100	0.07 0.08 0.08	89 64
Wheat Green Material	0	0.07 0.09 0.09 0.08 0.08		0.07 0.08 0.08 0.08 0.08	
	30	0.10 0.09 0.09	83 103	0.07 0.07 0.07	76 78
	89	0.07 0.07 0.09	98 109	0.08 0.08 0.09	95 87
	182	0.10 0.11 0.11	96 89	0.07 0.07 0.06	65 67
	363	0.09 0.09 0.10	89 88	0.08 0.08 0.08	83 86
	551	0.10 0.09 0.09	95 93	0.09 0.11 0.12	117 118
	769	0.07 0.08 0.07	82 87	0.06 0.06 0.06	67 65

[a] One recovery sample was identified as outlier, no RSD was calculated

[b] Mean of two measurements

Residues of fluopicolide and its metabolites M-04, M-01 and M-05 in samples of plant origin (wheat straw, grain, green material) are stable for at least 25 months (41 months for fluopicolide and M-01 in wheat straw) under deep-freezer storage conditions.

Stability in matrices of animal origin

The storage stability of residues in matrices from animal origin was investigated in the livestock feeding study (Cavaile and Rosati 2004). Samples of bovine tissues and milk were fortified with fluopicolide and metabolites M-01and M-02 at either 0.1 mg/kg (milk, muscle) or 0.5 mg/kg (liver, fat and kidney). Samples were analysed at different periods of frozen storage. Adequate storage stability of fluopicolide and metabolites M-01and M-02 has been demonstrated in deep frozen milk for up to 83 days, in deep frozen muscle and fat for up to 4 months and in deep frozen liver and kidney for up to 9 months.

Table 43 Freezer storage stability data for fluopicolide spiked into bovine tissue matrices and milk. Recorded residue levels are unadjusted for recoveries

Matrix	Storage interval	Fluopicolide (mg/kg)	Procedural recovery	M-01 (mg/kg)	Procedural recovery	M-02 (mg/kg)	Procedural recovery
Milk	0	0.093	92	0.108	111	0.090	89
	13 days	0.095	92	0.113	122	0.078	85
	51 days	–	–	0.118	130	0.093	106
	83 days	0.094	101	0.115	122	0.087	90
Liver	0	0.533	110	0.493	93	0.548	108
	9 months	0.498 0.403	92	0.473 0.470	100	0.535 0.515	86
Fat	0	0.45	92	0.493	86	0.488	93
	4 months	0.468 0.505	98	0.488 0.490		0.450 0.458	90
Kidney	0	0.463	92	0.460	100	0.473	103
	9 months	0.498 0.488	89	0.478 0.430	101	0.505 0.438	104
Muscle	0	0.090	92 86	0.095	107 91	0.106	107 109
	4 months	0.086 0.090	82	0.095 0.094	80	0.104 0.098	91

USE PATTERN

Table 44 Registered use patterns of fluopicolide in horticultural and field crops

Crop	Country	Form.	Conc (g ai/hL)	Rate fluopicolide (g ai/ha)	Water rate (L/ha)	N	Interval (days)	PHI
Brassica (head and stem)	United States	SC [c]		101–140 max. 420 g/ha/season	195–488 ground 49 air	1–4	7–14	2
Broccoli	Estonia	SC [b]		100		1–3	10–14	14
Brussels sprouts	Estonia	SC [b]		100		1–3	10–14	14
Bulb vegetables	United States	SC [c]		101–140 max. 420 g/ha/season	195–488 ground 49 air	1–4	7–14	2
Cabbage	Estonia	SC [b]		100		1–3	10–14	14
Cabbage, Chinese	Korea, Republic of	SC [b]		75	1200	1–2		14
Cabbage, cow	Guatemala	SC [b]		93.8	200–600	1–3		14
Cabbage, field	Guatemala	SC [b]		93.8	200–600	1–3		14
Cabbage, field	Nicaragua	SC [b]		93.8	200–600	1–3		14
Cabbage, head	Lithuania	SC [b]		100	300–600	1–3	10–14	14
Cabbage, leaf	Lithuania	SC [b]		100	300–600	1–3	10–14	14
Cauliflower	Estonia	SC [b]		100		1–3	10–14	14
Cauliflower	Lithuania	SC [b]		100	300–600	1–3	10–14	14
Chilli	Korea, Republic of	SC [e]		62.4	1500	1–2		7

Crop	Country	Form.	Conc (g ai/hL)	Rate fluopicolide (g ai/ha)	Water rate (L/ha)	N	Interval (days)	PHI
Chilli	Korea, Republic of	SC [b]		93.8	1500	1–2		7
Cucumber	China	SC [b]		56.3–70.3	675–900	1–3	7–10	3
Cucumber	Estonia	SC [b]	8.75		500–1500	1–3	10	indoor: 3
Cucumber	Estonia	SC [b]		100		1–3	10	outdoor: 3
Cucumber	Guatemala	SC [b]		93.8–93.8	200–600	1–3		14
Cucumber	Italy	SC [b]	8.8–10	88–100	1000	1–3	8–12	outdoor: 3
Cucumber	Italy	SC [b]	8.8–10	109–125	1250	1–3	8–12	indoor:. 3
Cucumber	Korea, Republic of	SC [e]		62.4	1500	1–3		2
Cucumber	Lithuania	SC [b]	8.75		500–1500	1–3	10	indoor: 1
Cucumber	Lithuania	SC [b]		100	500–700	1–3	10	outdoor: 3
Cucumber	Moldova, Republic of	SC [b]		75–100	300–500	1–3		10
Cucumber	Nicaragua	SC [b]		93.8	200–600	1–3		14
Cucumber	Romania	SC [b]	8.75	88	600–1000	1–3	7–10	Indoor: 4
Cucumber	Ukraine	SC [b]		87.5	200–300	1–3		10
Cucumber	Ukraine	SC [b]		75–100	300–500	1–2		10
Cucurbit vegetables	United States	SC [c]		101–140 max. 420 g/ha/season	195–488 ground 49 air	1–4	7–14	2
Fruiting vegetables	United States	SC [c]		101–140 max. 420 g/ha/season	195–488 ground 49 air	1–4	7–14	2**
Grape	Croatia	WG [a]		111–133	1000	1–3	12–14	42
Grape	Guatemala	SC [b]		93.8	200–600	1–3		14
Grape	Italy	WG [a]	10–13	100–133	1000	1–3	10–14	28
Grape	Korea, Republic of	SC [b]		250	4000	1–3		30
Grape	Moldova, Republic of	WG [a]		44.4	800–1000	1		20
Grape	Nicaragua	SC [b]		93.8	200–600	1–3		14
Grape	Slovenia	WG	11–13	111–133 (BBCH 53–BBCH 81)	1000	1–3		28
Grape	Taiwan	SC [b]		62.5–104	1200–2000	1–4		30
Grapes	United States	SC [c]		101–140 max. 420 g/ha/season	195–488 ground 49 air	1–4	7–14	21
Leafy vegetables	United States	SC [c]		101–140 max. 420 g/ha/season	195–488 ground 49 air	1–4	7–14	2[f]
Leek	Estonia	SC [b]		100		1–2	14–21	14
Leek	Lithuania	SC [b]		100	300–600	1–2	10–14	14
Lettuce	Guatemala	SC [b]		93.8	200–600	1–3		14
Lettuce	Nicaragua	SC [b]		93.8	200–600	1–3		14

Crop	Country	Form.	Conc (g ai/hL)	Rate fluopicolide (g ai/ha)	Water rate (L/ha)	N	Interval (days)	PHI
Lettuce	Romania	SC [b]	8.75	88 (until 70% head formed)	600–1000	1–2	7	Indoor: 14
Melon	Colombia	SC [b]		62.5–93.8	400–600	1–2		7
Melon	Colombia	WP [d]		72–108	400–600	1–3		14
Melon	Guatemala	SC [b]		93.8	200–600	1–3		14
Melon	Nicaragua	SC [b]		93.8	200–600	1–3		14
Melon, Makuwa	Korea, Republic of	SC [b]		75	1200	1–3		3
Onion	Colombia	SC [b]		93.8–125	not specified	1–3		7
Onion	Colombia	WP [d]		72–108	200–2000	1–3		7
Onion	Guatemala	SC [b]		93.8	200–600	1–3		14
Onion	Korea, Republic of	SC [b]		37.5	1200	1–3		14
Onion	Lithuania	SC [b]		100	300–600	1–2	7–12	7
Onion	Nicaragua	SC [b]		93.8	200–600	1–3		14
Pepper plant, common	Guatemala	SC [b]		93.8	200–600	1–3		14
Pepper plant, common	Nicaragua	SC [b]		93.8	200–600	1–3		14
Potato	Brazil	SC [b]		78.1–93.8	1000	1–3		14
Potato	Estonia	SC [b]		75–100		1–4	7–12	7
Potato	Italy	SC [b]	8.8–10	88–100	1000	1–3	7–10	7
Potato	Lithuania	SC [b]		75–100	200–400	1–4	7–12	7
Potato	Romania	SC [b]		88	300–400	1–3	8–12	7
Root vegetables (except carrot, potato and sugar beet)	United States	SC [c]		101–140 max. 420 g/ha/season	195–488 ground 49 air	1–4	7–14	2
Sweet potato	United States	SC [c]		101–140 max. 420 g/ha/season	195–488 ground 49 air	1–4	7–14	7
Sweet, Bell pepper / Pimento	Korea, Republic of	SC [e]		62.4	1500	1–2		7
Tomato	Brazil	SC [b]		78.1–93.8	600–800 until end of flowering 800–1000 from flowering	1–3		7
Tomato	China	SC [b]		56.3–70.3	675–900	1–3	7–10	3
Tomato	Colombia	SC [b]		93.8–125	400–600	1–3		7
Tomato	Colombia	WP [d]		72–108	400–600	1–3		14
Tomato	Estonia	SC [b]	8.75		500–1500	1–3	7–10	Indoor: 3
Tomato	Guatemala	SC [b]		93.8	200–600	1–3		14
Tomato	Italy	SC [b]	10	100	1000	1–3	7–10	field: 3
Tomato	Italy	SC [b]	10	125	1250	1–3	7–10	indoor:. 3
Tomato	Korea, Republic of	SC [b]		46.9	1500	1–3		3
Tomato	Lithuania	SC [b]	8.75		500–1500	1–3	7–10	indoor: 1
Tomato	Moldova, Republic of	SC [b]		75–100	300–500	1–2		14
Tomato	Nicaragua	SC [b]		93.8	200–600	1–3		14
Tomato	Romania	SC [b]	8.75	88	600–1000	1–3	7–10	7
Tomato	Ukraine	SC [b]		75–100	300–500	1–2		14

Crop	Country	Form.	Conc (g ai/hL)	Rate fluopicolide (g ai/ha)	Water rate (L/ha)	N	Interval (days)	PHI
Watermelon	Guatemala	SC [b]		93.8	200–600	1–3		14
Watermelon	Korea, Republic of	SC [b]		93.8	1500	1–3		14
Watermelon	Nicaragua	SC [b]		93.8	200–600	1–3		14

[a] WG 71.1 fluopicolide + fosetyl Al (44.4 + 666.7 g/kg)

[b] SC 687.5 fluopicolide + propamocarb (62.5 + 625 g/L)

[c] SC 480 fluopicolide 480 g/L

[d] WP 72.7 fluopicolide + propinep (60 + 667 g/kg)

[e] SC 166.4 fluopicolide + iprovalicarb (41.6 + 124.8 g/L)

[f] do not use on greenhouse crops

Brassica head and stem vegetables in the US classification system includes: broccoli, Brussels sprouts, cabbage, cauliflower, cavelo, broccoli, Chinese broccoli, Chinese (napa) cabbage, Chinese mustard cabbage, kohlrabi.

Bulb vegetables in the US classification system includes: Beltsville bunching onion, chive (fresh elaves), Chinese chives (fresh leaves), Chinese onion bulb, Daylily bulb, Elegans Hosta Fritillaria (bulb and leaves), garlic bulb, great headed garlic bulb, green onion, Kurrant, Lady's leek, leek, lily bulb, macrostem onion, onion (bulb and fresh), pearl onion, potato onion bulb, shallot (bulb and fresh leaves), serpent garlic bulb, tree onion tops, wild leek.

Leafy vegetables except brassicas in the US classification system includes: Head Lettuce, Leaf Lettuce, Spinach, Arugula, Chervil, Chinese spinach, Corn salad, Dandelion, Dock (sorrel), Edible chrysanthemum, Endive, Garden cress, Garden purslane, Garland Chrysanthemum, New Zealand spinach, Orach, Parsley, Red chicory, Upland cress, Vine spinach, Winter purslane, Cardoon, Celery, Celtuce, Chinese celery, Fennel, Rhubarb, Swiss chard.

Fruiting vegetables in the US classification system includes: Tomato/Cherry tomato, Sweet pepper, Bell pepper, Chilli pepper, Cooking pepper, Pimiento, Eggplant, Groundcherry, Pepino, Tomatillo

Cucurbit vegetables in the US classification system includes: Cantaloupe, Citron melon, Muskmelon, Watermelon, Chayote (fruit), Chinese waxgourd, Cucumber, Gherkin, Gourd, edible, Momordica spp., Pumpkin, Squash, summer, Squash, winter.

Root vegetables (tuber and corm) in the US classification includes: Arracacha, Arrowroot, Artichoke, Chinese, Artichoke, Jerusalem, Canna, edible, Cassava, bitter and sweet, Chayote (root), Chufa, Dasheen, Ginger, Leren, Sweet potato, Tanier, Turmeric, Yam bean, Yam, true,

Rotational crop restrictions for the USA are: cucurbit vegetables, fruiting vegetables, leafy vegetables, tuberous and corm vegetables (except potato, group 1D), none. Other crops: 18 months.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised field trials for fluopicolide on the following crops:

Commodity	Crop group	Table
Grapes	Berries and other small fruits	Tables 45–54
Onions, Welsh onions and leeks	Bulb vegetables	Tables 55–60
Brussels sprouts, broccoli, cabbage and cauliflower	Brassica vegetables	Tables 61–70
Cucumber, melons, summer squash and zucchini	Fruiting vegetables, Cucurbits	Tables 71–78
Tomatoes, peppers and chilli	Fruiting vegetables, other than Cucurbits	Tables 79–86
Lettuce and spinach	Leafy vegetables	Tables 87–94

Commodity	Crop group	Table
Carrots and radish	Root and tuber vegetables	Tables 95–96
Celery	Stalk and stem vegetables	Table 97

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

Conditions of the supervised residue trials were generally well reported in detailed field reports. Most trial designs used non-replicated plots. Most field reports provided data on the sprayers used, plot size, field sample size and sampling date.

Berries and other small fruits

Grapes

Fluopicolide was applied to grapevines at five sites in Northern Europe. The varieties chosen were wine grapes for all trials. Vines were sprayed three times with a WG formulation mixture with fosetyl aluminium at 0.125 kg ai/ha and at 14 day intervals. Sprayers were mist-blowers and air-blast sprayers. Plot sizes were 14–56 m^2. Grapes were sampled for analysis at nominal intervals of 0, 7, 14, 21 and 28 days after final application. The 21 and 28 day sampling occasions were equivalent to mature commercial harvest. Storage periods for samples in these trials were between 353 and 399 days. Analysis for fluopicolide and metabolites was by method 00782/M001.

Table 45 Results of residue trials conducted with fluopicolide in wine grapes in northern Europe (WG formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Doue la Fontaine, France 2001 Cabernet Franc	3 (14 14)	0.125 0.125 0.125	0.0502 0.0502 0.0502	250 250 250	83	bunch of grapes	0 7 14 21 28	0.26 0.22 0.27 0.32 <u>0.24</u>	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	01R284 01R284-3
Vernou Sur Brenne, France 2001 Chenin	3 (14 14)	0.125 0.125 0.125	0.0568 0.0568 0.0568	220 220 220	85	bunch of grapes	0 7 14 21 28	0.35 0.33 0.36 0.20 <u>0.27</u>	< 0.01 0.01 0.011 < 0.01 0.013	< 0.01 0.012 0.017 0.015 0.02	01R284 01R284-4
Brouillet, France 2001 Pinot Meunier	3 (13 14)	0.125 0.125 0.125	0.0125 0.0125 0.0125	1000 1000 1000	85	bunch of grapes	0 7 14 21 28	0.38 0.24 0.34 0.15 <u>0.21</u>	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	01R284 01R284-5
Neustadt–Mußbach, Germany 2001 Riesling	3 (14 14)	0.125 0.125 0.125	0.025 0.025 0.025	500 500 500	85	bunch of grapes	0 7 14 21 29	0.53 0.45 0.46 0.43 <u>0.52</u>	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	01R284 01R284-1
Ihringen, Germany 2001 Silvaner	3 (14 14)	0.125 0.125 0.125	0.025 0.025 0.025	500 500 500	85	bunch of grapes	0 7 14 21 29	0.39 0.54 0.41 0.37 <u>0.33</u>	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	01R284 01R284-2

Bunches of gapes = fruits plus stalks analysed

Fluopicolide, as a WG formulation with fosetyl aluminium, was applied to grapevines at five sites in Southern Europe at the EU GAP. The varieties chosen were wine grapes for four trials and table grapes at the remaining trial site. Vines were sprayed three times at 0.125 kg ai/ha with nominal spray intervals of 14 days using air-blast, mist-blower or motorised knapsack sprayers. Plot sizes were 14–68 m^2. Grapes were sampled for analysis at nominal intervals of 0, 7, 14, 21 and 28 days after final application. The 21 day sampling occasion was equivalent to mature commercial harvest. Storage periods for samples in these trials were between 371 and 464 days. Method 00782/M001 was for analysis of fluopicolide plus metabolites

Table 46 Results of residue trials conducted with fluopicolide in grapes in southern Europe (WG formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Mazeres, France 2001 Cabernet Sauvignon	3 (14 14)	0.125 0.125 0.125	0.0835 0.0835 0.0835	150 150 150	85	bunch of grapes	0 7 12 21 28	0.88 1.1 0.99 0.65 0.60	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	01R285 01R285-1
Chazay D'Azergues, France 2001 Chardonnay	3 (14 13)	0.138 0.125 0.125	0.062 0.0626 0.0626	222 200 200	79	bunch of grapes	0 7 14 21 28	0.33 0.20 0.23 0.28 0.27	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	01R285 01R285-2
Goumenisa–Kilkis, Greece 2001 Xinomavro	3 (14 13)	0.125 0.125 0.125	0.0156 0.0156 0.0156	800 800 800	81	bunch of grapes	0 7 14 22 28	0.39 0.56 0.13 0.068 0.11	< 0.01 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.017 0.019 < 0.01 0.017	01R285 01R285-5
San Prospero, Italy 2001 Lambrusco Di Sorbara	3 (13 14)	0.125 0.125 0.125	0.0125 0.0125 0.0125	1000 1000 1000	83	bunch of grapes	0 7 14 20 28	1.1 0.93 0.77 0.69 0.38	0.051 0.048 0.054 0.047 0.041	0.047 0.046 0.031 0.025 0.022	01R285 01R285-3
Godelleta, Spain 2001 Moscatel	3 (14 14)	0.125 0.125 0.125	0.0125 0.0125 0.0125	1000 1000 1000	83	bunch of grapes berry	0 7 14 22 28	0.27 0.36 0.38 0.10 0.21	< 0.01 0.015 0.02 0.021 0.026	0.011 0.019 0.026 0.02 0.038	01R285 01R285-4

Wine grapes analysed as fruit plus stalks, table grapes (Moscatel) as berries for the samples taken at commercial harvest

Fluopicolide was applied to grapevines at four sites in Northern Europe as a WG mixture formulation with fosetyl aluminium. Vines were sprayed three times at 0.125 kg ai/ha with spray intervals of 14 days using motorised knapsack sprayers. Plot sizes were 14–54 m^2. Grapes were sampled for analysis at nominal intervals of 0 and 21 days after final application, the latter equivalent to mature commercial harvest. Storage periods for samples in these trials were between 58 and 119 days. Method 00782/M001 was used for fluopicolide plus metabolites.

Table 47 Results of residue trials conducted with fluopicolide in grapes in northern Europe (WG)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Gueux, France 2002 Pinot Meunier	3 (14 14)	0.125 0.139 0.125	0.025 0.025 0.025	500 556 500	83	bunch of grapes	0 21	0.24 0.18	< 0.01 < 0.01	< 0.01 < 0.01	02R288 02R288-3
Epernay, France 2002 Chardonnay	3 (14 14)	0.125 0.125 0.125	0.025 0.025 0.025	500 500 500	83	bunch of grapes	0 21	0.47 0.33	< 0.01 < 0.01	< 0.01 < 0.01	02R288 02R288-4

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Neustadt–Mußbach, Germany 2002 Müller–Thurgau	3 (14 14)	0.125 0.125 0.125	0.025 0.025 0.025	500 500 500	83	bunch of grapes	0 21	0.43 0.50	< 0.01 < 0.01	< 0.01 < 0.01	02R288 02R288-1
Mühlhausen, Germany 2002 Spätburgunder	3 (14 14)	0.125 0.125 0.125	0.025 0.025 0.025	500 500 500	85	bunch of grapes	0 21	0.57 0.66	< 0.01 < 0.01	< 0.01 < 0.01	02R288 02R288-2

Wine grapes analysed as fruit plus stalks

Fluopicolide was applied to grapevines at four sites in Southern Europe. The varieties chosen were wine grapes for all trials. Fluopicolide, as a WG mixture formulation with fosetyl aluminium, was sprayed three times at 0.125 kg ai/ha with spray intervals of 14 days using motorised knapsack mist-blower sprayers. Plot sizes were 36–100 m^2. Grapes were sampled for analysis at intervals of 0 and 21 days after final application (mature commercial harvest). Storage periods for samples in these trials were between 71 and 184 days. Method 00782/M001 was used for analysis of fluopicolide plus metabolites

Table 48 Results of residue trials conducted with Fluopicolide in grapes in southern Europe (WG formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Chazay D'Azergues, France 2002 Gamay	3 (14 14)	0.125 0.125 0.125	0.0416 0.0416 0.0416	300 300 300	83	bunch of grapes	0 21	0.54 0.40	< 0.01 < 0.01	< 0.01 < 0.01	02R289 02R289-1
Graveson, France 2002 Carignan	3 (13 14)	0.125 0.125 0.125	0.0416 0.0416 0.0416	300 300 300	85	bunch of grapes	0 21	0.35 0.21	< 0.01 0.016	< 0.01 0.025	02R289 02R289-2
Andria, Italy 2002 Malvasia Leccese	3 (15 13)	0.125 0.125 0.125	0.0125 0.0125 0.0125	1000 1000 1000	85	bunch of grapes	0 21	1.0 1.1	< 0.01 < 0.01	< 0.01 < 0.01	02R289 02R289-3
Campo Arcís-Requena, Spain 2002 Macabeo	3 (14 14)	0.125 0.125 0.125	0.0167 0.0167 0.0167	750 750 750	83	bunch of grapes	0 21	0.52 0.21	0.012 0.019	0.011 0.02	02R289 02R289-4

Wine grapes analysed as fruit plus stalks

Fluopicolide as an SE formulation was applied to grapevines at six sites in Southern Europe. The varieties chosen were wine grapes for four trials and table grapes for the two remaining trials. Vines were sprayed three times at 0.133 kg ai/ha using motorised knapsack mist-blower sprayers. Plot sizes were 32–214 m^2. Grapes were sampled for analysis at 0, 3, 7, 14 and 21 days after final application. The 21 day sample was equivalent to mature commercial harvest. Additional grapes were

taken from the two trials on table grapes for processing into raisins by commercial drying processes (either sun dried or oven dried to between 25 and 30% of original mass). Grapes samples were also taken from three trials on wine grapes for further processing into wine. Storage periods for bunch of grape samples in these trials were between 551 and 637 days. Agredoc Number C024784 (IF-101/05424) with minor modifications was used for analysis of fluopicolide residues.

Table 49 Results of residue trials conducted with fluopicolide in grapes in southern Europe (SE formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
St Vincent de Paul, France 2000 Cabernet-Sauvignon	3 (10 11)	0.129 0.128 0.131	0.0383 0.0383 0.0361	337 334 363	85	bunch of grapes	0 3 7 21 21	0.89 0.56 0.51 0.46 0.40	< 0.01 < 0.01 < 0.01 < 0.01 0.02	< 0.01 < 0.01 < 0.01 < 0.01 0.02	DR00EUS00300FVIFRP04
Sorgues, France 2000 Grenache	3 (11 10)	0.131 0.131 0.130	0.0253 0.0253 0.0253	518 518 505	85	bunch of grapes	0 3 7 14 21	0.40 0.32 0.35 0.21 0.16	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 0.01 0.01 0.01	DR00EUS00300FVIFRP05
Lakoma, Greece 2000 Grenache Rouge	3 (12 10)	0.132 0.124 0.134	0.00859 0.00864 0.00867	1536 1435 1546	85	bunch of grapes	0 3 7 14 21 21	0.78 0.46 0.39 0.27 0.32 0.35	0.02 0.02 0.03 0.02 0.03 0.03	0.02 0.01 0.04 0.04 0.04 0.03	DR00EUS00300RF021/2
Utrera, Spain 2000 Cardenal	3 (12 13)	0.127 0.126 0.136	0.0127 0.0126 0.0126	1006 1000 1074	85	bunch of grapes	0 3 7 14 21 21	0.58 0.58 0.60 0.40 0.54 0.32	< 0.01 < 0.01 0.01 0.01 0.02 0.02	0.03 0.03 0.04 0.04 0.06 0.07	DR00EUS00300S041R
Neo Rysio, Greece 2000 Moshato	3 (12 10)	0.128 0.127 0.131	0.00992 0.00991 0.00983	1290 1281 1332	85	bunch of grapes raisin	0 3 7 14 21 21	0.61 0.15 0.17 0.15 0.20 1.3	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 0.03	< 0.01 < 0.01 < 0.01 0.02 0.02 0.05	DR00EUS00300RF021/1
Dos Hermanas, Greece 2000 Palieri	3 (12 13)	0.126 0.124 0.126	0.0140 0.0141 0.0140	900 881 900	83	bunch of grapes raisin	0 3 7 14 21 21	1.3 1.3 0.73 0.94 0.97 2.1	< 0.01 < 0.01 0.01 0.01 0.02 0.06	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 0.04	DR00EUS00300S040R

Fluopicolide as an SE formulation was applied to grapevines at five sites in Northern Europe. The varieties chosen were wine grapes all trials. Vines were sprayed three times at 0.133 kg ai/ha with spray intervals of 9 to 11 days using mist blower or air blast sprayers. Plot sizes were 14–54 m^2. Grapes were sampled for analysis at 0 and 21 days after final application (mature commercial harvest). Storage periods for samples in these trials were between 348 and 380 days. Method 00782/001 was used for analysis of fluopicolide plus metabolites.

Table 50 Results of residue trials conducted with fluopicolide in grapes in northern Europe (SE formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Doue la Fontaine, France 2001 Cabernet France	3 (10 10)	0.133 0.133 0.133	0.0532 0.0532 0.0532	250 250 250	83	bunch of grapes	0 21	0.79 0.48	< 0.01 0.01	< 0.01 < 0.01	01R280 01R280-3
Vernou Sur Brenne, France 2001 Chenin	3 (10 10)	0.133 0.133 0.147	0.0605 0.0605 0.0598	220 220 245	85	bunch of grapes	0 21	0.36 0.32	< 0.01 < 0.01	< 0.01 0.011	01R280 01R280-4
Brouillet, France, 2001 Pinot Meunier	3 (9 9)	0.133 0.133 0.133	0.0133 0.0133 0.0133	1000 1000 1000	85	bunch of grapes	0 21	0.34 0.20	< 0.01 < 0.01	< 0.01 < 0.01	01R280 01R280-5
Neustadt–Mußbach, Germany 2001 Riesling	3 (9 11)	0.133 0.133 0.133	0.0266 0.0266 0.0266	500 500 500	85	bunch of grapes	0 21	0.60 0.44	< 0.01 < 0.01	< 0.01 < 0.01	01R280 01R280-1
Ihringen, Germany 2001 Silvaner	3 (9 11)	0.133 0.133 0.133	0.0266 0.0266 0.0266	500 500 500	85	bunch of grapes	0 21	0.57 0.38	< 0.01 < 0.01	< 0.01 < 0.01	01R280 01R280-2

Fluopicolide, as an SE formulation, was applied to grapevines at five sites in southern Europe. The varieties chosen were wine grapes for four trials and table grapes for the remaining trial. Vines were sprayed three times at 0.133 kg ai/ha using motorised knapsack or air blast sprayers. Plot sizes were 14–60 m^2. Grapes were sampled for analysis at 0 and 20 to 22 days (nominal PHI 21 days) after final application. The nominal 21 day sample was equivalent to mature commercial harvest. Storage periods for samples in these trials were between 364 and 423 days. Method 00782/M001 was used for analysis of fluopicolide plus metabolites

Table 51 Results of residue trials conducted with fluopicolide in grapes in southern Europe (SE formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Mazeres, France 2001, Cabernet Sauvignon	3 (10 10)	0.133 0.133 0.133	0.0887 0.0887 0.0887	150 150 150	85	bunch of grapes	0 20	0.72 0.69	< 0.01 < 0.01	< 0.01 < 0.01	01R281 01R281-1
Chazay D'Azergues, France 2001 Gamay	3 (10 10)	0.133 0.133 0.133	0.0665 0.0665 0.0665	200 200 200	85	bunch of grapes	0 21	0.33 0.15	< 0.01 < 0.01	< 0.01 < 0.01	01R281 01R281-2
Goumenissa–Kilkis, Greece 2001 Xinomavro	3 (9 11)	0.133 0.133 0.133	0.0166 0.0166 0.0166	800 800 800	83	bunch of grapes	0 21	0.47 0.39	< 0.01 0.014	0.02 0.048	01R281 01R281-5
San Prospero, Italy 2001 Lambrusco Di Sorbara	3 (10 10)	0.133 0.133 0.133	0.0133 0.0133 0.0133	1000 1000 1000	83	bunch of grapes	0 21	1.5 1.2	0.023 0.037	0.014 0.018	01R281 01R281-3

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Godelleta, Spain 2001 Moscatel	3 (10 10)	0.133 0.133 0.133	0.0133 0.0133 0.0133	1000 1000 1000	83	bunch of grapes berry	0 22	0.28 0.11	< 0.01 0.015	< 0.01 0.015	01R281 01R281-4

Fluopicolide as a straight SE formulation was applied to grapevines at five sites in Northern Europe. The varieties chosen were wine grapes for all five trials. Vines were sprayed four times at 0.133 kg ai/ha with spray intervals of 10 to 13 days using motorised knapsack sprayers. Plot sizes were 17–210 m^2. Grapes were sampled for analysis at 0, 3, 7, 14 and 21 days after final application (mature commercial harvest). From three of the wine grape trials additional samples have been taken for processing into wine. Storage periods for bunch of grape samples in these trials were between 616 and 723 days. The analytical method used was Agredoc Number C024784 (IF-101/05424) with minor modifications.

Table 52 Results of residue trials conducted with fluopicolide in grapes in northern Europe (SE formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Juigne-sur-Loire, France, 2000, Chenin	4 (13 11 10)	0.121 0.126 0.128 0.131	0.0252 0.0253 0.0252 0.0252	480 499 507 519	85	bunch of grapes	0 4 7 14 21 21	1.7 1.1 1.1 0.75 0.83 0.62	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 0.02	0.01 0.01 0.01 0.01 0.01 0.02	DR00EUN002 BKA/683/00/REStest1
Vallet, France, 2000, Melon = Muscadet	4 (12 10 11)	0.126 0.119 0.132 0.124	0.0253 0.0253 0.0252 0.0252	500 471 523 489	81	bunch of grapes	0 3 7 14 21	0.60 0.73 0.47 0.34 0.32	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 0.01 < 0.01 0.01	DR00EUN002 BKA/683/00/REStest2
Geisenheim, Germany, 2000, Riesling	4 (10 11 11)	0.132 0.134 0.135 0.128	0.0158 0.0158 0.0157 0.0158	834 846 858 810	85	bunch of grapes	0 3 7 14 21 21	1.2 1.4 0.62 0.78 0.96 0.61	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 0.01	< 0.01 < 0.01 < 0.01 0.01 0.01 0.02	DR00EUN002 AT-00/021-1
Gau-Algesheim, Germany, 2000, Silvaner	4 (11 11 11)	0.133 0.136 0.137 0.132	0.0158 0.0158 0.0157 0.0158	839 859 870 837	85	bunch of grapes	0 3 7 14 21 21	0.48 < 0.01 0.053 0.46 0.44 0.51	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 0.01	< 0.01 n.d. < 0.01 0.01 0.01 0.01	DR00EUN002 AT-00/021-2
Dienheim, Germany, 2000, Kerner	4 (11 11 11)	0.125 0.132 0.132 0.124	0.0158 0.0158 0.0159 0.0158	792 837 832 787	85	bunch of grapes	0 3 7 14 21	0.44 0.46 0.43 0.41 0.56	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	DR00EUN002 AT-00/021-3

During the 2002 growing season, a total of five trials were performed on wine grapes in the field in different locations in Canada. Three grape varieties chosen were white varieties (Vidal, Pinot Gris and Riesling) and the two other grape varieties were red varieties (Foch, Cabernet Sauvignon). Fluopicolide was formulated as an SC formulation nominally containing 480 g ai/L. Three foliar spray applications of fluopicolide were made 5 ± 1 days apart at a nominal rate of 133 g ai/ha/application (actual 127–139 g ai/ha/application) or 399 g ai/ha/season. The spray volumes used per application were between 672 and 839 L/ha. The total residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to Method 00782. The storage period of deep frozen samples ranged between 164 and 181 days.

Table 53 Results of residue trials conducted with fluopicolide in/on wine grapes in Canada using an SC formulation (BCS04-03)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Niagara on the Lake, ON Canada 2002 Vidal	3 (4 5)	0.127 0.132 0.130	0.01654 0.01641 0.01678	770 806 778	85	bunch of grapes	21	0.26 0.20	< 0.01 < 0.01	< 0.01 < 0.01
Grimsby, ON Canada 2002 Foch	3 (4 5)	0.134 0.139 0.133	0.01625 0.01651 0.01635	824 839 815	85	bunch of grapes	21	0.22 0.32	< 0.01 < 0.01	< 0.01 < 0.01
Blenheim, ON Canada 2002 Cabernet Sauvignon	3 (4 5)	0.137 0.136 0.132	0.01789 0.01714 0.01692	764 796 780	83	bunch of grapes	20	0.25 0.22	< 0.01 < 0.01	< 0.01 < 0.01
Harrow, ON Canada 2002 Reisling	3 (4 4)	0.129 0.130 0.133	0.01915 0.01682 0.01691	673 774 788	85	bunch of grapes	21	0.56 0.32	< 0.01 < 0.01	< 0.01 < 0.01
Winfield, BC Canada 2002 Pinot Gris	3 (4 5)	0.129 0.130 0.128	0.01881 0.01881 0.01861	687 694 686	83	bunch of grapes	20	0.43 0.53	< 0.01 < 0.01	< 0.01 < 0.01

During the 2002 growing season, a total of 11 trials were performed on grapes in the field in different locations in the USA. Three foliar spray applications of fluopicolide were made 5 ± 1 days apart to each treated plot at a target rate of 133 g ai/ha/application or 399 g ai/ha/season. Plot sizes were 22–123 m^2. Sprays were made using air-blast sprayers except at three locations where boom and broadcast sprayers were used. Residues of fluopicolide, M-01 and M-02 were quantitated LC/MS/MS according to Method 00782. The storage period of deep frozen samples ranged between 156 and 219 days.

Table 54 Results of residue trials conducted with fluopicolide in/on wine grapes in the USA using an SC formulation (BCS04-03)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Dundee, NY USA 2002 Aurora	3 (5 5)	0.134 0.130 0.135	0.01894 0.01879 0.0191	705 694 695	81	bunch of grapes	21	0.44 0.32	< 0.01 < 0.01	< 0.01 < 0.01
North Rose, NY USA 2002 Elvira	3 (5 5)	0.126 0.135 0.136	0.01886 0.01927 0.01928	770 806 778	85	bunch of grapes	21	0.07 0.065	< 0.01 < 0.01	0.013 < 0.01
Fresno, CA, USA 2002 Cabernet	3 (5 5)	0.132 0.129 0.131	0.01881 0.01859 0.01717	704 694 764	85	bunch of grapes	21	0.10 0.13	< 0.01 < 0.01	< 0.01 < 0.01
Sanger, CA, USA 2002 Ruby Cabernet	3 (5 5)	0.133 0.130 0.132	0.01943 0.01764 0.01907	684 731 690	85	bunch of grapes	21	0.18 0.21	< 0.01 < 0.01	< 0.01 < 0.01
Kerman, CA USA 2002 Thompson Seedless	3 (6 5)	0.133 0.134 0.134	0.01480 0.01480 0.01484	901 902 899	77	bunch of grapes	21	0.10 0.077	< 0.01 < 0.01	< 0.01 < 0.01

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Bowles, CA USA 2002 Thompson Seedless	3 (6 5)	0.132 0.133 0.133	0.01470 0.01469 0.01483	899 903 899	[a]	bunch of grapes	21	0.12 <u>0.13</u>	< 0.01 < 0.01	< 0.01 0.01
Huron, CA USA 2002 Berger	3 (4 6)	0.134 0.133 0.134	0.01483 0.01476 0.01478	902 903 905	77	bunch of grapes	21	0.093 <u>0.098</u>	< 0.01 < 0.01	< 0.01 < 0.01
Gonzales, CA USA 2002 Chardonay	3 (6 4)	0.132 0.136 0.127	0.01651 0.01684 0.01618	800 808 784	85	bunch of grapes	20	0.98 <u>0.99</u>	< 0.01 < 0.01	< 0.01 < 0.01
San Luis Obispo, CA USA 2002 Chardonay	3 (4 6)	0.135 0.171 0.144	0.01690 0.01888 0.01731	796 904 831	85	bunch of grapes	21	0.85 <u>1.1</u>	< 0.01 < 0.01	< 0.01 < 0.01
Healdsburg, CA USA 2002 Cabernet	3 (5 5)	0.140 0.136 0.132	0.01879 0.01881 0.01761	746 722 751	85	bunch of grapes	21	<u>0.19</u> 0.15	< 0.01 < 0.01	< 0.01 < 0.01
Ephrata, WA USA 2002 Riesling	3 (5 5)	0.136 0.133 0.135	0.01961 0.01914 0.01950	696 695 693	85	bunch of grapes	21	<u>0.14</u> 0.13	< 0.01 < 0.01	< 0.01 < 0.01

[a] Majority of berries touching

Three trials used boom sprayers: Kerman, Bowles and Huron. Two used broadcast application, Gonzales and San Luis Obispo.

Bulb vegetables

Onions

In 2006 and 2007 a total of eight supervised residue trials were performed in the field in Northern Europe (Northern France 2, Germany 3, Belgium 1, United Kingdom 1 and the Netherlands 1) on onions. Plot sizes were 15–62 m^2 for the 2006 trials and 24–80 m^2 for the 2007 trials. An SC formulation was sprayed three times on onion plants with a water volume of 300–800 L/ha, corresponding to a fluopicolide use rate of 0.1 kg ai/ha per application. The applications were carried out with a spray interval of 7–8 days using knapsack and boom sprayers. The last application was at BBCH 47–49, seven days before the anticipated commercial harvest. Residues of fluopicolide and its metabolites M-02 and M-01 were determined according to method 00782/M001 for study RA-2306/06 and method 00782/M004 for study RA-2634/07. The LOQ for all three compounds was 0.01 mg/kg. The storage period of deep frozen samples ranged between 24 and 175 days.

Table 55 Results of residue trials conducted with fluopicolide in the field in Northern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Bouafle (Ile-de-France), France 2006 Jaunes des Cévennes	3 (7 7)	0.100 0.100 0.100	0.020 0.020 0.020	500 500 500	48	bulb	0 3 7	0.09 0.05 0.03	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2306/06 R 2006 0093 3 0093-06
Burscheid (Nordrhein-Westfalen), Germany	3 (7 7)	0.100 0.100 0.100	0.03331 0.03331 0.03331	300 300 300	47	bulb	0 3 7	0.08 0.02 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2306/06 R 2006 0094 1

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
2006 Stuttgarter Riesen											0094-06
Wangenies (Hainaut), Belgium 2006 Summit	3 (7 7)	0.100 0.100 0.100	0.02225 0.02225 0.02225	450 450 450	47	bulb	0 3 7	0.02 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2306/06 R 2006 0096 8 0096-06
Kohlhof (Rheinland-Pfalz) Germany 2006 Takstar	3 (7 7)	0.100 0.100 0.100	0.02000 0.02000 0.02000	500 500 500	49	bulb	0 3 7	0.05 0.03 0.02	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2306/06 R 2006 0097 6 0097-06
Champien (Picardie) France 2007 Boston	3 (7 7)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	48	bulb	0 3 7	0.01 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2634/07 R 2007 0336/8 0336-07
Burscheid (Nordrhein-Westfalen) Germany 2007 Stuttgarter Riesen	3 (7 7)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	47	bulb	0 3 7	0.03 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2634/07 R 2007 0378/3 0378-07
West Row/ BSE (Suffolk) UK 2007 Sherpa	3 (8 7)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	48	bulb	0 3 7	0.05 0.05 0.03	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2634/07 R 2007 0379/1 0379-07
Wieringerwerf (Noord-Holland) The Netherlands 2007 Hybell	3 (7 7)	0.100 0.100 0.100	0.0125 0.0125 0.0125	800 800 800	48	bulb	0 3 7	0.02 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2634/07 R 2007 0380/5 0380-07

Planting densities were 360k, 670k, 1500k and 480 k plants/ha for the 2007 Picardie, Nordrhein-Westfalen, Suffolk and Noord-Holland trials respectively.

In 2006 and 2007 a total of eight supervised residue trials were performed in the field in Southern Europe (Southern France 2, Spain 2, Italy 2 and Portugal 2) on onions. An SC formulation (with propamocarb) was sprayed three times on onion plants with a water rate of 500–800 L/ha, corresponding to a fluopicolide use rate of 0.1 kg ai/ha per application using knapsack sprayers with booms. The applications were carried out with a spray interval of 6–8 days. Plot sizes were 15–90 m^2 for 2006 trials and 15–72 m^2 for 2007 trials.

The first treatment was conducted at BBCH 43–47, whilst the last application was carried out at BBCH 47–48, seven days before the anticipated commercial harvest. In all trials, onion samples (bulbs) were taken at day 0, day 3–4 and at day 7 (the intended PHI) after the last application. Residues of fluopicolide and its metabolites M-02 and M-01 were determined according to method 00782/M001 for study RA-2307/06 and according to method 00782/M004 for study RA-2635/07. The LOQ for all three compounds was 0.01 mg/kg. The storage period of deep frozen samples ranged between 86 and 301 days.

Table 56 Results of residue trials conducted on onions with fluopicolide in the field in Southern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
St Jory (Midi-Pyrenees) France 2006 Elodie	3 (6 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	47	bulb	0 3 7	0.05 0.02 0.02	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2307/06 R 2006 0098 4 0098-06
Malgrat de Mar (Barcelona) (Cataluña) Spain 2006 Onion	3 (7 7)	0.100 0.100 0.100	0.0200– 0.0167 0.0167	500 600 600	48	bulb	0 3 7	0.06 0.04 0.0	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2307/06 R 2006 0099 2 0099-06
Bologna (Emilia–Romagna) Italy 2006 Density 5	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	48	bulb	0 3 7	0.02 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2307/06 R 2006 0101 8 0101-06
Alcochete (Ribatejo e Oeste) Portugal 2006 Cebola de Alcochete	3 (7 7)	0.108 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	47	bulb	0 4 7	0.05 0.02 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2307/06 R 2006 0102 6 0102-06
Sathonay Village (Rhone-Alpes) France 2007 Proteus	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	48	bulb	0 3 7	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2635/07 R 2007 0337/6 0337-07
Gava–Barcelona (Cataluña) Spain 2007 Figueras	3 (6 7)	0.100 0.092 0.093	0.01250 0.01250 0.01250	800 736 744	48	bulb	0 3 7	0.03 0.02 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2635/07 R 2007 0381/3 0381-07
Poggio Renatico (FE) (Emilia–Romagna) Italy 2007 Rossa di Toscana	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	48	bulb	0 4 7	0.02 0.02 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2635/07 R 2007 0382/1 0382-07
S. Francisco/Alcochete (Ribatejo e Oeste) Portugal 2007 Spring Star	3 (8 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	47	bulb	0 3 7	0.03 0.02 0.02	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2635/07 R 2007 0384/8 0384-07

Planting densities were 380 k, 100 k, 1100 k and 250 k plants/ha for the 2007 Rhone-Apls, Cataluña, Emilia–Romagna and Ribatejo e Oeste trials respectively.

During the 2002 and 2003 growing season, a total of 10 trials were performed on bulb onions (seven trials) and green onions (three trials, also known as Welsh onions) in the field in different locations in the USA. Fluopicolide was formulated as a suspension concentrate. Three foliar spray applications of fluopicolide were made 5 ± 1 days apart to each treated plot at a target rate of 133 g ai/ha/application (actual 131–139 g ai/ha/application) or 399 g ai/ha/season. Application was by backpack or tractor mounted CO_2 assisted sprayers. Plot sizes were 56–139 m^2. Residues of fluopicolide, M-01 and M-02 were quantitated according to Method 00782. The LOQ was 0.01 mg/kg. The storage period of deep frozen samples ranged between 877 and 1248 days.

Table 57 Results of residue trials conducted with fluopicolide (SC formulation) in/on bulb onions in the USA (02CU27780).

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Germansville, PA USA 2002 Stuttgarter	3 (5 6)	0.138 0.133 0.133	0.0718 0.0622 0.0622	192 214 214	Bulb enlargement	Bulb	2	0.013 0.013	< 0.01 < 0.01	< 0.01 < 0.01
Rincon, NM, USA 2002 Alabaster White	3 (5 5)	0.131 0.135 0.133	0.0790 0.0752 0.0728	166 179 183	79	bulb	2	0.029 0.048	< 0.01 < 0.01	< 0.01 < 0.01
King City, CA, USA 2002 Tamara	3 (5 4)	0.139 0.136 0.136	0.0716 0.0720 0.0716	194 188 189	49	bulb	2	0.071 0.050	< 0.01 < 0.01	< 0.01 < 0.01
Glenn, CA USA 2002 Yellow-bulb-cooking	3 (5 5)	0.132 0.133 0.132	0.0701 0.0723 0.0698	189 184 190	89	bulb	2	0.083 2.3[a]	< 0.01 < 0.01	< 0.01 < 0.01
Madras, OR USA 2002 Yellow Ebenezer	3 (5 5)	0.136 0.136 0.135	0.0716 0.0705 0.0700	189 193 192	89	bulb	2	0.582 0.408	< 0.01 < 0.01	< 0.01 < 0.01
Hermiston, OR USA 2002 Vaquero	3 (5 5)	0.133 0.139 0.131	0.0641 0.0669 0.0670	208 208 105	89	bulb	2	0.045 0.046	< 0.01 < 0.01	< 0.01 < 0.01
Raymondville, TX USA 2003 Texas Early Grano 502 PRR	3 (5 6)	0.135 0.137 0.137	0.0715 0.0716 0.0716	188 191 191	Large Bulbs	bulb	1 2 3 5 7	0.163 0.100 0.053 0.113 0.048 0.074	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01

Adjuvants (Stickers to enhance rainfastness) were added to tank mixes, Bond (Germanville, Ricon, Madras, Hermiston) and First-Choice (Castroville).

[a] Initial analyses reported high residues 2.3 mg/kg that were confirmed on reanalysis. Visual examination of the sample homogenates determined that the samples were greener than other bulb onion homogenates. The appearance of the second composite for sample the trial was similar to bulb macerates from other studies. Fluopicolide residues in this sample were 0.08 mg/kg. It was concluded that there was onion top material included in the samples with the high fluopicolide residues. The value 0.08 mg/kg is reported in the table.

Welsh green onions (bunching onions)

Table 58 Results of residue trials conducted with fluopicolide (SC formulation) in/on green (Welsh) onions in the USA (02CU27780).

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Raymondville, TX, USA 2002 (Welsh/ green) Texas Early Grano 502 PRR	3 (4 5)	0.136 0.136 0.133	0.0713 0.0716 0.0713	190 190 187	19	whole plant with root	2	4.50 4.47	< 0.01 0.01	< 0.01 < 0.01
Castroville, CA USA 2002 (Welsh /green) Emerald Isle	3 (5 5)	0.136 0.136 0.133	0.0721 0.0722 0.0717	188 188 186	49	whole plant with root	2	1.71 1.49	< 0.01 < 0.01	< 0.01 < 0.01

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Glenn, CA USA 2002 (Welsh/green) Bunching	3 (5 5)	0.132 0.133 0.132	0.0695 0.0693 0.0697	189 184 190	89	whole plant with root	1 2 3 5 7	1.41 2.08 1.61 1.78 1.46 1.24	0.013 0.014 0.014 0.018 0.018 0.021	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01

Adjuvants (Stickers to enhance rainfastness) were added to tank mixes Nu-Film 17 (Raymondville, Glenn) and First-Choice (Castroville).

Leeks

In 2005 and 2006 a total of eight supervised residue trials were performed in the field in Northern Europe (Germany 3, Northern France 2, the Netherlands 2 and Belgium) on leek. Fluopicolide SC (formulated with propamocarb) was sprayed three times on leek plants with a nominal rate of 0.1 kg ai/ha and a water volume of 300–600 L/ha using knapsack sprayers with booms. The applications were carried out with a spray interval of 6–8 days. Plot sizes for the 2006 trials were 24–45 m^2 and 16–45 m^2 for the 2006 trials. The first treatment was conducted at BBCH 43–47, whilst the last application was carried out at BBCH 44–49, two weeks before the anticipated commercial harvest. In the trials from 2005, leek samples (whole plants without roots) were taken at day 0, day 13–14 (the intended PHI) and at day 21–22 after the last application. In the 2006 trials, samples were taken at day 0 and at day 14-15 after the final treatment. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M001 and 00782/M004. The LOQ for all three molecules was 0.01 mg/kg for the whole leek plant without roots. The storage period of deep frozen samples ranged between 28 and 444 days.

Table 59 Results of residue trials conducted on leeks fluopicolide in Northern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Wayaux, Belgium 2005 Shelton	3 (7 7)	0.100 0.100 0.100	0.0222 0.0222 0.0222	450 450 450	47	whole plant without roots	0 3 7 14 21	0.28 0.45 0.23 0.08 0.07	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2111/05 R 2005 0560 4 0560-05
Zwaagdijk-Oost, The Netherlands 2005 Shelton	3 (8 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	48	whole plant without roots	0 3 7 14 21	0.75 0.97 0.60 0.63 0.18	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2111/05 R 2005 0561 2 0561-05
Langenfeld-Reusrath , Germnay 2005 Pandora	3 (7 7)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	47	whole plant without roots	0 14 21	0.30 0.06 0.03	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2111/05 R 2005 0564 7 0564-05
Faverolles, France 2005 Hiverna	3 (7 7)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	44	whole plant without roots	0[a] 13 22	1.7 0.59 0.45	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2111/05 R 2005 0565 5 0565-05
Faverolles, France 2006 Diana	3 (7 7)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	48	whole plant without roots	0 14	1.3 0.82	< 0.01 < 0.01	< 0.01 < 0.01	RA-2302/06 R 2006 0080 1 0080-06

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Langenfeld-Reusrath, Germany 2006 Pandora	3 (7 7)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	45	whole plant without roots	0 14	0.29 0.03	< 0.01 < 0.01	< 0.01 < 0.01	RA-2302/06 R 2006 0082 8 0082-06
Zwaagdijk-Oost, The Netherlands 2006 Roxton	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	48	whole plant without roots	0 14	0.62 0.18	< 0.01 < 0.01	< 0.01 < 0.01	RA-2302/06 R 2006 0083 6 0083-06
Bornheim–Sechtem, Germany 2006 Amundo	3 (7 6)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	49	whole plant without roots	0 15	0.86 0.31	< 0.01 < 0.01	< 0.01 < 0.01	RA-2302/06 R 2006 0084 4 0084-06

[a] 3 mm rain fell 6.3 h after the last spray

In 2005 a total of four supervised residue trials were performed in the field in Southern Europe (Italy, Southern France, Portugal and Spain) on leek. Fluopicolide SC was sprayed three times on leek plants with a nominal rate of 0.1 kg ai/ha and a spray volume of 300–600 L/ha using knapsack sprayers with booms. The applications were carried out with a spray interval of 7 days. Plot sizes were 22–68 m^2. The first treatment was conducted at BBCH 43–45, whilst the last application was carried out at BBCH 45–47, two weeks before the anticipated commercial harvest. In all trials leek samples (whole plants without roots) were taken at day 0, day 14 (the intended PHI) and at day 21 after the last application. In two trials additional samples were taken at day 3 and at day 7 after the final treatment. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M001. The LOQ for all three compounds was 0.01 mg/kg for the whole leek plant without roots. The storage period of deep frozen samples ranged between 392 and 472 days.

Table 60 Results of residue trials conducted with fluopicolide on leeks in Southern Europe (SC formulation)

	N	kg/ha (as)	kg/hL (as)	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Lusia, Italy 2005 Sabina	3	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	47	whole plant without roots	0 3 7 14 21	1.7 0.63 0.62 0.13 0.04	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2112/05 R 2005 0562 0 0562-05
Brenes Sevilla, Spain 2005 Heracles	3	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	45	whole plant without roots	0 3 7 14 21	1.8 [a] 1.7 1.6 1.2 0.65	0.01 0.01 0.01 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2112/05 R 2005 0563 9 0563-05
St Alban, France 2005 Davensy	3	0.100 0.100 0.100	0.0250 0.0250 0.0250	400 400 400	45	whole plant without roots	0 14 21	0.73 0.18 0.04	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2112/05 R 2005 0566 3 0566-05
Torres Novas, Portugal 2005 Lancelot	3	0.100 0.100 0.100	0.0250 0.0250 0.0250	400 400 400	47	whole plant without roots	0 14 21	0.60 0.15 0.06	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2112/05 R 2005 0567 1 0567-05

[a] 6 mm rain 15 h after last spray

Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead cabbages

Head Cabbages

In 2005 and 2006 a total of eight supervised field trials were performed in the field in Northern Europe (Northern France 2, the Netherlands 2, Germany 3 and Belgium) on savoy cabbage, round cabbage and red cabbage. Fluopicolide SC (formulated with propamocarb) was sprayed three times on cabbage plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 300–600 L/ha using knapsack boom sprayers. The applications were carried out with a spray interval of 9–11 days. Plot sizes were 24–75 m^2 for the trials conducted in 2006 and 32–75 m^2 in 2005. The first treatment was conducted at BBCH 19–46, whilst the last application was carried out at BBCH 42–48 two weeks before the anticipated commercial harvest. In all trials, cabbage samples (heads) were taken at day 0 and at day 13–14 after the last application, additional cabbage samples were taken at day 3–4, day 7 and day 21 after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M001 (LOQ for all three compounds was 0.01 mg/kg). The storage period of deep frozen samples ranged between 124 and 345 days.

Table 61 Results of residue trials conducted with fluopicolide SC on cabbage in Northern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Bornheim, Germany 2005 (Savoy) Alaska	3 (10 10)	0.100 0.100 0.100	0.0250 0.0250 0.0250	400 400 400	43	head	0 3 7 14 21	0.37 0.15 0.04 <u>0.01</u> 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2150/05 R 2005 0805 0 0805-05
Gembloux, Belgium 2005 (red) Regilus	3 (10 10)	0.100 0.100 0.100	0.0222 0.0222 0.0222	450 450 450	45	head	0 14 21	< 0.01 [a] <u>< 0.01</u> < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2150/05 R 2005 0806 9 0806-05
Ennemain, France 2005 (Savoy) Ice Prince	3 (10 10)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	48	head	0 3 7 14 21	0.04 0.04 0.05 <u>0.01</u> 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2150/05 R 2005 0869 7 0869-05
Zwaagdijk-Oost, The Netherlands 2005 (red) Integro	3 (10 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	48	head	0 14 21	0.03 [b] <u>< 0.01</u> < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2150/05 R 2005 0870 0 0870-05
Zwaagdijk-Oost, The Netherlands 2006 (Savoy) Pondusa	3 (11 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	48	head	0 14	0.09 <u>0.03</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2308/06 R 2006 0107 7 0107-06
Bornheim, Germany 2006 (Savoy) Visa	3 (10 9)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	47	head	0 13	0.57 <u>0.18</u>	< 0.01 < 0.01	0.02 0.02	RA-2308/06 R 2006 0108 5 0108-06
Bouafle, France 2006 (White) Premiére	3 (10 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	42	head	0 3 7 14 21	1.1 0.75 0.10 <u>0.03</u> 0.01	0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2308/06 R 2006 0111 5 0111-06

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Leichlingen, Germany 2006 (red) Rodima	3 (10 10)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	45	head	0 3 7 14 21	0.26 0.19 0.21 <u>0.08</u> 0.04	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2308/06 R 2006 0112 3 0112-06

[a] 13 mm rain at 6 h after the last spray;

[b] 3 mm rain at 16 h after the last spray.

Plant densities for the 2006 trials were 40 k plants/ha for Zwaagdijk-Oost, 42.9 k/ha for Bornheim, 25 k/ha for Bouafle and 40 k/ha for Leichlingen

In 2005 and 2006 a total of four supervised field trials were performed in the field in Southern Europe (Southern France, Italy, Greece and Spain) on round cabbage. Fluopicolide SC was sprayed three times on cabbage plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 300–600 L/ha. The applications were carried out with a spray interval of 9–12 days using knapsack sprayers with booms. Plot sizes were 49–60 m^2 for the 2005 trials and 35–60 m^2 for the 2006 trials. The first treatment was conducted at BBCH 41–44, whilst the last application was carried out at BBCH 47–48 two weeks before the anticipated commercial harvest. In all trials, cabbage samples (heads) were taken at day 0 and at day 14 after the last application, additional cabbage samples were taken in two trials at day 3, 7 and 21 after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M001 (LOQ for all three compounds was 0.01). The storage period of deep frozen samples ranged between 66 and 288 days.

Table 62 Results of residue trials on cabbage conducted with fluopicolide in Southern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
St Alban, France 2005 (white) Delus B285	3 (9 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	48	head	0 3 7 14 21	0.05 0.02 0.01 <u>0.01</u> < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2151/05 R 2005 0807 7 0807-05
Kato Agios Ioannis, Greece 2005 (white) Baner	3 (9 12)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	48	head	0 14 21	0.10 0.01 <u>0.02</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2151/05 R 2005 0836 0 0836-05
Gavà, Spain 2006 (white) Megaton	3 (9 12)	0.100 0.100 0.100	0.0200 0.0167 0.0167	500 600 600	47	head	0 14	0.05 <u>0.01</u>	< 0.01 < 0.010	< 0.01 < 0.010	RA-2309/06 R 2006 0109 3 0109-06
Andria, Italy 2006 (white) Sapalla	3 (10 10)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	47	head	0 14	0.11 <u>0.030</u>	< 0.01 < 0.010	< 0.01 < 0.010	RA-2309/06 R 2006 0110 7 0110-06

Plant densities were 40 k plants/ha for Gavà and 37.5 k/ha for Andria

During the 2002 growing season, a total of seven trials were performed on head cabbage in the field in different locations in the USA. Fluopicolide was formulated as a suspension concentrate.

Three foliar spray applications were made 4–6 days apart to each treated plot at a target rate of 0.133 kg ai/ha in spray volumes ranging from 163 to 191 L/ha using backpack and tractor mounted CO_2 assisted sprayers. Plot sizes were 59–134 m^2. Mature cabbage with and without wrapper leaves were harvested 2 days after the last application. Obviously decomposed or withered leaves were removed from cabbage samples. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to Bayer method 00782. The LOQ was 0.01 mg/kg for each analyte. The storage period of deep frozen samples ranged between 970 and 1220 days.

Table 63 Results of residue trials conducted with fluopicolide (SC formulation) in/on head cabbage in the USA (02CU33137).

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	AE C656948-pyridyl-carboxylic acid (mg/kg)
Arkansaw, WI, USA 2002 Quisto Hybrid	3 (5 5)	0.133 0.133 0.135	0.0709 0.0707 0.0712	188 189 184	49	head	2	0.057 <u>0.310</u>	< 0.01 < 0.01	< 0.01 < 0.01
						head, inner parts	2	< 0.01 0.014	< 0.01 < 0.01	< 0.01 < 0.01
Madison, FL USA 2002 Bravo	3 (5 5)	0.133 0.131 0.130	0.0791 0.0770 0.0780	168 170 166	49	head	2	0.81 <u>1.91</u>	< 0.01 < 0.01	< 0.01 < 0.01
						head, inner parts	2	0.89 1.11	< 0.01 < 0.01	< 0.01 < 0.01
Omega, GA, USA 2002 Bravo	3 (5 5)	0.132 0.132 0.135	0.0770 0.0805 0.0801	172 165 168	48	head	1 2 3 5 7	4.0 3.54 <u>3.93</u> 3.60 3.11 3.45 0.916 0.952 1.25 0.813	0.015 0.014 0.015 0.017 0.012 0.015 < 0.01 < 0.01 0.010 < 0.01	0.015 0.010 0.015 0.020 0.017 0.016 < 0.01 < 0.01 < 0.01 < 0.01
						head, inner parts	1 2 3 5 7	0.929 2.34 2.09 2.63 1.55 1.34 0.057 0.239 0.428 0.237	< 0.01 < 0.01 < 0.01 0.011 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.010 0.011 0.015 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Jamesville, NC, USA 2002 Blue Dynasty	3 (5 5)	0.132 0.136 0.135	0.0812 0.0821 0.0823	163 166 164	49	head	2	0.383 <u>1.22</u>	< 0.01 < 0.01	< 0.01 < 0.01
						head, inner parts	2	0.146 0.098	< 0.01 < 0.01	0.01 < 0.01
North Rose, NY USA 2002 Gourmet	3 (5 5)	0.130 0.135 0.131	0.0707 0.0707 0.0708	183 190 185	49	head	2	0.544 <u>0.614</u>	< 0.01 < 0.01	< 0.01 < 0.01
						head, inner parts	2	0.218 0.026	< 0.01 < 0.01	< 0.01 < 0.01
Uvalde, TX USA 2002 Pennant	3 (4 5)	0.135 0.131 0.137	0.0704 0.0709 0.0719	191 185 190	49	head	2	<u>0.36</u> 0.334	< 0.01 < 0.01	< 0.01 < 0.01
						head, inner parts	2	0.109 0.078	< 0.01 < 0.01	< 0.01 < 0.01
Santa Maria; CA, USA 2002 Supreme Vantage	3 (6 4)	0.136 0.133 0.133	0.0718 0.0705 0.0715	189 189 187	49	head	2	0.966 <u>2.29</u>	< 0.01 < 0.01	< 0.01 < 0.01
						head, inner parts	2	0.015 0.014	< 0.01 < 0.01	< 0.01 < 0.01

An adjuvant (spreader/sticker) was added to the tank mixes; Bond (North Rose, Jamesville, Arkansaw. Uvalde), Latron (Omega, Madison) and Break Thru (Santa Maria)

Brussels sprouts

In 2005 a total of four supervised field trials were performed in the field in Northern Europe (Northern France, the Netherlands and Germany). Fluopicolide SC (formulated with propamocarb) was sprayed three times on Brussels sprouts plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 300–600 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 9–10 days. Plot sizes were 30–66 m^2. The first treatment was conducted at BBCH 43-46, whilst the last application was carried out at BBCH 45–48 two weeks before the anticipated commercial harvest. In all trials, Brussels sprouts samples (sprouts) were taken at day 0, day 14-15 and at day 21 after the last application; additional Brussels sprouts samples were taken at day 3–4 and day 7 after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M001 (LOQ for all three compounds was 0.01 mg/kg). The storage period of deep frozen samples ranged between 196 and 306 days.

Table 64 Results of residue trials conducted on Brussels sprouts in Northern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Fontaine L'Etalon, France 2005 Maximus	3 (10 10)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	45	sprout	0 4 7 14 21	0.11[a] 0.04 0.02 <u>0.01</u> 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2152/05 R 2005 0809 3 0809-05
Zwaagdijk-Oost, The Netherlands 2005 Genius	3 (9 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	48	sprout	0 14 21	0.05 0.02 <u>0.03</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2152/05 R 2005 0810 7 0810-05
Werl-Westönnen, Germany 2005 Cyrus	3 (10 10)	0.106 0.100 0.100	0.0333 0.0333 0.0333	318 300 300	47	sprout	0 3 7 15 21	0.15 0.09 0.09 <u>0.04</u> 0.04	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2152/05 R 2005 0837 9 0837-05
Langenfeld-Reusrath, Germany 2005 Genius	3 (10 10)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	48	sprout	0 14 21	0.16 <u>0.13</u> 0.09	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2152/05 R 2005 0838 7 0838-05

[a] 3 mm rain at 19 h after last spray

In 2006 a total of four supervised field trials were performed in the field in Northern Europe (Germany (2), Northern France and Belgium). Fluopicolide SC (formulated with propamocarb) was sprayed three times on Brussels sprouts plants with nominal rate of 0.1 kg ai/ha and a spray volume of 300–450 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 9–10 days. Plot sizes were 21–66 m^2. The first treatment was conducted at BBCH 43-46, whilst the last application was carried out at BBCH 46–48, two weeks before the anticipated commercial harvest. In all trials, Brussels sprouts samples (sprouts) were taken at day 0 and at day 14 after the last application, additional Brussels sprouts samples were taken in two trials at day 3, day 7 and day 21 after the last application.

Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M001. The LOQ for all three molecules was 0.01 mg/kg. The storage period of deep frozen samples ranged between 41 and 184 days.

Table 65 Results of residue trials conducted on Brussels sprouts in Northern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Vechta–Langförden, Germany 2006 Camus	3 (10 9)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	48	sprout	0 14	0.11 <u>0.05</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2303/06 R 2006 0085 2 0085-06
Geer, Belgium 2006 Maximus	3 (10 10)	0.100 0.100 0.094	0.0222 0.0222 0.0222	450 450 423	48	sprout	0 14	0.06 [a] <u>0.03</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2303/06 R 2006 0086 0 0086-06
Fontaine l'Etalon, France 206 Louis	3 (10 10)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	48	sprout	0 3 7 14 21	0.08 0.12 0.06 <u>0.05</u> 0.05	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2303/06 R 2006 0087 9 0087-06
Langenfeld-Reusrath, Germany 2006 Genius	3 (10 10)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	46	sprout	0 3 7 14 21	0.08 0.07 0.08 <u>0.04</u> 0.04	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2303/06 R 2006 0088 7 0088-06

[a] 4 mm rainfall starting 9 h after the last spray

Broccoli

In 2005 a total of four supervised field trials were performed in the field in Northern Europe (Northern France, the Netherlands, Belgium and Germany) on broccoli. Fluopicolide SC (formulated with propamocarb) was sprayed three times on broccoli plants with nominal rate of 0.1 kg ai/ha and spray volumes of 300–600 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 10–14 days. Plot sizes were 30–60 m^2.

The first treatment was conducted at BBCH 18–34, whilst the last application was carried out at BBCH 41–55 two weeks before the anticipated commercial harvest. In all trials, broccoli samples (whole plant without roots, curd) were taken at day 0, day 14-15 and at day 21 after the last application, additional broccoli samples were taken in two trials at day 3 and day 7–8 after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M001 by HPLC-MS/MS. The LOQ for all three analytes was 0.01 mg/kg. The longest storage interval before analysis was 384 days.

Table 66 Results of residue trials conducted on broccoli in Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Fondettes, France 2005 Monaco	3 (10 10)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	41	curd whole plant without roots	14 21 0 3 8	<u>0.01</u> < 0.01 1.2 0.29 0.10	< 0.01 < 0.01 0.02 0.02 < 0.01	0.02 0.02 < 0.01 0.01 0.02	RA-2156/05 R 2005
Zwaagdijk-Oost, The Netherlands 2005 Montop	3 (10 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600		curd	0 15 21	0.46[a] <u>< 0.01</u> < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2156/05 R 2005 0819 0 0819-05

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Bornival, Belgium 2005 Monopoly	3 (10 14)	0.100 0.100 0.100	0.0222 0.0222 0.0222	450 450 450	43	curd	0 3 7 14 21	0.24 0.22 0.12 <u>0.10</u> 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.01 0.01 0.01 0.03 0.02	RA-2156/05 R 2005 0846 8 0846-05
Leichlingen, Germany 2005 Volta F1	3 (10 10)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500		curd	0 14 21	0.49 <u>0.02</u> < 0.01	< 0.01 < 0.01 < 0.01	0.01 0.01 0.02	RA-2156/05 R 2005 0847 6 0847-05

[a] 5 mm rainfall starting at 18 h after the last spray

In 2005 a total of four supervised field trials were performed in the field in Southern Europe (Southern France, Greece, Italy and Spain). Fluopicolide SC (formulated with propamocarb) was sprayed three times on broccoli plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 500–600 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 9–11 days except for trial 0820/4 in Greece were the interval between the 2nd and 3rd application was 21 days due to poor crop development. Plot sizes were 45–108 m^2. The first treatment was conducted at BBCH 37–43, whilst the last application was carried out at BBCH 43–60 two weeks before the anticipated commercial harvest. In all trials, broccoli samples (whole plant without roots, curd) were taken at day 0, day 14 and at day 21 after the last application, additional broccoli samples were taken in two trials at day 3 and day 7 after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M001 by HPLC-MS/MS. The LOQ for all three compounds was 0.01 mg/kg. The longest storage interval before analysis was 265 days.

Table 67 Results of residue trials conducted on broccoli in south Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Marathonas, Greece 2005 Marathon	3 (10 21)[a]	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	43	curd	0 3 7 14 21	0.22 0.09 0.03 <u>< 0.01</u> < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.01 0.01 < 0.01 0.01	RA-2157/05 R 2005 0820 4 0820-05
Fenouillet, France 2005 Empereur	3 (10 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	49	curd	0 14 21	0.31 <u>0.11</u> 0.07	< 0.01 < 0.01 < 0.01	0.01 0.01 0.01	RA-2157/05 R 2005 0821 2 0821-05
Lebrija Sevilla, Spain 2006 Marathon	3 (9 11)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	49	curd	0 3 7 14 21	0.25 0.17 0.12 <u>0.06</u> 0.04	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 0.01 0.01	RA-2157/05 R 2005 0848 4 0848-05
Catania, Italy 2005 Catanese	3 (10 10)	0.100 0.100 0.100	0.0200 0.0200 0.0167	500 500 600		curd	0 14 21	0.40 <u>0.04</u> 0.02	< 0.01 < 0.01 < 0.01	0.02 0.03 0.03	RA-2157/05 R 2005 0849 2 0849-05

[a] last spray delayed due to slow crop development

During the 2002 growing season, a total of six trials were performed on broccoli in the field in different locations in the USA. Fluopicolide was formulated as a suspension concentrate. Three foliar spray applications of fluopicolide were made 4–6 days apart to each treated plot at a target rate of 0.133 kg ai/ha in spray volumes ranging from 141 to 194 L/ha. Plot sizes were 69–116 m^2. Broccoli samples were harvested 2 days after the last application. For all trials, two treated and one control RAC sample were collected at this sampling interval. In addition, at one test site, broccoli samples were also harvested at 1, 3, 5, and 7 PHI to determine residue decline over time. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to Bayer method 00782 (LOQ 0.01 mg/kg for each analyte). The storage period of deep frozen samples ranged between 940 and 1065 days.

Table 68 Results of residue trials conducted with fluopicolide on broccoli in the USA (02CU33136) (SC formulation).

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Uvalde, USA 2002 Sprinter	3 (4 5)	0.136 0.133 0.130	0.0715 0.0711 0.0696	190 188 187	51	curd	2	0.503 0.480	< 0.01 < 0.01	0.014 0.012
Glenn, USA 2002 Greenbelt	3 (5 6)	0.133 0.133 0.133	0.0706 0.0711 0.0710	189 188 188	49	curd	1 2 3 5 7	0.487 0.538 0.178 0.122 0.147 0.103 0.066 0.063 0.077 0.101	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Fresno, USA 2002 Marathon	3 (5 4)	0.131 0.134 0.137	0.0719 0.0720 0.0720	183 188 190	88 80% fruits ripe	curd	2	0.454 0.428	< 0.01 < 0.01	0.014 0.017
Hickman, Stanislaus, USA 2002 Greenbelt	3 (5 5)	0.138 0.135 0.133	0.0712 0.0712 0.0715	194 189 187	48	curd	2	0.218 0.317	< 0.01 < 0.01	< 0.01 < 0.01
Live Oak, Sutter, USA 2002 Greenbelt	3 (5 5)	0.132 0.131 0.132	0.0939 0.0927 0.0929	141 141 142	28	curd	2	0.511 0.690	< 0.01 < 0.01	< 0.01 < 0.01
Corvallis, Benton, USA 2002 Emerald Pride	3 (5 5)	0.136 0.137 0.136	0.0719 0.0718 0.0708	184 191 192	49	curd	2	0.207 0.206	< 0.01 < 0.01	< 0.01 < 0.01

Cauliflower

In 2005 a total of four supervised field trials were performed in the field in Northern Europe (Northern France, the Netherlands, Belgium and Germany). Fluopicolide SC (with propamocarb) was sprayed three times on cauliflower plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 450–600 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 9–10 days. Plot sizes were 33–60 m^2. The first treatment was conducted at BBCH 19–37, whilst the last application was carried out at BBCH 43–55 two weeks before the anticipated commercial harvest. In all trials, cauliflower samples (whole plant without roots, curd) were taken at day 0, day 14 and at day 21 after the last application, additional cauliflower samples were taken at day 3–4 and day 7 after the

last application. Residues of fluopicolide and its metabolites M-02 and M-01 were determined according to method 00782/M001 by HPLC-MS/MS. The LOQ for all three compounds was 0.01 mg/kg. The storage period of deep frozen samples ranged between 207 and 384 days.

Table 69 Results of residue trials conducted on cauliflower in Northern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Fondettes, France 2005 Fargo	3 (10 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	43	curd	0 4 7 14 21	0.01[a] 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.01 0.01 0.01 0.01 0.01	RA-2154/05 R 2005 0813 1 0813-05
Zwaagdijk-Oost, The Netherlands 2005 Freemont	3 (10 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	41	curd whole plant without roots	14 21 0	< 0.01 < 0.01 0.92	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2154/05 R 2005 0815 8 0815-05
Bornival, Belgium 2005 Thalassa	3 (9 10)	0.100 0.100 0.100	0.0222 0.0222 0.0222	450 450 450	43	curd	0 3 7 14 21	0.03 0.02 0.03 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 0.01 0.02 0.02	RA-2154/05 R 2005 0841 7 0841-05
Leichlingen, Germany 2005 Veronie F1	3 (10 10)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	55	curd whole plant without roots	14 21 0	< 0.01 < 0.01 0.26	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 0.02	RA-2154/05 R 2005 0842 5 0842-05

[a]5 mm rainfall starting 15 h after last spray

In 2005 a total of four supervised field trials were performed in the field in Southern Europe (Southern France, Greece, Spain and Italy). Fluopicolide SC (formulated with propamocarb) was sprayed three times on cauliflower plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 500–600 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 9–10 days. Plot sizes were 60–135 m^2. The first treatment was conducted at BBCH 37–41, whilst the last application was carried out at BBCH 45–47 two weeks before the anticipated commercial harvest. In all trials, cauliflower samples (whole plant without roots, curd) were taken at day 0, day 14 and at day 21 after the last application, additional cauliflower samples were taken at day 3 and day 7 after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M001 by HPLC-MS/MS. The LOQ for all three compounds was 0.01 mg/kg. The storage period of deep frozen samples ranged between 58 and 280 days.

Table 70 Results of residue trials conducted on cauliflower in the field in Southern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Fenouillet, France 2005 Aviron	3 (9 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	45	curd	0 3 7 14 21	0.01 0.02 0.02 <u>0.01</u> 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.02 0.02 0.02 0.02 0.02	RA-2155/05 R 2005 0816 6 0816-05
Kato Souli, Greece 2005 White Magic	3 (10 10)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	47	curd	0 14 21	0.15 <u>0.06</u> 0.04	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 0.01	RA-2155/05 R 2005 0817 4 0817-05

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Gava, Spain 2006 Flora Blanca	3 (10 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	41	curd whole plant without roots	7 14 20 0 3	0.10 <u>< 0.01</u> < 0.01 1.2 0.86	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.02 0.01 0.01 0.01	RA-2155/05 R 2005 0843 3 0843-05
Catania, Italy 2005 Violetto	3 (10 10)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	45	curd	0 14 21	0.33 <u>< 0.01</u> < 0.01	< 0.01 < 0.01 < 0.01	0.01 0.02 0.02	RA-2155/05 R 2005 0844 1 0844-05

Fruiting vegetables, Cucurbits

Cucumbers

In 2005 a total of eight supervised residue trials were performed in the greenhouse in Europe (Italy 2, Spain 2, Germany 2, Greece and Portugal) on cucumbers. Fluopicolide SC (formulated with propamocarb) was sprayed three times on cucumber plants with a water rate adapted to the height of the leafy surface of the plants. The nominal application rate was 1.0 L product/(ha × m plant height) and 750 L water/(ha × m plant height). Considering a plant height of 2 m this corresponds to a maximum fluopicolide use rate of 0.125 kg ai/ha per application. Plot sizes were 13–48 m^2. In six of the eight trials the maximum use rate was applied at the last treatment. In two trials the application rate at the last treatment was slightly lower due to the lower plant height but the deviation is less than 25%. The applications were carried out with a spray interval of 6–7 days. The first treatment was conducted at BBCH 65–73, whilst the last application was carried out at BBCH 72–89 one day before the anticipated commercial harvest. In all trials, cucumber samples (fruits) were taken at day 0 and at day 1 (the intended PHI) after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The LOQ for all three analytes was 0.01 mg/kg. The storage period of deep frozen samples ranged between 362 and 554 days.

Table 71 Results of residue trials conducted on cucumbers in the greenhouse in Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Santa Croce Camerina, Italy 2005 Solverde	3 (7 7)	0.119 0.119 0.119	0.00831 0.00831 0.00831	1425 1425 1425	89	fruit	0 1	0.04 <u>0.04</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2162/05 R 2005 0834 4 0834-05
Molfetta, Italy 2005 Locale di Polignano	3 (7 7)	0.0938 0.125 0.125	0.00831 0.00831 0.00831	1125 1500 1500	76	fruit	0 1	0.03 <u>0.02</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2162/05 R 2005 0861 1 0861-05
Puebla de Vicar, Spain 2005 Argos	3 (7 7)	0.125 0.125 0.125	0.00831 0.00831 0.00831	1500 1500 1500	74	fruit	0 1	0.06 <u>0.04</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2162/05 R 2005 0863 8 0863-05
Sanlucar de Barrameda, Spain 2005 Alanis F1 Hibrido	3 (7 6)	0.104 0.100 0.1125	0.00831 0.00831 0.00831	975 1200 1350	89	fruit	0 1	0.04 <u>0.03</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2162/05 R 2005 0864 6 0864-05

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Vasilika, Greece 2005 Z14	3 (7 7)	0.0906 0.112 0.125	0.00831 0.00831 0.00831	1088 1350 1500	83	fruit	0 1	0.12 <u>0.09</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2162/05 R 2005 0865 4 0865-05
Leichlingen, Germany 2005 Aramon	3 (7 7)	0.100 0.125 0.125	0.00831 0.00831 0.00831	1200 1500 1500	72	fruit	0 1	0.05 <u>0.03</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2162/05 R 2005 0866 2 0866-05
Leichlingen, Germany 2005 Indira	3 (7 7)	0.112 0.125 0.125	0.00831 0.00831 0.00831	1350 1500 1500	73	fruit	0 1	0.03 <u>0.02</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2162/05 R 2005 0867 0 0867-05
Torres Vedras, Portugal 2005 Caman	3 (7 7)	0.0625 0.0831 0.125	0.00831 0.00831 0.00831	750 998 1500	87	fruit	0 1	0.09 <u>0.08</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2162/05 R 2005 0868 9 0868-05

In 2005 a total of four supervised field trials were performed in the field in Northern Europe (Germany and Belgium) on cucumbers. Fluopicolide SC (formulated with propamocarb) was sprayed three times on cucumber plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 300–600 L/ha using knapsack sprayers and wheelbarrow sprayers. The applications were carried out with a spray interval of 6–8 days. Plot sizes were 20–56 m^2.

The first treatment was conducted at BBCH 61–67, whilst the last application was carried out at BBCH 71–88, three days before the anticipated commercial harvest. In all trials, cucumber samples (fruits) were taken at day 0, 1 and at day 3 (the intended PHI) after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The LOQ for all three analytes was 0.01 mg/kg. The storage period of deep frozen samples ranged between 434 and 476 days.

Table 72 Results of residue trials conducted on cucumbers in the field in Northern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Düren–Eichtz, Germany 2005 Capra	3 (6 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	71	fruit	0 1 3	0.14[a] 0.03 <u>0.02</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2160/05 R 2005 0826 3 0826-05
Villers-Perwin, Belgium 2005 Comichon vert	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	88	fruit	0 1 3	0.04 [b] 0.03 <u>0.02</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2160/05 R 2005 0854 9 0854-05
Langenfeld-Reusrath, Germany 2005 Melody	3 (7 7)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	74	fruit	0 1 3	0.08 0.04 <u>0.03</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2160/05 R 2005 0856 5 0856-05

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Ruchheim, Germany 2005 Verona	3 (8 6)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	77	fruit	0 1 3	0.13 0.11 <u>0.08</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2160/05 R 2005 1032 2 1032-05

[a] 3 mm rainfall starting 6 h after last spray

[b] 4 mm rainfall starting 3 h after last spray

During the 2002 growing season, a total of six trials were performed on cucumbers in the field in different locations in the USA. Fluopicolide was formulated as a suspension concentrate. Three foliar spray applications of fluopicolide were made 3–6 days apart to each treated plot at a target rate of 0.133 kg ai/ha in spray volumes ranging from 156 to 189 L/ha using backpack or tractor mounted boom sprayers. Plot sizes were 56–186 m^2. Mature cucumber samples were harvested 2 days after the last application. In addition, at one test site, cucumber samples were also harvested at 1, 3, 5, and 7 PHI to determine residue decline over time. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to Method 00782/001 (LOQ 0.01 mg/kg for each analyte). Cucumber samples in this study were frozen a maximum of 597 days (20 months) prior to extraction.

Table 73 Results of residue trials conducted with fluopicolide on cucumber in the USA (02CU27779) (SC formulation).

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Rose Hill, NC USA 2002 Poinsett 76	3 (5 5)	0.135 0.135 0.136	0.0722 0.072 0.0751	186 186 180	74	fruit	2	0.016 <u>0.031</u>	< 0.01 < 0.01	< 0.01 < 0.01
Tifton, GA USA 2002 General Lee	3 (5 5)	0.131 0.133 0.127	0.0766 0.0766 0.0732	171 174 173	71	fruit	1 2 3 5 7	0.014 0.024 <u>0.013</u> < 0.01 < 0.01 < 0.01 0.011 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Madison, FL USA 2002 Straight Eight	3 (5 5)	0.133 0.133 0.132	0.0766 0.0783 0.0768	174 170 172	72	fruit	2	<u>0.016</u> 0.011	< 0.01 < 0.01	< 0.01 < 0.01
Wyoming, IL USA 2002 Indy F1	3 (3 6)	0.133 0.136 0.132	0.0848 0.0868 0.0846	157 156 156	73	fruit	2	0.024 <u>0.029</u>	< 0.01 < 0.01	< 0.01 < 0.01
Conklin, MI USA 2002 Marketmore 76	3 (5 5)	0.132 0.131 0.132	0.0703 0.0715 0.0703	188 183 188	73	fruit	2	<u>0.028</u> 0.015	< 0.01 < 0.01	< 0.01 < 0.01
Brookshire, TX USA 2002 Straight Eight	3 (5 6)	0.135 0.132 0.136	0.0719 0.0700 0.0721	187 189 188	85	fruit	2	<u>0.057</u> 0.043	< 0.01 < 0.01	< 0.01 < 0.01

Adjuvants (spreader/wetters) were added: NuFilm (Rose Hill, Conklin), Latron (Tifton, Madison) and Bond (Wyoming, Brookshire).

Zucchini

In 2005 a total of four supervised field trials were performed in the field in Southern Europe (Italy (2), Greece and Spain) on zucchini. Fluopicolide SC (formulated with propamocarb) was sprayed three times on zucchini plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 500–700 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 7 days. Plot sizes were 72–120 m^2. The first treatment was conducted at BBCH 63–81, whilst the last application was carried out at BBCH 76–83 three days before the anticipated commercial harvest. In all trials, zucchini samples (fruits) were taken at day 0, 1 and at day 3 (the intended PHI) after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The LOQ for all three compounds was 0.01 mg/kg. The storage period of deep frozen samples ranged between 503 and 534 days.

Table 74 Results of residue trials conducted on zucchini in the field in Southern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Ladispoli, Italy 2005 Nettuno	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	76	fruit	0 1 3	0.10 0.06 <u>0.03</u>	< 0.01 < 0.01 < 0.01	< 0.01 0.01 0.01	RA-2161/05 R 2005 0827 1 0827-05
Kato Souli, Greece 2005 Otto	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	81	fruit	0 1 3	0.11 0.07 <u>0.03</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2161/05 R 2005 0857 3 0857-05
Vilanova del Vallés, Spain 2005 Sophia	3 (7 7)	0.100 0.100 0.100	0.0143 0.0143 0.0143	700 700 700	83	fruit	0 1 3	0.08[a] 0.05 <u>0.01</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2161/05 R 2005 0858 1 0858-05
Andria, Italy 2005 President	3 (7 7)	0.100 0.100 0.100	0.0143 0.0143 0.0143	700 700 700	83	fruit	0 1 3	0.14 0.11 <u>0.08</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2161/05 R 2005 0860 3 0860-05

[a] 1.2 mm rainfall starting 8 h after the last spray

Squash

During the 2002 growing season, a total of six trials were performed on squash in the field in different locations in the USA. The test substance Fluopicolide was formulated as a suspension concentrate. Three foliar spray applications of fluopicolide were made 3–6 days apart to each treated plot at a target rate of 0.133 kg ai/ha in spray volumes ranging from 142 to 217 L/ha using backpack and tractor mounted sprayers. Plot sizes were 56–372 m^2. Mature squash samples were harvested 2 days after the last application. For all trials, two treated and one control RAC sample were collected at this sampling interval. In addition, at one test site, squash samples were also harvested at 1, 3, 5, and 7 PHI to determine residue decline over time. Two treated samples were collected at these additional sampling intervals. Residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to method 00782/001 (LOQ was 0.01 mg/kg for each analyte). Squash samples in this study were frozen a maximum of 624 days (21 months) prior to extraction.

Table 75 Results of residue trials conducted with fluopicolide on squash in the USA (02CU27824) (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Germansville, PA USA 2002 Superpik	3 (6 4)	0.135 0.136 0.135	0.0625 0.0625 0.0625	215 217 215	73	fruit	2	0.039 <u>0.051</u>	< 0.01 < 0.01	< 0.01 < 0.01
Rose Hill, NC USA 2002 Early Prolific Straightneck	3 (5 5)	0.133 0.135 0.132	0.0716 0.0719 0.0732	186 187 180	72	fruit	2	<u>0.014</u> 0.014	< 0.01 < 0.01	0.017 0.018
Enigma, GA USA 2002 Early Prolific	3 (5 5)	0.131 0.133 0.132	0.0766 0.0735 0.0752	171 181 176	72	fruit	1 2 3 5 7	0.032 0.018 0.017 0.027 <u>0.057</u> 0.021 0.011 0.019 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.024 0.010 0.021 0.031 0.040 0.015 0.027 < 0.01 < 0.01
Madison, FL USA 2002 Senator	3 (3 6)	0.135 0.135 0.133	0.0831 0.0753 0.0732	162 179 182	88	fruit	2	0.034 <u>0.042</u>	< 0.01 < 0.01	< 0.01 0.011
Wyoming, IL USA 2002 Revenue F1	3 (5 5)	0.133 0.135 0.132	0.0854 0.0871 0.0846	156 154 156	73	fruit	2	<u>0.040</u> 0.035	< 0.01 < 0.01	< 0.01 < 0.01
Live Oak, CA USA 2002 Yellow Straightneck	3 (5 5)	0.137 0.138 0.137	0.0961 0.0957 0.0955	142 144 143	73	fruit	2	0.019 <u>0.030</u>	< 0.01 < 0.01	< 0.01 < 0.01

Adjuvants (spreader/wetters) were added: NuFilm (Rose Hill, Live Oak), Latron (Enigma, Madison) and Bond (Germansville, Wyoming).

Melon

In 2005 a total of eight supervised residue trials were performed in the greenhouse in Europe (Italy 2, Southern France 2, the Netherlands, Spain 2 and Portugal) on melon. Fluopicolide SC (formulated with propamocarb) was sprayed three times on melon plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 600–1000 L/ha per application with knapsack sprayers. The applications were carried out with a spray interval of 4–5 days. Plot sizes were 24–264 m^2. The first treatment was conducted at BBCH 71–79, whilst the last application was carried out at BBCH 78–89 three days before the anticipated commercial harvest. In all trials, melon samples (whole fruit) were taken at day 0, 3 (the intended PHI) and at day 7 after the last application. Subsamples from day 3 and 7 from each trial were separated into peel and pulp and both matrices analysed separately. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The LOQ for all three compounds was 0.01 mg/kg. The storage period of deep frozen samples ranged from 520 to 578 days.

Table 76 Results of residue trials conducted on melon in the greenhouse in Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Molfetta, Italy 2005 Proteo	3 (5 5)	0.100 0.100 0.100	0.010 0.010 0.010	1000 1000 1000	82	fruit	0 3 7	0.05 0.05 0.03	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2119/05 R 2005 0609 0 0609-05

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
						peel	3	0.16	< 0.01	< 0.01	
							7	0.13	< 0.01	< 0.01	
						pulp	3	< 0.01	< 0.01	< 0.01	
							7	< 0.01	< 0.01	< 0.01	
Monte Algaida Sanlucar de Barrameda, Spain 2005 Liseta F1 hibrido	3 (5 5)	0.100 0.100 0.100	0.010 0.010 0.010	1000 1000 1000	87	fruit	0 3 7	0.07 0.08 0.08	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2119/05 R 2005 0610 4 0610-05
						peel	3	0.19	< 0.01	< 0.01	
							7	0.16	< 0.01	< 0.01	
						pulp	3	< 0.01	< 0.01	< 0.01	
							7	< 0.01	< 0.01	< 0.01	
Rockanje, The Netherlands 2005 Haon	3 (5 5)	0.100 0.100 0.100	0.010 0.010 0.010	1000 1000 1000	81	fruit	0 3 7	0.04 0.04 0.04	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2119/05 R 2005 0611 2 0611-05
						peel	3	0.06	< 0.01	< 0.01	
							7	0.06	< 0.01	< 0.01	
						pulp	3	< 0.01	< 0.01	< 0.01	
							7	0.01	< 0.01	< 0.01	
Vacquiers, France 2005 Anasta F1	3 (5 5)	0.100 0.100 0.100	0.010 0.010 0.010	1000 1000 1000	87	fruit	0 3 7	0.04 0.08 0.03	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2119/05 R 2005 0612 0 0612-05
						peel	3	0.16	< 0.01	< 0.01	
							7	0.17	< 0.01	< 0.01	
						pulp	3	< 0.01	< 0.01	< 0.01	
							7	< 0.01	< 0.01	< 0.01	
Torres Vedras, Portugal 2005 Galias	3 (5 4)	0.100 0.100 0.107	0.01669 0.01669 0.01669	600 600 642	78	fruit	0 3 7	0.05 0.03 0.02	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2119/05 R 2005 0613 9 0613-05
						peel	3	0.11	< 0.01	< 0.01	
							7	0.08	< 0.01	< 0.01	
						pulp	3	< 0.01	< 0.01	< 0.01	
							7	< 0.01	< 0.01	< 0.01	
Monteux, France 2005 Fidji	3 (5 5)	0.100 0.100 0.100	0.010 0.010 0.010	1000 1000 1000	89	fruit	0 3 7	< 0.01 0.01 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2119/05 R 2005 0614 7 0614-05
						peel	3	0.04	< 0.01	< 0.01	
							7	0.02	< 0.01	< 0.01	
						pulp	3	< 0.01	< 0.01	< 0.01	
							7	< 0.01	< 0.01	< 0.01	
Puebla de Vicar-Almeria, Spain 2005 Magenta	3 (5 5)	0.100 0.100 0.100	0.010 0.010 0.010	1000 1000 1000	81	fruit	0 3 7	0.05 0.03 0.02	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2119/05 R 2005 0615 5 0615-05
						peel	3	0.09	< 0.01	< 0.01	
							7	0.05	< 0.01	< 0.01	
						pulp	3	< 0.01	< 0.01	< 0.01	
							7	< 0.01	< 0.01	< 0.01	

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Zapponeta, Italy 2005 Proteo	3 (5 5)	0.100 0.100 0.100	0.010 0.010 0.010	1000 1000 1000	81	fruit	0 3 7	0.09 0.08 0.08	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2119/05 R 2005 0616 3 0616-05
						peel	3 7	0.21 0.35	< 0.01 < 0.01	< 0.01 < 0.01	
						pulp	3 7	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	

Plant densities were 11.1 k plants/ha, 22.7, 18.7, 13.9, 27.8, 13.3, 10 and 6.25 respectively.

In 2005 and 2006 a total of eight supervised residue trials were performed in the field in Southern Europe (Italy 2, Greece, Spain 3 and Portugal 2) on melon. Fluopicolide SC (formulated with propamocarb) was sprayed three times on melon plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 282–1000 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 5–7 days. Plot sizes were 60–488 m^2 for trials conducted in 2005 and 60–150 m^2 in 2006. The first treatment was conducted at BBCH 71–87, whilst the last application was carried out at BBCH 81–89, three days before the anticipated commercial harvest. In all trials, melon samples (whole fruit) were taken at day 0, and at day 3 (the intended PHI) after the last application. Subsamples from day 3 from each trial were separated into peel and pulp and both matrices analysed separately. In the 2005 trials additional samples were taken at day 7 after the last treatment. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The LOQ for all three molecules was 0.01 mg/kg for melon whole fruit, pulp and peel. The storage period of deep frozen samples ranged from 217 to 536 days.

Table 77 Results of residue trials conducted on melon in the field in Southern Europe (Sc formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Bologna, Italy 2005 Summer dream	3 (5 5)	0.100 0.100 0.100	0.010 0.010 0.010	1000 1000 1000	82	fruit	0 3 7	0.05 0.03 0.03	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2137/05 R 2005 0711 9 0711-05
						peel	3 7	0.06 0.06	< 0.01 < 0.01	< 0.01 < 0.01	
						pulp	3 7	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	
Alginet, Spain 2005 Sirio	3 (5 5)	0.100 0.100 0.100	0.0125 0.0125 0.0125	800 800 800	81	fruit	0 3 7	0.03 0.02 0.03	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2137/05 R 2005 0712 7 0712-05
						peel	3 7	0.04 0.05	< 0.01 < 0.01	< 0.01 < 0.01	
						pulp	3 7	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	
Can Cartro–Subirats, Spain 2005 Ruidera	3 (5 5)	0.094 0.100 0.100	0.0333 0.0333 0.0333	282 300 300	83	fruit	0 3 7	0.10 0.08 0.05	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2137/05 R 2005 0713 5 0713-05
						peel	3 7	0.22 0.21	< 0.01 < 0.01	< 0.01 < 0.01	
						pulp	3 7	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Caniceira-Vale de Cavalos, Portugal 2005 Branco do Ribatejo	3 (5 5)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	81	fruit peel pulp	0 3 7 3 7 3 7	0.04 0.04 0.02 0.07 0.04 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2137/05 R 2005 0714 3 0714-05 GLP yes 2005
Manfredonia, Italy 2006 Proteo	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	85	fruit peel pulp	0 3 3 3	0.030 0.02 0.10 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	RA-2301/06 R 2006 0075 5 0075-06
Gavà, Spain 2006 Seda	3 (7 7)	0.100 0.100 0.100	0.0125 0.0125 0.0111	800 800 900	89	fruit peel pulp	0 3 3 3	0.09 0.07 0.12 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	0.01 < 0.01 0.01 0.02	RA-2301/06 R 2006 0076 3 0076-06
Foros de Salva-terra, Portugal 2006 Leziria	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	87	fruit peel pulp	0 3 3 3	0.04 0.03 0.05 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	RA-2301/06 R 2006 0077 1 0077-06
Aronas–Pieria, Greece 2006 Velos F1	3 (7 7)	0.100 0.100 0.100	0.020 0.020 0.020	500 500 500	88	fruit peel pulp	0 3 3 3	0.06 0.10 0.14 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	RA-2301/06 R 2006 0079 8 0079-06

Planting densities for trials in 2006 were 7.1 k plants/ha, 5.3, 6.7 and 4.0 respectively.

During the 2002 growing season, a total of nine trials were performed on melons (cantaloupe) in the field in different locations in the USA. Fluopicolide was formulated as a suspension concentrate formulation. Three foliar spray applications of fluopicolide were made 5–6 days apart to each treated plot at a target rate of 0.133 kg ai/ha in spray volumes ranging from 141 to 193 L/ha. Application was by boom sprayers (backpack, or bicycle, ATV and tractor mounted). Plot sizes were 56–279 m^2. Mature melon samples were harvested 2 days after the last application (DALA). In addition, at one test site, melon samples were also harvested at 1, 3, 5, and 7 DALA to determine residue decline over time. Two treated samples were collected at these additional sampling intervals. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to method 00782/001. The LOQ was 0.01 mg/kg for each analyte. Melon samples in this study were frozen a maximum of 560 days (19 months) prior to extraction.

Table 78 Results of residue trials conducted with fluopicolide on melon in the USA (02CU27825) (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Jamesville, NC USA 2002 (cantaloupe) Ambrosia	3 (5 5)	0.135 0.133 0.131	0.0803 0.0775 0.0796	167 172 165	79	fruit	2	0.043 <u>0.069</u>	< 0.01 < 0.01	< 0.01 < 0.01
Carlyle, IL USA 2002 (cantaloupe) Hales Best	3 (5 5)	0.137 0.135 0.131	0.0855 0.0846 0.0876	160 159 150	73	fruit	2	<u>0.053</u> 0.048	< 0.01 < 0.01	< 0.01 < 0.01

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Brookshire, TX USA 2002 (cantaloupe) Hales Best	3 (5 5)	0.135 0.136 0.133	0.0698 0.0725 0.0709	193 187 188	86	fruit	2	0.066 0.040	< 0.01 < 0.01	< 0.01 < 0.01
East Bernard, TX USA 2002 (cantaloupe) TAM Uvalde	3 (5 5)	0.135 0.131 0.133	0.0831 0.0805 0.0739	162 163 180	82	fruit	2	0.030 0.060	< 0.01 < 0.01	< 0.01 < 0.01
Fresno, CA USA 2002 (cantaloupe) Top Mark	3 (5 5)	0.135 0.135 0.132	0.0715 0.0721 0.0716	188 183 186	88	fruit	2	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
Porterville, CA USA 2002 (cantaloupe) Hales Best Jumbo	3 (5 5)	0.133 0.133 0.132	0.0702 0.0707 0.0700	190 187 189	89	fruit	2	0.040 0.057	< 0.01 < 0.01	< 0.01 < 0.01
Live Oak, CA USA 2002 (cantaloupe) Ambrosia	3 (5 5)	0.132 0.133 0.132	0.0924 0.0944 0.0930	143 141 142	88	fruit	2	0.080 0.098	< 0.01 < 0.01	< 0.01 < 0.01
Westmoreland, CA USA 2002 (cantaloupe) Impact	3 (5 5)	0.131 0.132 0.131	0.0714 0.0710 0.0704	184 186 186	85	fruit	1 2 3 5 7	0.280 0.136 < 0.01 0.163 0.092 0.034 0.297 0.147 0.232 0.115	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Maricopa, USA AZ 2002 (cantaloupe) Esteem	3 (5 5)	0.134 0.132 0.135	0.0714 0.0707 0.0712	194 187 189	88	fruit	2	0.104 0.258	< 0.01 < 0.01	< 0.01 < 0.01

Adjuvants (stickers/wetters) were added to tank mixes: Bond (Jamesville, Brookshire, East Bernard), NuFilm (Carlyle, Fresno, Porterville, Live Oaks, Maricopa) and FirstChoice (Westmoreland)

Fruiting vegetables, other than Cucurbits

Tomatoes

Six outdoor trials were performed on tomato plants in 2003 in Brazil. Fluopicolide, formulated as a SC formulation, was sprayed six times on tomatoes with a single treatment rate of 0.144 kg ai/ha or 0.288 kg ai/ha. The applications were carried out with a spray interval of 7 days. Plot sizes were 18–30 m^2. The last application was carried out at BBCH 71-89, 7 days before the anticipated commercial harvest. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to method 00782/001. The LOQ was 0.01 mg/kg. The storage period of deep frozen samples ranged between 571 and 657 days.

Table 79 Results of residue trials conducted with fluopicolide in/on tomatoes in Brazil (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Sales de Oliveira–SP, Brazil 2003 Rio Grande	6	0.144 0.144 0.144 0.144 0.144 0.144	0.0144 0.0144 0.0144 0.0144 0.0144 0.0144	1000 1000 1000 1000 1000 1000	75	fruit	0 2 5 7 10	0.78 0.35 0.11 < 0.01 < 0.01	< 0.01 0.09 0.13 0.04 0.01	< 0.01 0.10 0.21 0.05 0.03	UNESP RA-908/05 FR03BRA002 BRA-FR03BRA002-C1-A
Sales de Oliveira–SP, Brazil 2003 Rio Grande	6	0.288 0.288 0.288 0.288 0.288 0.288	0.0288 0.0288 0.0288 0.0288 0.0288 0.0288	1000 1000 1000 1000 1000 1000	75	fruit	7	0.02	0.06	0.08	UNESP RA-908/05 FR03BRA002 BRA-FR03BRA002-C1-B
Paulinia–SP, Brazil 2003 Rio Grande	6	0.144 0.144 0.144 0.144 0.144 0.144	0.0144 0.0144 0.0144 0.0144 0.0144 0.0144	1000 1000 1000 1000 1000 1000	81	fruit	7	< 0.01	0.03	0.05	UNESP RA-909/05 FR03BRA002 BRA-FR03BRA002-P1-A
Paulinia–SP, Brazil 2003 Rio Grande	6	0.288 0.288 0.288 0.288 0.288 0.288	0.0288 0.0288 0.0288 0.0288 0.0288 0.0288	1000 1000 1000 1000 1000 1000	81	fruit	7	0.02	0.06	0.07	UNESP RA-909/05 FR03BRA002 BRA-FR03BRA002-P1-B
Hidrolandia–GO, Brazil 2003 Jumbo	6	0.144 0.144 0.144 0.144 0.144 0.144	0.0144 0.0144 0.0144 0.0144 0.0144 0.0144	1000 1000 1000 1000 1000 1000	89	fruit	7	< 0.01	0.03	0.04	UNESP RA-910/05 FR03BRA002 BRA-FR03BRA002-P2-A
Hidrolandia–GO, Brazil 2003 Jumbo	6	0.288 0.288 0.288 0.288 0.288 0.288	0.0288 0.0288 0.0288 0.0288 0.0288 0.0288	1000 1000 1000 1000 1000 1000	89	fruit	7	0.02	0.05	0.08	UNESP RA-910/05 FR03BRA002 BRA-FR03BRA002-P2-B

In 2005 a total of eight supervised residue trials were performed in the greenhouse in Europe (Greece, Italy, Germany 2, Spain, the Netherlands, Southern France and Belgium) on tomatoes. Fluopicolide SC (with propamocarb) was sprayed three times on tomato plants with a water rate adapted to the height of the leafy surface of the plants. The nominal application rate was 1.05 L product/(ha × m plant height) and 750 L water/(ha × m plant height). Considering a plant height of 2 m this corresponds to a maximum fluopicolide use rate of 0.131 kg ai/ha per application. The applications were carried out with a spray interval of 7 days. Application was by knapsack sprayers to

plot sizes 13–30 m^2. The first treatment was conducted at BBCH 71–81, whilst the last application was carried out at BBCH 74–83, one day before the anticipated commercial harvest. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The LOQ for all three molecules was 0.01 mg/kg for tomato fruits. The storage period of deep frozen samples ranged between 115 and 286 days.

Table 80 Results of residue trials conducted on tomatoes in the greenhouse in Europe (SC formulation).

	N	kg ai/ha	kg ai/hL		GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Esovalta, Greece 2005 Alma	3 (7 7)	0.0984 0.131 0.1313	0.00875 0.00875 0.00875	1125 1500 1500	83	fruit	0 1	0.086 <u>0.085</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2113/05 R 2005 0574 4 0574-05
Giovinazzo, Italy 2005 Piccadilly	3 (7 7)	0.131 0.131 0.131	0.00875 0.00875 0.00875	1500 1500 1500	83	fruit	0 1	0.19 <u>0.21</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2113/05 R 2005 0575 2 0575-05
St. Climent de Llobregat, Spain 2005 Juri	3 (7 7)	0.131 0.131 0.131	0.00875 0.00875 0.00875	1500 1500 1500	83	fruit	0 1	0.15 <u>0.14</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2113/05 R 2005 0576 0 0576-05
Wervershoof, The Netherlands 2005 Espero	3 (7 7)	0.131 0.131 0.131	0.00875 0.00875 0.00875	1500 1500 1500	82	fruit	0 1	0.065 <u>0.063</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2113/05 R 2005 0577 9 0577-05
Langenfeld, Germany 2005 Rogella	3 (7 7)	0.131 0.131 0.131	0.00875 0.00875 0.00875	1500 1500 1500	76	fruit	0 1	0.15 <u>0.093</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2113/05 R 2005 0578 7 0578-05
Euskirchen–DomEsch, Germany 2005 Mikano	3 (7 7)	0.131 0.131 0.131	0.00875 0.00875 0.00875	1500 1500 1500	81	fruit	0 1	0.32 <u>0.18</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2113/05 R 2005 0579 5 0579-05
St Remy de Provence, France 2005 Myriade	3 (7 7)	0.118 0.115 0.118	0.00875 0.00875 0.00875	1350 1313 1350	74	fruit	0 1	0.19 <u>0.20</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2113/05 R 2005 0580 9 0580-05
Villers-Perwin, Belgium 2005 Paola	3 (7 7)	0.0984 0.0984 0.0984	0.00875 0.00875 0.00875	1125 1125 1125	74	fruit	0 1	0.080 <u>0.080</u>	< 0.01 < 0.01	< 0.01 < 0.01	RA-2113/05 R 2005 0581 7 0581-05

Plant densities were 35.7, 33.3, 35.7, 40, 27.8, 10, 16.7 and 25 k plants/ha respectively

In 2005 a total of four supervised field trials were performed in the field in Northern Europe (Germany 2 and Northern France 2) on tomatoes. Fluopicolide SC (with propamocarb) was sprayed three times on tomato plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 500–750 L/ha per application. The applications were carried out with a spray interval of 7 days using knapsack sprayers. Plot sizes were 22–40 m^2. The first treatment was conducted at BBCH 65–81, whilst the last application was carried out at BBCH 72–85, three days before the anticipated commercial harvest. In all trials, tomato samples (fruits) were taken at day 0, 1 and at day 3 (the intended PHI) after the last

application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The storage period of deep frozen samples ranged between 172 and 198 days.

Table 81 Results of residue trials on tomatoes in the field in Northern Europe (SC formulation).

Loaction, year, variety	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	Reference
Langenfeld-Reusrath, Germany 2005 Matina	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	72	fruit	0 1 3	0.19 0.16 <u>0.23</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2114/05 R 2005 0582 5 0582-05
Langenfeld-Reusrath, Germany 2005 Harzfeuer	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	81	fruit	0 1 3	0.16 0.26 <u>0.22</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2114/05 R 2005 0583 3 0583-05
Fondettes, France 2005 Hector	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	85	fruit	0 1 3	0.069 0.037 <u>0.015</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2114/05 R 2005 0584 1 0584-05
Mâcon, France 2005 Pyros hybride F1	3 (7 7)	0.100 0.100 0.100	0.0133 0.0133 0.0133	750 750 750	84	fruit	0 1 3	0.16 0.12 <u>0.14</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2114/05 R 2005 0586 8 0586-05

In 2005 a total of four supervised field trials were performed in the field in Southern Europe (Greece, Italy, Spain and Portugal) on tomatoes. Fluopicolide SC (with propamocarb) was sprayed three times on tomato plants with a nominal rate of 0.1 kg ai/ha and spray volumes of 500–1060 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 6–7 days. Plot sizes were 15–45 m^2. The first treatment was conducted at BBCH 78–84, whilst the last application was carried out at BBCH 86–87, three days before the anticipated commercial harvest. In all trials, tomato samples (fruits) were taken at day 0, 1 and at day 3 (the intended PHI) after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The storage period of deep frozen samples ranged between 164 and 244 days.

Table 82 Results of residue trials conducted on tomatoes in the field in Southern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Katerini, Greece 2005 Gali	3 (7 7)	0.100 0.100 0.100	0.010 0.010 0.010	1000 1000 1000	86	fruit	0 1 3	0.20 0.036 <u>0.019</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2115/05 R 2005 0587 6 0587-05
Bologna, Italy 2005 Darck	3 (7 7)	0.100 0.100 0.100	0.010 0.010 0.010	1000 1000 1000	87	fruit	0 1 3	0.15 0.11 <u>0.046</u>	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2115/05 R 2005 0588 4 0588-05

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Lebrija Sevilla, Spain 2005 Elegy	3 (6 7)	0.100 0.109 0.100	0.010 0.010 0.010	1000 1090 1000	87	fruit	0 1 3	0.29 0.16 0.14	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2115/05 R 2005 0589 2 0589-05
Almeirim, Portugal 2005 H-9665	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	87	fruit	0 1 3	0.12 0.11 0.055	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2115/05 R 2005 0590 6 0590-05

In 2006 a total of four supervised field trials were performed in the field in Southern Europe (Southern France, Italy, Spain and Portugal) on tomatoes according to the critical GAP in this region. Fluopicolide SC (with propamocarb) was sprayed three times on tomato plants with a nominal rate of 0.131 kg ai/ha and spray volumes of 600–1080 L/ha per application using knapsack sprayers. The applications were carried out with a spray interval of 7–10 days. Plot areas were 15–50 m^2. The first treatment was conducted at BBCH 81–85, whilst the last application was carried out at BBCH 85–88, three days before the anticipated commercial harvest. In all trials, tomato samples (fruits) were taken at day 0 and at day 3 (the intended PHI) after the last application. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The storage period of deep frozen samples ranged between 136 and 179 days for fluopicolide and its metabolites.

Table 83 Results of residue trials conducted on tomatoes in the field in Southern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02	
Bari, Italy 2006 Leader	3 (7 7)	0.131 0.131 0.131	0.0131 0.0131 00131	1000 1000 1000	85	fruit	0 3	0.22 0.10	< 0.01 < 0.01	< 0.01 < 0.01	RA-2300/06 R 2006 0103 4 0103-06
Gava, Spain 2006 Virena	3 (9 10)	0.131 0.131 0.142	0.0131 0.0131 0.0131	1000 1000 1080	86	fruit	0 3	0.09 0.05	< 0.01 < 0.01	< 0.01 < 0.01	RA-2300/06 R 2006 0104 2 0104-06
Boé, France 2006 Perfect Peel	3 (7 7)	0.131 0.131 0.131	0.0219 0.0219 0.0219	600 600 600	88	fruit	0 3	0.11 0.09	< 0.01 < 0.01	< 0.01 < 0.01	RA-2300/06 R 2006 0105 0 0105-06
Foros de Salvaterra, Portugal 2006 H9144	3 (7 7)	0.131 0.131 0.131	0.0175 0.0175 0.0175	750 750 750	88	fruit	0 3	0.25 0.28	< 0.01 < 0.01	< 0.01 < 0.01	RA-2300/06 R 2006 0106 9 0106-06

Plant densities were 21.7, 10, 28.4 and 44.4 k plants/ha

During the 2001 growing season, a total of nine trials were performed on tomatoes and an additional three trials on cherry tomatoes in the field in different locations in the USA. Fluopicolide was formulated as a suspension concentrate nominally containing 480 g ai/L. Three foliar spray applications of fluopicolide were made 5–6 days apart to each treated plot at a target rate of 133 g ai/ha in spray volumes ranging from 186 to 424 L/ha using boom sprayers (backpack or tractor mounted). Plot sizes were 93–170 m^2. Mature tomato samples were harvested 2 days after the last

application. In addition, at two test sites, tomato samples were also harvested at 1, 3, 5, and 7 PHIs to determine residue decline over time. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to Method 00782 (LOQ 0.01 mg/kg for each analyte). M-02 was determined as the methyl ester (AE 0915899) after derivatisation of the free acid moiety with methanol/sulphuric acid and a clean up step. Tomato samples in this study were frozen a maximum of 646 days prior to extraction.

Table 84 Results of residue trials conducted with fluopicolide on tomato in the USA (01CU27776) (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Hamburg PA, USA 2001 Better Boy	3 (5 5)	0.1376 0.1351 0.1399	0.04700 0.04612 0.04523	292.8 293.0 309.4		Fruit	2	0.20 <u>0.28</u>	< 0.01 < 0.01	< 0.01 < 0.01
Elko SC, USA 2001 Celebrity	3 (5 5)	0.1333 0.1330 0.1332	0.04628 0.04572 0.04506	288.1 290.9 295.7		Fruit	2	<u>0.19</u> 0.19	< 0.01 < 0.01	< 0.01 < 0.01
Quincy FL, USA 2001 Mountain Spring	3 (5 5)	0.1337 0.1349 0.1327	0.05104 0.05480 0.05261	261.9 246.2 252.2		Fruit	2	<u>0.053</u> 0.041	< 0.01 < 0.01	< 0.01 < 0.01
Quincy FL, USA 2001 (cherry) BHN 286	3 (5 5)	0.1348 0.1356 0.1329	0.04583 0.04305 0.04581	294.1 314.9 290.1		Fruit	2	<u>0.17</u> 0.17	< 0.01 < 0.01	< 0.01 < 0.01
Conklin MI, USA 2001 Sun STX 7705	3 (5 5)	0.1331 0.1333 0.1341	0.04670 0.04646 0.04701	285.0 287.0 285.3		Fruit	2	<u>0.15</u> 0.13	< 0.01 < 0.01	< 0.01 < 0.01
Visalia CA, USA 2001 Haley 3155	3 (5 5)	0.1336 0.1329 0.1331	0.03151 0.03203 0.03265	423.9 414.9 407.7		Fruit	2	<u>0.081</u> 0.058	< 0.01 < 0.01	< 0.01 < 0.01
Five Points CA, USA 2001 Sun Seed 6117	3 (5 5)	0.1327 0.1326 0.1340	0.04718 0.04719 0.04848	281.2 280.9 276.4		Fruit	2	0.083 <u>0.10</u>	< 0.01 < 0.01	< 0.01 < 0.01
Live Oak CA, USA 2001 8892	3 (5 5)	0.1333 0.1329 0.1332	0.07174 0.07128 0.07136	185.9 186.4 186.7		Fruit	1 2 3 5 7	0.19 0.19 <u>0.19</u> 0.13 0.15 0.12 0.12 0.14 0.14 0.10	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 0.013 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Visalia CA, USA 2001 Ace 55 VF	3 (5 5)	0.1331 0.1337 0.1336	0.03149 0.03204 0.03266	422.7 417.2 408.9		Fruit	1 2 3 5 7	0.046 0.036 0.015 <u>0.062</u> 0.022 0.032 < 0.01 0.011 0.013 0.014	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Hickman CA, USA 2001 Shady Lady	3 (5 5)	0.1314 0.1320 0.1360	0.04739 0.04738 0.04741	277.3 278.6 286.9		Fruit	2	<u>0.17</u> 0.14	< 0.01 < 0.01	< 0.01 < 0.01
Live Oak CA, USA 2001 (chery) Red Cherry	3 (5 5)	0.1333 0.1361 0.1349	0.07124 0.07209 0.07133	187.2 188.9 189.1		Fruit	2	0.33 <u>0.42</u>	< 0.01 < 0.01	< 0.01 < 0.01
Visalia CA, USA 2001 (cherry) Red Cherry Large	3 (5 5)	0.1330 0.1330 0.1328	0.03150 0.03202 0.03266	422.2 415.3 406.5		Fruit	2	0.10 <u>0.15</u>	< 0.01 < 0.01	< 0.01 < 0.01

Adjuvants were added to tank mix: Bond (Hamberg), NuFilm (Elko, Conklin, Five Points), Latron (Quincy, Live Oak), DePloy (Visalia), Induce (Hickman)

Sweet Peppers

During the 2002 growing season, a total of seven trials were performed on sweet (bell) pepper in the field in different locations in the USA. Fluopicolide was formulated as a suspension concentrate. Three foliar spray applications of fluopicolide were made 4–6 days apart to each treated plot at a target rate of 133 g ai/ha in spray volumes ranging from 216 to 451 L/ha using boom sprayers (backpack or tractor mounted). Plot sizes were 46–186 m^2. Mature sweet pepper samples were harvested 2 days after the last application. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to Method 00782/001 (LOQ was 0.01 mg/kg for each analyte). Sweet pepper samples in this study were frozen a maximum of 554 days (19 months) prior to extraction.

Table 85 Results of residue trials conducted with fluopicolide on sweet pepper in the USA (02CU33132) (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Chula, GA USA 2002 Camelot	3 (5 5)	0.131 0.131 0.139	0.0326 0.0334 0.0310	402 393 448	89	fruit	2	0.047 0.041	< 0.01 < 0.01	< 0.01 < 0.01
Quincy, FL USA 2002 Camelot	3 (5 5)	0.133 0.132 0.136	0.0307 0.0293 0.0302	435 451 449	89	fruit	2	0.092 0.060	< 0.01 < 0.01	< 0.01 < 0.01
New Holland, OH USA 2002 Crusader	3 (5 4)	0.136 0.128 0.128	0.0571 0.0589 0.0591	237 217 216	72	fruit	2	0.167 0.095	< 0.01 < 0.01	< 0.01 < 0.01
Uvalde, TX USA 2002 Capistrano	3 (5 5)	0.133 0.133 0.133	0.0557 0.0550 0.0559	239 242 238	71	fruit	2	0.148 0.103	< 0.01 < 0.01	< 0.01 < 0.01
Fresno, CA USA 2002 Jupiter	3 (6 6)	0.131 0.133 0.133	0.0399 0.0402 0.0405	328 332 329	87	fruit	2	0.194 0.104	< 0.01 < 0.01	< 0.01 < 0.01
Visalia, CA USA 2002 Emerald Giant	3 (5 5)	0.133 0.132 0.133	0.0509 0.0492 0.0493	262 268 270	73	fruit	2	0.044 0.041	< 0.01 < 0.01	< 0.01 < 0.01
Madera, CA USA 2002 Emerald Giant	3 (5 5)	0.132 0.132 0.132	0.0413 0.0402 0.0404	325 332 327	89	fruit	1 2 3 5 7	0.555 0.587 0.489 0.557 0.571 0.522 0.536 0.426 0.394 0.396	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01

Adjuvants (spreaders/wetters) were added to tank mixes: NuFilm (Chula, Quincy, Fresno, Madera), Penetrate II (New Holland) and Bond (Uvalde, Visalia)

Chilli Peppers

During the 2002 growing season, a total of three trials were performed on chilli pepper in the field in different locations in the USA. Three foliar spray applications of fluopicolide were made 5 days apart to each treated plot at a target rate of 133 g ai/ha in spray volumes ranging from 282 to 390 L/ha using backpack sprayers. Plot sizes were 70–124 m^2. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to method 00782/001. The LOQ was 0.01 mg/kg for each analyte. Recoveries of fluopicolide for samples fortified at 0.01–0.75 mg/kg were low ranging from

63–73%. Chilli pepper samples in this study were frozen a maximum of 508 days (17 months) prior to extraction.

Table 86 Results of residue trials conducted with fluopicolide on chilli pepper in the USA (02CU33133) (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Levelland, USA 2002 Jalapeno M	3 (5 5)	0.135 0.138 0.135	0.0354 0.0353 0.0354	380 390 380	79	fruit	2	0.096 0.084	< 0.01 < 0.01	< 0.01 < 0.01
Bowie, USA 2002 B-58	3 (5 5)	0.133 0.133 0.132	0.0472 0.0470 0.0470	282 281 281	81	fruit	2	0.358 0.241	< 0.01 < 0.01	< 0.01 < 0.01
Madera, USA 2002 Santa Fe Grande	3 (5 5)	0.133 0.135 0.136	0.0411 0.0412 0.0413	324 326 328	89	fruit	2	0.456 0.576	< 0.01 < 0.01	< 0.01 < 0.01

The adjuvant (wetter/spreader) NuFilm was added

Leafy vegetables (including Brassica leafy vegetables)

Lettuce

In 2005 a total of eight supervised residue trials were performed in the greenhouse in Europe (Southern France 2, Italy, Spain, the Netherlands, Belgium, Greece and Germany) on head lettuce and leaf lettuce. Fluopicolide SC (with propamocarb) was sprayed three times on lettuce plants with a nominal rate of 0.1 kg ai/ha and spray volumes 500–1000 L/ha per application using knapsack sprayer. The applications were carried out with a spray interval of 7–8 days. Plot sizes were 10–100 m^2. The first treatment was conducted at BBCH 18–42, whilst the last application was carried out at BBCH 19–46, two weeks before the anticipated commercial harvest. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The LOQ for all three molecules was 0.01 mg/kg for lettuce heads. The storage period of deep frozen samples ranged between 55 and 233 days.

Table 87 Results of residue trials conducted on lettuce in the greenhouse in Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
RH Heiloo, The Netherlands 2005 (head) Varinka	3 (7 7)	0.100 0.100 0.100	0.0100 0.0100 0.0100	1000 1000 1000	46	head	0 14 21	5.0 4.9 4.3	0.01 0.011 0.011	< 0.01 < 0.01 < 0.01	RA-2116/05 R 2005 0591 4 0591-05
Monopoli, Italy 2005 (head) Tiziana	3 (7 7)	0.100 0.100 0.100	0.0143 0.0143 0.0143	700 700 700	41	head	0 14 21	4.1 0.68 0.27	0.015 0.017 0.013	< 0.01 < 0.01 < 0.01	RA-2116/05 R 2005 0592 2 0592-05
Brenes Sevilla, Spain 2005 (head) Intensite	3 (7 7)	0.100 0.120 0.100	0.0125 0.0125 0.0125	800 960 800	45	head	0 14 20	4.9 2.7 2.2	0.014 0.014 0.015	< 0.01 < 0.01 < 0.01	RA-2116/05 R 2005 0593 0 0593-05

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Gembloux, Belgium 2005 (head) Herman	3 (7 7)	0.100 0.100 0.100	0.0133 0.0133 0.0133	750 750 750	19	head	0 14 21	7.7 0.63 0.12	0.016 0.017 < 0.01	< 0.01 < 0.01 < 0.01	RA-2116/05 R 2005 0594 9 0594-05
Meckenbeuren, Germany 2005 Versaiie	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	42	head	0 14 21	2.8 0.40 0.024	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2116/05 R 2005 0595 7 0595-05
Chazay d'Azergues, France 2005 Exquise	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	41	head	0 14 21	3.3 0.40 0.16	0.020 0.018 0.013	< 0.01 < 0.01 < 0.01	RA-2116/05 R 2005 0597 3 0597-05
Kato Souli, Greece 2005 Manita	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	42	head	0 14 21	6.4 1.5 0.53	0.022 0.022 0.017	< 0.01 < 0.01 < 0.01	RA-2116/05 R 2005 0598 1 0598-05
St Rémy de Provence, France 2005 Lugano	3 (7 7)	0.100 0.100 0.100	0.0100 0.0100 0.0100	1000 1000 1000	44	head	0 14 21	8.5 4.0 3.7	0.022 0.020 0.024	< 0.01 < 0.01 < 0.01	RA-2116/05 R 2005 1007 1 1007-05

In 2005 and 2006 a total of eight supervised residue trials were performed in the field in Northern Europe (Northern France 2, the Netherlands 2, Germany 3 and the United Kingdom) on lettuce. Fluopicolide SC (with propamocarb) was sprayed three times on lettuce plants with 0.1 kg ai/ha and spray volumes 500–800 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 6–10 days. Plot sizes were 15–40 m^2. In trial R 2005 0600/7 in the Netherlands the interval between the 2nd and 3rd treatment was 22 days due to very cold weather and very slow growth of lettuce. The first treatment was conducted at BBCH 17–43, whilst the last application was carried out at BBCH 46–49, one week before the anticipated commercial harvest. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The LOQ for all three molecules was 0.01 mg/kg. The storage period of deep frozen samples ranged between 83 and 230 days.

Table 88 Results of residue trials conducted on lettuce in the field in Northern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Zwaagdijk-Oost, The Netherlands 2005 (butterhead) Naima	3 (7 22)	0.100 0.100 0.100	0.0125 0.0125 0.0125	800 800 800	46	head	0 3 **7** 10 14	2.0 1.2 0.31 0.18 0.05	< 0.01 0.010 0.011 0.011 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2117/05 R 2005 0600 7 0600-05
Little Shelford, UK 2005 (butterhead) Estelle	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	49	head	0 3 **7** 10 13	1.4 0.94 0.74 0.62 0.34	0.01 0.01 0.01 0.01 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2117/05 R 2005 0601 5 0601-05

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Schauernheim, Germany 2005 (butterhead) Casanova	3 (8 6)	0.100 0.100 0.100	0.0133 0.0133 0.0133	750 750 750	47	head	0 **7** 14	3.3 0.82 0.21	0.03 0.03 0.02	< 0.01 < 0.01 < 0.01	RA-2117/05 R 2005 0602 3 0602-05
Fondettes, France 2005 (butterhead) Sagess	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	48	head	0 **7** 14	1.2 0.07 < 0.010	0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	RA-2117/05 R 2005 0603 1 0603-05
Langenfeld-Reusrath, Germany 2006 (butterhead) Gisela	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	47	head	0* 0 3 **7** 10 14	0.13 1.7 0.79 0.60 0.42 0.15	< 0.01 < 0.01 < 0.01 0.01 0.01 0.02	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2117/06 R 2006 0510 2 0510-06
Cergy, France 2006 (loose leaf) Anikai	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	48	head	0* 0 3 **7** 10 13	0.91 2.6 0.64 0.36 0.27 0.11	0.01 0.02 < 0.01 0.01 0.01 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2117/06 R 2006 0512 9 0512-06
Meckenbeuren, Germany 2006 (butterhead) Jiska	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	46	head	0* 0 **7** 14	0.04 3.7 0.12 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	RA-2117/06 R 2006 0514 5 0514-06
Zwaagdijk-Oost, The Netherlands 2006 (loose leaf) Lollo rosso	3 (7 7)	0.100 0.100 0.100	0.0125 0.0125 0.0125	800 800 800	46	head	0* 0 **7** 14	1.3 3.8 0.41 0.10	0.01 0.02 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	RA-2117/06 R 2006 0516 1 0516-06

Plant densities for the 2005 trials were 101 k plants/ha, 111, 95.2 and 102 k plants/ha and for the 2006 trials 111 k, 133 k, 111 k and 111 k.

In 2005 and 2006 a total of eight supervised residue trials were performed in the field in Southern Europe (Spain 2, Italy 2, Portugal 2 and Greece 2) on lettuce. Fluopicolide SC (with propamocarb) was sprayed three times on lettuce plants with 0.1 kg ai/ha and spray volumes 500–800 L/ha per application using backpack sprayers. The applications were carried out with a spray interval of 7 days. Plot sizes were 15–80 m^2. The first treatment was conducted at BBCH 17–43, whilst the last application was carried out at BBCH 44–48, one week before the anticipated commercial harvest. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The LOQ for all three molecules was 0.01 mg/kg. The storage period of deep frozen samples ranged between 103 and 256 days.

Table 89 Results of residue trials conducted on lettuce in the field in Southern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Lusia, Italy 2005 (butterhead) Butterhead	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 00167	600 600 600	42	head	0 3 **7** 10 14	4.2 2.1 1.0 0.43 0.14	0.02 0.02 0.03 0.03 0.03	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2118/05 R 2005 0605 8 0605-05

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Vilanova del Vallés, Spain 2005 (butterhead) Trocadero	3 (7 7)	0.108 0.100 0.100	0.02000 0.01431 0.01250	540 700 800	43	head	0 3 **7** 10 14	3.0 1.9 0.41 0.06 0.01	0.02 0.02 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2118/05 R 2005 0606 6 0606-05
Póvoa da Isenta, Portugal 2005 (loose leaf) Joconda	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0200	500 500 500	44	head	0 **7** 14	1.8 0.14 0.06	0.01 0.01 0.02	< 0.01 < 0.01 < 0.01	RA-2118/05 R 2005 0607 4 0607-05
Marathonas, Greece 2005 (loose leaf) Grumsi	3 (7 7)	0.100 0.100 0.100	0.0200 0.0167 0.0167	500 600 600	41	head	0 **7** 14	2.2 1.8 0.36	0.013 0.016 < 0.01	< 0.01 < 0.01 < 0.01	RA-2118/05 R 2005 0608 2 0608-05
Gava, Spain 2006 (butterhead) Trocade ro Daguan	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	47	head	0 0 3 **7** 10 14	0.15 2.5 1.6 0.46 0.22 0.04	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2118/06 R 2006 0511 0 0511-06
Bologna, Italy 2006 (loose leaf) Funly	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	48	head	0 0 3 **7** 10 14	0.04 3.2 1.7 0.91 0.52 0.30	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2118/06 R 2006 0513 7 0513-06
Almargem do Bispo, Portugal 2006 (butterhead) Salakis	3 (7 7)	0.100 0.100 0.100	0.0125 0.0125 0.0125	800 800 800	47	head	0 0 **7** 14	0.41 3.1 0.07 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	RA-2118/06 R 2006 0515 3 0515-06
Marathonas, Greece 2006 (loose leaf) Parioli	3 (7 7)	0.100 0.100 0.100	0.0200 0.0200 0.0167	500 500 600	44	head	0 0 **7** 14	8.1 13 3.4 1.2	0.05 0.06 0.04 0.03	0.01 < 0.01 < 0.01 < 0.01	RA-2118/06 R 2006 0518 8 0518-06

Plant densities for 2005 trials were 143, 49.4, 86.6 and 95.2 k plants/ha, for 2006 trials 62.5, 100, 19 and 111 k plants/ha

During the 2002 growing season, a total of seven trials were performed on head lettuce in the field in different locations in the USA. Three foliar spray applications of fluopicolide were made 3–7 days apart to each treated plot at a target rate of 133 g ai/ha in spray volumes ranging from 186 to 218 L/ha using backpack boom sprayers. Plot sizes were 62–195 m^2. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to method 00782/001. The LOQ was 0.01 mg/kg. Head lettuce samples in this study were frozen for a maximum of 878 days (29 months) prior to extraction.

Table 90 Results of residue trials conducted with fluopicolide in/on head lettuce in the USA (02CU27778) (SC formulation)

Country	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	AE 0815899 (mg/kg)
North Rose, USA 2002 (head) Crispino	3 (5 5)	0.135 0.137 0.138	0.0722 0.0723 0.0726	186 189 190	crop size: 10–15 cm	head	2	2.08 2.45	< 0.01 < 0.01	< 0.01 < 0.01
						leaf, inner	2	0.324 0.293	< 0.01 < 0.01	< 0.01 < 0.01
Madera, USA 2002 (head) Empire	3 (7 3)	0.133 0.132 0.131	0.0612 0.0612 0.0609	218 216 215	49	head	2	1.18 2.33	< 0.01 0.012	< 0.01 < 0.01
						leaf, inner	2	0.022 0.056	< 0.01 < 0.01	< 0.01 < 0.01
Ojai, USA 2002 (head) Durango	3 (5 5)	0.136 0.140 0.133	0.0710 0.0710 0.0709	191 197 188	49	head	2	0.475 0.616	< 0.01 0.013	< 0.01 < 0.01
						leaf, inner	2	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
San Luis Obispo, CA USA 2002 (head) Cannery Row	3 (5 5)	0.137 0.135 0.131	0.0720 0.0705 0.0684	190 191 192	49	head	2	4.16 3.45	< 0.01 < 0.01	< 0.01 < 0.01
						leaf, inner	2	< 0.01 0.03	< 0.01 < 0.01	< 0.01 < 0.01
Nipomo, CA USA 2002 (head) Sniper	3 (4 5)	0.138 0.136 0.139	0.0719 0.0721 0.0718	192 191 192	49	head	2	4.32 2.88	< 0.01 < 0.01	< 0.01 < 0.01
						leaf, inner	2	0.066 0.011	< 0.01 < 0.01	< 0.01 < 0.01
Hickman, CA USA 2002 (head) Cannery Row	3 (5 5)	0.133 0.132 0.135	0.0713 0.0710 0.0718	187 186 188	49	head	2	5.52 7.15	< 0.01 < 0.01	< 0.01 < 0.01
						leaf, inner	2	0.141 0.122	< 0.01 < 0.01	< 0.01 < 0.01
Hobe Sound, FL USA 2002 (head) Iceburg #110	3 (7 3)	0.132 0.126 0.135	0.0612 0.0591 0.0656	216 212 205	49	head	1 2 3 5 7	0.452 0.455 0.500 2.28 1.27 0.395	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01
						leaf, inner	1 2 3 5 7	0.121 0.046 0.228 0.04 0.196 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01

Adjuvants were added to tank mixes: Bond (North Rose, Hobe Sound, San Luis Obispo), NuFilm (Madera), Latron (Ojai) and FirstChoice (Nipomo).

During the 2002 growing season, a total of seven trials were performed on leafy lettuce in the field in different locations in the USA. Three foliar spray applications of fluopicolide were made 3–7 days apart to each treated plot at a target rate of 133 g ai/ha in spray volumes ranging from 180 to 224 L/ha using backpack sprayers. Plot sizes were 56–93 m^2. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to method 00782/001. The LOQ was 0.01 mg/kg for each analyte. Lettuce samples in this study were frozen a maximum of 877 days (29 months) prior to extraction.

Table 91 Results of residue trials conducted with fluopicolide on leafy lettuce in the USA (02CU30473) (SC formulation)

Country	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
North Rose, NY USA 2002 (leaf) Black Seeded Simpson	3 (5 5)	0.137 0.130 0.129	0.0703 0.0709 0.0706	194 183 182	crop height 36–41 cm	leaf	2	7.86 11.7	< 0.01 0.015	< 0.01 < 0.01
Hobe Sound, FL USA 2002 (leaf) Romaine	3 (7 3)	0.133 0.133 0.132	0.0612 0.0596 0.0651	218 223 203	49	leaf	2	7.61 6.29	0.038 0.023	< 0.01 < 0.01
Madera, CA USA 2002 (leaf) Waldemanns Green	3 (5 5)	0.135 0.136 0.133	0.0622 0.0625 0.0612	216 217 218	49	leaf	1 2 3 5 7	5.50 4.33 3.33 2.03 2.90 2.33	0.012 0.011 < 0.01 < 0.01 0.018 0.036	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Camarillo, CA USA 2002 (leaf) Darkland	3 (5 7)	0.127 0.131 0.133	0.0705 0.0708 0.0709	180 185 188	49	leaf	2	4.99 0.444	0.012 < 0.01	< 0.01 < 0.01
San Luis Obispo, CA USA 2002 (leaf) Hacienda	3 (5 5)	0.138 0.133 0.139	0.0688 0.0672 0.0673	200 198 203	49	leaf	2	6.56 7.55	0.014 0.016	< 0.01 < 0.01
Spreckels, CA USA 2002 (leaf) Shining Star	3 (5 5)	0.136 0.137 0.135	0.0721 0.0716 0.0722	188 191 186	49	leaf	2	5.30 3.86	< 0.01 < 0.01	< 0.01 < 0.01
Hickman, CA USA 2002 (leaf) Shining Star	3 (5 5)	0.138 0.138 0.133	0.0712 0.0715 0.0714	194 193 185	49	leaf	2	9.02 10.30	< 0.01 < 0.01	< 0.01 < 0.01

Spinach

In 2006 and 2007 a total of four supervised residue trials were performed in the field in Northern Europe (Northern France 2 and Germany 2) on spinach. Fluopicolide SC (with propamocarb) was sprayed three times on spinach plants at 0.1 kg ai/ha with spray volumes 300–600 L/ha using knapsack sprayers. The applications were carried out with a spray interval of 7–8 days. Plot sizes were 33–120 m^2. The first treatment was conducted at BBCH 12–43, whilst the last application was carried out at BBCH 18–45, fourteen days before the anticipated commercial harvest. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The storage period of deep frozen samples ranged between 165 and 391 days.

Table 92 Results of residue trials conducted on spinach in the field in Northern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Champien (Picardie), France 2006 Eagle6-R2	3 (8 7)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	18	leaf	0 [b] 14	9.4 0.05	0.10 0.02	0.01 < 0.01	RA-2304/06 R 2006 0089 5 0089-06

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Weilerswist (Nordrhein-Westfalen), Germany 2006 Ventus	3 (7 8)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300		leaf	0 3 7 14 21	4.1 2.8 1.6 0.30 0.07	0.06 0.07 0.08 0.04 0.04	0.02 0.02 0.03 0.02 0.02	RA-2304/06 R 2006 0090 9 0090-06
Champien (Picardie), France 2007 Eagle	3 (7 7)	0.100 0.100 0.100	0.0333 0.0333 0.0333	300 300 300	29	leaf	0 [a] 0 3 7 14 21	0.81 8.0 1.6 0.52 0.15 0.05	0.08 0.09 0.09 0.07 0.08 0.06	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	RA-2636/07 R 2007 0338/4 0338-07
Langenfeld-Reusrath (Nordrhein-Westfalen), Germany 2007 Czezanne	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 00167	600 600 600	45	leaf	0 14	4.2 0.33	0.05 0.04	< 0.01 0.02	RA-2636/07 R 2007 0339/2 0339-07

[a] before last application

[b] 2 mm rainfall starting 5 h after the last spray

In 2006 and 2007 a total of four supervised residue trials were performed in the field in Southern Europe (Spain 2 and Italy 2) on spinach. Fluopicolide SC (with propamocarb) was sprayed three times on spinach plants at 0.1 kg ai/ha with spray volumes 377–600 L/ha per application using knapsack sprayers. The applications were carried out with a spray interval of 7 days. Plot sizes were 34–120 m^2. The first treatment was conducted at BBCH 16–41, whilst the last application was carried out at BBCH 33–45, fourteen days before the anticipated commercial harvest. Residues of fluopicolide and its metabolites M-01 and M-02 were determined according to method 00782/M004 by HPLC-MS/MS. The storage period of deep frozen samples ranged between 136 and 391 days.

Table 93 Results of residue trials conducted on spinach in the field in Southern Europe (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Badajoz (Extremadura), Spain 2006 Dolfin	3 (7 7)	0.100 0.100 0.100	0.0250 0.0250 0.0250	400 400 400	45	leaf	0 14	3.6 0.14	0.07 0.05	< 0.01 < 0.01	RA-2305/06 R 2006 0091 7 0091-06
Manfredonia (Foggia) (Puglia), Italy 2006 America	3 (7 7)	0.100 0.100 0.100	0.0167 0.0167 0.0167	600 600 600	43	leaf	0 3 7 14 21	5.3 3.8 2.5 1.7 1.2	0.03 0.04 0.03 0.03 0.03	0.01 0.02 0.01 0.02 0.02	RA-2305/06 R 2006 0092 5 0092-06
Manfredonia (Foggia) (Puglia) Italy 2007 America	3 (7 7)	0.100 0.100 0.100	0.0250 0.0250 0.0250	400 400 400	45	leaf	0 [a] 0 3 7 14 21	0.58 4.0 1.2 0.53 0.38 0.20	0.03 0.03 0.04 0.04 0.05 0.03	< 0.01 < 0.01 < 0.01 < 0.01 0.01 0.02	RA-2636/07 R 2007 0340/6 0340-07

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	Fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)	
Badajoz (Extremadura) Spain 2007 Silver Whale	3 (7 7)	0.094 0.095 0.100	0.02494 0.02488 0.02500	377 380 400	33	leaf	0 14	5.5 [b] 0.17	0.05 0.06	< 0.01 < 0.01	RA-2636/07 R 2007 0341/4 0341-07

[a] before last application

[b] 16 mm rainfall starting 5.5 h after the last spray

During the 2002 growing season, a total of seven trials were performed on spinach in the field in different locations in the USA. Three foliar spray applications of fluopicolide were made 4–6 days apart to each treated plot at a target rate of 0.133 kg ai/ha in spray volumes ranging from 147 to 196 L/ha using backpack sprayers. Plot sizes were 51–167 m^2. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to method 00782. The LOQ was 0.01 mg/kg for each analyte. Spinach samples in this study were frozen between 949 days and a maximum of 1176 days prior to extraction.

Table 94 Results of residue trials conducted with fluopicolide on spinach in the USA (02CU33135)– results are the mean of replicate samples (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Baptistown, NJ, USA 2002 Tyee F1	3 (4 6)	0.136 0.135 0.137	0.0710 0.0711 0.0708	191 189 193	NR	Leaf	2	6.86 6.13	0.073 0.086	0.018 0.023
Suffolk, VA USA 2002 Tyee Lot #18535J01	3 (5 5)	0.135 0.135 0.136	0.0763 0.0723 0.0720	177 185 188	19	leaf	1 2 3 5 7	17.4 11.8 15.5 15.1 14.6 9.74	0.175 0.152 0.188 0.200 0.201 0.156	0.074 0.062 0.090 0.119 0.140 0.142
Uvalde, TX USA 2002 F-380	3 (5 5)	0.133 0.132 0.135	0.0695 0.0722 0.0726	192 183 185	40	leaf	2	5.43 6.84	0.026 0.022	0.013 0.013
East Bernard, TX, USA 2002 Bloomsdale	3 (5 5)	0.133 0.133 0.135	0.0704 0.0682 0.0696	190 195 184	47	leaf	2	15.5 16.8	0.066 0.069	0.026 0.027
Wellington,CO, USA 2002 Unipack 151	3 (6 4)	0.133 0.135 0.136	0.0906 0.0909 0.0905	147 148 150	49	leaf	2	8.55 8.51	0.029 0.035	< 0.01 < 0.01

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Casa Grande, AZ, USA 2002 Bolero	3 (5 5)	0.138 0.137 0.135	0.0710 0.0708 0.0707	194 193 190	49	leaf	2	11.5 9.21	0.089 0.062	< 0.01 < 0.01
Fresno, CA USA 2002 Shasta	3 (5 6)	0.135 0.133 0.133	0.0720 0.0719 0.0719	187 185 185	39	leaf	2	6.48 6.78	0.051 0.064	< 0.01 < 0.01

NR not recorded

Root and tuber vegetables

Carrot

During the 2002 growing season, a total of seven trials were performed on carrots in the field in different locations in the USA. Three foliar spray applications of fluopicolide were made 4–6 days apart to each treated plot at a target rate of 133 g ai/ha in spray volumes ranging from 141 to 213 L/ha using CO_2 assisted broadcast sprayers. Plot sizes were 51–186 m^2. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to method 00782. The LOQ was 0.01 mg/kg for each analyte in carrots. Carrot samples in this study were frozen between 1082 days and a maximum of 1415 days prior to extraction.

Table 95 Results of residue trials conducted with fluopicolide on carrot in the USA (02CU33130) (SC formulation)

	N	kg/ha (as)	kg/hL (as)		GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Lake Park, GA, USA 2002 Choctaw	3 (5 5)	0.132 0.133 0.133	0.0780 0.0884 0.0946	169 151 141	49	Root	7	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01
New Holland, OH USA 2002 Chantenay Red	3 (6 5)	0.130 0.131 0.135	0.0896 0.0894 0.0920	130 131 135	48	root	7	0.144 0.106	< 0.01 < 0.01	< 0.01 < 0.01
Fresno, CA USA 2002 Bolero	3 (4 5)	0.131 0.132 0.135	0.0719 0.0718 0.0718	182 184 187	78	root	2 5 7 10 14	< 0.01 0.013 0.017 0.016 0.012 0.031 < 0.01 0.012 < 0.01 0.010	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Fresno, CA USA 2002 Bolero	3 (4 5)	0.131 0.133 0.132	0.0719 0.0720 0.0717	182 185 184	78	root	7	< 0.01 0.011	< 0.01 < 0.01	< 0.01 < 0.01
King City, CA, USA 2002 Danner's 126	3 (5 4)	0.131 0.133 0.136	0.0875 0.0694 0.0636	150 192 213	Root elongation	root	7	0.033 0.029	< 0.01 < 0.01	< 0.01 < 0.01
Greenfield, CA, USA 2002 Danver 126	3 (6 4)	0.132 0.133 0.1331	0.0706 0.0706 0.0705	287 189 186	49	root	7	0.025 0.029	< 0.01 < 0.01	< 0.01 < 0.01
Raymondville, TX, USA 2002 Sovereign	3 (5 5)	0.136 0.136 0.135	0.0710 0.0712 0.0708	191 191 190	49	root	7	0.028 0.047	< 0.01 < 0.01	< 0.01 < 0.01

Adjuvants were added to tank mixes: Latron (Lane Park), New Holland (Penetrate), NuFilm (Raymondville, Fresno, King City) and BreakThru (Greenfield).

Fresno same site same dates for sprays, side-by-side trials?

Radish

During the 2002 growing season, a total of six trials were performed on radish in the field in different locations in the USA. Three foliar spray applications of fluopicolide were made 5–6 days apart to each treated plot at a target rate of 0.133 kg ai/ha in spray volumes ranging from 141 to 225 L/ha using backpack and tractor mounted CO_2 boom sprayers. Plot sizes were 70–149 m^2. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to method 00782. The LOQ was 0.01 mg/kg for each analyte. Radish root and radish top samples in this study were frozen between 1260 days and a maximum of 1379 days prior to extraction.

Table 96 Results of residue trials conducted with fluopicolide on radish in the USA (02CU33129) (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
North Rose, NY, USA 2002 (small) Champion	3 (5 5)	0.136 0.138 0.132	0.0707 0.0711 0.0710	192 194 186	46	root	7	0.051 0.055	< 0.01 < 0.01	< 0.01 < 0.01
						leaf	7	5.49 7.03	0.012 0.020	0.014 0.021
Oviedo, FL, USA 2002 (small) Early Scarlett Globe	3 (5 5)	0.130 0.132 0.133	0.0588 0.0592 0.0593	221 224 224	47	root	2	0.092 0.113	< 0.01 < 0.01	< 0.01 < 0.01
							4	0.069 0.089	< 0.01 < 0.01	< 0.01 < 0.01
							7	0.103 0.069	< 0.01 < 0.01	< 0.01 < 0.01
							10	0.033 0.026	< 0.01 < 0.01	< 0.01 < 0.01
							14	0.029 0.021	< 0.01 < 0.01	< 0.01 < 0.01
						leaf	2	7.02 4.89	0.095 0.089	0.029 0.025
							4	8.68 7.27	0.030 0.039	0.013 0.011
							7	6.03 5.58	0.069 0.071	0.014 0.013
							10	3.66 2.41	0.071 0.052	0.024 0.018
							14	1.45 1.38	0.060 0.070	0.017 0.015
Oviedo, FL, USA 2002 (small) Altaglobe	3 (5 5)	0.129 0.135 0.133	0.0596 0.0598 0.0593	216 225 224	46	root	7	0.031 0.032	< 0.01 < 0.01	0.010 0.011
						leaf	7	3.71 3.97	0.149 0.163	0.012 0.014
Winter Garden, FL, USA 2002 (small) Sparkler	3 (4 5)	0.133 0.129 0.133	0.0705 0.0703 0.0704	189 183 189	48	root	7	0.017 0.017	< 0.01 < 0.01	< 0.01 < 0.01
						leaf	7	2.33 2.98	0.016 0.026	< 0.01 0.011
Arkansas, WI, USA 2002 (small) Crunchy Royale	3 (5 4)	0.133 0.135 0.132	0.0710 0.0710 0.0711	188 189 186	16	root	7	0.020 0.025	< 0.01 < 0.01	< 0.01 < 0.01
						leaf	7	2.39 2.32	0.038 0.035	0.013 0.017
Live Oak, CA, USA 2002 (small) Crimson	3 (5 5)	0.136 0.136 0.136	0.0960 0.0961 0.0960	359 360 359	49	root	7	0.025 0.022	< 0.01 < 0.01	< 0.01 < 0.01
						leaf	7	10.2 7.32	0.109 0.052	0.028 0.018

Adjuvants were added to tank mixes: Bond (North Rose, Oviedo, Arkansas) and NuFilm (Winter Garden, Live Oak)

Oviedo trials same dates, locations, side-by-side trials?

Stalk and Stem vegetables

Celery

During the 2002 growing season, a total of seven trials were performed on celery in the field in different locations in the USA. Three foliar spray applications of fluopicolide were made 3–7 days apart to each treated plot at a target rate of 133 kg ai/ha in spray volumes ranging from 183 to 238 L/ha using backpack and tractor mounted CO_2 boom sprayers. Plot sizes were 53–93 m^2. The residues of fluopicolide, M-01 and M-02 were quantitated by LC/MS/MS according to method 00782. Celery samples in this study were frozen between 964 days and a maximum of 1150 days prior to extraction.

Table 97 Results of residue trials conducted with fluopicolide on celery in the USA (02CU33134) (SC formulation)

	N	kg ai/ha	kg ai/hL	L/ha	GS	Portion analysed	PHI (days)	fluopicolide (mg/kg)	M-01 (mg/kg)	M-02 (mg/kg)
Hobe Sound, FL, USA 2002 Junebell	3 (7 3)	0.132 0.133 0.135	0.0554 0.0650 0.0632	238 205 210	19	stalk	2	4.90 <u>5.20</u>	0.037 0.041	0.017 0.024
Grant, MI, USA 2002 Green Bay	3 (5 5)	0.136 0.136 0.135	0.0720 0.0736 0.0722	188 184 186	19	stalk	2	1.11 <u>1.35</u>	< 0.01 < 0.01	< 0.01 < 0.01
Fresno, CA USA 2002 Conquistador	3 (6 6)	0.136 0.135 0.132	0.0715 0.0717 0.0715	190 188 185	76	stalk	2	<u>6.68</u> 6.53	0.026 0.027	< 0.01 < 0.01
Ojai, CA USA 2002 Conquistador	3 (5 5)	0.131 0.131 0.135	0.0711 0.0710 0.0709	184 184 190	49	stalk	2	0.983 <u>1.03</u>	< 0.01 < 0.01	< 0.01 < 0.01
San Luis Obispo, CA USA 2002 Conquistador	3 (4 5)	0.132 0.141 0.135	0.0722 0.0716 0.0720	183 197 187	79	stalk	2	<u>0.762</u> 0.325	< 0.01 < 0.01	< 0.01 < 0.01
Santa Maria, CA, USA 2002 Conquistador	3 (5 5)	0.135 0.135 0.140	0.0710 0.0705 0.0705	190 191 199	market able	stalk, trimmed	1 2 3 5 7	0.063 0.037 0.040 0.106 <u>0.163</u> 0.136	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Hickman, CA USA 2002 Matador	3 (5 5)	0.135 0.137 0.131	0.0711 0.0716 0.0711	189 191 184	53	stalk	2	6.10 <u>13.6</u>	< 0.01 0.01	< 0.01 < 0.01

FATE OF RESIDUES IN STORAGE AND PROCESSING

Residues after Processing

Processing studies are necessary according to the uses and the residues of fluopicolide on raw agricultural commodities. The fate of fluopicolide residues during processing of raw agricultural commodities was investigated in grapes and tomatoes.

As a measure for the transfer of residues into processed products, a transfer factor was used, which is defined as

$$TF = \frac{\text{Residue in processed product (mg/kg)}}{\text{Residue in raw agricultural commodity (mg/kg)}}$$

A concentration of residues takes place when TF > 1.

Van der Gaauw (2001) studied the degradation of fluopicolide under simulated processing conditions. Samples of standard buffer solutions at pH values of 4, 5 and 6 were fortified with [^{14}C]fluopicolide and hydrolysed at varying temperatures and durations. The distribution of [^{14}C]fluopicolide in the respective buffer solutions is shown below.

Table 98 The distribution of [^{14}C]fluopicolide in buffered solutions

Substrate	Temperature (˚C)	Incubation time (min.)	Simulation of	Mean % of applied radioactivity determined as fluopicolide
pH 4 buffer	90	20	pasteurisation	99
pH 5 buffer	100	60	baking, brewing or boiling	104
pH 6 buffer	120	20	sterilisation	100

Greater than 98% of radioactivity was accounted for as unchanged parent compound.

Effects of processing on the level of residues

Residues of fluopicolide were determined in processed commodities of grapes and tomatoes in Europe and/or the USA. Processing data have been generated simulating both household practices and industrial practices on a laboratory scale.

Grapes

The effect of processing red wine grapes on fluopicolide residues was studied by Zietz (2003). Grapes (red varieties) were sampled from vines at three sites in Southern Europe following application of the formulated SE product. Sufficient quantities of fruit was taken to enable processing at a pilot plant into fractions of pomace, must, yeast, young wine and mature wine. These fractions and the RAC samples were analysed for fluopicolide and its metabolites M-01 and M-02 using an analytical method with LC/MS/MS determination.

Grapes were de-stemmed, crushed and the mash stabilized with up to 25 mg/L SO_2. The mash was heated to 60–75 °C and then allowed to cool down to room temperature overnight. Must was separated by pressing the mash. Up to 25 mg/L of SO_2 was added to the must. For grapes from Spain impurities were allowed to precipitate overnight at ambient temperature. The clear must was transferred into glass vessels and yeast added (approximately 10 g/hL). Fermentation occurred at 16–18 °C and when complete the young wine was separated from yeast and sludge (first racking). Bentonite was added to the young wine which was allowed to clarify again. Finally the clarified wine was filtered using a filter press (second racking) and filled into smaller glass vessels. After an ageing period of 6–7 weeks after the 2nd racking the wine was filtrated again and bottled (young wine). The wine was allowed to mature within the bottles for a further 4 months (mature wine).

Table 99 Results from processing studies on red grapes in Europe

Country, year (trial ref)	Rate kg as/ha	Fraction analysed	Residue level (mg/kg)			Report reference
			fluopicolide	M-01	M-02	
Spain, 2000 (00S041R)	3 × 0.13	RAC	0.32	0.02	0.07	M-218649-01-1
		must	0.12	0.02	0.08	
		pomace	2.1	0.03	0.07	
		yeast	1.2	< 0.01	0.04	
		young wine	0.08	0.01	0.07	
		mature wine	0.09	0.01	0.07	
Greece, 2000 (00RF021/2)	3 × 0.13	RAC	0.35	0.03	0.03	M-218649-01-1
		must	0.20	0.03	0.03	
		pomace	2.2	0.05	0.04	
		yeast	3.1	0.04	0.05	
		young wine	0.11	0.03	0.03	
		mature wine	0.11	0.03	0.03	
France, 2000 (00 F VI FR P04)	3 × 0.13	RAC	0.40	0.02	0.02	M-218649-01-1
		must	0.15	0.02	0.02	
		pomace	2.0	0.03	0.03	
		yeast	2.4	0.02	0.03	
		young wine	0.15	0.02	0.02	
		mature wine	0.15	0.02	0.02	

The residue transfer in absolute terms was used to establish a mass balance in each of the three trials. The mass balance values ranged from 87 to 137% across the three trials in terms of fluopicolide residues.

Table 100 Processing factors during wine processing

Fraction	Processing factor		
	Spain, 2000 (00S041R)	Greece, 2000 (00RF021/2)	France, 2000 (00 F VI FR P04)
RAC	–	–	–
must	0.38	0.57	0.38
pomace	6.6	6.3	5.0
yeast	3.8	8.9	6.0
young wine	0.25	0.31	0.38
mature wine	0.28	0.31	0.38

Following commercially representative processing of wine grapes, treated with fluopicolide, into mature wine, residues of fluopicolide and its metabolites were found in all fractions. Fluopicolide residues in mature wine ranged from 0.09 to 0.15 mg/kg.

Processing factors for the transfer of fluopicolide residues (parent only) from RAC into mature wine ranged from 0.28 to 0.38 (mean value of 0.32).

A further processing study on white grapes was carried out by Zietz (2003). Grapes were sampled from vines at three sites in Northern Europe following application of the formulated SE product. Sufficient quantities of fruit were taken to enable processing at a pilot plant into fractions of pomace, must, yeast, young wine and mature wine. These fractions and the RAC samples were analysed for fluopicolide and its metabolites M-01 and M-02 using an analytical method with LC/MS/MS determination.

The grapes of white varieties were crushed without de-stemming. After pressing of the mash, the must was stabilised with up to 41 mg/L of SO_2 and divided into two parts for processing as pasteurised and non-pasteurised must. The portion for pasteurisation was heated to 85 ± 1 °C and kept at this temperature for 3 minutes. Thereafter the must was allowed to cool down to about 30 °C. After this step the processing of pasteurised and non-pasteurised must was the same. The clear must was

transferred into glass vessels and pure culture yeast was added (approximately10 g/hL). The fermentation was at 13–18 °C. When the fermentation was complete the young wine was separated from yeast and sludge (first racking). Bentonite was added to the young wine which was allowed to clarify again. Finally the clarified wine was filtered using a filter press (second racking) and filled into smaller glass vessels. After an ageing period of 5–8 weeks after the 2nd racking the wine was filtered again and bottled (young wine). After maturation of the wine within the bottles for approximately 4 months, a sample of mature wine was collected.

Table 101 Results from processing studies on white grapes in Europe

Country, year (trial ref)	Rate kg ai/ha	Fraction analysed	Residue level (mg/kg)			Report reference
			fluopicolide	M-01	M-02	
France, 2000 (BKA/683/00/RES 1)	4 × 0.13	RAC	0.62	0.02	0.02	M-222674-01-1
		pomace	1.1	0.01	0.03	
		must (np)	0.27	< 0.01	0.01	
		yeast (np)	4.2	0.01	0.03	
		young wine (np)	0.28	0.01	< 0.01	
		mature wine (np)	0.25	< 0.01	< 0.01	
		must (p)	0.18	< 0.01	< 0.01	
		yeast (p)	2.3	0.01	0.01	
		young wine (p)	0.15	< 0.01	< 0.01	
		mature wine (p)	0.15	0.01	< 0.01	
Germany, 2000 (AT-00/021-1)	4 × 0.13	RAC	0.61	0.01	0.02	M-222674-01-1
		pomace	1.4	0.01	0.02	
		must (np)	0.29	< 0.01	< 0.01	
		yeast (np)	3.7	< 0.01	0.02	
		young wine (np)	0.25	< 0.01	< 0.01	
		mature wine (np)	0.26	< 0.01	< 0.01	
		must (p)	0.19	< 0.01	< 0.01	
		yeast (p)	2.1	< 0.01	< 0.01	
		young wine (p)	0.14	< 0.01	< 0.01	
		mature wine (p)	0.14	< 0.01	< 0.01	
Germany, 2000 (AT-00/021-2)	4 × 0.13	RAC	0.51	0.01	0.01	M-222674-01-1
		pomace	0.80	0.01	0.03	
		must (np)	0.33	< 0.01	0.01	
		yeast (np)	4.8	0.02	0.06	
		young wine (np)	0.32	< 0.01	< 0.01	
		mature wine (np)	0.31	< 0.01	< 0.01	
		must (p)	0.20	< 0.01	0.01	
		yeast (p)	3.2	0.01	0.02	
		young wine (p)	0.13	< 0.01	0.01	
		mature wine (p)	0.22	< 0.01	0.01	

(np) = non-pasteurised

(p) = pasteurised

The residue transfer in absolute terms was used to establish a mass balance in each of the three trials. The mass balance values ranged from 66 to 86% across the three trials in terms of fluopicolide residue values.

Table 102 Residue processing factors during wine processing

Fraction	Processing factor		
	France, 2000 (BKA/683/00/RES 1)	Germany, 2000 (AT-00/021-1)	Germany, 2000 (AT-00/021-2)
RAC	–	–	–
pomace	1.8	2.3	1.6
must (np)	0.44	0.48	0.65

Fraction	Processing factor		
	France, 2000 (BKA/683/00/RES 1)	Germany, 2000 (AT-00/021-1)	Germany, 2000 (AT-00/021-2)
yeast (np)	6.8	6.1	9.4
young wine (np)	0.45	0.41	0.63
mature wine (np)	0.40	0.43	0.61
must (p)	0.29	0.31	0.39
yeast (p)	3.7	3.4	6.3
young wine (p)	0.24	0.23	0.25
mature wine (p)	0.24	0.23	0.43

Following processing of white wine grapes treated with fluopicolide according to commercial procedures, residues of fluopicolide were found in all fractions. The metabolites M-01 and M-02 were found in some fractions but not at significant levels. Fluopicolide residues in mature wine ranged from 0.14 to 0.31 mg/kg. The processing factors for fluopicolide residues (parent only) from RAC into mature white wine (both non-pasteurised and pasteurised) ranged from 0.23 to 0.61 (mean value of 0.39). Achieved mass balance figures ranged from 66 to 86%.

Tomato

Balance studies on processing of tomato into juice, preserve and puree were conducted to determine the transfer of fluopicolide (fluopicolide) and its metabolites (M-01 and M-02) and propamocarb from tomato fruits into processed fractions (Billian 2008). Only the results for fluopicolide are reported here.

In 2007 four supervised residue trials were conducted on field grown tomatoes (Italy, Spain, Greece and Portugal). Fluopicolide (as an SC formulation) was sprayed three times on tomato plants at an exaggerated rate of 0.39 kg ai/ha and in spray volumes of 800–1155 L/ha. The applications were carried out with a spray interval of 7 days. The first treatment was conducted at BBCH 81–84, whilst the last application was carried out at BBCH 82–89, one day before the anticipated commercial harvest. In all trials, tomato samples (fruits) were taken at day 0 and at day 1 (the intended PHI) after the last application.

The processing of tomato samples into fruit, washed; washing water; raw juice; juice; fruit, peeled; peel, peeling water; preserves; strain rest, wet; raw puree and purée was performed in the Food Processing Laboratory (FPL) of BCS-D-ROCS in Monheim am Rhein. The washing and peeling of tomatoes was done using household practice. The preparation of juice, preserves, and puree simulated the industrial practice at a laboratory scale.

The tomatoes were washed in lukewarm standing water. The washed tomatoes were cut with a knife into small pieces and were heated after addition of water to 98–100 °C for 40 min in order to prevent enzymatic reactions. After this blanching process, the tomato pulp was passed through a strainer to separate raw juice and strain the rest. Sodium chloride (0.5–0.7% (w/w)) was added to the raw juice. An aliquot of the raw juice was taken. One part of the remaining raw juice was used for the processing into preserves (see below). Another portion of the remaining raw juice was filled into 1/1 preserving cans and pasteurised. After pasteurisation an aliquot of the juice was taken.

For the processing of tomato into preserves, another portion of the deep-frozen tomatoes were washed in warm standing water. After a few minutes the peel could be removed however, for these samples the peel was very difficult to remove and a lot of peel remained on the fruit. Aliquots of peel, peeling water and peeled fruit were taken. After addition of raw juice a part of the remaining peeled tomatoes (ratio fruit/juice = 1/0.86) was filled into 1/1 preserving cans and pasteurised. After pasteurisation, the tomato preserves were minced with a hand mixer. An aliquot of tomato preserve was taken.

For the processing of tomato fruits into purée, tomatoes samples were washed in lukewarm standing water. The washed tomatoes were cut with a knife into small pieces and were heated after addition of water to 98–100 °C for 40 min in order to prevent enzymatic reactions. After this

blanching process the tomato pulp was passed through a strainer to separate raw juice and strain rest. The obtained tomato raw juice was mixed up with sodium chloride. An aliquot of the raw juice was concentrated (100–200 mbar, 75 °C) while stirring to obtain tomato raw purée (dry weight: 16%).

Residues of fluopicolide and its metabolites M-02 and M-01 were determined according to method 00782/M004 by HPLC-MS/MS. The storage period of deep frozen samples ranged between 206 and 354 days.

In tomato fruits used for processing, residues of fluopicolide were between 0.17 and 0.43 mg/kg. During tomato juice production a mean of 60% of the absolute residue was recovered in the washing water. Approximately 34% of the initial fluopicolide residue remained in the washed fruit and was transferred into raw juice, leading to fluopicolide values between 0.05 and 0.09 mg/kg in the final product (juice).

With tomato preserves approximately 72% of the initial fluopicolide residue was found in the peel water and 32% in the peel. Approximately 3% of the initial residue remained in the peeled fruit, leading to values between 0.02 and 0.03 mg/kg in preserves. During tomato purée production about 16% of the initial residue was recovered in the material collected on straining with 13% found in the raw purée, leading to fluopicolide values between 0.07 and 0.15 mg/kg in purée. Average processing factors of 0.3, 0.1 and 0.4 were calculated for the transfer of fluopicolide from tomato fruits into juice, preserve and purée respectively.

Table 103 Residues of fluopicolide (and its metabolites) in tomato fruits and processed commodities of tomato juice, preserve and puree production

Study No. Trial No.	Portion analysed	PHI (days)	Residues (mg/kg) fluopicolide	M-01	M-02
Italy RA-3639/07 R 2007 0343/0	fruit	0	0.36	< 0.01	0.01
	fruit	1	0.43	0.02	0.02
	raw juice	1	0.06	0.01	< 0.01
	washings	1	0.12	< 0.01	< 0.01
	fruit, washed	1	0.14	0.01	< 0.01
	juice	1	0.07	0.01	< 0.01
	peel	1	0.50	0.02	0.01
	preserve	1	0.03	< 0.01	< 0.01
	fruit, peeled	1	0.02	< 0.01	< 0.01
	peeling water	1	0.12	< 0.01	< 0.01
	purée	1	0.12	0.02	0.01
	raw purée	1	0.11	0.02	0.01
	strain rest	1	0.85	0.01	< 0.01
Spain RA-3639/07 R 2007 0367/8	fruit	0	0.21	< 0.01	< 0.01
	fruit	1	0.28	< 0.01	< 0.01
	raw juice	1	0.10	< 0.01	< 0.01
	washings	1	0.08	< 0.01	< 0.01
	fruit, washed	1	0.08	< 0.01	< 0.01
	juice	1	0.09	< 0.01	< 0.01
	peel	1	1.5	< 0.01	< 0.01
	preserve	1	0.03	< 0.01	< 0.01
	fruit, peeled	1	< 0.01	< 0.01	< 0.01
	peeling water	1	0.12	< 0.01	< 0.01
	purée	1	0.15	< 0.01	< 0.01
	raw purée	1	0.12	< 0.01	< 0.01
	strain rest	1	1.1	< 0.01	< 0.01
Greece RA-3639/07 R 2007 0368/6	fruit	0	0.14	< 0.01	< 0.01
	fruit	1	0.22	< 0.01	0.01
	raw juice	1	0.05	< 0.01	< 0.01
	washings	1	0.03	< 0.01	< 0.01
	fruit, washed	1	0.04	< 0.01	< 0.01

Study No. Trial No.	Portion analysed	PHI (days)	Residues (mg/kg) fluopicolide	M-01	M-02
	juice	1	0.06	< 0.01	< 0.01
	peel	1	0.76	< 0.01	< 0.01
	preserve	1	0.02	< 0.01	< 0.01
	fruit, peeled	1	< 0.01	< 0.01	< 0.01
	peeling water	1	0.07	< 0.01	< 0.01
	purée	1	0.07	< 0.01	< 0.01
	raw purée	1	0.08	< 0.01	< 0.01
	strain rest	1	0.47	< 0.01	< 0.01
Portugal RA-3639/07 R 2007 0369/4	fruit	0	0.31	< 0.01	< 0.01
	fruit	1	0.17	< 0.01	< 0.01
	raw juice	1	0.05	< 0.01	< 0.01
	washings	1	0.08	< 0.01	< 0.01
	fruit, washed	1	0.07	< 0.01	< 0.01
	juice	1	0.05	< 0.01	< 0.01
	peel	1	0.36	< 0.01	< 0.01
	preserve	1	0.02	< 0.01	< 0.01
	fruit, peeled	1	< 0.01	< 0.01	< 0.01
	peeling water	1	0.06	< 0.01	< 0.01
	purée	1	0.08	< 0.01	< 0.01
	raw purée	1	0.08	< 0.01	< 0.01
	strain rest	1	0.57	< 0.01	< 0.01

Table 104 Processing factors for the residue of fluopicolide in processed commodities of tomato juice, preserve and purée production

Sample material	Processing factors for residues of fluopicolide				
	R 2007 0343/0 Italy	R 2007 0367/8 Spain	R 2007 0368/6 Greece	R 2007 0369/4 Portugal	Mean
fruit, washed	0.3	0.3	0.2	0.4	0.4
washing water	0.3	0.3	0.1	0.5	0.3
raw juice	0.1	0.3	0.2	0.3	0.2
Juice	0.2	0.3	0.3	0.3	0.3
fruit, peeled	0.04	< 0.04 [a]	< 0.05 [a]	< 0.06 [a]	0.05
Peel	1.2	5.4	3.5	2.1	3.1
peeling water	0.3	0.4	0.3	0.3	0.3
preserve	0.1	0.1	0.1	0.1	0.1
strain rest, wet	2.0	4.0	2.1	3.3	2.9
raw purée	0.2	0.4	0.4	0.5	0.4
purée	0.3	0.5	0.3	0.5	0.4

[a] For calculation of the transfer factor the residue in the processed product was set at the LOQ (0.01 mg/kg).

A study was carried out in the USA to determine the transfer of fluopicolide residues on processing of tomatoes (Norris 2003). Tomato plants were sprayed three times with an SC formulation of fluopicolide at a rate of 667 g ai/ha at five day intervals. Tomato fruit was collected at a 2-day pre-harvest interval (PHI) and processed to tomato puree and tomato paste.

The first processing step was to wash the tomatoes.

The washed tomatoes were introduced into a grinder which discharged crushed tomatoes into a surge tank. The crush was heated to 93 °C and the hot crush processed through a finisher equipped with a screen having 0.084 cm perforations which removed peel and seeds (wet pomace) from the crush, producing juice. Concentration of juice to purée was done using a vacuum evaporator. The juice was recirculated through the evaporator until it was condensed to purée. Natural tomato soluble

solids (NTSS) were measured on the juice at the start of concentration and during concentration to purée. When the NTSS was within the specified range for purée (8 to 16%), the purée was collected into a drum and weighed. The NTSS for the purée fractions was 11% for the control and 11.6% for the treated. A weighed portion of purée (3.5 kg for control, and 7.1 kg for treated) was taken to produce the canned purée fraction sample. The remainder of the purée was transferred to a vacuum kettle evaporator for condensing to paste.

The weighed portion of the control purée was transferred to a steam jacketed kettle, heated while stirring to 89 °C and filled into three cans; the after-heating NTSS was 11.8%. The cans were sealed and then inverted. After 6 minutes, the cans were water-cooled. When cool, the NFL Sample No. 07 fraction sample cans were dried, labelled and frozen.

The residues of fluopicolide, M-01 (BAM) and M-02 (PCA) were quantitated by LC/MS/MS according to method 00782. The LOQ was 0.01 mg/kg for each analyte in all commodities. Residues for M-02 were determined as AE 0815899 and calculated as M-02. Processed samples analysed in this study were held in frozen storage between 366 and 380 days prior to extraction.

The fluopicolide residue level in the tomato RAC sampled on day 2 after the last treatment was between 0.23 and 0.34 mg/kg (unwashed fruit). Fluopicolide residues were concentrated during processing into tomato purée (0.48–0.49 mg/kg) and tomato paste (0.59–0.79 mg/kg). This corresponds to a mean processing factor of 1.8 for the processing into purée and 2.5 for the processing into tomato paste. Residues of M-01 and M-02 were below the LOQ (< 0.01 mg/kg) except for residues of 0.011 mg/kg of M-02 in one tomato paste sample. This terminal fraction is the result of the removal of a lot of water with heat which may have hydrolysed traces of the parent fungicide. Concentration of the solids in the paste fraction also increased the concentration of the analyte to detectable, but not to significant, levels.

Table 105 Results from processing studies on tomato in USA

Reference	Country (year)	PHI (days)	Portion analysed	fluopicolide (mg/kg)	PF	M-01 (mg/kg)	M-02 (mg/kg)
01CU27782 27782-01(A)	USA 2001	2	fruit	0.23	–	< 0.01	< 0.01
			purée	0.49	2.2	< 0.01	< 0.01
			paste	0.79	3.5	< 0.01	0.011
01CU27782 27782-01(B)	USA 2001	2	Fruit	0.28	–	< 0.01	< 0.01
			purée	0.48	1.8	< 0.01	< 0.01
			paste	0.59	2.2	< 0.01	< 0.01
01CU27782 27782-01(C)	USA 2001	2	Fruit	0.34	–	< 0.01	< 0.01
			purée	0.49	1.5	< 0.01	< 0.01
			paste	0.63	1.9	< 0.01	< 0.01

Fluopicolide residues were concentrated during processing into tomato purée (mean transfer factor of 1.8) and tomato paste (mean transfer factor of 2.5). Residues of M-01 and M-02 were below the LOQ (< 0.01 mg/kg) except for residues of 0.011 mg/kg of M-02 in one tomato paste sample.

Livestock feeding studies

Fluopicolide was administered orally (within gelatine capsules) to lactating Red Holstein Fleckvieh or Simmentaler Fleckvieh dairy cows (2–7 years old, 480–740 kg) for 27–28 days. Capsules were prepared by adding acetone solutions to capsules and the solvent evaporated. Daily doses were approximately 10, 30 and 100 mg/cow and were split into two and administered twice daily. Based on daily feed consumption of 17.6–20.3 kg/d the doses were equivalent to 0.5, 1.7 and 5.7 ppm in the

feed. Average milk production for each group ranged from 16.8 to 19.2 kg/d. Milk samples were pooled from each cow on a daily basis (evening and morning milkings) for residue analysis. Cows were sacrificed within 24 hours of the last dose at the end of the feeding period to provide samples of tissues for analysis. Tissue samples taken for analysis were muscle (meat), liver, kidney and fat. Aliquots of milk from the day 22 5.7 ppm dose group and control group samples were separated to yield milk fat (cream) and skimmed milk so that the distribution of any residues could be established. Pooled milk samples from cows in the 5.7 ppm dose group were analysed in the first instance from the following dosing days of the study: –1, 1, 4, 7, 10, 13, 16, 19, 22, 25 and 28 days as were samples of skeletal muscle (meat), fat (composite of mesenterial, perirenal and where possible subcutaneous fats), liver and kidney. Analytical method AR 303-2 was used for the analysis of fluopicolide, plus metabolites M-01 and M-02 in milk and cattle tissues

All residues of M-01 and M-02 in milk from the 5.7 ppm dose group were below the LOQ of 0.01 mg/kg. Residues of fluopicolide were also all below the same LOQ of 0.01 mg/kg with the exception of one cow at day 4 which gave 0.01 mg/kg fluopicolide and one at day 28 which gave 0.02 mg/kg fluopicolide. Milk samples from the lower dose groups (0.5 and 1.7 ppm) were analysed from days –1, 1, and 4 as well as samples from days 7 and 10 for the 1.7 ppm dose group. All these results for fluopicolide were below the LOQ of 0.01 mg/kg.

Whole milk from all three cows from 5.7 ppm dose group for day 22 was separated into milk fat (cream) and skimmed milk. Residues were below the LOQ of 0.01 mg/kg for M-01 and M-02 in both the cream and skimmed milk. Residues of fluopicolide were below the LOQ in skimmed milk and 0.016 mg/kg (mean of three values) in cream.

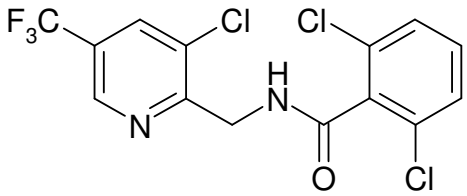
No residues above LOQ (0.05 mg/kg) were detected for fluopicolide, M-01 and M-02 in samples of fat (composites), liver and kidney for the 5.7 ppm dose group. As no residues above LOQ (0.05 mg/kg) were detected for the high dose group samples from the lower dose groups were not subject to analysis. Samples of muscle were analysed for all three dose groups. Residues of fluopicolide, M-01 and M-02 were all below the LOQ of 0.02 mg/kg.

APPRAISAL

Fluopicolide belongs to the benzamide and pyridine class of fungicide. It is a meso-systemic fungicide; it translocates toward the stem tips via the xylem but it does not translocate toward the roots. Fluopicolide is effective against a wide range of Oomycete (Phycomycete) diseases including downy mildews (Plasmopara, Pseudoperonospora, Peronospora and Bremia), late blight (Phytophthora), and some Pythium species. The Meeting received information on fluopicolide metabolism and environmental fate, methods of residue analysis, freezer storage stability, national registered use patterns, supervised residue trials, farm animal feeding studies and fates of residues in processing.

The 2009 JMPR established ADIs for fluopicolide and 2,6-dichlorobenzamide of 0–0.08 and 0–0.02 mg/kg bw respectively. For fluopicolide the ARfD is 0.6 mg/kg bw for women of child-bearing age with an ARfD not necessary for other groups of the population. The Meeting set an ARfD for 2,6-dichlorobenzamide of 0.6 mg/kg bw for the general population.

Fluopicolide is 2,6-dichloro-N-{[3-chloro-5-(trifluoromethyl)-2-pyridinyl]methyl}benzamide.



The following abbreviations are used for the metabolites discussed below:

M-01 or BAM: 2,6-dichlorobenzamide

M-02: 3-chloro-5-(trifluoromethyl)pyridine-2-carboxylic acid

M-04: 2,6-dichloro-3-hydroxybenzamide

M-05: 3-(methylsulfinyl)-5-(trifluoromethyl)pyridine-2-carboxylic acid

M-06 2,6-dichloro-N-[(3-chloro-5-trifluoromethylpyridin-2-yl) methyl]-3-hydroxybenzamide

M-07 2,6-dichloro-N-[(3-chloro-5-trifluoromethylpyridin-2-yl) methyl]-4-hydroxybenzamide

M-18 2,4-dichloro-3-[({[3-chloro-5-(trifluoromethyl)pyridin-2-yl]methyl}amino)carbonyl] phenyl hydrogen sulphate or 3,5-dichloro-4-[({[3-chloro-5-(trifluoromethyl)pyridin-2-yl]methyl}amino)carbonyl] phenyl hydrogen sulfate

M-19 3,5-dichloro-4-[({[3-chloro-5-(trifluoromethyl)pyridin-2-yl]methyl}amino)carbonyl] hydroxyphenyl hydrogen sulfate

Animal metabolism

Radiolabelled fluopicolide (separately ^{14}C-labelled at the [pyridyl-2,6-^{14}C]- and [phenyl-U-^{14}C]-rings) was used in the metabolism and environmental studies. The metabolism of laboratory animals was qualitatively the same as for farm animals though some species-related differences were noted.

Lactating cows were orally dosed with [pyridyl-2,6-^{14}C]- or [phenyl-U-^{14}C]-fluopicolide at doses equivalent to approximately 1 or 10 ppm in the feed for 7 consecutive days.

The majority of the administered doses were recovered in excreta (55–69% in faeces, 11–19% in urine) with an additional 0.87–2.1% recovered from the cage wash. Radioactivity retained in tissues, bile or secreted in milk accounted for less than 1% of the administered dose. Overall 76–84% of administered radioactivity was accounted for.

Radiocarbon content in various tissues were highest in liver followed by kidney, fat and muscle while in milk radioactive residues were low, being lower than those observed in muscle. Following dosing equivalent to 10 ppm in the diet radioactivity was 0.45–0.64 mg/kg in liver, 0.2–0.3 mg/kg in kidney, 0.04 mg/g in fat, 0.01–0.02 mg/kg in muscle and 0.01–0.02 mg/kg in milk. Fluopicolide was the major component of the extracted radioactivity identified in muscle (5.1%), fat (64–78%) and milk (37%) samples and was also present in liver (0.9–2.9%) and kidney (0.7–1.8%). A large number of metabolites were present in extracts of liver and kidney, each accounting for less than 10% of the TRR, most notably mono- and di-hydroxy-glucuronides of fluopicolide as well as mono- and dihydroxy-sulphate conjugates of fluopicolide (M-18, M-19).

Investigations into polar metabolites in liver and kidney demonstrated that they were associated with amino acids, peptides and proteins. There was no significant association of the radioactive residues of fluopicolide with RNA or DNA.

Laying hens were orally dosed with [pyridyl-2,6-^{14}C]- or [phenyl-U-^{14}C]-fluopicolide at doses equivalent to approximately 1 or 10 ppm in the feed for 14 days. The majority of the administered radioactivity was excreted (82–95% over the 14 day dosing period), with 0.6–2.8% recovered from cage wash and approximately 0.08–0.13% in eggs (white and yolks). In tissues from the 10 ppm dose groups, the highest concentrations of radioactivity were in liver (0.28–0.98 mg/kg), followed by fat (0.03–0.06 mg/kg) and muscle (0.01–0.04 mg/kg). Fluopicolide represented 11% of the radioactivity in yolks and 0–2.5% in egg whites. The major component of the radioactivity in egg whites (51%) was tentatively assigned to a methylsulphone conjugate of fluopicolide; the conjugate was also present in fat (38% TRR). A large number of degradates were present in the eggs and tissues, most notably M-01 (37% liver TRR), M-06 in liver (5.4% TRR) and skin plus fat (38% TRR), M-07 in egg

white (41% TRR), egg yolk (9.6–16% TRR), liver (5.9% TRR) and fat (47% TRR). Monohydroxy-sulphate (M-18 10% TRR in yolk and liver) and dihydroxy-sulphate conjugates (M-19 23% egg white TRR, 15–34% yolk TRR) were also observed but no mono- and dihydroxy-glucuronides.

As with lactating cows, investigations into polar metabolites in liver demonstrated that they were associated with amino acids, peptides and proteins and that there was no significant association of the radioactive residues of fluopicolide with RNA or DNA.

In summary, in livestock the majority of the administered radioactivity was recovered in the excreta (75–95% of dose) leaving only low levels of radioactivity in the tissues (0.06–0.78%), milk (0.08–0.14%) and eggs (0.08–0.13%). The highest tissue concentrations were consistently observed in the liver of cow and hen at both dose levels. There was no evidence of any accumulation of radioactivity in milk, eggs or edible tissues.

The identified metabolites of fluopicolide in the cow and hen are thought to be formed by hydroxylation of the chlorophenyl ring in the meta- and para- positions to give metabolites M-07 and M-06, respectively. Each of these metabolites is conjugated with sulphate or hydroxylated in a second position to give a proposed dihydroxy intermediate, which is further metabolised to a sulphate conjugate. In the cow, conjugation with glucuronic acid was also observed. Additionally a methyl sulphone conjugate of fluopicolide and M-01 have been observed in the hen.

Plant Metabolism

The Meeting received information on the fate of [^{14}C]fluopicolide after foliar application to grapes, lettuce and potato and also as a soil drench to lettuce.

Metabolism studies in grapes, lettuce and potato demonstrated that following foliar application, fluopicolide was not metabolised to any great extent. With up to three consecutive foliar applications of fluopicolide to grapes, lettuce and potato, parent compound was the major component of the radioactive residues at 87–95%, 96% and 51–70% of the TRR respectively for grapes (berries), lettuce (leaves) and potato (tubers). When applied as a soil drench to lettuce parent compound was the major component of the TRR in lettuce at harvest (72% TRR). Minor metabolites (< 0.035 mg/kg) identified in the studies were M-01 (1.3–25% TRR), M-02 (0.6–26% TRR) and M-06 (0.1–2.8% TRR) with the higher levels of metabolites resulting from uptake from soil (lettuce following a soil drench or in potato tubers following foliar sprays). Surface washes of samples removed the majority of the residue, decreasing with time after spraying.

Metabolism of fluopicolide is proposed to occur through hydrolysis of the amide bond of fluopicolide to form metabolites M-01 and M-02 and hydroxylation in position 3 of the phenyl ring to form metabolite M-06.

Environmental fate

Photolytic degradation of fluopicolide occurs to some extent and may contribute to its degradation. Fluopicolide is considered stable to hydrolysis.

The aerobic degradation of fluopicolide in soil is primarily via oxidative cleavage to produce, M-01 and M-02. Ultimately mineralisation to $^{14}CO_2$ occurs. The half-life for disappearance of parent fluopicolide in soil is estimated to be > 200 days. Fluopicolide is considered to be persistent.

Residues in succeeding crops

The log K_{ow} of fluopicolide (log K_{ow} 2.9) and the results of the lettuce and potato metabolism studies suggest fluopicolide may be translocated in plants. In confined and field rotational crop studies, residues of fluopicolide were found in leafy and brassica vegetables, root vegetables, and cereal and pulse grain at harvest. In confined rotational crop studies with radiolabelled fluopicolide metabolites M-01, M-02 and M-04 occurred at levels higher than fluopicolide in some matrices, principally wheat grain and forage. In lettuce and radish (root and tops), the main residues were fluopicolide and M-01.

Residues of M-06, M-08 and M-09 were also detected but the levels were lower than for fluopicolide. The levels of fluopicolide and metabolites in field rotational crop studies on wheat were < 0.01–0.12 mg/kg for fluopicolide, < 0.01–0.06 mg/kg for M-01, < 0.01–0.02 mg/kg for M-02, < 0.01–0.09 mg/kg for M-04 and < 0.01–0.08 mg/kg for M-05 in forage, straw and grain. For cabbage, faba beans (shoots, pods and dried seed) and radish (root and tops) residues were < 0.01–0.03 mg/kg for fluopicolide, < 0.01–0.10 mg/kg for M-01 and < 0.01–0.02 mg/kg for M-02. It is concluded that rotational crops may contain low levels of residues of fluopicolide and metabolites.

Analytical methods

Several different analytical methods have been reported for the analysis of fluopicolide and selected metabolites/degradates in plant material (M-01, M-02) and fluopicolide in animal commodities. The basic approach employs extraction by homogenisation with acetonitrile:water, and column clean-up using SPE. Residues are determined by liquid chromatography with mass spectra detection. The methods for fluopicolide and selected metabolites have been validated with for a range of substrates with LOQs of 0.01 mg/kg for each analyte. Studies on extraction efficiency indicated greater than 80% of the residue is able to be extracted with acetone:water.

The official German multi-residue method (DFG-S19) with LC-MS/MS detection was validated for fluopicolide; M-01, M-02 in plant, and fluopicolide in animal commodities. LOQs were also 0.01 mg/kg for each analyte.

Stability of pesticide residues in stored analytical samples

Freezer storage stability was tested for a range of representative substrates. Fluopicolide, M-01 and M-02 residues are stable in grapes, potatoes, cabbages and wheat grain for at least 30 months frozen storage. Fluopicolide, M-01, M-04 and M-05 are stable in wheat straw for at least 18 months frozen storage. Data on freezer storage stability showed that fluopicolide, M-01 and M-02 residues are stable in milk for at least 2 months, in fat and muscle for at least 4 months and in liver and kidney for at least 9 months.

Residue definition

The metabolism of fluopicolide in a range of crops has been studied following both foliar and soil drench application. Studies were conducted with leafy vegetables (lettuce), root vegetables (potatoes) and fruit crops (grape vine). Each was conducted with both phenyl- and pyridyl-radiolabelled fluopicolide. The rate of degradation on plants is low and the parent compound was always the major component (51–96% TRR). Metabolites M-01 and M-02 were present at 1.3–25% and 0.6–26% respectively. Minor metabolites M-04, M-05, M-08 and M-09 were found in plant matrices at low levels (≤ 2.8% TRR) but not in rat metabolism studies.

In rotational crop studies fluopicolide and M-01 were generally the main components of the residue. The Meeting considered the acute and long term toxicity of M-01 is higher than fluopicolide while the available data show that the metabolites M-02, M-04 and M-05 are less toxic than the parent compound. The Meeting decided to include M-01 in the residue definition for risk assessment. However, the metabolite M-01 is not unique to fluopicolide, e.g. M-01 is also a metabolite of dichlobenil. Therefore, it was proposed not to include M-01 in the residue definition for compliance. The Meeting considered the majority of dietary exposure to residues of toxicological concern would be accounted for when measuring residues of fluopicolide and M-01.

In the lactating cow metabolism study, fluopicolide is the major component of the residue in muscle (5.1%), fat (64–78%) and milk (37%) and was also present in liver (0.9–2.9%) and kidney (0.7–1.8%) and in the laying hen study represented 11% of the radioactivity in yolks and 0–2.5% in

egg whites. Parent fluopicolide is present in most tissues and considered a good indicator compound for enforcement purposes.

The Meeting recommended that the residue definition for plant and animal commodities for compliance with MRLs should be fluopicolide.

The Meeting recommended that the residue definition for plant and animal commodities for dietary risk assessment should be fluopicolide and M-01.

The log K_{ow} of fluopicolide (log K_{ow} 2.9, pH 7) suggests that fluopicolide might be borderline fat soluble. The ratio of fluopicolide residues in muscle and fat observed in the livestock metabolism studies (lactating cow 1:32–1:49) support the conclusion that fluopicolide is fat soluble.

Proposed definition of the residue (for compliance with MRL for plant and animal commodities): fluopicolide.

Proposed definition of the residue (for estimation of dietary intake for plant and animal commodities): fluopicolide and 2,6-dichlorobenzamide measured separately.

The residue is fat soluble.

Results of supervised trials on crops

Dietary risk assessment requires separate STMR and HR values for fluopicolide and M-01. Supervised trials were available for the use of fluopicolide on: grapes, onions, leeks, Brassica vegetables (broccoli, Brussels sprouts, cabbage and cauliflower), cucumber, melon and summer squash including zucchini, chilli peppers, sweet peppers, tomatoes, lettuce, spinach, carrots, radish, and celery. Residue trial data was made available from Brazil, Canada, member states of the European Union and the USA.

The NAFTA calculator was used as a tool in the estimation of the maximum residue levels from the selected residue data sets obtained from trials conducted according to GAP. As a first step, the Meeting reviewed all relevant factors related to each data set in arriving at a best estimate of the maximum residue level with the calculator using expert judgement. Then, the NAFTA calculator was employed. If the statistical calculation spreadsheet suggested a different value than that recommended by the JMPR, a brief explanation of the deviation was supplied. Some common factors that may lead to rejection of the statistical estimate include when the number of data points in a data set is < 15 or when there are a large number of values < LOQ.

Grapes

Data were available from supervised trials on grapes in member states of the European Union, Canada and the USA.

The GAPs of Italy and Slovenia are similar at one to three sprays at 133 g ai/ha and a PHI of 28 days. Residues in grapes from trials in southern Europe matching GAP of Italy and Slovenia were (n=20): 0.11, 0.11, 0.15, 0.16, 0.20, 0.21, 0.21, 0.21, 0.27, 0.35, 0.38, 0.39, 0.40, 0.46, 0.54, 0.60, 0.69, 0.97, 1.1 and 1.2 mg/kg. M-01 residues were < 0.01 (12), 0.014, 0.015, 0.02 (2), 0.026, 0.03, 0.037 and 0.04 mg/kg. Residues in grapes from trials in northern Europe matching GAP of Italy and Slovenia were (n=19): 0.18, 0.20, 0.21, 0.24, 0.27 (0.013), 0.32, 0.32, 0.33, 0.33, 0.38, 0.44, 0.48 (0.01), 0.50, 0.51 (0.01), 0.52, 0.56, 0.66, 0.83 and 0.96 mg/kg. Residues of M-01 were: < 0.01 (16), 0.01 (2) and 0.013 mg/kg. The residue populations for trials conducted in northern and southern Europe were similar (Mann-Whitney U test) and the Meeting decided to combine the data for the purposes of estimating a maximum residue level (n=39) 0.11, 0.11, 0.15, 0.16, 0.18, 0.2, 0.2, 0.21, 0.21, 0.21, 0.21, 0.24, 0.27, 0.27, 0.32, 0.32, 0.33, 0.33, 0.35, 0.38, 0.38, 0.39, 0.4, 0.44, 0.46, 0.48, 0.5, 0.51, 0.52, 0.54, 0.56, 0.6, 0.66, 0.69, 0.83, 0.96, 0.97, 1.1 and 1.2 mg/kg. Residues of M-01 were: ≤ 0.01 (28), 0.01 (2), 0.013, 0.014, 0.015, 0.02 (2), 0.026, 0.03, 0.037 and 0.04 mg/kg.

The GAP of the USA was used to evaluate trials on grapes from Canada and the USA (USA GAP: 140 g ai/ha, PHI 21 days with a maximum seasonal application of 420 g ai/ha). The intervals

between sprays in the trials were 4 to 5 days compared with the minimum specified for GAP of 7 days. The meeting noted the DT_{50} for residues in grapes from trials in Europe were approximately 21 days and concluded the shorter interval between sprays would have minimal impact on observed residues at harvest. Residues of fluopicolide in grapes from 16 trials in Canada and the USA approximating GAP of the USA, in rank order, were: 0.07, 0.10, 0.10, 0.13, 0.13, 0.14, 0.19, 0.21, 0.25, 0.26, 0.32, 0.44, 0.53, 0.56, 0.99 and 1.1 mg/kg. No residues of M-01 were detected, LOQ = 0.01 mg/kg.

Residues according to the GAP of Canada and the USA were similar to those for Italy and Slovenia and the larger dataset of trials conducted in Europe was used to estimate residue values. The Meeting considered a value of 2 mg/kg appropriate as a maximum residue using a mixture of expert judgement and information on initial residue deposits. Use of the NAFTA calculator yielded a value of 1.4 mg/kg which agreed with the estimate of 2 mg/kg made by the Meeting (after rounding up to one figure). The Meeting estimated a maximum residue level for fluopicolide in grapes of 2 mg/kg. The corresponding HR values are 1.2 mg/kg for fluopicolide and 0.04 mg/kg for M-01, and STMRs are 0.38 mg/kg for fluopicolide and 0.01 mg/kg for M-01.

Bulb vegetables

Data were available from supervised trials on onions in member states of the European Union and the USA. Details of GAP for countries from the European Union were not available and the data from these trials were not further evaluated.

The GAP of the USA is foliar application at a maximum rate of 140 g ai/ha, PHI 2 days with a maximum seasonal application of 420 g ai/ha and a minimum interval between sprays of 7 days. In trials conducted in the USA the interval between sprays was lower (4–6 days) than the minimum; however, the meeting noted that the DT_{50} for residues in decline trials from Europe was of the order of 4 days and therefore it is the last spray that has the greatest influence on residues. Residues of fluopicolide in onions from seven trials in the USA complying with GAP were (in rank order, median underlined): 0.01, 0.05, 0.05, 0.07, 0.08, 0.11 and 0.58 mg/kg. No residues of M-01 were detected, < 0.01 (7) mg/kg.

The Meeting suggested a value of 1 mg/kg would be appropriate noting the size of the dataset and variability in residues. Using the NAFTA calculator a proposal of 0.51 mg/kg was derived assuming a lognormal distribution however, inspection of plots indicated the data did not follow this distribution type. The Meeting estimated maximum residue level for fluopicolide in onions of 1 mg/kg. The corresponding HR values are 0.58 mg/kg (fluopicolide) and 0.01 mg/kg (M-01) and STMR values of 0.07 mg/kg for fluopicolide and 0.01 mg/kg for M-01.

Additionally three trials were available on bunching onions (Welsh onions). Residues according to the GAP of the USA for bulb vegetables were: 1.7, 2.1 and 4.5 g/kg. Corresponding residues of M-01 were < 0.01, ≤ 0.01 and 0.01 mg/kg respectively. The Meeting noted the small dataset and suggested a value of 10 mg/kg would be suitable as a maximum residue level. The estimate using the NAFTA calculator was 8.3 mg/kg. The Meeting considered the uncertainty of estimates based on very small datasets and considered the higher estimate more appropriate.

The Meeting estimated maximum residue level for fluopicolide in Welsh onions of 10 mg/kg, HR values of 4.5 mg/kg (fluopicolide) and 0.01 mg/kg (M-01) and STMRs of 2.1 mg/kg for fluopicolide and 0.01 mg/kg for M-01.

Residue trials were provided from Europe for use of fluopicolide on leeks but no GAP was available.

Brassica vegetables

In Estonia and Lithuania, fluopicolide is registered for use on cabbage at a maximum of three sprays of 100 g ai/ha with a PHI of 14 days. Residues in head cabbage from northern Europe complying with GAP were: < 0.01, < 0.01, 0.01, 0.01, 0.03, 0.03, 0.08 and 0.18 mg/kg. Residues of M-01 were not

detected. Residues in head cabbage from southern Europe complying with GAP were: 0.01, 0.01, 0.02, and 0.03 mg/kg. Residues of M-01 were not detected. The residue populations for trials conducted in northern and southern Europe were similar (Mann-Whitney U test) and the Meeting decided to combine the data for the purposes of estimating a maximum residue level (n=12): < 0.01, < 0.01, 0.01, 0.01, 0.01, 0.01, 0.02, 0.03, 0.03, 0.03, 0.08 and 0.18 mg/kg.

Fluopicolide is registered in the USA for use on cabbage (Brassica vegetables) at 140 g ai/ha, PHI 2 days with a maximum seasonal application of 420 g ai/ha. Trials were available from the USA in which crops were treated three times at four to six day intervals at 133 g ai/ha with harvest 2 days after the last spray. Residues in head cabbage (with wrapper leaves) were: 0.31, 0.36, 0.61, 1.2, 1.9, 2.3 and 3.9 mg/kg. Residues of M-01 were < 0.01 (6) and 0.02 mg/kg.

The Meeting noted the data from the US for head cabbage had the higher residues and decided to use this dataset to estimate a maximum residue level. The Meeting considered a value of 7 mg/kg appropriate as a maximum residue using a mixture of expert judgement and initial residue deposits. Use of the NAFTA calculator yielded a value of 8.85 mg/kg. The Meeting estimated a maximum residue value for fluopicolide in head cabbages of 7 mg/kg. The corresponding HR values are 4.0 and 0.02 mg/kg respectively for fluopicolide and M-01. The STMRs are 1.2 mg/kg for fluopicolide and 0.01 mg/kg for M-01.

Trials reported from Europe on Brussels sprouts were assessed according to the GAP of Estonia (maximum of three sprays of 100 g ai/ha with a PHI of 14 days). Residues that approximated GAP of Estonia were (n=8): 0.01, 0.03, 0.03, 0.04, 0.04, 0.05, 0.05 and 0.13 mg/kg. Residues of M-01 were < 0.01 (8) mg/kg.

The Meeting considered a value of 0.2 mg/kg appropriate as a maximum residue noting the distribution of residue values. The estimate using the NAFTA calculator was also 0.2 mg/kg. The Meeting estimated maximum residue level for fluopicolide in Brussels sprouts of 0.2 mg/kg, HR values of 0.13 and 0.01 mg/kg for fluopicolide and M-01 respectively, and STMRs of 0.04 mg/kg for fluopicolide and 0.01 mg/kg for M-01.

In Estonia and Lithuania, fluopicolide is registered for use on cauliflower and broccoli at a maximum of three sprays of 100 g ai/ha with a PHI of 14 days. Residues in broccoli from northern Europe trials complying with GAP were: < 0.01, 0.01, 0.02, and 0.10 mg/kg. Corresponding residues of M-01 were all < 0.01 mg/kg. Residues in broccoli from southern Europe trials complying with GAP were: < 0.01, 0.04, 0.06 and 0.11 mg/kg. Corresponding residues of M-01 were all < 0.01 mg/kg.

In Estonia and Lithuania, fluopicolide is registered for use on cauliflower at a maximum of three sprays of 100 g ai/ha with a PHI of 14 days. Residues in cauliflower from northern Europe trials complying with GAP were: < 0.01, < 0.01, < 0.01, and 0.01 mg/kg. Corresponding residues of M-01 were all < 0.01 (4) mg/kg. Residues in cauliflower from southern Europe trials complying with GAP were: < 0.01, < 0.01, 0.01 and 0.06 mg/kg. Corresponding residues of M-01 were all < 0.01 (4) mg/kg.

Fluopicolide is registered in the USA for use on broccoli (Brassica vegetables) at 140 g ai/ha, PHI 2 days with a maximum seasonal application of 420 g ai/ha. Trials were available from the USA in which crops were treated three times at four to six day intervals at 133 g ai/ha with harvest 2 days after the last spray. Residues in broccoli were: 0.18, 0.21, 0.32, 0.45, 0.50 and 0.69 mg/kg. Residues of M-01 were not detected (< 0.01 (6) mg/kg).

The Meeting agreed to extrapolate the USA data for broccoli to establish a maximum residue level for Flowerhead brassicas. The Meeting considered a value of 2 mg/kg appropriate as a maximum residue. The value using the NAFTA calculator agreed with the estimate of 2 mg/kg made by the Meeting (after rounding up to one figure (NAFTA = 1.2 mg/kg). The Meeting estimated a maximum residue level, HR and an STMR value of 2 mg/kg for fluopicolide in Flowerhead brassicas. The corresponding HR values are 0.69 mg/kg for fluopicolide and 0.01 mg/kg for M-01. The STMRs are 0.385 mg/kg for fluopicolide and 0.01 mg/kg for M-01.

Fruiting vegetables, Cucurbits

Fluopicolide is registered in Estonia for use on cucumbers at 100 g ai/ha or 10 g ai/hL, PHI 3 days for field use. Trials were available from northern Europe that complied with GAP of Estonia. Residues in field grown cucumbers were: 0.02, 0.02, 0.03 and 0.08 mg/kg. Residues of M-01 were not detected (< 0.01 mg/kg).

In Lithuania, fluopicolide is registered for use on cucumbers grown under protected cover at a maximum of three sprays at 8.8 g ai/hL with a PHI of 1 day. Trials were available from Europe that complied with GAP of Lithuania with residues of: 0.02, 0.02, 0.03, 0.03, 0.04, 0.04, 0.08 and 0.09 mg/kg. Residues of M-01 were not detected (< 0.01 mg/kg).

Trials on cucumber were reported from the USA (USA GAP for cucurbits: 140 g ai/ha, PHI of 2 days and a maximum application per season of 420 g ai/ha). Fluopicolide residues on cucumbers in six trials from the USA matching GAP in rank order were: 0.01, 0.02, 0.03, 0.03, 0.03 and 0.06 mg/kg. Residues of M-01 were not detected (< 0.01 mg/kg).

Residue trials were provided from Europe for use of fluopicolide on melons but no GAP was available.

Residues on melons (cantaloupe) in nine trials from the USA matching GAP in rank order were: < 0.01, 0.05, 0.06, 0.06, 0.07, 0.07, 0.10, 0.26 and 0.30 mg/kg. Residues of M-01 were not detected (< 0.01 mg/kg).

Trials were available from Greece, Italy and Spain on zucchini but did not match GAP.

Fluopicolide residues on summer squash (including zucchini) in six trials from the USA matching GAP in rank order were: 0.01, 0.03, 0.04, 0.04, 0.05 and 0.06 mg/kg. Residues of M-01 were not detected (< 0.01 mg/kg).

The use-pattern in the USA is for fruiting vegetables, (cucurbits) and the Meeting decided to use the data on the crop with the highest residues (melons) to estimate a maximum residue level for the group. The Meeting considered a value of 0.5 mg/kg appropriate as a maximum residue using a mixture of expert judgement and initial residue deposit data. The estimate using the NAFTA calculator was also 0.5 mg/kg. The Meeting estimated a maximum residue level for fluopicolide in fruiting vegetables, cucurbits of 0.5 mg/kg.

The commodity group encompasses fruit with both edible and inedible peel. For fruit with edible peel the HR and STMRs listed above should be used. Data on residues in the edible portion for melons in trials complying with USA GAP were not available; however, in trials from Europe with similar residues in melons, no residues of fluopicolide or M-01 were detected in the edible portion (LOQ 0.01 mg/kg). For fruit with inedible peel the HR and STMRs are all 0.01 mg/kg and for fruit with edible peel the HR and STMRs are 0.3, 0.07 (fluopicolide) and 0.01, 0.01 (M-01) mg/kg respectively. This is consistent with fluopicolide being a surface residue on crops if applied by foliar application.

Fruiting vegetables, other than Cucurbits

Trials on tomatoes were made available from Brazil but did not match GAP for that country. Fluopicolide is registered in Italy for use on tomatoes at 100 g ai/ha or 10 g ai/hL, PHI 3 days for field use, and 125 g ai/ha or 10 g ai/hL, PHI 3 days for crops grown under protected cover. Trials were available from Europe that complied with GAP of Italy. Residues in field grown tomatoes from trials conducted in northern Europe were: 0.015, 0.14, 0.22, and 0.23 mg/kg. Residues of M-01 were not detected (< 0.01 mg/kg). Residues in field grown tomatoes from trials conducted in southern Europe were: 0.019, 0.046, 0.05, 0.055, 0.09, 0.10, 0.14 and 0.28 mg/kg. Residues of M-01 were not detected (< 0.01 mg/kg). The residue populations for trials conducted in northern and southern Europe were similar (Mann-Whitney U test) and the Meeting decided to combine the data for the purposes of estimating a maximum residue level (n=12): 0.015, 0.019, 0.046, 0.05, 0.055, 0.09, 0.10, 0.14, 0.14, 0.22, 0.23 and 0.28 mg/kg.

In Lithuania, fluopicolide is registered for use on tomatoes grown under protected cover at a maximum of three sprays at 8.8 g ai/hL with a PHI of 1 day. Trials were available from Europe that complied with GAP of Lithuania with residues of: 0.063, 0.08, 0.085, 0.093, 0.14, 0.18, 0.20 and 0.21 mg/kg. Residues of M-01 were not detected (< 0.01 mg/kg).

Trials on tomatoes (including cherry tomatoes) were reported from the USA (USA GAP: 140 g ai/ha, PHI of 2 days and a maximum application per season of 420 g ai/ha). Fluopicolide residues in twelve trials from the USA matching GAP in rank order were: 0.05, 0.06, 0.08, 0.10, 0.15, 0.15[c], 0.17[c], 0.17, 0.19, 0.19, 0.28 and 0.42[c] mg/kg ([c] = cherry tomatoes). Residues of M-01 were not detected (< 0.01 mg/kg).

Trials on sweet peppers were reported from the USA (GAP: 140 g ai/ha, PHI of 2 days and a maximum application per season of 420 g ai/ha). Fluopicolide residues in seven trials on sweet peppers (including Bell peppers) from the USA matching GAP in rank order were: 0.04, 0.05, 0.09, 0.15, 0.17, 0.19 and 0.57 mg/kg. Residues of M-01 were not detected (< 0.01 mg/kg).

Fluopicolide residues in chilli peppers in three trials from the USA matching GAP in rank order were: 0.10, 0.36 and 0.58 mg/kg. Residues of M-01 were not detected (< 0.01 mg/kg).

The Meeting decided that the trials in tomatoes, sweet and chilli peppers could be used to support a group maximum residue level for fruiting vegetables other than cucurbits except mushrooms and sweet corn. The Meeting decided to use the data on the crop with the highest residues (sweet and chilli peppers) to estimate a maximum residue level for the group (fluopicolide residues: 0.04, 0.05, 0.09, 0.10, 0.15, 0.17, 0.19, 0.36, 0.57 and 0.58 mg/kg; M-01 residues < 0.01 (10) mg/kg).

The Meeting considered a value of 1 mg/kg appropriate as a maximum residue using a mixture of expert judgement and initial residue deposit data. Use of the NAFTA calculator yielded a value of 0.8 mg/kg. The Meeting estimated a maximum residue level for fluopicolide in fruiting vegetables other than cucurbits (except mushrooms and sweet corn) of 1 mg/kg. The HR values are 0.58 mg/kg for fluopicolide and 0.01 mg/kg for M-01. The STMRs are 0.16 mg/kg for fluopicolide and 0.01 mg/kg for M-01.

Leafy vegetables

In Romania, fluopicolide is registered for use on lettuce grown under protected cover at a maximum of two sprays at 7 day intervals and at 8.8 g ai/hL (88 g ai/ha) with a PHI of 14 days. Noting that growth dilution would ensure a spray made 28 days before harvest would make a negligible contribution to the final residues; the Meeting agreed that the trials from Europe with three sprays at 7 day intervals could be evaluated against the GAP of Romania. Trials were available from Europe that complied with GAP of Romania with residues of: 0.40, 0.40, 0.63, 0.68, 1.5, 2.7, 4.0 and 4.9 mg/kg. Corresponding residues of M-01 were: < 0.01, 0.018, 0.017, 0.017, 0.022, 0.014, 0.020 and 0.011 mg/kg).

Trials on lettuce and spinach were reported from the USA (GAP: 140 g ai/ha, PHI of 2 days and a maximum application per season of 420 g ai/ha). Fluopicolide residues in seven trials on head lettuce from the USA matching GAP in rank order were: 0.62, 2.3, 2.3, 2.4, 4.2, 4.3 and 7.2 mg/kg. Corresponding residues of M-01 were: < 0.01 (5) and 0.01 (2) mg/kg.

Residues of fluopicolide in seven trials on leaf lettuce from the USA matching GAP were higher than in head lettuce and were (in rank order): 4.3, 5.0, 5.3, 7.6, 7.6, 10 and 12 mg/kg. Corresponding residues of M-01 were: 0.01, 0.01, < 0.01, 0.02, 0.04, < 0.01 and 0.02 mg/kg.

Residue trials were provided from Europe for use of fluopicolide on spinach but no GAP was available.

Fluopicolide residues in seven trials on spinach from the USA matching GAP in rank order were: 6.8, 6.8, 6.9, 8.6, 12, 16 and 17 mg/kg. Corresponding residues of M-01 in rank order were: 0.02, 0.03, 0.06, 0.07, 0.07, 0.09 and 0.19 mg/kg.

The Meeting noted that the registered use of fluopicolide in the USA is for leafy vegetables and decided to recommend a group MRL. The Meeting decided to use the data on the crop with the highest residues (spinach) to estimate a maximum residue level for the group. The Meeting considered a value of 30 mg/kg appropriate as a maximum residue using a mixture of expert judgement and initial residue deposit data. Use of the NAFTA calculator yielded a value of 25.3 mg/kg which, on rounding, also leads to a value of 30 mg/kg. The Meeting estimated a maximum residue level for fluopicolide in leafy vegetables of 30 mg/kg. The HR values are 17 mg/kg for fluopicolide and 0.19 mg/kg for M-01, while the STMRs are 8.6 mg/kg for fluopicolide and 0.07 mg/kg for M-01.

Root and tuber vegetables

Trials on carrot and radish were made available from the USA. No carrot trials matched GAP (no GAP available) and one trial on radish matched GAP in the USA (GAP: 140 g ai/ha, PHI of 2 days and a maximum application per season of 420 g ai/ha) with residues of 0.11 mg/kg (M-01 < 0.01 mg/kg). The Meeting decided that a single trial constitutes an insufficient dataset to estimate a maximum residue level.

Celery

Fluopicolide residues in seven trials on celery from the USA matching GAP (the USA crop group 'leafy vegetables' includes celery) in rank order were (median underlined): 0.16, 0.76, 1.0, 1.4, 5.2, 6.7 and 14 mg/kg. Residues of M-01 were < 0.01 (4), 0.01, 0.03 and 0.04 mg/kg. The Meeting considered a value of 20 mg/kg appropriate as a maximum residue using a mixture of expert judgement. Use of the NAFTA calculator yielded a value of 10.15 mg/kg, which is less than the highest observed residues. The Meeting estimated a maximum residue level for fluopicolide in celery of 20 mg/kg. The HR values are 14 mg/kg for fluopicolide and 0.04 mg/kg for M-01, and STMRs 1.4 mg/kg for fluopicolide and 0.01 mg/kg for M-01.

Rotational crops

Residues of fluopicolide are persistent in soil and may be taken up by succeeding crops. In the USA the total seasonal application rate for crops is 420 g ai/ha. Studies of residues in rotational crops were made available to the meeting where in confined rotational crop studies bare soil was treated at 400 g ai/ha, and in field studies preceding potato crops were treated four times at 100 g ai/ha (400 g ai/ha). It is likely that soil residues would require several years to reach plateau levels and residues in succeeding crops could be higher than those observed in the rotational crop following a single season of applications.

Residues in brassica vegetables grown as a rotational crop were < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 (0.02) and < 0.01 (0.04) mg/kg in cabbage (figures in brackets are for M-01). The levels in brassica vegetables from rotational crops are adequately covered by the recommendations for Head cabbages (5 mg/kg), Flowerhead brassicas (2 mg/kg) and Brussels sprouts (0.2 mg/kg). In addition, if the levels found in cabbage are representative of those taken up by leafy vegetables, considering the magnitude of the maximum residue level recommended for leafy vegetables, it is concluded that residues taken up from soil are a minor contribution for leafy vegetables and adequately covered by the recommendation for leafy vegetables.

Residues in follow-crop cereal grains were < 0.01 mg/kg in 17 trials on wheat. No residues of M-01 were detected. As the residues were all below the LOQ, the Meeting decided it is not necessary to recommend a maximum residue level for cereals grown as rotational crops.

Corresponding residues in cereal forage (wheat) were: < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, 0.01, 0.01, 0.01, 0.01, 0.02, 0.02, 0.02, 0.02, 0.02, 0.03, 0.04 and 0.04 mg/kg. The Meeting decided to recommend STMR and highest residue values of 0.015 and 0.04 mg/kg respectively for forage of cereals (or 0.06 and 0.16 mg/kg on a dry weight basis respectively and assuming 25% dry matter content).

Corresponding residues in cereal straw (wheat) were: < 0.01, 0.01, 0.02, 0.02, 0.03, 0.04, 0.05, 0.05, 0.06, 0.06, 0.06, 0.07, 0.07, 0.07, 0.08, 0.09 and 0.12 mg/kg. The estimated STMR and highest residue values for straw of cereals are 0.06 (or 0.07 mg/kg on a dry weight basis) and 0.12 (or 0.14 mg/kg on a dry weight basis assuming 88% dry matter content) mg/kg respectively. The Meeting recommended a maximum residue level for straw and hay of cereals of 0.2 mg/kg.

Eight trials on residues in pulses (faba bean) grown as rotational crops were available with residues in seed of < 0.01(8) mg/kg. No residues of M-01 were detected. The Meeting decided it is not necessary to recommend a maximum residue level for pulses grown as rotational crops. Residues in forage were < 0.01 (5), 0.01, 0.02 and 0.03 mg/kg. The Meeting also estimated STMR and highest residue values of 0.01 and 0.03 mg/kg respectively for legume animal feeds, or 0.04 and 0.12 mg/kg on a dry weight basis respectively, assuming 25% dry matter content.

Metabolism studies on rotational crops suggested residues of fluopicolide and metabolites would be present in root and tuber crops; however, no field studies were available. The Meeting did not have sufficient information to evaluate residue levels in root and tuber crops or other rotational crops not mentioned above.

Fate of residues during processing

The effect of processing on the nature of residues was investigated in buffer solutions under conditions simulating pasteurisation, boiling and sterilisation. Fluopicolide was shown to be stable under these conditions.

The fate of fluopicolide residues has been examined in grapes and tomato processing studies. Processing of tomatoes into purée and paste showed an increase of fluopicolide residues in the processed commodities compared to the raw commodity, whilst there was a decrease in residues found in the corresponding juice and ketchup. Grapes showed a decrease in residues found in wine, but an increase in pomace. Estimated processing factors and STMR-Ps are summarised below.

Raw agricultural commodity (RAC)	Processed commodity	Calculated processing factors	PF (Mean, median or best estimate)	Fluopicolide RAC-STMR (mg/kg)	Fluopicolide STMR-P (mg/kg)	M-01 STMR-P (mg/kg)[a]
Grape	Pomace wet	1.6 1.8 2.3 5.0 6.3 6.6	3.65 (median)	0.38	1.387	0.01
	Raisin	2.2, 6.5	6.5 (highest)		2.47	0.045
	White wine (np)	0.40 0.43 0.61	0.43 (median)		0.1634	0.01
	Red wine	0.28 0.31 0.38	0.31 (median)		0.1178	0.01
Tomato	Preserve	0.1 0.1 0.1 0.1 0.1	0.1 (median)	0.16[c]	0.016	0.01
	Juice	0.2 0.2 0.3 0.3 0.3	0.3 (median)		0.048	0.01
	Purée[b]	(0.3 0.3 0.4 0.5 0.5) 1.5 1.8 2.2	1.8 (median US)		0.288	0.01
	Paste	1.9 2.2 3.5	2.2 (median)		0.352	0.01

np = non-pasteurised

[a] values in brackets are for 2,6-dichlorobenzamide residues observed in processed commodities from processing trials. Residues were scaled to the application rate for GAP for the crop from which the RAC was derived.

[b] higher tomato values are from US study

[c] STMR for USA tomato trials

On processing tomatoes, fluopicolide concentrated in tomato purée and paste. For grapes, residues concentrated in raisins and pomace. The Meeting decided to estimate a maximum residue level for dried grapes of 10 mg/kg based on a highest residue for grapes of 1.2 mg/kg and a processing factor of 6.5 (1.2 mg/kg × 6.5 = 7.8 mg/kg). The highest residue observed for M-01 in grapes from

vines treated according to GAP and processed was 0.06 mg/kg. The STMR-P for residues of fluopicolide in dried grapes is 2.47 mg/kg while that for M-01 is 0.045 mg/kg (average of the two residue values for M-01 observed in the trials that processed grapes into raisins).

Residues in grape pomace were estimated to be 0.785 mg/kg on a wet weight basis and 5.2 mg/kg (assuming a default 15% dry matter content) when expressed on a dry weight basis. The Meeting decided to recommend a maximum residue level for grape pomace (dry) of 7 mg/kg.

The Meeting also decided to estimate a maximum residue for chilli pepper (dried) of 7 mg/kg following application of a default dehydration factor of 7 to the estimated maximum residue level of 1 mg/kg for chilli pepper (7 × 1 mg/kg = 7 mg/kg). The STMR for residues of fluopicolide in chilli peppers (dry) is estimated to be 7 × 0.13 mg/kg = 0.91 mg/kg. As residues of M-01 were < 0.01 in peppers, the HR and STMR for chilli pepper (dried) is also estimated to be 0.01 mg/kg.

Residues in animal commodities

Farm animal dietary burden

The Meeting estimated the dietary burden of fluopicolide in farm animals on the basis of the diets listed in Annex 6 of the 2006 JMPR Report (OECD Feedstuffs Derived from Field Crops). Residues of M-01 are extremely low and considered unlikely to transfer from feed to tissues, milk and eggs. Calculation from highest residue, STMR (some bulk commodities) and STMR-P values provides the levels in feed suitable for estimating MRLs, while calculation from STMR and STMR-P values for feed is suitable for estimating STMR values for animal commodities. The percentage dry matter is taken as 100% when the highest residue levels and STMRs are already expressed as dry weight.

Estimated maximum and mean dietary burdens of farm animals

Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are provided in Annex 6 of the 2009 JMPR Report. The calculations were made according to the animal diets from US-Canada, EU and Australia in the OECD Table (Annex 6 of the 2006 JMPR Report).

		Animal dietary burden, fluopicolide, ppm of dry matter diet		
		US-Canada	EU	Australia
Beef cattle	max	0.08	5.1[a]	2.0
	mean	0.03	1.1	1.9[c]
Dairy cattle	max	0.09	5.1[b]	2.0
	mean	0.05	1.1	1.9[d]
Poultry – broiler	max	0.01	1.3[e]	0.01
	mean	0.01	0.28[f]	0.01
Poultry – layer	max	0.01	0.03[g]	0.01
	mean	0.01	0.02[h]	0.01

[a] Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian tissues

[b] Highest maximum dairy cattle dietary burden suitable for MRL estimates for mammalian milk

[c] Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian tissues.

[d] Highest mean dairy cattle dietary burden suitable for STMR estimates for milk.

[e] Highest maximum poultry dietary burden suitable for MRL estimates for poultry tissues.

[f] Highest mean poultry dietary burden suitable for STMR estimates for poultry tissues.

[g] Highest maximum poultry dietary burden suitable for MRL estimates for poultry eggs.

[h] Highest mean poultry dietary burden suitable for STMR estimates for poultry eggs.

The fluopicolide dietary burdens for animal commodity MRL and STMR estimation (residue levels in animal feeds expressed on dry weight) are: beef cattle 5.1 and 1.1 ppm, dairy cattle 5.1 and 1.9 ppm and poultry 1.3 and 0.28 ppm (for eggs 0.03 and 0.02 ppm).

Farm animal feeding studies

The Meeting received information on the residue levels arising in animal tissues and milk when dairy cows were dosed with fluopicolide for 28 days at the equivalent of 0.5, 1.7 and 5.7 ppm in the diet. Average residues of fluopicolide in milk for the 5.7 ppm dose group were < 0.01 mg/kg. Residues of fluopicolide in milk were detected for one sample at day 4 and one at day 28 of dosing; levels were 0.01 and 0.02 mg/kg respectively. No residues of the metabolites M-01 and M-02 were detected in milk (LOQ 0.01 mg/kg). No residues of fluopicolide or the metabolites M-01 and M-02 were detected in tissues (LOQ 0.02 mg/kg).

The Meeting also received information on the residue levels arising in tissues and eggs when laying hens were dosed with ^{14}C-fluopicolide for 14 days at levels equivalent to 1 and 10 ppm in the diet. At the high dose residues of fluopicolide in eggs and tissues were below the LOQ for the analytical method, 0.01 mg/kg.

Animal commodity maximum residue levels

The maximum dietary burden for beef and dairy cattle is 5.1 ppm, so the levels of residues in tissues can be obtained directly from the 5.7 ppm feeding level. Maximum residues expected in tissues are: fat, muscle, liver and kidney are 0 mg/kg and the mean residue for milk 0 mg/kg. The Meeting estimated maximum residue levels for meat (from mammals other than marine mammals) 0.01* mg/kg; edible offal (mammalian) 0.01* mg/kg and milks 0.02 mg/kg. Estimated HRs for short term intake estimations for fluopicolide are all 0 mg/kg for tissues. No residues of M-01 are expected, HR values are 0 mg/kg.

No residues are expected to be detected on exposure to the mean dietary burden and estimated STMRs for fluopicolide and M-01 are 0 mg/kg for meat (from mammals other than marine mammals), fat (from mammals other than marine mammals), edible offal (mammalian) and milk.

The maximum dietary burden for broiler poultry is 1.3 ppm. No residues above the LOQ of the analytical method are expected for fluopicolide or M-01.

The Meeting estimated maximum residue levels for poultry meat 0.01* mg/kg; poultry offal 0.01* and eggs 0.01* mg/kg. The mean dietary burden for poultry is 0.28 ppm. No residues are expected in poultry tissues and eggs of birds at the mean dietary burden. HRs and STMRs for fluopicolide and M-01 in poultry meat, skin/fat, edible offal and eggs are all 0 mg/kg.

RECOMMENDATIONS

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

Definition of the residue for plant and animal commodities (for compliance with MRL): *fluopicolide.*

Definition of the residue for plant and animal commodities (for estimation of dietary intake): *fluopicolide and 2,6-dichlorobenzamide measured separately.*

The residue is fat soluble.

	Commodity	Recommended MRL mg/kg		STMR or	HR [a]
CCN	Name	New	Prev	STMR-P [a]	
VB 0402	Brussels sprouts	0.2		0.04 (0.01)	0.13 (0.01)
VB 0041	Cabbages, Head	7		1.2 (0.01)	4 (0.02)
VS 0624	Celery	20		1.4 (0.01)	14 (0.04)
PE 0112	Eggs	0.01*		0 (0)	0 (0)
VB 0042	Flowerhead brassicas	2		0.385 (0.01)	0.69 (0.01)
VC 0045	Fruiting vegetables, Cucurbits	0.5		0.07 (0.01)[b] 0.01 (0.01)[c]	0.3 (0.01)[b] 0.01 (0.01)[c]
VO 0050	Fruiting vegetables, other than Cucurbits (except mushrooms and sweet corn)	1		0.16 (0.01)	0.58 (0.01)
	Tomato juice			0.048 (0.01)	
	Tomato purée			0.288 (0.01)	
	Tomato paste			0.352 (0.01)	
FB 0269	Grapes	2		0.38 (0.01)	1.2 (0.04)
DF 0269	Dried grapes (= currants, raisins and sultanas)	10		2.47 (0.045)	7.8 (0.06)
	White wine			0.16 (0.01)	
	Red wine			0.12 (0.01)	
AB 0269	Grape pomace, dry	7			
VL 0053	Leafy vegetables	30		8.6 (0.07)	17 (0.19)
MO 0105	Edible offal (Mammalian)	0.01*		0 (0)	0 (0)
ML 0106	Milks	0.02		0 (0)	
MM 0095	Meat (from mammals other than marine mammals)	0.01* (fat)		0 (0)	0 (0)
VB 0385	Onion, bulb	1		0.07 (0.01)	0.58 (0.01)
VB 0387	Onion, Welsh	10		2.1 (0.01)	4.5 (0.01)
HS 0444	Peppers Chilli, dried	7		0.91 (0.01)	7 (0.01)
PM 0110	Poultry meat	0.01*		0 (0)	0 (0)
PO 0111	Poultry, edible offal of	0.01*		0 (0)	0 (0)
AS 0081	Straw and fodder (dry) of cereal grains	0.2			

* the MRL is estimated at or about the LOQ

[a] values in brackets are for residues of 2,6-dichlorobenzamide

[b] values are for fruit with edible peel

[c] values are for fruit with inedible peel

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intake (IEDI) for fluopicolide was calculated for the food commodities for which STMRs or HRs were estimated and for which consumption data were available. The results are shown in Annex 3 of the 2009 JMPR Report.

The International Estimated Daily Intakes of fluopicolide and 2,6-dichlorobenzamide for the 13 GEMS/Food regional diets, based on estimated STMRs were 1–10% of the maximum ADI of 0.08 mg/kg bw for fluopicolide and 0–1% of the maximum ADI of 0.02 mg/kg bw for 2,6-dichlorobenzamide (Annex 3 of 2009 JMPR Report). The Meeting concluded that the long-term intake of residues of fluopicolide from uses that have been considered by the JMPR is unlikely to present a public health concern.

Long-term intake

The International Estimated Short-term Intake (IESTI) for fluopicolide was calculated for the food commodities for which STMRs or HRs were estimated and for which consumption data were available. The results are shown in Annex 4 of the 2009 Report of the JMPR.

For fluopicolide the IESTI varied from 0–70% of the ARfD (0.6 mg/kg bw) for women of child bearing age when using intake figures for the general population. An ARfD was unnecessary for the other groups of the population. For 2,6-dichlorobenzamide the IESTI varies from 0–1% of the ARfD (0.6 mg/kg bw) for the general population and 0–2% for children. The Meeting concluded that the short-term intake of residues of fluopicolide from uses considered by the Meeting is unlikely to present a public health concern.

REFERENCES

Code	Author	Year	Title, Institute, Report reference
C008406 M-197457-01-1	Bright, AAS	2000	Vapour pressure–AE C638206 (99.6 percent w/w)–Code: AE C638206 00 1B99 0002, Aventis CropScience UK Limited; Physical and Theoretical Chemistry, Saffron Walden, Essex, UK, BCS, Report No.: C008406, Report includes Trial Nos.: 00040605 Edition Number: M-197457-01-1, 2000, GLP, unpublished
C008405 M-197456-01-1	Bright, AAS.	2000	Dissociation constant AE C638206 99.6% w/w Code: AE C638206 00 1B99 0002, Aventis CropScience UK Limited; Essex, UK, BCS, Report No.: C008405, Report includes Trial Nos.: 00040604, Edition Number: M-197456-01-1, 2000, GLP, unpublished
C034149 M-234474-01-1	Muehlberger, B	2003	Spectral data (UV / VIS, IR, 1H-NMR, 13C-NMR, MS) and molar extinction coefficient Code: AE C638206 00 1B99 0002, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C034149, Edition Number: M-234474-01-1, 2003, GLP, unpublished
C034161 M-234496-01-1	Muehlberger, B	2003	Water solubility of AE C638206 at pH4, pH 7 and pH 9 (Column-elution method) Code: AE C638206 00 1B99 0002, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C034161, Edition Number: M-234496-01-1, 2003, GLP, unpublished
C031136 M-229073-01-1	Muehlberger, B	2003	Solubility in organic solvents Code: AE C638206 00 1B99 0002, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C031136, Edition Number: M-229073-01-1, 2003, GLP, unpublished
C032556 M-231643-01-1	Muehlberger, B	2003	Partition coefficient 1-octanol/water (HPLC-method) Code: AE C638206 00 1B99 0002, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C032556, Edition Number: M-231643-01-1, 2003, GLP, unpublished
C031788 M-230264-01-1	Muehlberger, B and Eyrich, U	2003	Physical characteristics, colour, appearance and odour–Code: AE C638206 00 1C96 0001–Substance, technical, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C031788, Edition Number: M-230264-01-1, 2003, GLP, unpublished
C031787 M-230262-01-1	Muehlberger, B and Eyrich, U	2003	Physical, characteristics colour, appearance and odour substance, pure Code: AE C638206 00 1B99 0002, Bayer CropScience GmbH, Frankfurt am Main, Germany, Report No.: C031787, Edition Number: M-230262-01-1, 2003, GLP, unpublished
C031788 M-230264-01-1	Muehlberger, B and Eyrich, U	2003	Physical characteristics, colour, appearance and odour–Code: AE C638206 00 1C96 0001–Substance, technical, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C031788, Edition Number: M-230264-01-1, 2003, GLP, unpublished
C031787 M-230262-01-1	Muehlberger, B and Eyrich, U	2003	Physical, characteristics colour, appearance and odour substance, pure Code: AE C638206 00 1B99 0002, Bayer CropScience GmbH, Frankfurt am Main, Germany, Report No.: C031787, Edition Number: M-230262-01-1, 2003, GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
C037664 M-223275-01-1	Renaud, D	2003	Henry's law constant calculation AE C638206, Bayer CropScience S.A., Lyon, France, Report No.: C037664, Edition Number: M-223275-01-1, 2003, Non GLP, unpublished
B004202 M-241162-01-1	Runes, H and Shepler, K	2002	Hydrolysis of [^{14}C]- AE C638206 at pH 4,5,7 and 9, PTRL West, Inc., USA, Report No.: B004202, Report includes Trial Nos.: 1124W, Edition Number: M-241162-01-1, 2002, GLP, unpublished
B004201 M-241161-01-1	Runes, H and Shepler, K	2003	Photolysis and Quantum Yield of [^{14}C]- AE C638206 in Buffered Aqueous Solution, PTRL West, Inc., USA, Report No.: B004201, Edition Number: M-241161-01-1, 2003, GLP, unpublished
B004201 M-241161-01-1	Runes, H and Shepler, K	2003	Photolysis and Quantum Yield of [^{14}C]- AE C638206 in Buffered Aqueous Solution, PTRL West, Inc., USA, Report No.: B004201, Edition Number: M-241161-01-1, 2003, GLP, unpublished
B004573 M-241479-01-1	Rupprecht, JK	2004	Estimation of the Reaction of AE C638206 with Photochemically Produced Hydroxyl Radicals in the Atmosphere, Bayer CropScience LP, RTP, NC, USA, Report No.: B004573, Report includes Trial Nos.: 04MEACX003, Edition Number: M-241479-01-1, 2004, GLP, unpublished
C034152 M-234480-01-1	Smeykal, H	2003	Melting point/melting range AE C638206 substance, pure Code: AE C638206 00 1B99 0002, Siemens Axiva GmbH & Co. KG, DEU; Sicherheitstechnik, Frankfurt, Report No.: C034152, Edition Number: M-234480-01-1, 2003, GLP, unpublished
C034153 M-234482-01-1	Smeykal, H	2003	Boiling point/boiling range Thermal stability AE C638206 substance, pure Code: AE C638206 00 1B99 0002, Siemens Axiva GmbH & Co. KG, DEU; Sicherheitstechnik, Frankfurt, Report No.: C034153, Edition Number: M-234482-01-1, 2003, GLP, unpublished
C034153 M-234482-01-1	Smeykal, H	2003	Boiling point/boiling range Thermal stability AE C638206 substance, pure Code: AE C638206 00 1B99 0002, Siemens Axiva GmbH & Co. KG, DEU; Sicherheitstechnik, Frankfurt, Report No.: C034153, Edition Number: M-234482-01-1, 2003, GLP, unpublished
C034154 M-234484-01-1	Smeykal, H	2003	Relative density AE C638206 substance, pure Code: AE C638206 00 1B99 0002, Siemens Axiva GmbH & Co. KG, Frankfurt am Main, Germany, BCS, Report No.: C034154, Edition Number: M-234484-01-1, 2003, GLP, unpublished
C033117 M-232634-01-1	Smeykal, H	2003	Flammability (solids) AE C638206; substance technical Code: AE C638206 00 1C96 0001, Siemens Axiva GmbH & Co. KG, DEU; Sicherheitstechnik, Frankfurt, Report No.: C033117, Edition Number: M-232634-01-1, 2003, GLP, unpublished
C033119 M-232638-01-1	Smeykal, H	2003	Auto-flammability (Solids–Determination of relative self-ignition temperature) AE C638206; substance technical Code: AE C638206 00 1C96 0001, Siemens Axiva GmbH & Co. KG, DEU; Sicherheitstechnik, Frankfurt, Report No.: C033119, Edition Number: M-232638-01-1, 2003, GLP, unpublished
20060164.01 M-269406-01-1	Smeykal, H	2006	Fluopicolide (AE C638206); Substance, technical–Product Code: AE C638206-TE-01–Explosive properties A.14. Siemens AG, Frankfurt am Main, Germany, BCS, Report No.: 20060164.01, Edition Number: M-269406-01-1, 2006, GLP, unpublished
C033116 M-232632-01-1	Smeykal, H	2003	Surface tension AE C638206; substance technical Code: AE C638206 00 1C96 0001, Siemens Axiva GmbH & Co. KG, DEU; Sicherheitstechnik, Frankfurt, Report No.: C033116, Edition Number: M-232632-01-1, 2003, GLP, unpublished
C033120 M-232640-01-1	Smeykal, H	2003	Oxidizing properties AE C638206; substance technical Code: AE C638206 00 1C96 0001, Siemens Axiva GmbH & Co. KG, DEU; Sicherheitstechnik, Frankfurt, Report No.: C033120, Edition Number: M-232640-01-1, 2003, GLP, unpublished
C008855 M-197858-01-1	D'Souza, R	2000	Preliminary toxicokinetic studies in the rat Code: (^{14}C)-AE C638206, Aventis CropScience UK Ltd., Saffron Walden, Essex, England, BCS, Report No.: C008855, Report includes Trial Nos.: TOX99217, Edition Number: M-197858-01-1, 2000, GLP, unpublished
C036983 M-221892-01-1	Fisher, PJ	2003	(phenyl-U-^{14}C)-AE C638206 Rat tissue kinetic study, Bayer CropScience S.A., Sophia Antipolis, France, BCS, Report No.: C036983, Edition Number: M-221892-01-1, 2003, GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
C036980 M-221885-01-1	Fisher, PJ	2003	(2,6-pyridyl-^{14}C)-AE C638206 Rat tissue kinetic study, Bayer CropScience S.A., Sophia Antipolis, France, BCS, Report No.: C036980, Edition Number: M-221885-01-1, 2003, GLP, unpublished
C039580 M-227023-02-1	Fisher, PJ	2004	[Pyridyl-2,6-^{14}C]-AE C638206: Rat metabolism following administration of a single oral low dose, Bayer CropScience S.A., Sophia Antipolis, France, BCS, Report No.: C039580, Edition Number: M-227023-02-1, 2004 Amended, GLP, unpublished
C039582 M-227025-02-1	Fisher, PJ	2004	[Phenyl-U-^{14}C]-AE C638206: Rat metabolism following administration of a single oral high dose, Bayer CropScience S.A., Sophia Antipolis, France, BCS, Report No.: C039582, Edition Number: M-227025-02-1, 04 Amended GLP, unpublished
C039583 M-227026-02-1	Fisher, PJ	2004	[Phenyl-U-^{14}C]-AE C638206: Rat metabolism following administration of a single oral low dose, Bayer CropScience S.A., Sophia Antipolis, France, BCS, Report No.: C039583, Edition Number: M-227026-02-1, 2004 Amended, GLP, unpublished
C039584 M-227027-02-1	Fisher, PJ	2004	[Phenyl-U-^{14}C]-AE C638206: Repeat oral low dose A.D.M.E. study in the rat, Bayer CropScience S.A., Sophia Antipolis, France, BCS, Report No.: C039584, Report includes Trial Nos.: SA01288, Edition Number: M-227027-02-1, 2004, Amended, GLP, unpublished
C036987 M-221902-01-1	Fisher, PJ and Vinck, K	2003	(phenyl-U-^{14}C)-AE C638206 and (pyridyl-2,6-^{14}C)-AE C638206: Rat blood and plasma kinetics study, Bayer CropScience S.A., Sophia Antipolis, France, BCS, Report No.: C036987, Edition Number: M-221902-01-1, 2003, GLP, unpublished
21552 M-233361-02-1	Gedik, L and McCombe, WS	2003	The distribution and metabolism of (^{14}C)-AE C638206 in the laying hen, Inveresk Research Int. Ltd., Tranent, Scotland, BCS, Report No.: 21552, Edition Number: M-233361-02-1, 2003, Amended: 2009, GLP, unpublished
21582 M-233391-02-1	Gedik, L and McCombe, WS	2003	The distribution and metabolism of (^{14}C)-AE C638206 in the lactating cow, Inveresk Research Int. Ltd., Tranent, Scotland, BCS, Report No.: 21582, Edition Number: M-233391-02-1, 2003, Amended: 2009, GLP, unpublished
C032181 M-230976-01-1	Gutierrez, L	2003	Single oral low dose rat bile excretion study Code: (Pyridyl-2,6-^{14}C)-AE C638206, Bayer CropScience S.A., Sophia Antipolis, France, BCS, Report No.: C032181, Edition Number: M-230976-01-1, 2003, GLP, unpublished
C035247 M-218352-01-1	Gutierrez, L	2003	(Phenyl-U-^{14}C)-AE C653711 (BAM): Single oral high dose A.D.M.E. study in the rat, Bayer CropScience S.A., Sophia Antipolis, France, Report No.: C035247, Edition Number: M-218352-01-1, 2003, GLP, unpublished
C035245 M-218350-01-1	Gutierrez, L	2003	(Phenyl-U-^{14}C)-AE C653711 (BAM): Single oral low dose A.D.M.E. study in the rat, Bayer CropScience S.A., Sophia Antipolis, France, Report No.: C035245, Edition Number: M-218350-01-1, 2003, GLP, unpublished
C035920 M-219491-01-1	Gutierrez, L	2003	Repeat oral low dose A.D.M.E. study in the rat Code: (phenyl-U-^{14}C)-AE C653711, Bayer CropScience S.A., Sophia Antipolis, France, Report No.: C035920, Edition Number: M-219491-01-1, 2003, GLP, unpublished
C024615 M-217250-01-1	Gutierrez, L	2002	Single oral low dose A.D.M.E. study [Pyridyl-2,6-^{14}C]-AE C657188 (PCA), Bayer CropScience S.A., Sophia Antipolis, France, Report No.: C024615, Edition Number: M-217250-01-1, 2002, GLP, unpublished
C040386 M-228807-01-1	Hellpointner, E	2004	Phototransformation of [pyridyl-2,6-^{14}C]AE C638206 in sterile water buffered at pH 7, Report No.: C040386, Edition Number: M-228807-01-1, 2004, GLP, unpublished
C012385 M-202609-02-1	Le Lain, R	2001	[Pyridyl-2,6–^{14}C]-AE C638206–Single oral low dose rat A.D.E. study, Aventis CropScience S.A., Sophia Antipolis, France, BCS, Report No.: C012385, Edition Number: M-202609-02-1, 2001, Amended, GLP, unpublished
B004552 M-240707-03-1	Meyer, BN	2003	Uptake of [^{14}C]-AE C638206 Residues in Soil by Rotational Crops Under Confined Conditions, Aventis CropScience USA LP, RTP, NC, USA, Report No.: B004552, Report includes Trial Nos.: 501CU, CU99E501, Edition Number: M-240707-03-1, 2003, Amended, GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
2014/004-D1145 M-233977-03-1	Needham, D and Hardwick, T	2003	(^{14}C)-AE C638206: Absorption, distribution, metabolism and excretion following repeated oral administration to the laying hen, Covance Laboratories Ltd., Harrogate, United Kingdom, BCS, Report No.: 2014/004-D1145, Edition Number: M-233977-03-1, 2003, Amended: 2009, GLP, unpublished
2014/040-D1145 M-218626-02-1	Needham, D and Hardwick, T	2003	(^{14}C)-AE C638206: Absorption, distribution, metabolism and excretion following repeated oral administration to the lactating cow, Covance Laboratories Ltd., Harrogate, United Kingdom, BCS, Report No.: 2014/040-D1145, Edition Number: M-218626-02-1, 2003 Amended: 2008, GLP, unpublished
B004202 M-241162-01-1	Runes, H and Shepler, K	2002	Hydrolysis of [^{14}C]- AE C638206 at pH 4,5,7 and 9, PTRL West, Inc., USA, Report No.: B004202, Report includes Trial Nos.: 1124W, Edition Number: M-241162-01-1, 2002, GLP, unpublished
B004201 M-241161-01-1	Runes, H and Shepler, K	2003	Photolysis and Quantum Yield of [^{14}C]- AE C638206 in Buffered Aqueous Solution, PTRL West, Inc., USA, Report No.: B004201, Edition Number: M-241161-01-1, 2003, GLP, unpublished
B004861 M-241269-02-1	Rupprecht, JK	2004	Metabolism of [U-^{14}C-phenyl]- and [2,6-^{14}C pyridinyl]-AE C638206 in Lettuce (Amended report replacing report 505CU, Document B004330), AgrEvo USA Company; AgrEvo Research Center, Report No.: B004861, Report includes Trial Nos.: CU99E505, Edition Number: M-241269-02-1, 2004 Amended, GLP, unpublished
B004860 M-241268-02-1	Rupprecht, JK	2004	Metabolism of [U-^{14}C-phenyl]- and [2,6-^{14}C pyridinyl]-AE C638206 in Vines (Amended Report replacing report CU99E503, Document B004329), AgrEvo USA Comp. Pikeville, NC, USA, BCS, Report No.: B004860, Report includes Trial Nos.: CU99E503A, Edition Number: M-241268-02-1, 2004, GLP, unpublished
B004913 M-241267-03-1	Rupprecht, JK	2004	Metabolism of [U-^{14}C-phenyl]- and [2,6-^{14}C pyridinyl]-AE C638206 in Potatoes (Amended Report Replacing Report 502CUA, Document B004859), AgrEvo USA Company; AgrEvo Research Center, BCS, Report No.: B004913, Report includes Trial Nos.: CU99E502, Edition Number: M-241267-03-1, 2004 Amended: 2005, GLP, unpublished
C017703 M-204781-01-2	Totis, M	2001	[phenyl-U-^{14}C]–AE C638206: Single high & low dose rat A.D.E. study, Aventis CropScience, Sophia-Antipolis; France, BCS, Report No.: C017703, Edition Number: M-204781-01-2, 2001, GLP, unpublished
C021984 M-212243-01-1	Totis, M	2002	Rat bile excretion study (Phenyl-U-14C)-AE C638206, Aventis CropScience S.A.,Sophia Antipolis, France, BCS, Report No.: C021984, Edition Number: M-212243-01-1, 2002, GLP, unpublished
	Allan JG		Route and Rate of Degradation of [2,6-^{14}C-pyridinyl] and [U-^{14}C-benzoyl]-AE C638206 in a European Sandy Loam Under Laboratory Aerobic Conditions at 20 °C and Determination of Aged in situ Kd Values at 25 °C
P963G M-262176-01-1	Bacher, R	2005	Independent Laboratory Validation of Multi-Residue Method DFG S19 for the Determination of residues of fluopicolide (AE C638206) in materials of animal origin, PTRL Europe, Ulm, Germany, BCS, Report No.: P963G, Edition Number: M-262176-01-1, 2006, GLP, unpublished
RAACX039 M-242519-02-1	Ford, CA	2005	Final report–PAM I multiresidue protocol testing for AE C638206 (fluopicolide) and its metabolites AE C653711 (BAM), AE C657378 (BAM-OH), AE C657188 (PCA), and AE 1344122 (P1X), Pyxant Labs Inc., Colorado springs, CO., USA, BCS, Report No.: RAACX039, Edition Number: M-242519-02-1, 2005, GLP, unpublished
BAY-0517 M-256235-01-1	Klimmek, S	2005	AE C638206: Examination of the applicability of DFG methods S 19 (extended and revised revision) for the determination of residues of AE C638206, Specht & Partner Chemische Laboratorien GmbH, Hamburg, Germany, BCS, Report No.: BAY-0517, Edition Number: M-256235-01-1, Method Report No.: BAY-0517, Method Report No.: G05-0094, 2005, GLP, unpublished
00086/M074 M-259495-01-1	Klimmek, S	2005	Validation of multi-residue method DFG S19 (L 00.00-34) for the determination of residues of AE C638206 in animal tissues with GC MSD detection, Chemische Laboratorien GmbH, Hamburg, Germany, BCS, Report No.: 00086/M074, Edition Number: M-259495-01-1, 2005, GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
02CU27780 M-284110-01-1	Kowalsky, J	2006	Fluopicolide: Magnitude of residues in onion RAC resulting from foliar applications of EXP 11067B under maximum proposed label specifications (2002), Pyxant Labs Inc., Colorado Springs, CO, USA, BCS, Report No.: 02CU27780, Edition Number: M-284110-01-1, 2006, GLP, unpublished
C038576 M-225282-01-1	Peatman, MH And Harrand, C	2003	AE C638206: validation of the DFG multi-residue analytical report S19 for the determination of residues in grapes, potatoes and cereal grain, Covance Laboratories Ltd; Report No.: C038576, Edition Number: M-225282-01-1, 2003, GLP, unpublished
C017634 M-204661-01-1	Queyrel, I and Rosati, D	2001	Analytical method for the determination of residues in soil (Method AR 265-01) AE C638206 and its metabolites: AE C657188 (PCA), AE C653711 (BAM), and RPA 427967 (hydroxy). (method and validation), Aventis CropScience S.A., Lyon, France, Report No.: C017634, , Report includes Trial Nos.: 01-03, AR265-01, Edition Number: M-204661-01-1, 2001, GLP, unpublished
C046034 M-237604-01-1	Reiner, H	2004	Extraction efficiency testing (radiovalidation) of the residue method for the determination of AE C638206 residues in plant samples using aged radioactive residues, BCS, Report No.: C046034, Report includes Trial Nos.: M9991415-8, Edition Number: M-237604-01-1, 2004, GLP, unpublished
G06-0150 M-280096-01-1	Rzepka, S	2006	Independent Laboratory Validation of an Analytical Method for the Determination of Residues of Fluopicolide (AE C638206) in Foodstuffs of Plant Origin (Grapes, Potato (tuber) and Wheat (grain)), Eurofins Analytik GmbH, Hamburg, Germany BCS, Report No.: G06-0150, Edition Number: M-280096-01-1, 2006, GLP, unpublished
C031433 M-229630-01-1	Schoening, R and Billian, P	2003	Modification M001 of the residue analytical method 00782 for the determination of residues of AE C638206 and its metabolites AE C657188 and AE C653711 in/on grape and potato by HPLC-MS/MS, BCS, Report No.: C031433, Edition Number: M-229630-01-1, 2003, GLP, unpublished
00782/M002 M-226098-02-1	Schoening, R and Billian, P	2003	Validation of the modification M002 to the analytical method 00782 for the determination of residues of AE C638206 and its metabolites AE C657188, AE C653711 and AE 1344122 in/on wheat by HPLC-MS/MS, Report No.: 00782/M002, Report includes Trial Nos.: P602034701, Edition Number: M-226098-02-1, 2003 Amended: 2008, GLP, unpublished
C038960 M-226108-01-1	Schoening, R Billian, P	2003	Modification M003 to the analytical method 00782 for the determination of residues of AE C657378 (3-OH-BAM) in/on cereals (wheat) by HPLC-MS/MS, BCS, Report No.: C038960, Report includes Trial Nos.: P602034709, Edition Number: M-226108-01-1, 2003, GLP, unpublished
C040209 M-228497-01-1	Taylor, NW	2004	Independent Laboratory validation for the determination of residues of AE C638206 in grapes and potatoes, and evaluation and validation of the method for apples and oilseed rape, based on the DFG S19 multi-residue enforcement method, Synergy Laboratories, Essex, UK; Report No.: C040209, Report includes Trial Nos.: SYN/0273, Edition Number: M-228497-01-1, 2004, GLP, unpublished
00782 M-217563-02-1	Zietz, E and Billian, P	2002	Determination of the residues of AE C638206 and metabolites in wheat (straw and grain), grapes and cabbage using LC/MS/MS–Method validation, Institut Fresenius Chem.und Biolog. Lab. AG, Taunusstein, Germany, BCS, Report No.: 00782, Report includes Trial Nos.: 01-009, Edition Number: M-217563-02-1, 2002 Amended: 2007, GLP, unpublished
RA-2151/05 M-278494-01-1	Billian, P	2006	Determination of the residues of AE C638206 and propamocarb-hydrochloride in/on round cabbage after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Southern France and Greece, BCS, Report No.: RA-2151/05, Report includes Trial Nos.: 0807-05, 0836-05, R 2005 0807/7, R 2005 0836/0, Edition Number: M-278494-01-1, 2006, GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
RA-2150/05 M-279586-01-1	Billian, P	2006	Determination of the residues of AE C638206 and propamocarb-hydrochloride in/on savoy cabbage and red cabbage after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Germany, Belgium, Northern France and the Netherlands, BCS, Report No.: RA-2150/05, Report includes Trial Nos.: 0805-05, 0806-05, 0869-05, 0870-05, R 2005 0805/0, R 2005 0806/9, R 2005 0869/7, R 2005 0870/0, Edition Number: M-279586-01-1, 2006, GLP, unpublished
RA-2152/05 M-280137-01-1	Billian, P	2006	Determination of the residues of AE C638206 and propamocarb-hydrochloride in/on Brussels sprouts after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Northern France, the Netherlands and Germany, BCS, Report No.: RA-2152/05, Report includes Trial Nos.: R 2005 0809/3 = 0809–05, R 2005 0810/7 = 0810–05, R 2005 0837/9 = 0837–05, R 2005 0838/7 = 0838–05, Edition Number: M-280137-01-1, 2006, GLP, unpublished
RA-2156/05 M-279693-01-1	Billian, P	2006	Determination of the residues of AE C638206 and propamocarb-hydrochloride in/on broccoli after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Northern France, the Netherlands, Belgium and Germany, BCS, Report No.: RA-2156/05, Report includes Trial Nos.: R 2005 0818/2 = 0818–05, R 2005 0819/0 = 0819–05, R 2005 0846/8 = 0846–05, R 2005 0847/6 = 0847–05, Edition Number: M-279693-01-1, 2006, GLP, unpublished
RA-2157/05 M-280045-01-1	Billian, P	2006	Determination of the residues of AE C638206 and propamocarb-hydrochloride in/on broccoli after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Greece, Southern France, Spain and Italy, BCS, Report No.: RA-2157/05, Report includes Trial Nos.: R 2005 0820/4 = 0820–05, R 2005 0821/2 = 0821–05, R 2005 0848/4 = 0848–05, R 2005 0849/2 = 0849–05, Edition Number: M-280045-01-1, 2006, GLP, unpublished
RA-2307/06 M-293122-02-1	Billian, P Raecker, T and Erler, S	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on onion after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Southern France, Spain, Italy and Portugal, BCS, Report No.: RA-2307/06, Report includes Trial Nos.: R 2006 0098/4 = 0098–06, R 2006 0099/2 = 0099–06, R 2006 0101/8 = 0101–06, R 2006 0102/6 = 0102–06, Edition Number: M-293122-02-1, 2007 Amended: 2008 GLP, unpublished
MR-178/04 M-274729-02-1	Billian, P and Schoening, R	2006	Storage stability of AE C638206 and its metabolites AE C657378 (3-OH-BAM), AE C653711 (BAM) and AE 1344122 (P1x) in/on cereals (rest of plant, grain, straw) for 25 months, Bayer CropScience, Report No.: MR-178/04, Edition Number: M-274729-02-1, 2006 Amended: 2007, GLP, unpublished
RA-2306/06 M-292503-02-1	Billian, P and Wolters, A	2007	Determination of the residues of AE C638206 and propamocarb-hydrochloride in/on onion after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Northern France, Germany and Belgium, BCS, Report No.: RA-2306/06, Report includes Trial Nos.: R 2006 0093/3 = 0093–06, R 2006 0094/1 = 0094–06, R 2006 0096/8 = 0096–06, R 2006 0097/6 = 0097–06, Edition Number: M-292503-02-1, 2007, Amended: 2008, GLP, unpublished
RA-2302/06 M-289482-02-1	Billian, P and Wolters, A	2007	Determination of the residues of AE C638206 and propamocarb-hydrochloride in/on leek after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Northern France, Germany and The Netherlands, BCS, Report No.: RA-2302/06, Report includes Trial Nos.: R 2006 0080/1 = 0080–06, R 2006 0082/8 = 0082–06, R 2006 0083/6 = 0083–06, R 2006 0084/4 = 0084–06, Edition Number: M-289482-02-1, 2007, Amended: 2008, GLP, unpublished
RA-2154/05 M-280030-01-1	Billian, P and Wolters, A	2006	Determination of the residues of AE C638206 and Propamocarb-hydrochloride in/on cauliflower after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Northern France, the Netherlands, Belgium and Germany, BCS, Report No.: RA-2154/05, Report includes Trial Nos.: R 2005 0813/1 = 0813-05, R 2005 0815/8 = 0815-05, R, 2005 0841/7 = 0841-05, R2005 0842/5 = 0842–05, Edition Number: M-280030-01-1, 2006, GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
RA-2155/05 M-280060-01-1	Billian, P and Wolters, A	2006	Determination of the residues of AE C638206 and propamocarb-hydrochloride in/on cauliflower after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Southern France, Greece, Spain and Italy, BCS, Report No.: RA-2155/05, Report includes Trial Nos.: R 2005 0816/6 = 0816–05, R 2005 0817/4 = 0817–05, R 2005 0843/3 = 0843–05, R 2005 0844/1 = 0844–05, Edition Number: M-280060-01-1, 2006, GLP, unpublished
RA-2303/06 M-291863-02-1	Billian, P, Wolters, A and Telscher, M	2007	Determination of the residues of AE C638206 and propamocarb-hydrochloride in/on Brussels sprouts after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Germany, Belgium and Northern France, BCS, Report No.: RA-2303/06, Report includes Trial Nos.: R 2006 0085/2 = 0085–06, R 2006 0086/0 = 0086–06, R 2006 0087/9 = 0087–06, R 2006 0088/7 = 0088–06, Edition Number: M-291863-02-1, 2007, GLP, unpublished
RA-2111/05 M-281159-01-1	Cavaillé, C	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on leek after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Belgium, Netherlands, Germany and Northern France, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2111/05, Report includes Trial Nos.: R 2005 0560/4 = 0560–05, R 2005 0561/2 = 0561–05, R 2005 0564/7 = 0564–05, R 2005 0565/5 = 0565–05, Edition Number: M-281159-01-1, 2006, GLP, unpublished
RA-2112/05 M-281536-01-1	Cavaillé, C	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on leek after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Italy, Spain, France and Portugal, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2112/05, Report includes Trial Nos.: R 2005 0562/0 = 0562–05, R 2005 0563/9 = 0563–05, R 2005 0566/3 = 0566–05, R 2005 0567/1 = 0567–05, Edition Number: M-281536-01-1, 2006, GLP, unpublished
RA-2119/05 M-283011-01-1	Cavaillé, C	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on melon after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the greenhouse in Italy, Spain, Netherlands, France and Portugal, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2119/05, Report includes Trial Nos.: R 2005 0609/0 = 0609–05, R 2005 0610/4 = 0610–05, R 2005 0611/2 = 0611–05, R 2005 0612/0 = 0612–05, R 2005 0613/9 = 0613–05, R 2005 0614/7 = 0614–05, R 2005 0615/5 = 0615–05, R 2005 0616/3 = 0616–05, Edition Number: M-283011-01-1, 2007, GLP, unpublished
RA-2137/05 M-282198-01-1	Cavaillé, C	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on melon after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Italy, Spain and Portugal, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2137/05, Report includes Trial Nos.: R 2005 0711/9 = 0711–05, R 2005 0712/7 = 0712–05, R 2005 0713/5 = 0713–05, R 2005 0714/3 = 0714–05, Edition Number: M-282198-01-1, 2007, GLP, unpublished
RA-2118/05 M-279580-01-1	Cavaillé, C	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on head lettuce after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Italy, Spain, Portugal and Greece, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2118/05, Report includes Trial Nos.: R 2005 0605/8 = 0605–05, R 2005 0606/6 = 0606–05, R 2005 0607/4 = 0607–05, R 2005 0608/2 = 0608–05, Edition Number: M-279580-01-1, 2006, GLP, unpublished
C035907 M-219457-01-1	Cavaillé, C and Rosati, D	2004	Residues of AE C638206 and major metabolites in milk and edible cattle tissues following 28 days dosing of technical product to lactating cows; 2002. Final report. Bayer CropScience S.A., Lyon, France, Report No.: C035907, Report includes Trial Nos.: R&D/CRLD/AN/0315145, Edition Number: M-219457-01-1, 2004, GLP, unpublished
RA-2115/05 M-280866-01-1	Cavaillé, C and Wieland, K	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on tomato after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Greece, Italy, Spain and Portugal, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2115/05, Report includes Trial Nos.: R 2005 0587/6 = 0587–05, R 2005 0588/4 = 0588–05, R 2005 0589/2 = 0589–05, R 2005 0590/6 = 0590–05, Edition Number: M-280866-01-1, 2006, GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
RA-2117/05 M-280861-01-1	Cavaillé, C and Wieland, K	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on lettuce after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Netherlands, United Kingdom, Germany and France, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2117/05, Report includes Trial Nos.: R 2005 0600/7 = 0600–05, R 2005 0601/5 = 0601–05, R 2005 0602/3 = 0602–05, R 2005 0603/1 = 0603–05, Edition Number: M-280861-01-1, 2006, GLP, unpublished
RA-2162/05 M-281542-01-1	Cavaillé, C and Wieland, K	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on cucumber after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in the greenhouse in Italy, Spain, Greece, Germany and Portugal, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2162/05, Report includes Trial Nos.: R 2005 0834/4 = 0834–05, R 2005 0861/1 = 0861–05, R 2005 0863/8 = 0863–05, R 2005 0864/6 = 0864–05, R 2005 0865/4 = 0865–05, R 2005 0866/2 = 0866–05, R 2005 0867/0 = 0867–05, R 2005 0868/9 = 0868–05, Edition Number: M-281542-01-1, 2006, GLP, unpublished
RA-2160/05 M-281534-01-1	Cavaillé, C and Wieland, K	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on cucumber after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Germany and Belgium, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2160/05, Report includes Trial Nos.: R 2005 0826/3 = 0826–05, R 2005 0854/9 = 0854–05, R 2005 0856/5 = 0856–05, R 2005 1032/2 = 1032–05, Edition Number: M-281534-01-1, 2006, GLP, unpublished
RA-2161/05 M-281541-01-1	Cavaillé, C and Wieland, K	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on zucchini after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Italy, Greece and Spain, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2161/05, Report includes Trial Nos.: R 2005 0827/1 = 0827–05, R 2005 0857/3 = 0857–05, R 2005 0858/1 = 0858–05, R 2005 0860/3 = 0860–05, Edition Number: M-281541-01-1, 2006, GLP, unpublished
RA-2113/05 M-281162-01-1	Cavaillé, C and Wieland, K	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on tomato after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the greenhouse in Greece, Italy, Spain, Netherlands, Germany, France and Belgium, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2113/05, Report includes Trial Nos.: R 2005 0574/4 = 0574–05, R 2005 0575/2 = 0575–05, R 2005 0576/0 = 0576–05, R 2005 0577/9 = 0577–05, R 2005 0578/7 = 0578–05, R 2005 0579/5 = 0579–05, R 2005 0580/9 = 0580–05, R 2005 0581/7 = 0581–05, Edition Number: M-281162-01-1, 2006, GLP, unpublished
RA-2114/05 M-281167-01-1	Cavaillé, C and Wolters, A	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on tomato after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Germany and Northern France, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2114/05, Report includes Trial Nos.: R 2005 0582/5 = 0582–05, R 2005 0583/3 = 0583–05, R 2005 0584/1 = 0584–05, R 2005 0586/8 = 0586–05, Edition Number: M-281167-01-1, 2006, GLP, unpublished
RA-2116/05 M-281171-01-1	Cavaillé, C and Wolters, A	2006	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on head lettuce and lettuce after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the greenhouse in Netherlands, Italy, Spain, Belgium, Germany, Northern France, Greece and Southern France, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2116/05, Report includes Trial Nos.: R 2005 0591/4 = 0591–05, R 2005 0592/2 = 0592–05, R 2005 0593/0 = 0593–05, R 2005 0594/9 = 0594–05, R 2005 0595/7 = 0595–05, R 2005 0597/3 = 0597–05, R 2005 0598/1 = 0598–05, R 2005 1007/1 = 1007–05, Edition Number: M-281171-01-1, 2006, GLP, unpublished
UNESP RA-908/05 M-276166-01-2	Galhiane, MS and de Sousa, SL	2005	Fluopicolide; 480 SC; tomato; BBA; Brazil, Universidade Estadual Paulista (UNESP), Bauru, Brazil, Report No.: UNESP RA-908/05, Report includes Trial Nos.: BRA-FR03BRA002-C1-A, BRA-FR03BRA002-C1-B, FR03BRA002-C1, Edition Number: M-276166-01-2, 2005, Non GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
UNESP RA-909/05 M-276170-01-2	Galhiane, MS and de Sousa, SL	2005	Fluopicolide; 480 SC; tomato; BBA; Brazil, Universidade Estadual Paulista (UNESP), Bauru, Brazil, Report No.: UNESP RA-909/05, Report includes Trial Nos.: BRA-FR03BRA002-P1-A, BRA-FR03BRA002-P1-B, FR03BRA002-P1, Edition Number: M-276170-01-2, 2005, Non GLP, unpublished
UNESP RA-910/05 M-276171-01-2	Galhiane, MS and de Sousa, SL	2005	Fluopicolide; 480 SC; tomato; BBA; Brazil, Universidade Estadual Paulista (UNESP), Bauru, Brazil, Report No.: UNESP RA-910/05, Report includes Trial Nos.: BRA-FR03BRA002-P2-A, BRA-FR03BRA002-P2-B, FR03BRA002-P2, Edition Number: M-276171-01-2, 2005, Non GLP, unpublished
RA-2300/06 M-288408-02-1	Gateaud, L	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on tomato after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in (the) Italy, Spain, Southern France and Portugal–Amendment no. 1, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2300/06, Report includes Trial Nos.: R 2006 0103/4 = 0103–06, R 2006 0104/2 = 0104–06, R 2006 0105/0 = 0105–06, R 2006 0106/9 = 0106–06, Edition Number: M-288408-02-1, 2007, GLP, unpublished
RA-2309/06 M-288563-01-1	Gateaud, L and Portet, M	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on round cabbage after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in (the) Spain and Italy, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2309/06, Report includes Trial Nos.: R 2006 0109/3 = 0109–06, R 2006 0110/7 = 0110–06, Edition Number: M-288563-01-1, 2007, GLP, unpublished
RA-2301/06 M-288560-01-1	Gateaud, L and Portet, M	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on melon after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in (the) Italy, Spain, Portugal and Greece, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2301/06, Report includes Trial Nos.: R 2006 0075/5 = 0075–06, R 2006 0076/3 = 0076–06, R 2006 0077/1 = 0077–06, R 2006 0079/8 = 0079–06, Edition Number: M-288560-01-1, 2007, GLP, unpublished
RA-2117/06 M-287994-01-1	Gateaud, L and Portet, M	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on lettuce after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in (the) Germany, Northern France and Netherlands, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2117/06, Report includes Trial Nos.: R 2006 0510/2 = 0510–06, R 2006 0512/9 = 0512–06, R 2006 0514/5 = 0514–06, R 2006 0516/1 = 0516–06, Edition Number: M-287994-01-1, 2007, GLP, unpublished
RA-2308/06 M-288004-01-1	Gateaud, L and Ratajczak, M	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on savoy cabbage, round cabbage and red cabbage after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in the Netherlands, Germany an Northern France, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2308/06, Report includes Trial Nos.: R 2006 0107/7 = 0107–06, R 2006 0108/5 = 0108–06, R 2006 0111/5 = 0111–06, R 2006 0112/3 = 0112–06, Edition Number: M-288004-01-1, 2007, GLP, unpublished
RA-2118/06 M-288551-01-1	Gateaud, L and Ratajczak, M	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on lettuce after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in (the) Spain, Italy, Portugal and Greece, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2118/06, Report includes Trial Nos.: R 2006 0511/0 = 0511–06, R 2006 0513/7 = 0513–06, R 2006 0515/3 = 0515–06, R 2006 0518/8 = 0518–06, Edition Number: M-288551-01-1, 2007, GLP, unpublished
RA-2304/06 M-292444-01-1	Gateaud, L and Ratajczak, M	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on spinach after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in (the) Northern France and Germany, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2304/06, Report includes Trial Nos.: R 2006 0089/5 = 0089–06, R 2006 0090/9 = 0090–06, Edition Number: M-292444-01-1, 2007, GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
RA-2305/06 M-292456-01-1	Gateaud, L and Ratajczak, M	2007	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on spinach after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in (the) Spain and Italy, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2305/06, Report includes Trial Nos.: R 2006 0091/7 = 0091–06, R 2006 0092/5 = 0092–06, Edition Number: M-292456-01-1, 2007, GLP, unpublished
02CU27780 M-284110-01-1	Kowalsky, J	2006	Fluopicolide: Magnitude of residues in onion RAC resulting from foliar applications of EXP 11067B under maximum proposed label specifications (2002), Pyxant Labs Inc., Colorado Springs, CO, USA, BCS, Report No.: 02CU27780, Edition Number: M-284110-01-1, 2006, GLP, unpublished
02CU33137 M-283956-01-1	Kowalsky, J	2006	Fluopicolide: Magnitude of residues in/on cabbage RAC resulting from foliar application of EXP11067B under maximum proposed label specifications, Pyxant Labs. Inc., Colorado Springs, CO, USA, BCS, Report No.: 02CU33137, Edition Number: M-283956-01-1, 2006, GLP, unpublished
02CU33136 M-284052-01-1	Kowalsky, J	2006	Fluopicolide: Magnitude of residues in/on broccoli RAC resulting from foliar applications of EXP 11067B under maximum proposed label specifications (2002), Pyxant Labs Inc., Colorado Springs, CO, USA, BCS, Report No.: 02CU33136, , Edition Number: M-284052-01-1, 2006, GLP, unpublished
02CU33135 M-284212-01-1	Kowalsky, J	2005	Fluopicolide: Magnitude of residues in spinach resulting from foliar applications of EXP 11067B under maximum proposed label specifications (2002), Pyxant Labs. Inc., Colorado Springs, CO, USA, BCS, Report No.: 02CU33135, Edition Number: M-284212-01-1, 2005, GLP, unpublished
02CU33130 M-284048-01-1	Kowalsky, J	2006	Fluopicolide: Magnitude of residues in/on carrot RAC resulting from foliar applications of EXP 11067B under maximum proposed label specifications (2002), Pyxant Labs. Inc., Colorado Springs, CO, USA, BCS, Report No.: O2CU33130, Edition Number: M-284048-01-1, 2006, GLP, unpublished
02CU33129 M-284022-01-1	Kowalsky, J	2006	Fluopicolide: Magnitude of residues in/on radish RAC resulting from foliar applications of EXP 11067B under maximum proposed label specifications (2002), Pyxant Labs. Inc., Colorado Springs, CO, USA, BCS, Report No.: 02CU33129, Edition Number: M-284022-01-1, 2006, GLP, unpublished
02CU33134 M-284205-01-1	Kowalsky, J	2005	Fluopicolide: Magnitude of residues in celery resulting from foliar applications of EXP 11067B under maximum proposed label specifications (2002), Pyxant Labs. Inc., Colorado Springs, CO, USA, BCS, Report No.: 02CU33134, Edition Number: M-284205-01-1, 2005, GLP, unpublished
B004631 M-241525-01-1	Mackie, SJW	2004	AE C638206: Magnitude of Residues in Cucumber Resulting from Foliar Applications of EXP 11067B under Maximum Proposed Label Specifications (2002), Bayer CropScience LP, RTP, NC, USA, Report No.: B004631, Report includes Trial Nos.: 02CU27779, Edition Number: M-241525-01-1, 2004, GLP, unpublished
B004632 M-241526-01-1	Mackie, SJW	2004	AE C638206: Magnitude of Residues in Squash Resulting from Foliar Applications of EXP 11067B under Maximum Proposed Label Specifications (2002), Bayer CropScience LP, RTP, NC, USA, Report No.: B004632, Report includes Trial Nos.: 02CU27824, Edition Number: M-241526-01-1 2004, GLP, unpublished
B004633 M-241527-01-1	Mackie, SJW	2004	AE C638206: Magnitude of Residues in Cantaloupe Resulting from Foliar Applications of EXP 11067B under Maximum Proposed Label Specifications (2002) Bayer CropScience LP, RTP, NC, USA, Report No.: B004633, Report includes Trial Nos.: 02CU27825, Edition Number: M-241527-01-1, 2004, GLP, unpublished
B004634 M-241528-01-1	Mackie, SJW	2004	AE C638206: Magnitude of Residues in/on Bell Pepper RAC Resulting from Foliar Application of EXP 11067B (2002), Bayer CropScience LP, RTP, NC, USA, Report No.: B004634, Report includes Trial Nos.: 02CU33132, Edition Number: M-241528-01-1, 2004, Non GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
B004635 M-241529-01-1	Mackie, SJW	2004	AE C638206: Magnitude of Residues in/on Chilli Pepper RAC Resulting from Foliar Application of EXP 11067B (2002), Bayer CropScience LP, RTP, NC, USA, Report No.: B004635, Report includes Trial Nos.: 02CU33133, Edition Number: M-241529-01-1, 2004, GLP, unpublished
B004798 M-251279-01-1	Mackie, SJW	2005	AE C638206: Magnitude of Residues in Head Lettuce Resulting from Foliar Applications of EXP 11067B under Maximum Proposed Label Specifications (2002), Bayer CropScience LP, RTP, NC, USA, Report No.: B004798, Report includes Trial Nos.: 02CU27778, Edition Number: M-251279-01-1, 2005, GLP, unpublished
B004799 M-251280-01-1	Mackie, SJ.W	2005	AE C638206: Magnitude of Residues in Leaf Lettuce Resulting from Foliar Applications of EXP 11067B under Maximum Proposed Label Specifications (2002), Bayer CropScience LP, RTP, NC, USA, Report No.: B004799, Report includes Trial Nos.: 02CU30473, Edition Number: M-251280-01-1, 2005, GLP, unpublished
RA-2634/07 M-307615-01-1	Melrose, I and Portet, M	2008	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on onion after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Northern France, Germany, United Kingdom and Netherlands, Bayer CropScience S.A., Lyon, France, Bayer CropScience, Report No.: RA-2634/07, Report includes Trial Nos.: R 2007 0336/8 = 0336–07, R 2007 0378/3 = 0378–07, R 2007 0379/1 = 0379–07, R 2007 0380/5 = 0380–07, Edition Number: M-307615-01-1, 2008, GLP, unpublished
RA-2635/07 M-307731-01-1	Melrose, I and Portet, M	2008	Determination of the residues of AE C638206 and Propamocarb hydrochloride in/on onion after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Southern France, Spain, Italy and Portugal, Bayer CropScience S.A., Lyon, France, BCS, Report No.: RA-2635/07, Report includes Trial Nos.:, R2007 0337/6=0337-07, R2007 0381/3=0381-07, R2007 0382/1=0382-07, R2007 0384/8=0384-07, Edition Number: M-307731-01-1, 2008, GLP, unpublished
RA-2636/07 M-307614-01-1	Melrose, I and Portet, M	2008	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on spinach after spraying of AE B066752 04 SC61 A1 (687.5 SC) in the field in Northern France, Germany, Italy and Spain, Bayer CropScience S.A., Lyon, France, Bayer CropScience, , Report No.: RA-2636/07, Report includes Trial Nos.: R 2007 0338/4 = 0338–07, R 2007 0339/2 = 0339–07, R 2007 0340/6 = 0340–07, R 2007 0341/4 = 0341–07, Edition Number: M-307614-01-1, 2008, GLP, unpublished
B004934 M-251281-01-1	Milo, J and Belyk, M	2005	Magnitude of residues on grapes treated with three applications of the fungicide EXP11067B (AE C638206) with a 21 day PHI, Enviro-Test Laboratories, Alberta, Canada, Report No.: B004934, Report includes Trial Nos.: 02AC03, Edition Number: M-251281-01-1, 2005, GLP, unpublished
B004934 M-251281-01-1	Milo, J and Belyk, M	2005	Magnitude of residues on grapes treated with three applications of the fungicide EXP11067b (AE C638206) with a 21 day PHI, Enviro-Test Laboratories, Alberta, Canada, Report No.: B004934, Report includes Trial Nos.: 02AC03, Edition Number: M-251281-01-1, 2005, GLP, unpublished
B004413 M-241334-01-1	Norris, FA	2003	AE C638206: Magnitude of Residues in/on Tomato RAC Resulting from Foliar Application of EXP 110678B (2001) Agricultural Advisor's Inc.; Report No.: B004413, Report includes Trial Nos.: 01CU27776, Edition Number: M-241334-01-1 2003, GLP, unpublished
C034684 M-235371-01-1	Scharm, M and Zietz, E	2003	Determination of the residues in white grapes following four treatments under field conditions in Northern Europe 2000 Code: AE C638206 00 SE10 A3, Institut Fresenius Chem.und Biolog. Lab. AG, Taunusstein, Germany, Report No.: C034684, Report includes Trial Nos.: DR00EUN002, Edition Number: M-235371-01-1, 2003, GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
C039706 M-227140-01-1	Schoening, R, Dorff, M and Billian, P	2004	Determination of the residues of AE C 638206 and metabolites in potatoes and rotational crop following treatment with AE C 638206 00 SC18 A1 under field conditions in southern and northern Europe 2000, Aventis CropScience GmbH, Frankfurt am Main, Germany, Report No.: C039706, Report includes Trial Nos.: DR00EUN005, IF-100/10685-00, MR-150/03, Edition Number: M-227140-01-1, 2004, GLP, unpublished
C028242 M-214899-01-1	Sonder, K	2003	Residue behaviour in grapevine European Union (Northern zone) 2001 AE C638206 + fosetyl-aluminium water dispersible granule (WG) 4.44 % + 66.7% w/w Code: AE F053616 06 WG71 A101 (EXP11074B), Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C028242, Edition Number: M-214899-01-1, 2003, GLP, unpublished
C028243 M-214901-02-1	Sonder, K	2003	Residue behaviour in table grapes and wine grapes European Union (Southern zone) 2001 Fosetyl-aluminium + AE C638206 water dispersible granule (WG) 66.7% + 4.44% w/w Code: AE F053616 06 WG71 A101, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C028243, Edition Number: M-214901-02-1, 2003, GLP, unpublished
C028236 M-214887-01-1	Sonder, K	2003	Residues at harvest in grapevine European Union (northern zone) 2001 AE C638206 Suspo-emulsion (SE) 95 g/L Code: AE C638206 00 SE10 A303, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C028236, Edition Number: M-214887-01-1, 2003, GLP, unpublished
C028237 M-214888-01-1	Sonder, K	2003	Residues at harvest in table grapes and wine grapes European Union (Southern zone) 2001 AE C638206 suspo-emulsion (SE) 95 g/L Code: AE C638206 00 SE10 A303, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C028237, Edition Number: M-214888-01-1, 2003, GLP, unpublished
C032071 M-230759-01-1	Sonder, KH	2003	Residue behaviour in grapevine European Union (Northern zone) 2002 AE C638206 + fosetyl-aluminium water dispersible granule (WG) 4.44% + 66.7% w/w Code: AE F053616 06 WG71 A102, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C032071, Edition Number: M-230759-01-1, 2003, GLP, unpublished
C032072 M-230761-01-1	Sonder, KH	2003	Residue behaviour in grapevine European Union (Southern zone) 2002 AE C638206 + fosetyl-aluminium water dispersible granule (WG) 4.44% + 66.7% w/w Code: AE F053616 06 WG71 A102, Bayer CropScience GmbH, Frankfurt am Main, Germany, BCS, Report No.: C032072, Edition Number: M-230761-01-1, 2003, GLP, unpublished
C045739 M-237350-01-1	Zietz, E	2004	Final report—Determination of the storage stability of AE C638206 and the metabolites AE C653711 (BAM) and AE C657188 (PCA) in grape, potato, cabbage, and wheat grain, Institut Fresenius Chem.und Biolog. Lab. AG, Taunusstein, Germany, Bayer CropScience, Report No.: C045739, Edition Number: M-237350-01-1, 2004, GLP, unpublished
C031908 M-230472-01-1	Zietz, E	2003	Determination of the residues in red grapes following three treatments under field conditions in Southern Europe 2000 Code: AE C638206 00 SE10 A3, Institut Fresenius Chem.und Biolog. Lab. AG, Taunusstein, Germany, BCS, Report No.: C031908, Report includes Trial Nos.: DR00EUS003, Edition Number: M-230472-01-1 2003, GLP, unpublished
C036940 M-221798-01-1	Zietz, E and Klimmek, S	2003	Determination of the residues of AEC638206 and metabolites in potatoes and rotational crop following treatment with AE C638206 00 SC18 A1 under field conditions in southern and northern Europe 2000, Institut Fresenius Chem.und Biolog. Lab. AG, Taunusstein, Germany, Report No.: C036940, Report includes Trial Nos.: DR00EUN005, Edition Number: M-221798-01-1, 2003, GLP, unpublished
C038284 M-224665-01-1	Zietz, E and Klimmek, S	2003	Determination of the residues of AE C638206 and metabolites in potatoes and rotational crop following treatment with AE C638206 00 SE10 A303 under field conditions in northern Europe 2001, Institut Fresenius Chem.und Biolog. Lab. AG, Taunusstein, Germany, Report No.: C038284, Report includes Trial Nos.: 01R026, Edition Number: M-224665-01-1, 2003, GLP, unpublished

Code	Author	Year	Title, Institute, Report reference
RA-3639/07 M-307290-01-1	Billian, P	2008	Determination of the residues of AE C638206 and propamocarb hydrochloride in/on tomato fruit and fruit for processing and the processed fractions (raw juice; washings; fruit, washed; juice; peel; preserve; fruit, peeled; peeling water. BCS, Report No.: RA-3639/07, Report includes Trial Nos.: R 2007 0343/0 = 0343–07, R 2007 0367/8 = 0367–07, R 2007 0368/6 = 0368–07, R 2007 0369/4 = 0369–07, Edition Number: M-307290-01-1, 2008, GLP, unpublished
B004412 M-241333-01-1	Norris, FA	2003	AE C638206: Determination of the Magnitude of Residues in/on Tomato Processed Fractions Resulting from Foliar Application of EXP 11067B, The National Food Laboratory, Dublin, CA, USA, Report No.: B004412, Report includes Trial Nos.: 01CU27782, Edition Number: M-241333-01-1, 2003, GLP, unpublished
C013665 M-205032-01-1	van der Gaauw, A	2001	Simulated processing (14C)-AE C638206 RCC Ltd., Itingen, CHE; Environmental Chemistry & Pharmanalytics Division, Report No.: C013665, Edition Number: M-205032-01-1, 2001, GLP, unpublished
C035551 M-218649-01-1	Zietz, E	2003	Determination of the residues in processed fractions derived from red grapes following three treatments under field conditions in Southern Europe 2000 AE C638206 Code: AE C638206 00 SE10 A3, Institut Fresenius Chem.und Biolog. Lab. AG, Taunusstein, Germany, BCS, Report No.: C035551, Report includes Trial Nos.: DR00EUS056, Edition Number: M-218649-01-1, 2003, GLP, unpublished
C037343 M-222674-01-1	Zietz, E	2002	Determination of the residues in processed fractions derived from white grapes following four treatments under field conditions in Northern Europe 2000 Code: AE C638206 00 SE10 A3, Institut Fresenius Chem.und Biolog. Lab. AG, Taunusstein, Germany, Report No.: C037343, Edition Number: M-222674-01-1, 2002, GLP, unpublished