METRAFENONE (278)

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EXPLANATION

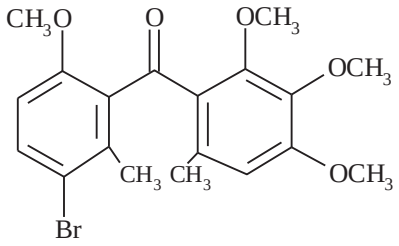
Metrafenone is a benzophenone fungicide, active mainly against powdery mildews and eyespot, inhibiting mycelium growth, leaf penetration, haustoria formation and sporulation.

Authorisations exist for the use of metrafenone on cereals, grapes, strawberries and fruiting vegetables in over 50 countries in Europe, the Americas, Asia and the Pacific.

Metrafenone was scheduled by the Forty-fifth Session of the CCPR as a new compound for consideration by the 2014 JMPR. Residue and analytical aspects of metrafenone were considered for the first time by the present meeting. The manufacturer submitted studies on metabolism, analytical methods, supervised field trials, processing, freezer storage stability, environmental fate in soil and rotational crop residues.

In this evaluation, the values presented in the tables are as reported in the various studies, but in the accompanying text, they have generally been rounded to two significant digits.

IDENTITY

ISO common name:	Metrafenone
Code number	BASF 560 F
IUPAC name:	3′-bromo-2,3,4,6′-tetramethoxy-2′,6-dimethylbenzophenone
Chemical Abstracts name:	(3-bromo-6-methoxy-2-methylphenyl) (2,3,4-trimethoxy-6-methylphenyl)-methanone
CAS number	220899-03-6
CIPAC number	752
Molecular mass:	409.3
Molecular formula	$C_{19}H_{21}O_5Br$
Structural formula:	

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

A detailed chemical and physical characterisation of the active ingredient, technical grade and selected metabolites are given in Tables 1 and 2.

Table 1 Physical and chemical data of metrafenone (active ingredient) and metabolites CL 377160, CL 4084564 and CL 375816

Test or Study & Annex point	Test material purity and specification	Findings and comments	Reference
Melting point	Pure ai (99.5%)	99.2–100.8 °C	1998/7000370
Boiling point	Pure ai (99.5%)	No boiling point measured decomposition at *ca*. 310 °C (to a black tar)	1998/7000371
Relative density	Pure ai (99.7%)	1.45	1999/7000299
Vapour pressure	Pure ai (99.7%)	$1.53 \cdot 10^{-4}$ Pa at 20 °C $2.56 \cdot 10^{-4}$ Pa at 25 °C	2001/5002313

Test or Study & Annex point	Test material purity and specification	Findings and comments	Reference
Henry's law constant	calculated	K_H = 0.132 Pa m³ mol^{-1} (20 °C)	2002/7004412
Appearance	Pure ai (99.5%)	White to chalky-white crystalline solid, light musty smell	1998/7000367 1998/7000369
Solubility in water	Pure ai (99.5%)	0.474 mg/L in deionized water 0.552 mg/L in pH 5 buffer 0.492 mg/L in pH 7 buffer 0.457 mg/L in pH 9 buffer	1998/7000347
	CL 377160 metabolite (97%)	1.1 mg/L in deionized water (pH ca. 4.0, 20 °C) 1.0 mg/L in acidified water (pH 2.8, 20 °C 175 mg/L in basified water (pH 11.6, 20 °C)	2001/1019497
n-octanol/water partition coefficient	Pure ai (99.5%)	Log K_{ow} 4.3 (pH 4.0, 25 °C)	1999/7000293
	CL 4084564 Metabolite	Log K_{ow} 3.52 (neutral form)—pH ca 8 Log K_{ow} 0.37 (ionized form)—pH ca 8	2002/7005227
	CL 375816 Metabolite	Log K_{ow} 3.01 (neutral form) Log K_{ow} 1.09 (ionized form) pH dependent—dissociation of the carboxylic acid function.	2002/7005228
Hydrolysis (sterile buffer in the dark)	^{14}C labelled pure ai (> 99%) radiolabel purity 98.3%	Stable to hydrolysis in the dark after incubation for 5 days at 50 °C in pH 4, pH 7, pH 9 buffers	1999/7000284
Photolysis in sterile water	^{14}C labelled pure ai (> 98%)	Extensive degradation in sterile water after irradiation by simulated sunlight (15 days, pH 7, 22 °C) First order kinetics, rate constant: 0.225 day^{-1}, DT_{50} : 3.1 days, DT_{90} : 10.2 days) Multiple photoproducts observed, all < 10% AR After 15 days irradiation ca 97% conversion to very polar anionic materials and CO_2.	2002/7005112
Photolysis in natural water	^{14}C labelled pure ai, radiochemical purity of > 99%	Rapid degradation in natural water under light at 22 °C (DT_{50}: 2.6 days, DT_{90}: 8.5 days) Many degradation products were formed, all< 10% AR. Main degradates included CL 377160, CL 377095, CL 377096, CL 4084564, and CL 375816. Maximum $^{14}CO_2$ formation ca. 5%.	2002/7004458
Dissociation in water	Pure ai (99.5%)	No evidence of dissociation—no hydrogens or basic groups present in the molecule and no appreciable differences in the UV spectra of the ai over a pH range of 1.0–13.0	1998/7000353
	CL 4084564 Metabolite	Estimated pKa : 9.63 ± 0.3	2002/7005227
	CL 375816 Metabolite	Estimated pKa : 3.35 ±0.2.	2002/7005228

Table 2 Physical and chemical data of metrafenone (technical grade material) and metabolites CL 377160, CL 4084564 and CL 375816

Test or Study & Annex point	Test material purity and specification	Findings and comments	Reference
Relative density	Technical (95.86%)	1.45	1999/7000296
Appearance	Technical (95.86%)	Yellow-white powdery, fine-crystalline solid, light musty smell	1998/7000368 1999/7000312 1999/7000311 1999/7000313
Solubility in organic solvents (g/L, 20 °C)	Technical (97.1%)	Dichloromethane: 1950 Acetone: 403 Toluene: 363 Ethyl acetate: 261 Acetonitrile: 165 Methanol: 26.1 n-Hexane: 4.8	1998/7000349

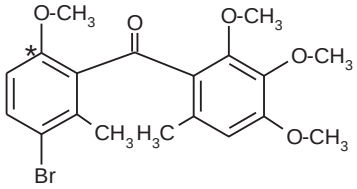
Formulations

Formulations of metrafenone are available for use as foliar applications, both as solo products or co-formulated with other actives.

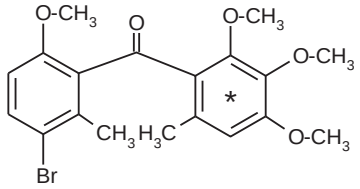
Formulation type	Active substance/s and content	Other active ingredients
SC (Soluble Concentrate)	Metrafenone 300 g/L Metrafenone 500 g/L Metrafenone 100 g/L	– – Epoxiconazole 83 g/L
SE (Suspo-emulsion)	Metrafenone 75 g/L	Fenpropimorph 200 g/L + Epoxiconazole 62.5 g/L

METABOLISM

The Meeting received metrafenone metabolism studies on animals (rats, lactating goats and laying hens), plants (grape, cucumber and wheat), soil and rotational crops. Metrafenone radiolabelled on the bromophenyl or the trimethoxyphenyl groups were used in these studies. The label positions are given below:



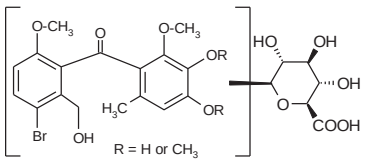
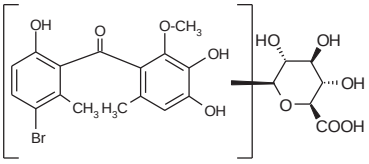
[Bromphenyl-6-^{14}C]-metrafenone
(Bromophenyl-label)
* = location of the radiolabel

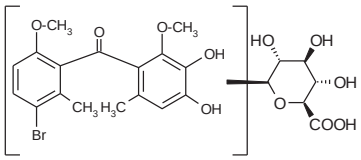
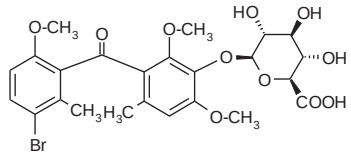
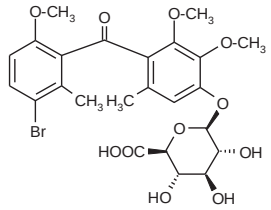
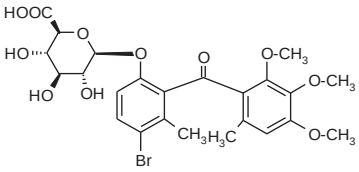
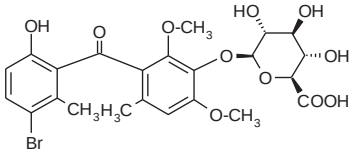
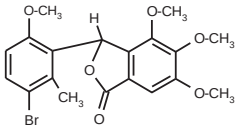
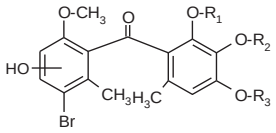
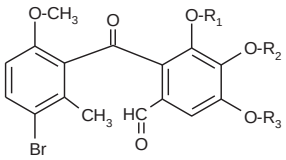
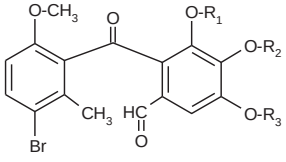


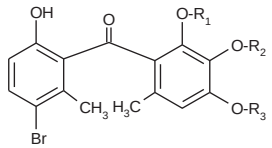
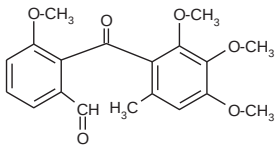
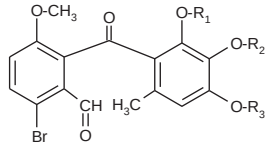
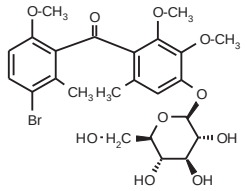
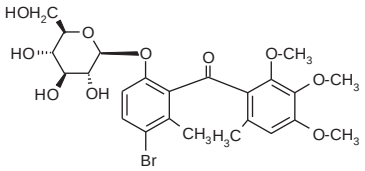
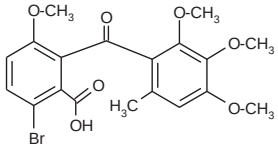
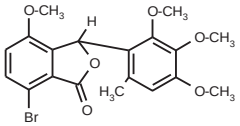
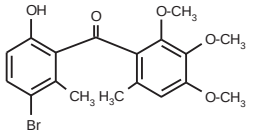
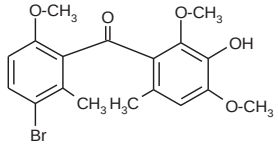
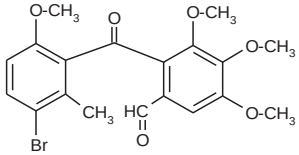
[Trimethoxyphenyl-U-^{14}C]-metrafenone
(Trimethoxyphenyl-label)
* = location of the radiolabel

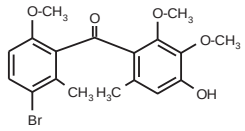
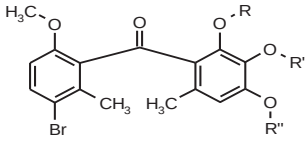
Major metabolites identified in these studies and discussed in this evaluation are listed below.

Table 3 Major metrafenone metabolites identified in plant, animal and soil matrices

CODE	STRUCTURE	CHEMICAL NAME	OCCURRENCE
CL 1023361		3-[3-bromo-2-(hydroxymethyl)-6-methoxybenzoyl]-2,6-dimethoxy-4- methylphenyl β-D-glucopyranosiduronic acid 3-[3-bromo-2-(hydroxymethyl)-6-methoxybenzoyl]-6-hydroxy-2-methoxy-4-methylphenyl β-D-glucopyranosiduronic acid 4-[3-bromo-2-(hydroxymethyl)-6-methoxybenzoyl]-2-hydroxy-3-methoxy-5-methylphenyl β-D-glucopyranosiduronic acid 4-[3-bromo-2-(hydroxymethyl)-6-methoxybenzoyl]-2,3-dimethoxy-5- methylphenyl β-D-glucopyranosiduronic acid	goat
CL 1023362		4-(3-bromo-6-hydroxy-2-methylbenzoyl)-2-hydroxy-3-methoxy-5-methylphenyl β-D-glucopyranosiduronic acid 3-(3-bromo-6-hydroxy-2-methylbenzoyl)-6-hydroxy-2-methoxy-4-methylphenyl β-D-glucopyranosiduronic acid	goat

CODE	STRUCTURE	CHEMICAL NAME	OCCURRENCE
CL 1023363		3-(3-bromo-6-methoxy-2-methylbenzoyl)-6-hydroxy-2-methoxy-4-methylphenyl β-D-glucopyranosiduronic acid 4-(3-bromo-6-methoxy-2-methylbenzoyl)-2-hydroxy-3-methoxy-5-methylphenyl β-D-glucopyranosiduronic acid	goat
CL 1500698		3-(3-bromo-6-methoxy-2-methylbenzoyl)-2,6-dimethoxy-4-methylphenyl β-D-glucopyranosiduronic acid	rat goat
CL 1500699		Methanone, (3-bromo-6-methoxy-2-methylphenyl)[4-(β-D-glucopyranurosyloxy)-2,3-dimethoxy-6-methylphenyl])-	goat
CL 1500701		Methanone, [3-bromo-6-(β-D-glucopyranurosyloxy)-2-methylphenyl](2,3,4-trimethoxy-6-methylphenyl)-	goat
CL 1500702		3-(3-bromo-6-hydroxy-2-methylbenzoyl)-2,6-dimethoxy-4-methylphenyl β-D-glucopyranosiduronic acid	goat
CL 1500831		1(3H)-isobenzofuranone, 4,5,6-trimethoxy-3-(3-bromo-6-methoxy-2-methylphenyl)-	wheat
CL 1500832	 R_1, R_2, R_3 = 1H, $2CH_3$	Methanone, [3-bromo-6-methoxy-(4 or 5)-hydroxy-2-methylphenyl](2,3,4-trimethoxy-6-methylphenyl-	wheat
CL 1500833	 R_1, R_2, R_3 = 1H, $2CH_3$	Methanone, [3-bromo-6-methoxy-2-methylphenyl] (2, 3 or 4)-hydroxy-[2, 3 or 4-dimethoxy-6-formylphenyl-	wheat
CL 1500834	 R_1, R_2, R_3 = 1H, $2CH_3$	Benzaldehyde, 6-bromo-3-hydroxy-2-(2,3,4-trimethoxy-6-methylbenzoyl-	wheat

CODE	STRUCTURE	CHEMICAL NAME	OCCURRENCE
CL 1500835	 R_1, R_2, R_3 = 1H, $2CH_3$	Methanone, [3-bromo-6-hydroxy-2-methylphenyl] (2, 3 or 4)-hydroxy-[2, 3 or 4-dimethoxy-6-methylphenyl-	wheat
CL 1500836		3-methoxy-2-(2,3,4-trimethoxy-6- methylbenzoyl) benzaldehyde	wheat grape
CL 1500837	 R_1, R_2, R_3 = 1H, $2CH_3$	Benzaldehyde, 6-bromo-3-methoxy-2-(2,3 or 4-dimethoxy-6-methylbenzoyl)-	wheat
CL 1500838		Methanone, (3-bromo-6-methoxy-2-methylphenyl)[4-(β-D-glucopyranosyloxy)-2-methylphenyl](2,3,4-trimethoxy-6-methylphenyl)-	wheat (glucose conjugate)
CL 1500839		Methanone, (3-bromo-6-(β-D-glucopyranosyloxy)-2-methylphenyl](2,3,4-trimethoxy-6-methylphenyl)-	wheat
CL 197675		Methanone, (3-bromo-6-methoxy-2-carboxyl)(2,3,4-trimethoxy-6-methylphenyl)-	grape
CL 3000402		7-bromo-4-methoxy-3-(2,3,4-trimethoxy-6-methylphenyl)-2-benzofuran-1(3H)-one	wheat grape
CL 376991		Methanone, (3-bromo-6-methoxy-2-methylphenyl)(2,3,4-trimethoxy-6-methylphenyl)-	rat wheat
CL 377160		Methanone, (3-bromo-6-methoxy-2-methylphenyl)(3-hydroxy-2,4-dimethoxy-6-methylphenyl)-	wheat
CL 379395		2-(3-bromo-6-methoxy-2-methylbenzoyl)- 3,4,5-trimethoxybenzaldehyde	grape

CODE	STRUCTURE	CHEMICAL NAME	OCCURRENCE
CL 434223		Methanone, (3-bromo-6-methoxy-2-methylphenyl)(4-hydroxy-2,3-dimethoxy-6-methylphenyl)-	wheat
M560F06	 R = H, R' and R" = CH_3 or R' = H, R and R" = CH_3 or R" = H, R and R' = CH_3	Methanone, (3-bromo-6-methoxy-2-methylphenyl)(2-hydroxy-3,4-dimethoxy-6-methylphenyl)- or Methanone, (3-bromo-6-methoxy-2-methylphenyl)(3-hydroxy-2,4-dimethoxy-6-methylphenyl)- or Methanone, (3-bromo-6-methoxy-2-methylphenyl)(4-hydroxy-2,3-dimethoxy-6-methylphenyl)-	hen

Animal metabolism

The Meeting received animal metabolism studies on rats, lactating goats and laying hens, following oral dosing with [bromophenyl-6 (^{14}C)] metrafenone or [trimethoxyphenyl-(U-^{14}C)] metrafenone. As no cleavage of the molecule was observed in these metabolism studies, the results for both radiolabels are reported together.

Rats

The metabolism of metrafenone in rats was evaluated by the WHO Core Assessment Group of the 2014 JMPR. Absorption of metrafenone is rapid and complete (> 88%) at the low dose of 10 mg/kg bw, limited to 15–20% at the high dose of 1000 mg/kg bw suggesting saturation of the absorption processes. Metrafenone is widely distributed in the body, with highest residue levels mainly found in the gastro-intestinal (GI) tract, liver and fat. There is no evidence of accumulation. The labelled material is relatively rapidly excreted into the GI tract via the bile (85–90%) resulting in extensive excretion via faeces. Excretion via urine is relatively low (5–6% depending on radiolabel position), and even lower at the high dose level (*ca.* 1%). Metrafenone is extensively metabolised, with most of the radioactivity (ca 80%) not identified, consisting of many (11–26) different components and totalling < 0.1 ppm at the low dose and < 1 ppm at the high dose. The identified metabolites, mostly < 1.0 mg eq/kg, included metrafenone and glucuronic acid conjugates in fat, liver and kidney.

Lactating goats

In a study reported by Fung, 2002 [Ref: 2002/7005114], the metabolism and distribution of [^{14}C]metrafenone were investigated in lactating goats following repeated oral administration of radiolabelled metrafenone in gelatin capsules over five consecutive days at nominal dose levels equivalent to 10 ppm and 70 ppm in the diet (based on an average feed consumption of 2 kg per goat per day). The goat body weights ranged from 46–55 kg prior to treatment and 45–54 kg at sacrifice (21–23 hours after the last dose), and mean feed consumptions ranged from 1.5–2.3 kg.

[Bromphenyl-6-^{14}C]-metrafenone, enriched with C^{13} (49%) as a mass marker to assist in mass spectometric analysis of metabolites was administered to two goats at daily doses equivalent to 13 ppm or 87 ppm feed and [trimethoxyphenyl-(U-C^{14})] metrafenone enriched with C^{13} (49%) was administered to two goats at doses equivalent to 8 ppm or 87 ppm in the diet.

The majority of the radioactivity (76–86% AR) was excreted, mainly through the faeces. The highest residue levels were found in liver (0.21–0.23 mg eq/kg at the lower dose and 0.72–1.3 mg eq/kg at the higher dose) and kidney (0.05–0.06 mg eq/kg at the low dose and 0.16–0.33 mg eq/kg at the higher dose). Residues were significantly lower in fat (0.015–0.022 mg eq/kg)

and were < 0.01 mg eq/kg in muscle and up to 0.01 mg eq/kg in milk regardless of the dose rate. In milk, a plateau level not higher than 0.01 mg eq/kg was reached within about 3 days.

Table 4 Total radioactive residues in dissected tissues, excreta and milk of lactating goats following five daily oral administrations of [^{14}C]metrafenone

	Treatment Groups			
Group ID	B	D	C	E
Radiolabel	Trimethoxyphenyl-label	Bromophenyl-label	Trimethoxyphenyl-label	Bromophenyl-label
Dose Group	Low	Low	High	High
Dose Rate (ppm)	8	13	60	87
Sample type	Total Radioactive Residues (TRR mg eq/kg)			
Liver	0.208	0.231	0.718	1.278
Kidneys	0.047	0.06	0.157	0.329
Muscle	< 0.005	< 0.005	0.006	0.008
Adipose tissue	< 0.005	< 0.005	0.022	0.015
Milk (Day 1)	< 0.005	< 0.005	0.005	0.009
Milk (Day 2)	< 0.005	< 0.005	0.006	0.009
Milk (Day 3)	< 0.005	< 0.005	0.006	0.009
Milk (Day 4)	< 0.005	< 0.005	0.006	0.008
Milk (Day 5)	< 0.005	< 0.005	0.006	0.01
Sample type	Excretion (% total dose)			
Urine + Faeces	85.7%	84.0%	82.2%	75.7%

Liver and kidney samples from the higher dose groups were sequentially extracted with acetonitrile, acetonitrile:water (80:20), methanol:acetone:water:trimethylamine (24:24:50:2) and methanol:water:trifluoroacetic acid (99:30:1). The post extraction solids were subject to pepsin hydrolysis followed by extraction with hydrochloric acid in methanol. Fat samples were triple-extracted with methanol. Milk samples were extracted with acetone, concentrated, redissolved in acetonitrile and partitioned with hexane, with the aqueous layer retained and the hexane extract partitioned with methanol. The two aqueous layers were then combined for analysis. The sample extracts were analysed by HPLC with a variable wavelength detector and radio detector within 15 days of sampling and the fractions were isolated for LC-MS analysis. A storage stability study indicated that residues of the glucuronide metabolites were stable in frozen storage for up to 3 months in liver, 6 months in kidney and that metrafenone was stable for up to 10 months in fat.

In liver, 95–97% TRR was able to be extracted (0.7–1.2 mg eq/kg) and 98–101% TRR (0.15–0.33 mg eq/kg) was extractable from kidney. The two sequential extractions of milk with acetone accounted for 99.9% TRR (ca 0.01 mg eq/kg).

Metrafenone was the predominant residue in fat (0.01–0.02 mg eq/kg), making up 60–85% TRR but was only found at 2.7–4.4% TRR in liver and kidney (0.025–0.035 mg eq/kg in liver and 0.005–0.014 mg eq/kg in kidney).

In liver and kidney, the predominant residues were two metabolites (CL 1500698 and CL 1023363) which together represented 15–21% of the TRR in liver (max 0.27 mg eq/kg) and 26–28% of the TRR in kidney (max 0.09 mg eq/kg). An additional group of three metabolites (CL 1023361, CL1023362 and CL 1500702) were found at up to 13% of TRR (0.17 mg eq/kg) in liver. While a number of other metabolites were present, these generally made up < 10% TRR.

In milk, residues of parent (24% TRR) and metabolites (up to 10% TRR) were all < 0.005 mg eq/kg and no metabolites were found in fat above 0.005 mg eq/kg (9% TRR).

Table 5 Characterisation and identification of radioactive residues in goat liver and kidney following five daily oral administrations of [^{14}C]metrafenone

Sample Type	Liver				Kidney			
Dose Group (Rate in Diet)	C (60 mg/kg)		E (87 mg/kg)		C (60 mg/kg)		E (87 mg/kg)	
Radiolabel	Trimethoxyphenyl		Bromophenyl		Trimethoxyphenyl		Bromophenyl	
Fractions	%TRR	mg eq./kg	% TRR	mg eq./kg	% TRR	mg eq./kg	% TRR	mg eq./kg
TRR	100	0.718	100	1.278	100	0.157	100	0.329
Combined extracts	96.8	0.695	94.6	1.21	97.7	0.153	100.6	0.331
Distribution of Extractable Radioactive Residues								
ROI-1 (Unknown)	5.99	0.043	3.60	0.046	5.54	0.009	6.00	0.020
ROI-2 (Unknown)	3.76	0.027	2.97	0.038	0.61	0.001	1.23	0.004
ROI-3 (Unknown)	11.7	0.084	5.94	0.076	1.21	0.002	1.82	0.006
ROI-4 (Unknown)	4.18	0.030	4.77	0.061	3.12	0.005	7.39	0.024
ROI-5 (Unknown)	5.01	0.036	3.60	0.046	3.82	0.006	5.23	0.017
ROI-6 (Unknown)	2.64	0.019	3.68	0.047	4.97	0.008	4.16	0.014
ROI-7 (Unknown)	4.73	0.034	5.09	0.065	1.53	0.002	1.25	0.004
ROI-8 (Unknown)	2.92	0.021	2.97	0.038	4.33	0.007	3.80	0.013
ROI-9A (CL 1023361) + ROI-9B1 (CL 1023362) + ROI-9B2 (CL 1500702	9.89	0.071	13.23	0.169	13.57	0.021	9.51	0.031
ROI-10 (Unknown)	2.65	0.019	2.35	0.030	2.80	0.004	4.80	0.016
ROI-11 (Unknown)	2.93	0.021	12.11	0.027	1.66	0.003	2.13	0.007
ROI-12 (Unknown)	2.23	0.016	1.96	0.025	5.67	0.009	3.10	0.010
ROI-13A1 (CL 1500698) + ROI-13A2 (CL 1023363) + Unknown	14.77	0.106	21.05	0.269	28.15	0.044	26.29	0.087
ROI-14 (Unknown)	3.35	0.024	2.90	0.037	4.14	0.007	4.32	0.014
ROI-15 (Unknown)	2.09	0.015	1.88	0.024	4.08	0.006	1.43	0.005
ROI-16A (CL 1500701) + ROI-16B (CL 1500699) + Unknown	6.41	0.046	7.12	0.091	1.46	0.002	4.19	0.014
ROI-17 (Unknown)	1.53	0.011	1.72	0.022	0.64	0.001	1.22	0.004
ROI-18 (Unknown)	1.53	0.011	1.25	0.016	0.63	0.001	1.49	0.005
ROI-19 (Unknown)	0.98	0.007	0.70	0.009	0.49	0.001	1.28	0.004
ROI-20 (Unknown)	1.81	0.013	1.80	0.023	1.21	0.002	2.16	0.007
ROI-21 (Unknown)	1.67	0.012	1.33	0.017	2.36	0.004	2.28	0.008
ROI-22 (Metrafenone)	3.49	0.025	2.74	0.035	3.25	0.005	4.35	0.014

Table 6 Characterisation and identification of radioactive residues in goat milk and fat following five daily oral administrations of [^{14}C]metrafenone

Sample Type	Milk				Fat			
Dose Group (Rate in Diet)	C (60 mg/kg)		E (87 mg/kg)		C (60 mg/kg)		E (87 mg/kg)	
Radiolabel	Trimethoxyphenyl		Bromophenyl		Trimethoxyphenyl		Bromophenyl	
Fractions	%TRR	mg eq./kg	% TRR	mg eq./kg	% TRR	mg eq./kg	% TRR	mg eq./kg
TRR	100	0.006	100	0.010	100	0.022	100	0.015
Combined extracts [a]	NP	NP	98.9	~0.010	116	~0.026	112.6	0.020
Distribution of Extractable Radioactive Residues								
ROI-1 (Unknown)	NP	NP	5.3	< 0.005	8.0	< 0.005	9.1	< 0.005
ROI-2 (Unknown)	NP	NP	1.8	< 0.005	ND	ND	ND	ND
ROI-3 (Unknown)	NP	NP	2.2	< 0.005	ND	ND	ND	ND

Sample Type	Milk				Fat			
Dose Group (Rate in Diet)	C (60 mg/kg)		E (87 mg/kg)		C (60 mg/kg)		E (87 mg/kg)	
Radiolabel	Trimethoxyphenyl		Bromophenyl		Trimethoxyphenyl		Bromophenyl	
Fractions	%TRR	mg eq./kg	% TRR	mg eq./kg	% TRR	mg eq./kg	% TRR	mg eq./kg
TRR	100	0.006	100	0.010	100	0.022	100	0.015
Combined extracts [a]	NP	NP	98.9	~0.010	116	~0.026	112.6	0.020
Distribution of Extractable Radioactive Residues								
ROI-4 (Unknown)	NP	NP	2.9	< 0.005	ND	ND	ND	ND
ROI-5 (Unknown)	NP	NP	1.4	< 0.005	ND	ND	ND	ND
ROI-6 (Unknown)	NP	NP	1.6	< 0.005	ND	ND	ND	ND
ROI-7 (Unknown)	NP	NP	1.1	< 0.005	ND	ND	ND	ND
ROI-8 (Unknown)	NP	NP	2.0	< 0.005	ND	ND	ND	ND
ROI-9A (CL 1023361) + ROI-9B1 (CL 1023362) + ROI-9B2 (CL 1500702	NP	NP	2.8	< 0.005	ND	ND	ND	ND
ROI-10 (Unknown)	NP	NP	1.0	< 0.005	ND	ND	ND	ND
ROI-11 (Unknown)	NP	NP	1.2	< 0.005	ND	ND	ND	ND
ROI-12 (Unknown)	NP	NP	1.3	< 0.005	ND	ND	ND	ND
ROI-13A1 (CL 1500698) + ROI-13A2 (CL 1023363) + Unknown	NP	NP	10.7	< 0.005	ND	ND	ND	ND
ROI-14 (Unknown)	NP	NP	2.8	< 0.005	ND	ND	ND	ND
ROI-15 (Unknown)	NP	NP	7.2	< 0.005	ND	ND	ND	ND
ROI-16A (CL 1500701) + ROI-16B (CL 1500699) + Unknown	NP	NP	3.8	< 0.005	ND	ND	ND	ND
ROI-17 (Unknown)	NP	NP	2.6	< 0.005	ND	ND	ND	ND
ROI-18 (Unknown)	NP	NP	5.0	< 0.005	ND	ND	ND	ND
ROI-19 (Unknown)	NP	NP	4.3	< 0.005	ND	ND	ND	ND
ROI-20 (Unknown)	NP	NP	6.7	< 0.005	ND	ND	ND	ND
ROI-21 (Unknown)	NP	NP	5.5	< 0.005	5.4	< 0.005	5.3	< 0.005
ROI-22 (Metrafenone)	NP	NP	24.1	< 0.005	85.4	0.019	60.0	0.009

NP–not performed

[a] For milk, combined acetone extracts analysed by HPLC, for adipose tissues combined methanol extracts analysed by HPLC

In summary, when goats were treated orally for five consecutive days with metrafenone, the majority (76–86%) of the dose was excreted, with TRR being highest in liver and 0.01 mg eq/kg or less in milk and muscle. Metrafenone made up about 3–4% of the TRR in liver and kidney and was the main component in fat. Most of the residues in liver and kidney were the glucuronide conjugates of metrafenone (CL 1500698, CL 1023363) which together made up 15–30% TRR, with several other conjugates also found at lower levels.

The proposed metabolic pathway includes hydroxylation and demethylation of the methyl groups and the phase II glucuronidation of the hydroxylated metabolites to various mono-O-glucuronides, qualitatively similar to the metabolic pathway in the rat.

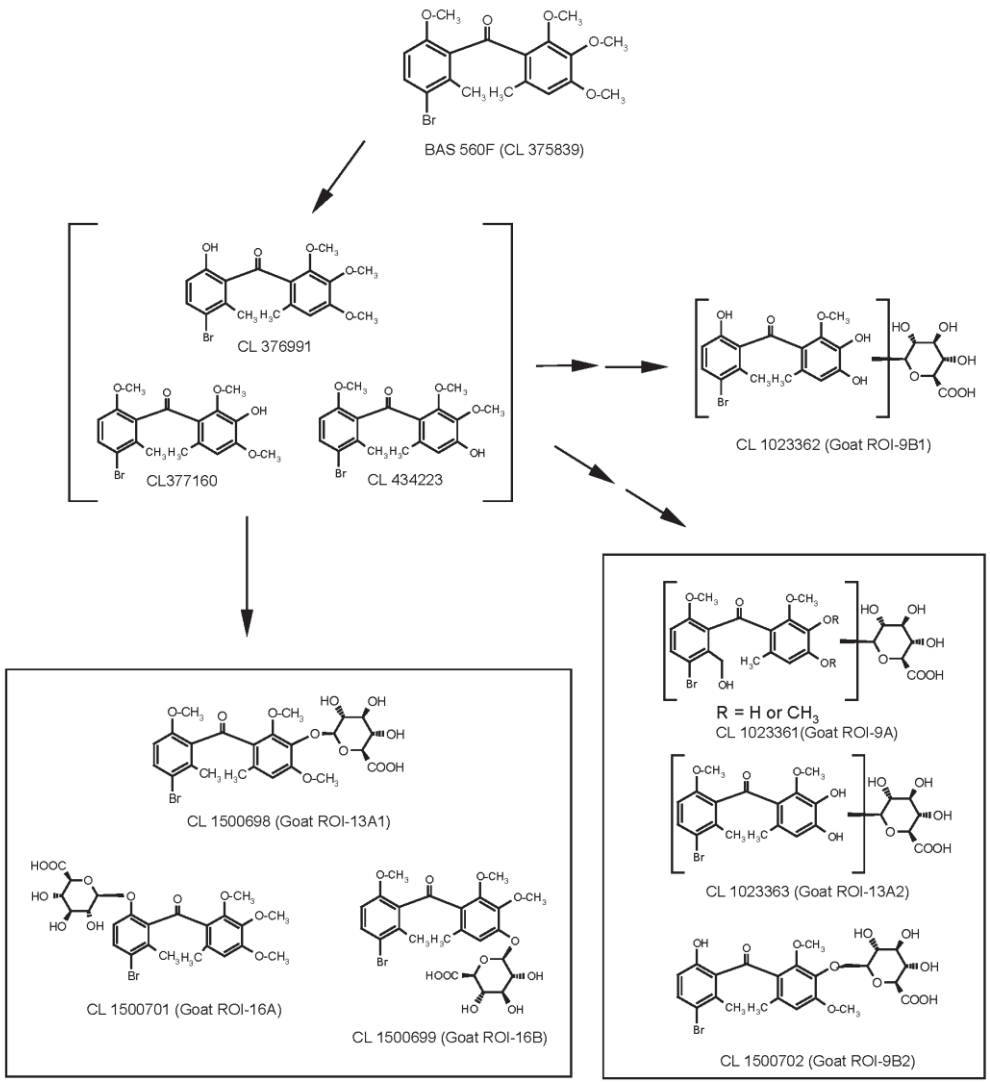


Figure 1Metabolic pathway in lactating goats

Laying hens

In a study reported by Hoefs, 2008 [Ref: 2005/1026047], the metabolism and distribution of [^{14}C]metrafenone were investigated in laying hens following repeated oral administration of radiolabelled metrafenone in gelatin capsules over twelve consecutive days at nominal dose levels equivalent to 12 ppm in the diet (based on an average feed consumption of 120 g per hen per day). The actual dose rates for the two groups of eight laying hens were 14.2 mg/kg (trimethoxyphenyl label) and 13.9 mg/kg (bromophenyl label). Average body weights for the two dose groups were 1.55 kg and 1.64 kg prior to treatment and 1.58 kg and 1.66 kg at sacrifice (22 hours after the last dose), and mean feed consumptions ranged from 102–185 g/day.

Overall recoveries of radioactivity were approximately 96 and 86% of the total applied dose for the trimethoxyphenyl and bromophenyl labels, respectively. Radioactivity was rapidly eliminated within 24 hours with 95% (trimethoxyphenyl label) and 86% (bromophenyl label) of the administered dosed recovered in the excreta. About 0.25% AR was found in eggs and 0.06–0.09% AR was measured in liver. Radioactivity in skin + fat was < 0.01% AR and muscle contained 0.003% AR. TRRs in eggs reached a plateau about day 9–10.

Table 7 Total radioactive residues in dissected tissues, excreta and eggs of laying hens following 12 daily oral administrations of [^{14}C]metrafenone

Matrix	Dose Group A trimethoxyphenyl label		Dose Group B bromophenyl label	
	mg eq./kg	% AR	mg eq./kg	% AR
Eggs (Day 1)	< 0.001		< 0.001	
Eggs (Day 2)	0.016	0.003	0.018	0.003
Eggs (Day 3)	0.026	0.004	0039	0.009
Eggs (Day 4)	0.054	0.013	0.055	0.012
Eggs (Day 5)	0.072	0.019	0.064	0.014
Eggs (Day 6)	0.086	0.024	0.102	0.025
Eggs (Day 7)	0.095	0.02	0.094	0.024
Eggs (Day 8)	0.097	0.027	0.106	0.031
Eggs (Day 9)	0.107	0.034	0.115	0.03
Eggs (Day 10)	0.109	0.028	0.117	0.035
Eggs (Day 11)	0.106	0.032	0.118	0.031
Eggs (Day 12)	0.110	0.032	0.118	0.036
Eggs (Days 9–12 pooled)	0.099	0.25	0.118	0.236
Muscle	0.010	0.003	0.013	0.003
Skin with fat	0.060	0.006	0.084	0.009
Liver	0.489	0.088	0.326	0.063
Bile	10.214	0.027	10.641	0.028
Excreta (Days 6–12 pooled)	14.758	85.9	13.289	95.1

Tissue and egg samples were extracted sequentially with three aliquots of methanol and two aliquots of water, with the combined methanol extracts and the combined water extracts being analysed by LSC. Residues in the post extraction solids were determined by LSC after combustion. Eggs were homogenized with an equal weight of water before extraction.

Extraction of pooled eggs (days 9–12) yielded 63% TRR (0.06–0.07 mg eq/kg) in the methanol extract and a further 17% (0.017 to 0.02 mg eq/kg) in water, giving a total of 80% TRR (0.079 to 0.094 mg eq/kg) as extractable residues. Unextractable residues accounted for about 20% TRR.

Low levels of radioactivity (0.01–0.013 mg eq/kg) were found in muscle with about 27–31% TRR extracted with methanol and a further 1–1.8% TRR extracted in water. Unextractable residues accounted for about 68–72% TRR (0.007 to 0.009 mg eq/kg).

About 58–61% TRR in skin + fat was able to be extracted and overall extractability in liver was about 30% TRR.

HPLC analysis of acetone-extracted egg samples and bile extracts stored for more than 19 months showed comparable metabolite patterns to those from samples analysed within 8 days of extraction.

Table 8 Extractability of [^{14}C]metrafenone residues in hen matrices following 12 daily oral administrations of [^{14}C]metrafenone.

Matrix	TRR [a]	Methanol	Water	ERR [b]	PES [c]	TRR [d] Recovery
	mg eq./kg	mg eq./kg (% TRR)	mg eq./kg (% TRR)	mg eq./kg (% TRR)	mg eq./kg (% TRR)	mg eq./kg [%]
Trimethoxyphenyl Label						
Eggs pooled (days 9–12)	0.099	0.062 (62.6)	0.017 (17.2)	0.079 (79.8)	0.020 (20.2)	0.099 (100)
Muscle	0.010	0.003 (26.8)	0.0001 (1.0)	0.003 (27.8)	0.007 (72.2)	0.010 (100)
Skin with fat	0.060	0.033 (53.9)	0.002 (4.1)	0.035 (58.0)	0.025 (42.0)	0.060 (100)
Liver	0.489	0.058 (11.8)	0.099 (20.2)	0.157 (32.0)	0.333 (68.0)	0.490 (100)
Excreta pool (days 6–12)	14.758	11.656 (79.0)	1.567 (10.6)	13.233 (89.6)	1.535 (10.4)	14.758 (100)
Bromophenyl Label						
Eggs pooled (days 9–12)	0.118	0.074 (62.7)	0.020 (16.9)	0.094 (79.7)	0.024 (20.3)	0.118 (100)
Muscle	0.013	0.004 (30.7)	0.0002 (1.8)	0.004 (32.5)	0.009 (67.5)	0.013 (100)
Skin with fat	0.084	0.048 (57.7)	0.002 (2.9)	0.050 (60.6)	0.033 (39.4)	0.083 (100)
Liver	0.326	0.036 (11.0)	0.060 (18.6)	0.096 (29.6)	0.230 (70.4)	0.326 (100)
Excreta pool (days 6–12)	13.289	9.965 (75.0)	1.548 (11.6)	11.513 (86.6)	1.776 (13.4)	13.289 (100)

[a] TRR values reported as sum of radioactivity on methanol and water extract measured directly by LSC and in post extraction solids after combustion

[b] ERR—extractable radioactive residues (sum of methanol and water extracts)

[c] PES—Post extraction solids remaining after extraction with methanol and water

[d] Sum of all extracts and post extraction solids

Characterisation of metabolites was performed by LC-MS and LC-MS/MS analysis. Metrafenone was found only in eggs (1.8–2.2% TRR) and in skin + fat (1.9% TRR). A comparison with the retention times and metabolite patterns for the components in the methanol extract of excreta (bromophenol-label), allowed the assignment of the metabolite M560F06 in the skin + fat extracts (at about 6–11% TRR) and tentatively in eggs (unquantifiable). With the exception of one unknown component in eggs (found at about 14% TRR and 0.015 mg eq/kg) all other components were below 10% TRR (< 0.01 mg eq/kg) in all tissues and eggs.

Table 9 Residues of metrafenone and other characterised components in hen matrices following following 12 daily oral administrations of [^{14}C]metrafenone.

Matrix	Metrafenone		Characterised (Methanol extract)		Characterised (Aqueous extract)	
	mg/kg	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR
Trimethoxyphenyl Label						
Eggs pooled (days 9–12)	0.002	2.2	0.04 [a]	37.5	0.009 [b]	8.4
Muscle	NA	NA	0.003	26.8	0.0001	1.0
Skin with fat	0.001	1.9	0.034 [c]	48.6		
Liver			0.097 [d]	17.3	0.07 [e]	12.5

Matrix	Metrafenone		Characterised (Methanol extract)		Characterised (Aqueous extract)	
	mg/kg	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR
Bromophenyl Label						
Eggs pooled (days 9–12)	0.002	1.8	0.041 [f]	35.1	0.01 [g]	8.0
Muscle	NA	NA	0.004	30.7	0.0002	1.8
Skin with fat	< 0.001	< 0.001	0.042 [h]	42.9		
Liver	< 0.001	< 0.001	0.096 [i]	27.8	0.058 [j]	16.6

[a] Includes nine peaks, each < 0.01 mg eq/kg or < 1.5% TRR, including 1 peak tentatively identified as M560F06
[b] Includes eight peaks, each < 0.01 mg eq/kg or < 3% TRR
[c] Includes 12 peaks, each < 7% TRR, and one peak identified as M560F06 (0.008 mg eq/kg, 11.4% TRR)
[d] Includes 10 peaks, each < 3.7% TRR
[e] Includes 12 peaks, each < 1.6% TRR
[f] Includes six peaks, each < 0.01 mg eq/kg or < 3% TRR, including one peak identified as M560F06
[g] Includes eight peaks, each < 0.01 mg eq/kg or < 2.7% TRR
[h] Includes 12 peaks, each < 9% TRR, and one peak identified as M560F06 (0.006 mg eq/kg (5.8% TRR)
[i] Includes six peaks, each < 4.5% TRR
[j] Includes five unknown peaks, each < 4.1% TRR

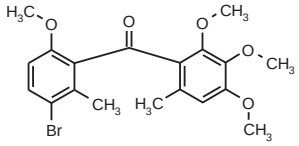
In summary, after 12 consecutive daily oral administrations of [^{14}C]metrafenone to laying hens, there was rapid absorption and almost complete excretion within 24 hours. The total radioactive residues in edible tissues and organs were about 0.11 mg eq/kg in eggs, up to 0.57 mg eq/kg in liver, about 0.012 mg eq/kg in muscle, and up to 0.1 mg eq/kg in skin with adhering fat.

Metrafenone made up about 2% of the TRR in eggs and skin + fat (0.002 mg/kg) and the M560F06 metabolite was tentatively identified in skin + fat and eggs. The proposed metabolic pathway for metrafenone involves:

Hydroxylation at the bromophenyl ring or the attached methyl group to form M560F05, which can be demethylated and conjugated with glucuronic acid in bile to form M560F07

Demethylation at the trimethoxyphenyl ring to form M560F06, with glucuronic acid conjugation in bile to form the metabolites M560F08 and M560F09

Oxidation of the methyl group on the bromomethoxytoluene ring to the carboxylic acid (via the respective isomer of M560F05) to form M560F03.

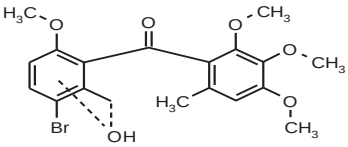


BAS 560 F

Hydroxylation

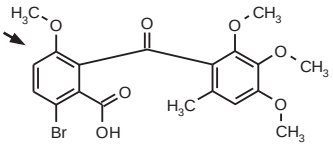
Methyl group oxidation

Demethylation

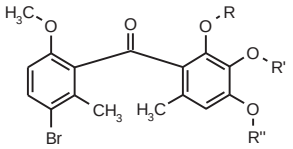


M560F05

Oxidation



M560F03



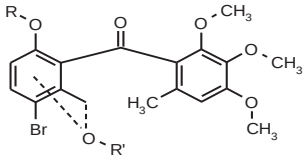
M560F06

R = H, R' and R" = CH_3

or R' = H, R and R" = CH_3

or R" = H, R and R' = CH_3

Demethylation, Glucuronylation (Bile)



M560F07

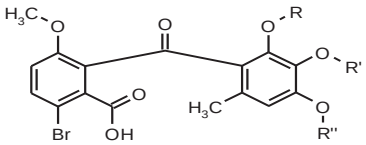
R = H, R' = GlcA

or R = GlcA, R' = H

Demethylation

Methyl group oxidation

Glucuronylation (Bile)

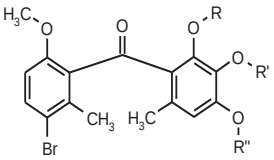


M560F01 / M560F02

R = H, R' and R" = CH_3

or R' = H, R and R" = CH_3

or R" = H, R and R' = CH_3



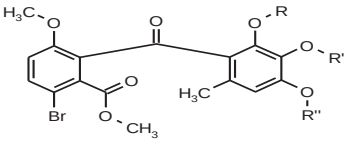
M560F08 / M560F09

R = GlcA, R' and R" = CH_3

or R' = GlcA, R and R" = CH_3

or R" = GlcA, R and R' = CH_3

Methyl ester formation



M560F04

R = H, R' and R" = CH_3

or R' = H, R and R" = CH_3

Plant metabolism

The Meeting received plant metabolism studies on grapes, cucumbers and wheat following foliar treatments with with [bromophenyl-6 (^{14}C)] metrafenone or [trimethoxyphenyl-(U-^{14}C)] metrafenone.

Grape

In a study reported by Class & Schluter, 2001 [Ref: 2001/7000342], the metabolism of metrafenone in outdoor grapevines was investigated following five foliar applications at 10–11 day intervals of about 0.2 kg ai/ha of [^{14}C]metrafenone (trimethoxyphenyl-label or bromophenyl-label, both being diluted with ^{13}C as a mass marker). Grape and leaf samples were taken immediately after each application; nineteen days after the last treatment (61 days after the first application, BBCH 85) and at maturity, 35 days after the last application (77 days after the first application, BBCH 89).

Grapes from the second and third samples were separated into juice and marc, and the marc was sequentially extracted with acetone, methanol:water (4:1) and then water. Leaves were surface washed with acetone and then sequentially extracted with acetone, methanol:water (4:1) and water. The post-extraction solids from the mature leaf and grape samples were further extracted with HCl:methanol and then sequentially treated with pepsin, cellulose, surfactant and refluxed with 6 M HCl. Radioactivity was analysed by LSC or combustion LSC and characterisation of the radioactive residues was conducted by TLC and HPLC-UV and HPLC-MS.

TRRs (calculated from extracted and non-extracted radioactivity) immediately after the last treatment were 0.6–0.77 mg eq/kg in grapes immediately after the last treatment and about 40 mg eq/kg in leaves. At maturity, 35 days after the last treatment, TRRs were 0.28–0.44 mg eq/kg in grapes and 25–38 mg eq/kg in leaves (with about 39–45% TRR present in the leaf surface wash).

Table 10 Radioactive residues (mg eq./kg) in grapes and grape leaves following five foliar applications of [^{14}C]metrafenone

Sample	Bromophenyl-label					Trimethoxyphenyl-label				
	Grapes		Leaves			Grapes		Leaves		
	TRR	TER [a]	TRR	Surface [b]	TER [a]	TRR	TER [a]	TRR	Surface [b]	TER [a]
0 DAT1	0.43	0.361 (83.8)	30.67	26.87 (87.6)	30.64 (99.9)	0.552	0.55 (99.6)	21.92	18.93 (86.4)	21.96 (100.0)
0 DAT2	1.07	0.998 (93.7)	25.9	14.79 (57.1)	23.88 (92.2)	0.471	0.421 (89.4)	20.41	13.27 (65.0)	19.31 (94.6)
0 DAT3	0.386	0.341 (88.3)	42.58	23.77 (55.8)	37.94 (89.1)	0.326	0.283 (86.8)	37.43	22.79 (60.9)	33.94 (90.7)
0 DAT4	0.241	0.2 (83.0)	59.22	32.27 (54.5)	54.31 (91.7)	2.1	1.61 (76.5)	52.41	33.62 (64.1)	49.14 (93.8)
0 DAT5	0.768	0.745 (97.0)	39.82	18.88 (47.4)	31.34 (78.7)	0.604	0.487 (80.6)	42.37	19.98 (47.2)	35.66 (84.2)
19 DAT5	0.314	0.26 (82.8)	59.11	22.23 (37.6)	45.68 (77.3)	0.15	0.135 (90.0)	55.48	23.78 (42.9)	43.59 (78.6)
35 DAT5	0.442	0.389 (88.0) [c]	38.13	17.14 (44.9)	35.88 (94.1) [c]	0.275	0.256 (93.1) [c]	24.74	9.57 (38.7)	22.75 (91.9) [c]

[a] TER = Total extracted radioactivity in mg eq./kg (%TRR)
[b] Extracted radioactivity in acetone surface wash in mg eq./kg (%TRR)
[c] Includes enzyme/acid extraction

Table 11 Radioactive residues in grape juice and marc following five foliar applications of [^{14}C]metrafenone

Sample	Juice		Grape solids (marc)		Non-extractable residue	
	mg eq./kg	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR
Bromophenyl-label						
0 DAT1	NA	NA	0.361	83.8	0.070	16.2

Sample	Juice		Grape solids (marc)		Non-extractable residue	
	mg eq./kg	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR
0 DAT2	0.031	2.9	0.967	90.7	0.088	6.4
0 DAT3	0.024	6.3	0.317	82.1	0.045	11.6
0 DAT4	0.021	8.7	0.178	73.8	0.042	17.4
0 DAT5	0.054	7.1	0.690	89.9	0.023	3.0
19 DAT5	0.060	19.2	0.201	63.9	0.053	16.9
35 DAT5	0.080	18.0	0.277	62.6	0.086	19.4
Trimethoxyphenyl-label						
0 DAT1	NA	NA	0.550	99.7	0.002	0.3
0 DAT2	0.012	2.6	0.408	86.7	0.050	10.7
0 DAT3	0.019	5.8	0.264	81.1	0.043	13.1
0 DAT4	0.224	10.7	1.384	65.9	0.493	23.5
0 DAT5	0.075	12.5	0.413	68.3	0.116	19.3
19 DAT5	0.049	32.6	0.086	57.5	0.015	9.8
35 DAT5	0.070	25.3	0.174	63.1	0.032	11.6

NA = not applicable

Characterisation of the residues in juice indicated the presence of several metabolites more polar than parent. One of these, CL197675, made up about 9% TRR (0.006 mg eq/kg), with the others present at lower concentrations. Metrafenone was not found. Low levels of radioactivity precluded further investigation.

In pomace extracts, metrafenone was the major residue, making up about 23–25% TRR (0.06–0.11 mg eq/kg), with other, more polar fractions not exceeding 0.05 mg eq/kg (12–17% TRR). These fractions were not investigated further.

Analysis of leaf samples showed rapid metabolism to several polar compounds. At maturity (35 days after the last treatment), unchanged parent had decreased to about 15% TRR (5.8 mg/kg) and 11% (2.7 mg/kg) for the bromophenyl-label and trimethoxyphenyl-label, respectively. None of the degradation products could be positively identified against the reference standards. However analysis of fragmentation patterns allowed for the proposal of several metabolite structures, identified as CL3000402, CL379395 and CL1500836. As with grapes, no other extracts could be investigated due to low levels of radioactivity.

Table12 Residues of unchanged metrafenone in grape leaf samples following five foliar applications of [^{14}C]metrafenone

Sample	Bromomethyl-label				Trimethoxyphenyl-label			
	Metrafenone		Other metabolites		Metrafenone		Other metabolites	
	mg/kg	%TRR	mg eq./kg	%TRR	mg/kg	%TRR	mg eq./kg	%TRR
0 DAT1	26.6	86.9	4.07	13.3	20.3	92.4	1.62	7.4
0 DAT2	9.6	36.9	16.3	62.9	10.6	52.2	9.81	48.1
0 DAT3	15.6	36.6	26.98	63.4	13.9	37.2	23.53	62.9
0 DAT4	20.2	33.7	39.22	66.2	17.1	32.7	35.31	67.4
0 DAT5	14.2	35.6	25.62	64.3	14.2	33.5	28.17	66.5
19 DAT5	8.4	14.2	50.71	85.8	9.8	17.6	45.68	82.3
35 DAT5	5.8	15.2	32.33	84.8	2.7	11.0	22.04	89.1

In summary, after five foliar applications of about 0.2 kg ai/ha of [^{14}C]metrafenone, TRRs in mature grapes, 35 days after the last application were about 0.3–0.4 mg eq/kg, with parent being the major component (0.06 to 0.11 mg/kg) in the marc, but not found in juice. Unidentified polar

metabolites did not exceed 0.05 mg eq/kg (12–17% TRR) in mature grape pomace and in juice, CL197675 made up about 9% TRR (0.006 mg eq/kg).

The proposed metabolic pathway involves oxidation of the methyl groups on the bromophenyl and trimethoxyphenyl rings to yield the corresponding aldehydes. In the case of the bromophenyl ring, the aldehyde can undergo further oxidation to the carboxylic acid, cyclization to form the lactone, and/or dehalogenation to form the des-bromo aldehyde.

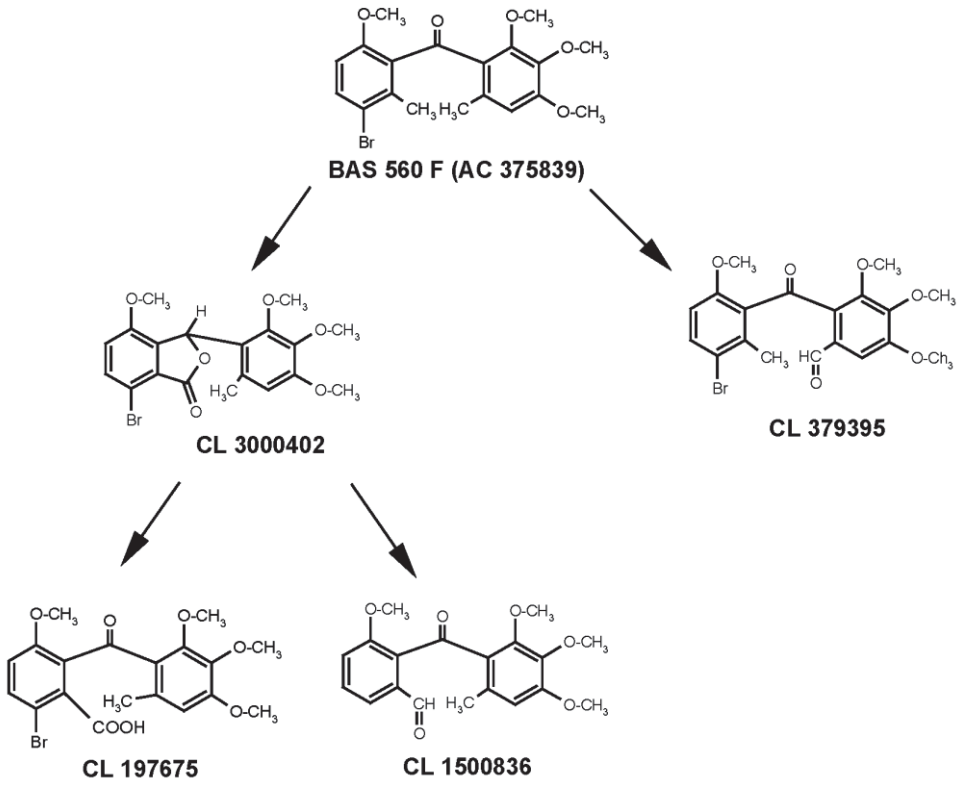


Figure 3 Metabolic pathway for metrafenone in grapevines

Cucumber

A metrafenone metabolism study in cucumber was reported by Grosshans & Ockert, 2010 [Ref: 2010/1054630]. Cucumber plants were treated with two foliar applications equivalent to 0.2 kg ai/ha (48 g ai/100L) [^{14}C]metrafenone (trimethoxyphenyl-label), 17 and 3 days before harvest. Leaf samples were taken immediately after the first application and cucumbers were sampled just before the second application (14 DAT1). At maturity, 3 days after the second application, whole plants (without roots) were sampled to investigate residues in cucumber peel, pulp and the vines.

Samples were sequentially extracted three times with methanol and twice with water and radioactivity was measured by LSC or combustion LSC and characterisation of the radioactive residues was by HPLC. Samples were stored frozen for up to 50 days before extraction and a further 36 days before analysis.

TRRs (calculated from extracted and non-extracted radioactivity) in leaves sampled directly after the first application were 6.4 mg eq/kg. In cucumber fruit sampled at maturity, 3 days after the second application, the TRR in whole fruit was 0.05 mg eq/kg with 0.013 mg eq/kg in pulp and 0.26 mg eq/kg in the peel. The TRR in the vines (rest of the plant) was 8.8 mg eq/kg.

Methanol extraction efficiency ranged from 87.5% to 93% in fruit, 91% in peel and pulp, 98.8% in leaves (0DAT1) and 92.6% in vines (rest of plant) at harvest. Up to an additional 1.6% TRR in cucumbers (whole fruit, peel and pulp) was able to be extracted with water.

Table13 Extractability of radioactive residues in cucumber samples after two foliar applications of [^{14}C]metrafenone

Matrix	DAT [a]	TRR [b]	Methanol extract		Aqueous extract		ERR [c]		RRR [d]	
		mg eq./kg	mg eq./kg	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR
Leaf	0DAT1	6.397	6.319	98.78	0.020	0.31	6.339	99.09	0.058	0.91
Fruit	14DAT1	0.016	0.014	87.46	0.000	1.55	0.015	89.01	0.002	10.99
Fruit	3DAT2	0.051	0.047	92.86	0.001	1.42	0.048	94.27	0.003	5.73
Pulp	3DAT2	0.013	0.012	91.09	0.000	1.12	0.012	92.21	0.001	7.79
Peel	3DAT2	0.263	0.240	91.16	0.003	1.07	0.243	92.23	0.020	7.77
Vines [e]	3DAT2	8.807	8.151	92.56	0.282	3.20	8.433	95.76	0.374	4.24

[a] DAT = Days after treatment
[b] TRR calculated as the sum of ERR and RRR
[c] ERR = Extractable Radioactive Residue
[d] RRR = Residual Radioactive Residue
[e] Vines = Whole plant without roots and fruit

Metabolite identification and characterisation in leaves (0DAT1) and fruit (14DAT1) was achieved by HPLC co-chromatography with metrafenone and peak assignment in the other samples was done by comparison of the retention times and the HPLC elution profiles with those of the extracts investigated by co-chromatography.

Metrafenone was the main residue component in leaves immediately after the first application (95% TRR) and represented 80% TRR in vines. In fruit at harvest, metrafenone was also the predominant residue, making up 42% TRR (0.022 mg/kg) in whole fruit, 61% TRR (0.16 mg/kg) in peel. In pulp, metrafenone was found at 0.0009 mg/kg or 6.5% TRR, with the majority of the residue being polar or medium polar components (23 peaks), each below 0.002 mg eq/kg.

Table 14 Residues of metrafenone and other characterised components in cucumber matrices following foliar applications of [^{14}C]metrafenone

Matrix	DAT [a]	Metrafenone		Characterised (total) (Methanol extract)		Characterised (total) (Aqueous extract)	
		mg/kg	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR
Leaf	0DAT1	6.076	95.0	0.243 [b]	3.8	0.0197	0.3
Fruit	14DAT1	0.002	12.6	0.011 [c]	66.1	0.0003	1.6
Fruit	3DAT2	0.022	42.4	0.019 [d]	36.5	0.0007	1.4
Pulp	3DAT2	0.0009	6.5	0.011 [e]	83.7	0.0001	1.1
Peel	3DAT2	0.161	61.0	0.048 [f]	18.3	0.0028	1.1
Vines [8)]	3DAT2	7.084	80.4	1.301 [g]	14.8		

[a] DAT = Days after treatment
[b] 4 peaks, each ≤ 2.1% TRR
[c] 17 peaks, each ≤ 8.9% TRR
[d] 22 peaks, each ≤ 7.3% TRR
[e] 23 peaks, each ≤ 12.1% TRR, 0.0016 mg eq/kg
[f] 20 peaks, each ≤ 2.9% TRR
[g] 26 peaks, each ≤ 3.1% TRR
[h] Vines = Whole plant without roots and fruit

In summary, after two foliar applications 0.2 kg ai/ha [^{14}C]metrafenone to cucumber plants, TRR in mature fruit, sampled 3 days after the second application were about 0.05 mg/kg (TRR), with 0.013 mg eq/kg present in pulp and 0.26 mg eq/kg in peel. More than 89% TRR was able to be extracted with methanol. Metrafenone was the only identified residue component, making up 42% of

the TRR in mature fruit (0.02 mg/kg), mostly in the peel (61% TRR, 0.16 mg/kg). Numerous polar and medium polar metabolites at low concentrations (each less than 9% TRR) were characterized by their retention time behaviour in HPLC or by extractability with water.

Wheat

The metabolism and distribution of metrafenone in wheat was investigated in a study reported by Zulalian, 2002 [Ref: 2002/7005253]. Spring wheat plants were treated with three foliar applications of [^{14}C]metrafenone (trimethoxyphenyl-label or bromophenyl-label, both being diluted with ^{13}C as a mass marker), at nominal rates of 0.3, 0.3 and 0.2 kg ai/ha, applied at 13–14 day intervals with the last application being 35 days before harvest.

Wheat plants (without roots) were sampled immediately after each application and forage samples were also taken 3 days after the first application. Wheat plants (hay) were cut 14 days after the second application and dried for about 33 hours before being collected as samples. Straw (including chaff) and seed were collected at mature harvest, 35 days after the last application. Analysis for total radioactive residues (TRR) was conducted by combustion and liquid scintillation counting (LSC) and residues were characterized and identified by HPLC and where possible, by mass spectrometry.

Highest radioactive residues were found in the straw (*ca* 8 to 9 mg eq/kg), with similar levels (5–8 mg eq/kg) in forage and straw, and lower levels of 0.2 to 0.4 mg eq/kg measured in grain. Methanol:water extraction was able to release about 95% TRR in forage, 78% TRR in hay, 61% TRR in straw and 35% TRR in grain. Additional extraction with hexane and acidified methanol was able to release a further 12–14% TRR in grain.

Table 15 Extractability of radioactive residues in wheat matrices after three foliar applications of [^{14}C]metrafenone

Radiolabel		Bromophenyl				Trimethoxyphenyl			
Matrix		Forage	Hay	Straw	Grain	Forage	Hay	Straw	Grain
DAT [a]		3DAT1	14DAT2	35DAT3	35DAT3	3DAT1	14DAT2	35DAT3	35DAT3
TRR [b]	mg eq./kg	8.17	7.78	8.91	0.21	5.27	8.5	8.25	0.4
Main Extracts									
Hexane	% mg eq./kg	NC	NC	NC	6.4 0.013	NC	NC	NC	3.5 0.014
Methanol:Water	% mg eq./kg	96.6 7.89	79.2 6.17	60.3 5.39	35.8 0.075	92.6 4.88	77.0 6.55	62.0 5.11	34.7 0.138
Methanol:2% HCl	% mg eq./kg	NC	NC	NC	8.0 0.017	NC	NC	NC	8.0 0.032
ERR [c]	% mg eq./kg	96.6 7.89	79.2 6.17	60.3 5.39	50.2 0.11)	92.6 1(4.88)	77.0 6.55)	62.0 5.11	46.2 0.184
RRR [d]	% mg eq./kg	3.4 0.278	20.8 1.62	39.6 3.53	49.8 0.1	7.4 0.388	23.0 1.95	38.1 3.14	53.8 0.215

[a] DAT = Days after treatment; 3DAT1=3 days after the 1st treatment
[b] TRR was calculated as the sum of ERR and RRR
[c] ERR = Extractable Radioactive Residue
[d] RRR = Residual Radioactive Residue
NC–Extraction not conducted

Metrafenone was the main component of the TRR in all matrices, making up 3–7.7% TRR in grain (0.013–0.016 mg/kg), 59–64% TRR in forage (3.1–5.3 mg/kg), 13–26% TRR in hay (1.1–2.0 mg/kg) and 7.7–14% TRR in straw (0.64–1.2 mg/kg). While TRRs in several regions of interest were each found at 10–20% TRR, these were described as metabolites more polar than the parent compound and consisted of up to five unidentified components. All other components in all matrices were present at less than 10% TRR. Significant single metabolites in forage, hay and straw were identified as the CL 3000402, CL 434223 and CL 1500831, each present at less than 7% TRR

(0.6 mg eq/kg) in these matrices. In grain, although no identified metabolites were found above 0.004 mg eq/kg, up to half the TRR was not solvent-extracted and while additional residues were released by alpha-amylase treatment of the post-extraction solids, these were not quantified. However HPLC analysis of the alpha-amylase extract showed that the radioactive residues were made up of multiple minor components.

Table 16 Characterisation and identification of radioactive residues in wheat matrices after three foliar applications of [^{14}C]metrafenone (bromophenol-label)

Matrix	Forage		Hay		Straw		Grain	
Sampling Time	3DAT1		14DAT2		35DAT3		35DAT3	
	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR	mg eq./kg
TRR	100	8.17	100	7.78	100	8.9	100	0.21
TRR in extract (ERR)	96.6	7.889	79.2	6.168	60.3	5.387	35.8	0.075
ROI-12 (Metrafenone)	64.4	5.261	26.0	2.021	13.6	1.215	7.7	0.016
ROI-1 (Unknowns) [a]	4.3	0.355	15.0	1.165	8.3	0.740	15.2	0.045
ROI-2 (Unknowns) [a]	3.9	0.320	11.5	0.896	10.5	0.934	< 2.0	< 0.004
ROI-3A (CL 1500837) + ROI-3B (CL 1500836)	4.2	0.342	3.7	0.291	4.6	0.412	< 2.0	< 0.004
ROI-4 (CL 3000402)	4.7	0.381	4.7	0.367	2.3	0.203	< 2.0	< 0.004
ROI-5 (CL 1500838), Conjugate of ROI 8	1.1	0.091	4.2	0.328	3.2	0.289	< 2.0	< 0.004
ROI-6A (CL 1500839) + ROI-6B (1500832)	1.6	0.132	3.7	0.289	1.5	0.132	< 2.0	< 0.004
ROI-7A1 (CL 1500833) + ROI-7A2 (CL 1500834) + ROI-7A3 (CL 1500835) + ROI-7B (CL 377160) + ROI-7C (Unknown) +	2.0	0.159	3.1	0.245	4.9	0.434	< 2.0	< 0.004
ROI-8 (CL 434223)	3.0	0.243	0.8	0.065	2.5	0.219	< 2.0	< 0.004
ROI-9 (CL 376991)	0.3	0.024	0.4	0.033	0.7	0.062	< 2.0	< 0.004
ROI-10 (CL 1500831)	1.4	0.114	1.5	0.119	0.7	0.066	< 2.0	< 0.004
ROI-11 (Unknowns)	0.8	0.067	1.4	0.107	0.2	0.020	< 2.0	< 0.004
Total Identified	91.7	7.489	76	5.926	53.0	4.726	42.9	0.093
PES	3.4	0.278	20.8	1.615	39.6	3.527	49.8	0.104

[a] Consisting of at least five minor unknown components

Table 17 Characterisation and identification of radioactive residues in wheat matrices after three foliar applications of [^{14}C]metrafenone (trimethoxyphenyl-label)

Matrix	Forage		Hay		Straw		Grain	
Sampling Time	3DAT1		14DAT2		35DAT3		35DAT3	
	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR	mg eq./kg
TRR	100	5.27	100	8.5	100	8.25	100	0.4
TRR in extract (ERR)	92.6	4.877	77.0	6.545	62.0	5.109	38.2	0.152
ROI-12 (metrafenone)	58.78	3.101	12.7	1.078	7.7	0.635	3.1	0.013
ROI-1 (Unknowns) [a]	3.9	0.203	17.4	1.478	9.1	0.751	20.3	0.081
ROI-1 (Unknowns) [a]	3.1	0.163	12.5	10.61	10.6	0.876	< 2.0	< 0.004
ROI-3A (CL 1500837) + ROI-3B (CL 1500836)	4.5	0.238	4.7	0.403	5.0	0.410	< 2.0	< 0.004
ROI-4 (CL 3000402)	4.2	0.219	6.6	0.564	3.9	0.319	< 2.0	< 0.004
ROI-5 (CL 1500838), Conjugate of ROI 8	2.0	0.103	5.0	0.429	4.1	0.338	< 2.0	< 0.004

Matrix	Forage		Hay		Straw		Grain	
Sampling Time	3DAT1		14DAT2		35DAT3		35DAT3	
	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR	mg eq./kg	%TRR	mg eq./kg
ROI-6A (CL 1500839) + ROI-6B (1500832)	2.4	0.127	5.3	0.446	2.3	0.194	< 2.0	< 0.004
ROI-7A1 (CL 1500833) + ROI-7A2 (CL 1500834) + ROI-7A3 (CL 1500835) + ROI-7B (CL 377160) + ROI-7C (Unknown) +	2.6	0.136	3.2	0.275	6.5	0.540	< 2.0	< 0.004
ROI-8 (CL 434223)	3.4	0.177	1.2	0.105	2.3	0.189	< 2.0	< 0.004
ROI-9 (CL 376991)	0.2	0.011	0.4	0.033	0.2	0.016	< 2.0	< 0.004
ROI-10 (CL 1500831)	0.4	0.021	1.8	0.153	0.6	0.046	< 2.0	< 0.004
ROI-11 (unknowns)	0.9	0.046	1.7	0.147	0.3	0.023	< 2.0	< 0.004
Total Identified	86.3	4.536	72.5	6.171	52.6	4.337	43.0	0.133
PES	7.4	0.388	23.0	1.952	38.1	3.139	53.6	0.214

[a] Consisting of at least five minor unknown components

In summary, after three foliar applications of [^{14}C]metrafenone to wheat (totalling 0.8 kg ai/ha), highest radioactive residues (up to 9 mg eq/kg) were found in hay and straw, with the lowest residues found in the grain (0.2 to 0.4 mg eq/kg). The TRR in forage (3DAT1) amounted to *ca*. 5 to 8 mg eq/kg. Metrafenone was the major component in all matrices, comprising up to 64% TRR in forage, up to 26% TRR in hay, up to 14% in straw and up to about 8% TRR in grain. In forage, hay and straw, other characterized or identified metabolites represented less than 10% TRR. In grain, no identified metabolites were found above 0.004 mg eq/kg and although only about 50% of the radioactivity was extracted, further investigation showed that the unextracted residue was made up of multiple minor components.

The proposed metabolic pathway involves oxidative demethylation of the parent to form CL 434223, CL 376991, and CL 377160 and subsequently CL 1500835. The 1actones CL 3000402 and CL 1500831 are formed by oxidation at each benzylic carbon followed by cyclization. Oxidation of the methyl groups on either of the two phenyl rings gives rise to the aldehyde derivatives, CL 1500833, CL 1500834 and CL 1500837. Aromatic oxidation and oxidative de-methylations can produce CL 1500832. Additionally, CL 1500836 is formed by oxidation at the benzylic carbon of the bromophenyl ring followed by reductive de-bromination. The oxidations are proposed to be either enzymatic and/or chemical (photolysis) in nature. Subsequent glucoside conjugation reactions yield the conjugates CL 1500838 and CL 1500839 from their corresponding aglycones, CL 434223 and CL 376991.

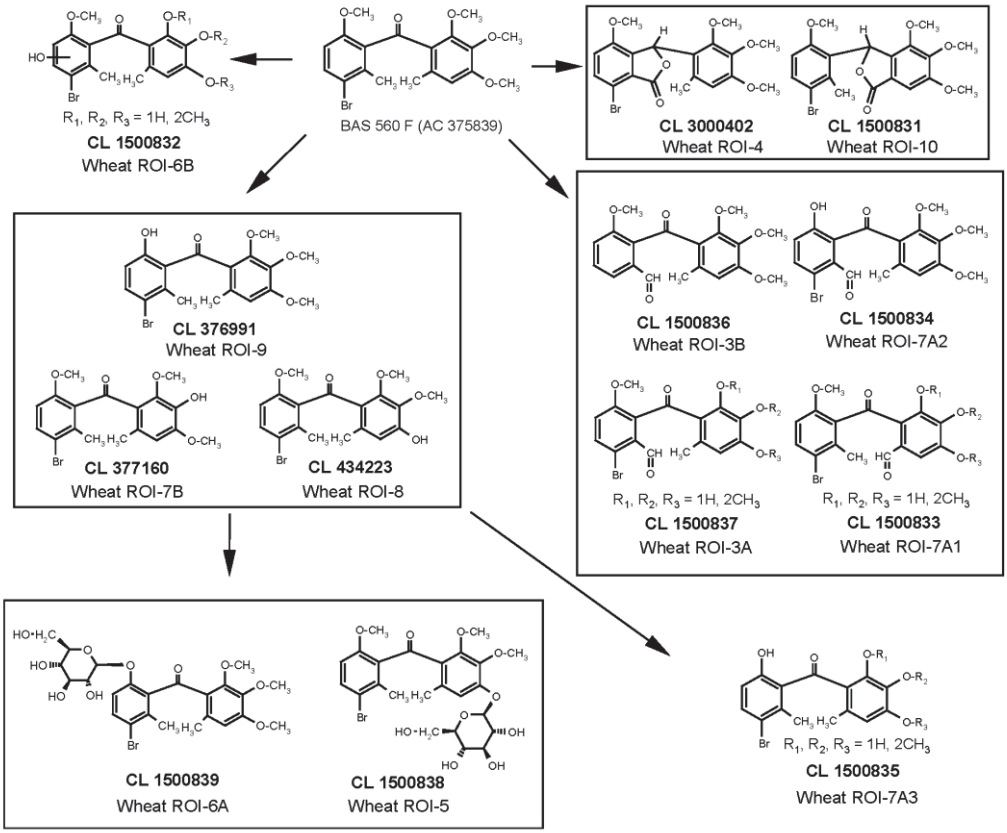


Figure 4 Metabolic pathway for metrafenone in wheat

Environmental fate

The Meeting received information the environmental fate and behaviour of metrafenone, including hydrolytic stability, photolysis in aqueous solutions, aerobic metabolism and rotational crop metabolism studies.

Hydrolysis

The hydrolysis of metrafenone was evaluated in a study reported by An, 1999 [Ref: 1999/7000284]. Sterile buffered solutions of 0.2 mg/L [bromophenyl-6-^{14}C]-metrafenone at pH 4, 7, and 9 were incubated in the dark under sterile conditions at 50 °C, sampled after 5 days and analysed by reversed phase radio-HPLC.

There was no loss of radioactivity during the course of the incubation at any pH values with metrafenone making up 97–106% of the applied radioactivity after 5 days of incubation.

Table 18 Hydrolytic stability of [bromophenyl-6-^{14}C]-metrafenone in sterile buffer solutions at 50 °C

pH	DAT	metrafenone	others	Total Recovery
4	0	99.7	0.1	99.8
	5	104.4	1.2	105.6
7	0	90.8	1.9	92.7
	5	97.8	2.7	100.5
9	0	96.8	0.1	96.9
	5	100.1	0.6	100.7

DAT = Days after treatment

Aerobic soil metabolism

In a study reported by Steinfuehrer, 2000 [Ref: 2000/7000152], a silty loam soil (pH 7.5, 2.03% organic C, CEC 18 meq/100 g soil and MWHC 47.3 g water/100 g dry soil) was treated with the 0.9 mg/kg dry soil [trimethoxy-label]-metrafenone or 0.98 mg/kg dry soil [bromophenyl-label]-metrafenone and incubated at 20 ± 2 °C in the dark for up to 210 days. The soil moisture was maintained at about 50% of maximum water holding capacity (MWHC). The application rates corresponded to 0.675 kg ai/ha and 0.735 kg as/ha respectively, assuming a soil mixing depth of 5 cm and a soil density of 1.5 g/cm3.

Duplicate soil samples were taken at treatment and after incubation for 4, 7, 14, 28, 60, 120, and 210 days and exhaustively extracted using acetone, methanol:water (4:1), water, and/or acetonitrile:0.5 N HCl (1:1). The various soil extracts were concentrated by rotary evaporation and analysed separately by radio-TLC (except most water and acetonitrile/HCl extracts, which were not analysed because of low radioactivity content. HPLC and LC/MS were used for metabolite identification. In addition, the non-extracted (bound) radioactivity in the day 210 soil samples was further characterized by fractionation of the extracted soil between fulvic acids, humic acids and humin. The fulvic acid fraction was partitioned into methylene chloride and analysed by TLC.

Between 92–106% of the applied radioactivity (% AR) was able to be recovered and extractable residues accounted for approximately 100% AR up to 14 days, but thereafter decreased steadily to 61% AR after 210 days for both labels. Accordingly, non-extractable (bound) residues increased to 28 and 29% AR at the end of the study. $^{14}CO_2$ reached 3.3% and 2.9% AR after 210 days, showing that both labels were eventually mineralized.

The levels of metrafenone in the extractable residues decreased to 55–57% AR at the end of the 201-day study and the metabolite fraction (< 0.2% AR) detected with TLC in the 210-day methanol/water and water extracts and was shown by HPLC analysis to consist of the substituted benzoic acids CL 197675 and CL 197676, formed by oxidation of the respective methyl group.

The characterization of bound residues in the day 210 samples showed that approximately two-thirds of the radioactivity (18.5–20% AR) was in the humin fraction, while 2–3% AR was in the humic acid fraction and 4–5% AR was in the fulvic acid fraction. Approximately half of the radioactivity in the fulvic fraction was partitioned into methylene chloride and analysed by TLC, which showed a small amount of metrafenone and a polar fraction.

Table 19 Recovery and distribution of radioactivity in soil treated with [^{14}C]metrafenone and incubated under aerobic conditions in the dark at 20 °C

DAT	$^{14}CO_2$	Extractable Residues (mg/eq./kg)				Bound residues	Total Recovery
		Metrafenone	CL 197675 + CL 197676	Unidentified [a]	Total		
Trimethoxyphenyl-U-^{14}C							
0	n.a.	97.8	n.d.	2.6	100.4	4.7	105.1
4	< 0.1	96.8	n.d.	5.2	102.0	1.7	103.7
7	< 0.1	97.1	n.d.	4.3	101.4	2.5	103.9
14	< 0.1	93.0	n.d.	7.0	100.0	4.1	104.1
28	0.3	86.3	n.d.	8.3	94.6	7.3	102.2
60	0.7	77.5	n.d.	8.7	86.2	13.1	100.0
120	1.8	66.2	n.d.	7.3	73.5	19.4	94.7
210	3.3	54.7	0.15	5.9	60.8	27.7	91.8
Bromophenyl-6-^{14}C							
0	n.a.	99.4	n.d.	2.3	101.7	4.7	106.4
4	< 0.1	99.9	n.d.	3.7	103.6	1.7	105.3
7	< 0.1	97.4	n.d.	5.2	102.6	2.6	105.2

14	< 0.1	94.6	n.d.	5.8	100.4	4.3	104.7
28	0.2	90.5	n.d.	6.6	97.1	7.4	104.7
60	0.6	81.1	n.d.	6.6	88.4	14.3	102.6
120	1.5	69.0	n.d.	4.9	73.9	22.8	98.2
210	2.9	57.4	0.15	3.7	61.3	29.2	93.4

DAT = Days after treatment
[a] Unidentified radioactivity consists of radioactivity in non-analysed water and acetonitrile/HCl extracts, radioactivity remaining at TLC origin and radioactivity lost during sample work-out.
n.a. = not analysed
n.d. = not detected

In a similar study reported by Steinfuehrer, 2000 [Ref: 2000/7000151], three soils (loamy sand, sandy loam, and clay loam) were treated with [bromophenyl-6-^{14}C]-metrafenone at a concentration of 1.48 mg/kg dry soil (corresponding to field application rates of 1.11 kg ai/ha) and incubated in the dark at 20 ± 2 °C and 40–50% MWHC. Duplicate soil samples taken at treatment time and after incubation for 3, 7, 14, 28, 58, 90, and 120 days were exhaustively extracted with acetone, methanol:water (4:1), and water using ultrasonication. The acetone and methanol:water extracts were concentrated by rotary evaporation and analysed by radio-TLC.

Total recoveries for the three soils were 94–100% of the applied radioactivity and the levels of extractable radioactivity continuously decreased over the incubation period to 67–78% AR after 120 days. Accordingly, increasing amounts of bound residues were formed in the three soils, accounting for up to 17.4–24.8% AR at the end of the 120-day study period. Mineralization was also observed with evolved $^{14}CO_2$ accounting for 2.7 to 5.3% AR after 120 days of incubation for the three soils.

Table 20 Recovery and distribution of radioactivity in three soils treated with [^{14}C]metrafenone and incubated under aerobic conditions in the dark at 20 °C

Soil	DAT	Extractable Residues (mg eq./kg)				CO_2	Bound Residues	Total Recovery
		Acetone	MeOH/Water	Water	Total			
Sporkenheim loamy sand pH: 6.2 Organic C: 0.63% CEC: 8 meq/100 g MWHC: 32.8%	0	93.7	5.4	0.4	99.5	n.a.	0.3	99.8
	3	82.3	14.3	0.9	97.5	< 0.1	1.2	98.7
	7	75.3	17.8	1.4	94.5	0.1	2.6	97.1
	14	85.3	5.0	1.0	91.3	0.3	4.3	95.9
	28	65.0	18.5	2.3	85.8	0.8	9.1	95.8
	58	71.1	5.0	2.3	78.4	2.2	13.9	94.5
	90	56.2	12.1	3.6	71.9	3.5	19.7	95.1
	120	50.6	12.3	3.7	66.6	5.3	24.8	96.8
Binger Pfad sandy loam pH: 7.1 Organic C: 1.02% CEC: 13 meq/100 g MWHC: 33.6%	0	92.0	6.4	0.6	99.1	n.a.	0.7	99.8
	3	82.7	12.6	1.2	96.5	< 0.1	1.9	98.4
	7	77.5	16.7	1.4	95.6	0.1	2.8	98.5
	14	84.9	4.7	0.9	90.5	0.2	3.7	94.4
	28	73.1	13.8	2.5	89.4	0.5	7.4	97.3
	58	74.3	9.2	2.3	85.8	1.2	11.0	97.9
	90	65.7	12.6	3.1	81.4	1.8	14.0	97.2
	120	62.8	11.9	2.9	77.6	3.0	17.4	98.1
Gensingen Pfad clay loam pH: 7.3 Organic C: 0.96% CEC: 18 meq/100 g	0	89.2	8.1	1.1	98.4	n.a.	1.4	99.8
	3	87.9	8.1	1.1	97.1	< 0.1	1.8	98.9
	7	85.7	9.3	1.2	96.2	< 0.1	2.8	99.0
	14	81.3	6.6	1.3	89.2	0.1	4.5	93.8
	28	80.9	9.1	1.9	91.9	0.3	8.3	100.4

Soil	DAT	Extractable Residues (mg eq./kg)				CO_2	Bound Residues	Total Recovery
		Acetone	MeOH/Water	Water	Total			
MWHC: 40.5%	58	71.9	7.0	2.5	81.4	1.0	14.3	96.7
	90	69.6	7.6	2.7	79.9	1.5	17.5	98.9
	120	64.5	7.6	3.2	75.3	2.7	21.8	99.8

DAT = Days after treatment
n.a. = Not analysed

Metrafenone accounted for approximately 90% AR in the extracts at day 0 and slowly decreased to 56.1–68.7 % AR after 120 days. Only one minor metabolite fraction was observed at various sampling times in the three soils, this accounting for less than 0.9% AR and was not identified.

Table 21 Metrafenone residues (%AR) in soils treated with [bromophenyl-6-^{14}C]-metrafenone and incubated under aerobic conditions in the dark at 20 °C

Time (days)	Sporkenheim	Binger Pfad	Gensingen
0	89.4	90.4	89.5
3	90.0	85.2	87.7
7	86.4	85.0	84.7
14	80.7	79.8	79.7
28	69.1	77.7	81.9
58	67.9	75.1	70.8
90	62.2	72.5	71.3
120	56.1	68.7	65.7
1st order DT50 (r^2)	182 days (0.8824)	365 days (0.8637)	289 days (0.8705)

In a further study reported by Steinfuehrer, 2000 [Ref: 2000/7000150], a loamy sand soil (pH: 6.3, Organic C: 0.72%, CEC: 8 meq/100 g and MWHC: 34.2 g water/100 g dry soil) was treated with [bromophenyl-6-^{14}C]-metrafenone at a concentration of 1.52 mg/kg dry soil (corresponding to field application rates of 1.14 kg ai/ha) and incubated in the dark at a lower temperature of 10 ± 2 °C and moisture content was maintained at 40–50% MWHC. Duplicate soil samples taken at treatment time and after incubation for 3, 7, 14, 28, 48, 90, and 120 days were exhaustively extracted with acetone, methanol:water (4:1), and water using ultrasonication. The acetone and methanol:water extracts were concentrated by rotary evaporation and analysed by radio-TLC.

Total recoveries were in the range of 100–102% AR and the levels of extractable radioactivity continuously decreased over the incubation period to about 91% AR after 120 days with bound residues increasing to up to 8.2% AR at the end of the 120-day study. Mineralization was also observed, with evolved $^{14}CO_2$ accounting for 1.4% AR after 120 days.

Metrafenone accounted for 93.4% AR at day 0 and slowly decreased to 82.0% AR after 120 days, with no other defined peaks or metabolite fractions observed in the TLC chromatograms at any sampling time.

Table 22 Recovery and distribution of radioactivity in soil treated with [^{14}C]metrafenone and incubated under aerobic conditions in the dark at 10 °C

Soil	Time (days)	Extractable Residues (mg eq./kg)			CO_2	Bound Residues	Total Recovery
		Metrafenone	Others [a]	Total			
Sporkenheim	0	93.4	6.3	99.7	n.a.	1.5	102.2
	3	91.8	7.3	99.1	< 0.1	1.3	100.4

	7	89.9	9.0	98.9	< 0.1	1.5	100.5
	14	91.4	7.6	99.0	0.1	1.5	100.5
	28	89.1	8.2	97.3	0.2	2.5	100.0
	58	87.5	8.1	95.6	0.5	4.5	100.6
	90	82.6	11.5	94.1	0.9	6.5	101.6
	120	82.0	8.6	90.6	1.4	8.2	100.2

[a] Others include radioactivity lost during sample work-up, unresolved background in TLC traces and radioactivity in extracts that were not analysed by TLC. It does not consist of defined peaks.
n.a. = Not analysed

In summary, metrafenone degraded slowly in the loamy sand, sandy loam and clay loam soils incubated for up to 210 days under aerobic laboratory conditions at 10 °C and 20 °C. About 66–69% AR was still present as the parent compound at the end of the 20 °C study and about 82% AR remaining as metrafenone at the end of the 10 °C study. Calculated half-lives (1st order kinetics) ranged from 182–365 days.

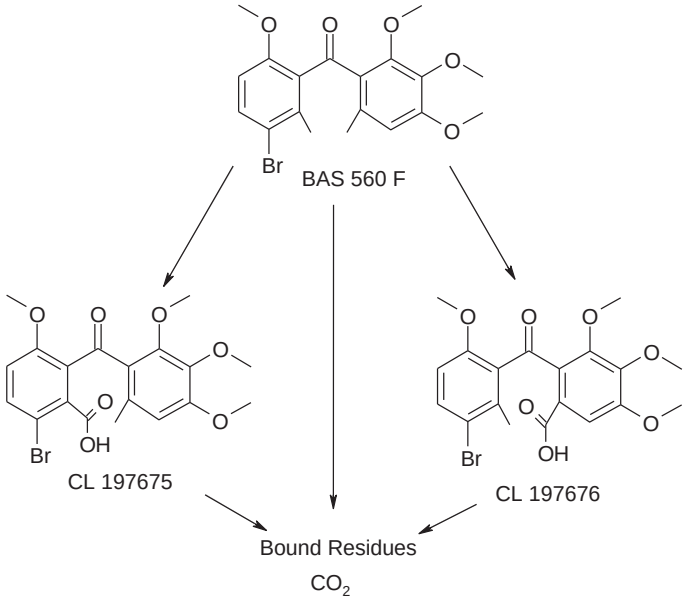


Figure 5 Proposed pathway of degradation in soil under aerobic laboratory conditions for metrafenone

Residues in rotational crops

Rotational crops metabolism

The Meeting received information on the fate of residues in lettuce, radish and canola grown as rotational crops in metrafenone-treated soil.

In an outdoor confined rotational crop study with ^{14}C labelled metrafenone reported by Zulalian, 2002 [Ref: 2002/7005187], representative leafy vegetable crop (lettuce), root crop (radish) and oil crop (canola) were planted back at various time intervals (30, 60, 90 and 365 days) after a single application of [trimethoxy-label]-metrafenone or [bromophenyl-label]-metrafenone to bare soil at a rate equivalent to 0.625 kg ai/400 L/ha.

Harvested samples were homogenised with dry ice and the TRR determined by combustion of aliquots to yield $^{14}CO_2$, followed by quantification by liquid scintillation counting (LSC). For characterization and identification, samples were extracted with mixtures of methanol:water or hexane and methanol:HCl. The extracts were then subjected to HPLC and resolved into fractions which were

quantified by LSC. Identification was performed by co-chromatography with known reference standards. The TRR of the post extraction solid (PES) was determined either by LSC or combustion.

In general, the highest total radioactive residues (TRR) were found in plants sampled from the 30-day plant back interval, while the lowest residues (< 0.01 mg eq/kg) were detected in plants from the 365 DAT plant back interval. The canola straw/pod contained the highest residues, while very low residues were detected in canola seed at all sampling intervals. In soil, TRR declined by about 50% after 90 days, mostly found in the top 10 cm of soil samples.

Highest TRRs in the 30-day plant back samples residues were 0.048 mg eq/kg in canola straw/pods, 0.008 mg eq/kg in canola seed, 0.023–0.025 mg eq/kg in radish root and top and 0.006 mg eq/kg in lettuce. In the 365 day plant back samples, highest TRRs were < 0.004 mg eq/kg in canola straw/pods, 0.008 mg eq/kg in canola seed, 0.005–0.007 mg eq/kg in radish root and top and < 0.004 mg eq/kg in lettuce.

Table 23 Total Radioactive Residues in rotational crops planted in soil treated with [^{14}C]metrafenone at a rate equivalent to 0.625 kg ai/ha

Crop	RAC	Bromophenyl-label TRR (mg eq./kg)				Trimethoxyphenyl-label TRR (mg eq./kg)			
		Days after treatment (DAT)				Days after treatment (DAT)			
		30	60	90	365	30	60	90	365
Lettuce		0.006	< 0.004	0.034	< 0.004	0.005	< 0.004	0.030	< 0.004
Radish	Top	0.025	0.007	0.023	0.007	0.015	0018	0.024	0.005
	Root	0.023	0.020	0.010	0.005	0.012	0.015	0.009	0.004
Canola	Straw/Pod	0.048	0.027	0.033	0.023	0.037	0.023	0.029	0.029
	Seed	0.007	0.004	0.010	0.005	0.008	0.005	0.009	0.008
	Plant	NA	0.005	NA	NA	NA	0.006	NA	NA

NA = Not analysed

Characterisation of the radioactive residue in the rotational crop samples containing more than 0.01 mg eq/kg TRR was conducted using reversed phase HPLC/^{14}C analysis of the solvent extracts. With the exception of canola seed, extraction with methanol:water and methanolic HCl was able to recover 64–88% TRR. Hexane and methanol:water extraction recovered 42–86% TRR in canola seed.

The HPLC results showed that the residue was comprised of unchanged metrafenone and a group of polar compounds (designated ROI 1 (Region of Interest 1). These were not investigated further because of the low concentrations of the individual peaks. Metrafenone accounted for < 0.005 mg/kg of the TRR in lettuce and radish roots. The major portion of the extractable residues in most of the crops was shown to contain multiple components, all present at < 0.02 mg eq/kg. All other components of the extractable residues were < 0.01 mg eq/kg. The non-extractable residues were less than 0.01 mg eq/kg for all crops.

Table 24 Extraction and identification of radioactive residues in lettuce planted as a rotational crop after soil treatment with [^{14}C]metrafenone at a rate equivalent to 0.625 kg ai/ha

Plant Back Interval	30DAT		60DAT		90DAT		365DAT	
	% TRR	mg eq./kg	% TRR	mg eq./kg	% TRR	mg eq./kg	% TRR	mg eq./kg
	Bromophenol-label							
TRR	100	0.006	100	< 0.004	100	0.034	100	< 0.004
MeOH: H_2O	82.3	0.005	NA	NA	65.0	0.022	NA	NA
Metrafenone		< 0.001			11.08	0.004		
ROI -1(Unknown)	17.2	0.001			8.1	0.003		
ROI -2(Unknown)	ND	ND			ND	ND		
MeOH: 2% HCl	NA	NA	NA	NA	16.3	0.006	NA	NA

Plant Back Interval	30DAT		60DAT		90DAT		365DAT	
	% TRR	mg eq./kg	% TRR	mg eq./kg	% TRR	mg eq./kg	% TRR	mg eq./kg
Total ERR	82.3	0.005	NA	NA	81.3	0.028	NA	NA
Total RRR	17.7	0.001	NA	NA	18.7	0.006	NA	NA
	Trimethoxyphenyl-label							
TRR	100	0.005	100	< 0.004	100	0.030	100	< 0.004
MeOH: H_2O	82.3	0.004	NA	NA	70.2	0.021	NA	NA
Metrafenone		< 0.001			ND	ND		
ROI -1(Unknown)	17.3	0.001			10.73	0.003		
ROI -2(Unknown)	ND	ND			11.91	0.004		
MeOH: 2% HCl	17.7	NA	NA	NA	9.5	0.003	NA	NA
Total ERR	82.3	0.004	NA	NA	79.7	0.024	NA	NA
Total RRR	17.7	0.001	NA	NA	19.6	0.006	NA	NA

ERR–Extractable Radioactive Residues
RRR–Residual Radioactive Residues
NA–Not analysed
ND–Not detected

Table 25 Extraction of radioactive residues in radish planted as a rotational crop after soil treatment with [^{14}C]metrafenone at a rate equivalent to 0.625 kg ai/ha

Plant Back Interval	30DAT		60DAT		90DAT		365DAT	
Radish tops	Bromophenyl-label							
TRR	%	mg eq./kg	%	mg eq./kg	%	mg eq./kg	%	mg eq./kg
	100	0.025	100	0.007	100	0.023	100	0.007
MeOH: H_2O	68.9	0.017	70.7	0.005	85.2	0.020	NA	NA
Metrafenone			ND	ND	ND	ND		
ROI -1(Unknown)			15.3	0.001	43.7	0.01		
ROI -2(Unknown)			8.8	ND	20.0	0.005		
MeOH: 2% HCl	10.3	0.003	NA	NA	NA	NA	NA	NA
Total ERR	79.2	0.020	70.7	0.005	85.2	0.020	NA	NA
Total RRR	20.8	0.005	29.3	0.002	14.8	0.003	NA	NA
Radish tops	Trimethoxyphenyl-label							
TRR	%	mg eq./kg	%	mg eq./kg	%	mg eq./kg	%	mg eq./kg
	100	0.015	100	0.018	100	0.024	100	0.005
MeOH: H_2O	67.7	0.010	64.0	0.012	81.5	0.20	NA	NA
Metrafenone	ND	ND	ND	ND	ND	ND		
ROI -1(Unknown)	17.9	0.003	10.3	0.002	14.29	0.003		
ROI -2(Unknown)	ND	ND	ND	ND	ND	ND		
MeOH: 2% HCl	14.7	0.002	NA	NA	NA	NA	NA	NA
Total ERR	82.4	0.012	64.0	0.012	81.5	0.020	NA	NA
Total RRR	17.6	0.003	36.0	0.006	18.5	0.004	NA	NA
Radish roots	Bromophenyl-label							
TRR	%	mg eq./kg	%	mg eq./kg	%	mg eq./kg	%	mg eq./kg
	100	0.023	100	0.020	100	0.010	100	0.005
MeOH: H_2O	80.2	0.018	65.9	0.013	70.9	0.007	NA	NA
Metrafenone	16.1	0.004	9.2	0.002		< 0.001		
ROI -1(Unknown)	19.4	0.004	19.1	0.004	16.6	0.002		
ROI -2(Unknown)	ND	ND	ND	ND	ND	ND		
MeOH: 2% HCl	NA	NA	9.3	0.002	NA	NA	NA	NA
Total ERR	80.2	0.018	75.2	0.015	70.9	0.007	NA	NA

Plant Back Interval	30DAT		60DAT		90DAT		365DAT	
Total RRR	19.8	0.005	25.0	0.005	29.1	0.003	NA	NA
Radish roots	Trimethoxyphenyl-label							
TRR	%	mg eq./kg	%	mg eq./kg	%	mg eq./kg	%	mg eq./kg
	100	0.012	100	0.015	100	0.009	100	0.004
MeOH: H_2O	75.0	0.009	62.1	0.009	68.8	0.006	NA	NA
Metrafenone	27.7	0.003	3.9	0.001		< 0.001		
ROI -1(Unknown)	16.8	0.002	25,7	0.004	26.5	0.002		
ROI -2(Unknown)	ND	ND	12.8	0.002	ND	ND		
MeOH: 2% HCl	NA	NA	6.4	0.001	NA	NA	NA	NA
Total ERR	75.0	0.009	68.5	0.01	68.8	0.006	NA	NA
Total RRR	25.0	0.003	31.8	0.005	31.2	0.003	NA	NA

ERR–Extractable Radioactive Residues
RRR–Residual Radioactive Residues
NA–Not analysed
ND–Not detected

Table 26 Extraction of radioactive residues in canola planted as a rotational crop after soil treatment with [^{14}C]metrafenone at a rate equivalent to 0.625 kg ai/ha

Plant Back Interval	30DAT		60DAT		90DAT		365DAT	
	%	mg eq./kg	%	mg eq./kg	%	mg eq./kg	%	mg eq./kg
Canola straw/pod	Bromophenyl-label							
TRR	100	0.048	100	0.027	100	0.033	100	0.023
MeOH: H_2O	76.9	0.037	74.3	0.020	64.0	0.021	66.2	0.015
Metrafenone	ND	ND	ND	ND	ND	ND	ND	ND
ROI -1(Unknown)	27.0	0.013	32.7	0.009	39.1	0.013	31.2	0.007
ROI -2(Unknown)	9.6	0.005	ND	ND	10.3	0.003	ND	ND
MeOH: 2% HCl	11.0	0.005	16.1	0.004	18.1	0.006	18.5	0.004
Total ERR	87.9	0.042	81.8	0.022	82.1	0.027	84.7	0.019
Total RRR	11.8	0.006	18.2	0.005	17.9	0.006	14.3	0.004
Canola straw/pod	Trimethoxyphenyl-label							
TRR	100	0.037	100	0.023	100	0.029	100	0.029
MeOH: H_2O	76.1	0.028	67.8	0.016	64.6	0.019	64.7	0.019
Metrafenone	ND	ND	ND	ND	ND	ND	ND	ND
ROI -1(Unknown)	40.0	0.015	42.2	0.01	25.1	0.007	26.5	0.008
ROI -2(Unknown)	12.4	0.005	ND	ND	ND	ND	ND	ND
MeOH: 2% HCl	11.5	0.004	12.0	0.003	19.9	0.006	5.9	0.002
Total ERR	87.6	0.035	79.8	0.019	84.5	0.025	70.6	0.021
Total RRR	12.5	0.005	20.1	0.004	15.5	0.004	29.4	0.008
Canola seed	Bromophenyl-label							
TRR	100	0.007	100	0.004	100	0.010	100	0.005
Hexane	61.5	0.004	41.9	0.002	51.6	0.005	NA	NA
MeOH: H2O	<1.0	< 0.001	NA	NA	NA	NA	NA	NA
Total ERR	61.5	0.004	41.9	0.002	51.6	0.005	NA	NA
Total RRR	38.5	0.003	58.1	0.002	48.4	0.005	NA	NA
Canola seed	Trimethoxyphenyl-label							
TRR	100	0.008	100	0.005	100	0.009	100	0.008
Hexane	45.6	0.004	86.2	0.004	47.9	0.004	NA	NA
MeOH: H2O	24.5	0.002	NA	NA	NA	NA	NA	NA
Total ERR	70.1	0.006	86.2	0.004	47.9	0.004	NA	NA

Total RRR	29.9	0.002	13.8	0.001	52.1	0.005	NA	NA
Canola plant	Bromophenyl-label							
TRR			100	0.005				
MeOH: H_2O			76.1	0.004				
MeOH: 2% HCl			NA	NA				
Total ERR			76.1	0.004				
Total RRR			23.9	0.001				
Canola plant	Trimethoxyphenyl-label							
TRR			100	0.006				
MeOH: H_2O			< 0.1	< 0.001				
MeOH: 2% HCl			NA	NA				
Total ERR			< 0.1	< 0.001				
Total RRR			100	0.006				

ERR–Extractable Radioactive Residues
RRR–Residual Radioactive Residues
NA–Not analysed
ND–Not detected

In summary, translocation of radiolabelled metrafenone from soils to representative rotational crops (lettuce, radish, canola) was low, with TRRs ranging from < 0.004 to 0.048 mg eq/kg (in canola pods), generally highest in the samples from the 30-day plant back interval. In soil, radioactive residues declined by about 50% after 90 days, and were mostly found in the top 10 cm of soil samples.

Total extractable residues ranged from 64.0 to 88% TRR in the majority of the samples (42–86% TRR in canola seed) and comprised mostly of multiple unidentified polar components, all present at < 0.02 mg eq/kg. Metrafenone accounted for 0.004 mg/kg of the TRR in lettuce (90DAT) and radish roots (30DAT) and was not found in canola.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The meeting received analytical method descriptions and validation data for metrafenone in crop and animal commodities and in soil and water. A summary of the analytical methods for plant and animal commodities is provided below.

Table 27 Summary of metrafenone analytical methods developed for plant and animal matrices

Matrix	Analyte	Method	Principle	LOQ (mg/kg)	Reference
Wheat forage Wheat straw Wheat grain Barley forage Barley straw Barley grain Barley products	Metrafenone CL 3000402 CL 434223 CL 376991	RLA 12619.02 RLA 12619.03V (993/0)	Methanol/water extraction Dichloromethane partition SPE clean-up LC-MS/MS analysis Metrafenone m/z 409 → m/z 209 / m/z 411 → m/z 209 CL 3000402 m/z 423 → m/z 241 / m/z 425 → m/z 243 CL 434223 m/z 395 → m/z 195 / m/z 397 → m/z 195 CL 376991 m/z 395 → m/z 209 / m/z 397 → m/z 209	0.01	2001/7001048, 2001/7001770, 2002/1004080

Grape Wine Barley grain	Metrafenone	DFG S19	Aqueous acetone extraction Acetone/ethyl acetate/cyclohexane partition GPC and silica gel column clean-up GC-ECD analysis	0.01	2000/7000136
Grapes	Metrafenone	RLA 12612V (99105V)	n-heptane/acetone extraction SPE clean-up GC-ECD or GC-MS analysis	0.05	2000/7000111
Wheat forage Wheat straw Wheat grain Cucumber Lemon Beans Oilseed rape (seed) Hops (dry cones)	Metrafenone	QuEChERS 1	Acetonitrile extraction (pH 5-5.5 buffer) SPE clean-up LC-MS/MS analysis m/z 409 → m/z 209 / m/z 409 → m/z 227 m/z 409 → m/z 209 / m/z 411→ m/z 209 for dry hop cones	0.01	2011/7007816
Hops (green cones) Hops (dry cones) Beer	Metrafenone	535/3 (L0076/03)	Methanol/water/HCl extraction cyclohexane partition (alkaline) HPLC-MS/MS analysis m/z 411 → m/z 209 / m/z 411 → m/z 229	0.01	2010/1089964
Eggs Meat Milk	Metrafenone	DFG S19	Aqueous acetone extraction Ethyl acetate/cyclohexane partition GPC clean-up GC-MS analysis m/z 377 → 395 / m/z 377 → m/z 408	0.05 0.05 0.01	2001/7000486

Data collection methods

RLA 12619.02

This method for measuring residues of metrafenone and major metabolites (CL 3000402, CL 434223 and CL 376911) in cereal matrices and was described and validated by Smalley, 2001 [Ref: 2001/7001048], by Kang, 2001 [Ref: 2001/7001770] and for measuring residues of metrafenone in barley 'processing products' by Pollmann, 2002 [Ref: 2002/1004080]. Residues were extracted with methanol:water (80:20), filtered and reduced by rotary evaporation before partitioning into dichloromethane and final clean up through a strong anion exchange cartridge. Residues were measured using LC/APCI mass spectrometry (LC-MS/MS) calculating results using bracketing standards.

Average recovery rates in samples spiked with 0.01–0.1 mg/kg metrafenone ranged from 88–98% (RSD ≤ 13.3%) and the LOQ was 0.01 mg/kg for grain and barley 'processing products' and 0.1 mg/kg for forage and straw.

Table 28 Metrafenone analytical recovery rates for analytical method RLA 12619.02 and RLA 12619.03

Sample Matrix	Method	Analyte	Fortification (mg/kg)	Average recovery (%)	RSD (%)	No	Reference
Wheat whole plant	LC-MS/MS	Metrafenone	0.1 1.0	88 88	11.7 2.8	5 5	2000/7001048
		CL 3000402	0.1 1.0	78 95	12.7 2.6	5 5	
		CL 434223	0.1 1.0	75 76	18.1 4.3	5 5	
		CL 376911	0.1 1.0	82 91	10.6 4.8	5 5	
Wheat grain	LC-MS/MS	Metrafenone	0.01 0.1	95 98	13.3 3.4	5 5	2000/7001770

Sample Matrix	Method	Analyte	Fortification (mg/kg)	Average recovery (%)	RSD (%)	No	Reference
Wheat straw	LC-MS/MS	Metrafenone	0.1 1.0	86 91	9.1 8.2	5 5	2000/7001048
		CL 3000402	0.1 1.0	90 90	0.8 4.2	5 5	
		CL 434223	0.1 1.0	94 87	1.7 5.2	5 5	
		CL 376911	0.1 1.0	92 86	6.7 3.1	5 5	
Barley grain	LC-MS/MS	Metrafenone	0.01 0.1	100 100	- -	2 2	2002/1004080
Malt	LC-MS/MS	Metrafenone	0.01 0.1	81 83	- -	2 2	
Brewers grain	LC-MS/MS	Metrafenone	0.01 1.0	91 98	- -	2 2	
Spent hops	LC-MS/MS	Metrafenone	0.01 0.1	59 62	- -	2 2	
Brewer's yeast	LC-MS/MS	Metrafenone	0.01 0.1	85 77	- -	2 2	
Beer	LC-MS/MS	Metrafenone	0.01 0.1	90 93	- -	2 2	
Pearl barley	LC-MS/MS	Metrafenone	0.01 0.1	91 106	- -	2 2	
Pearl barley abrasion	LC-MS/MS	Metrafenone	0.01 0.1	106 116	- -	2 2	

MRM DFG S19 (plant matrices)

The German multi-residue method DFG S19 with modified extraction was described and reported by Hausmann & Class, 2000 [Ref: 2000/7000136] as suitable for as a data-collection method to measure residues of metrafenone in wheat and barley grain, grapes and wine, with an LOQ of 0.01 mg/kg.

Residues in barley grain, grapes, and wine were extracted with water:acetone (1:2) and partitioned into acetone/ethyl acetate/cyclohexane. Gel permeation chromatography was used to eliminate fat and macromolecules (as described in DFG clean-up method 6) with further silica gel column clean-up before GC/ECD analysis using a 5% phenyl methyl silicone column (non-polar stationary phase). Confirmatory analysis used a methyl siloxane column (non-polar stationary phase) and the 393 m/z ion was the target ion for quantitation.

Average recovery rates in samples spiked with 0.01–0.2 mg/kg metrafenone ranged from 88–128% (RSD ≤ 13%) and the LOQ was 0.01 mg/kg.

This method was independently validated in a study reported by Steinhauer & Pelz, 2001 [Ref: 2001/7001286] with average recovery rates in samples spiked with 0.02–0.2 mg/kg metrafenone (barley grain, grapes) or 0.01–0.1 mg/kg (wine) ranged from 88–114% (RSD ≤ 17%).

Table 29 Metrafenone analytical recovery rates for analytical method DFG S19 (modified extraction)

Sample Matrix	Method	Fortification (mg/kg)	Average recovery (%)	RSD (%)	No	Reference
Wheat grain	GC/ECD	0.01 0.1	95 98	13.3 3.4	5 5	2000/7000136
Barley Grain	GC/ECD	0.01 0.02 0.20	91 91 88	4 3 3	5 5 5	2000/7000136
		0.02 0.2	92 88	4.9 2.5	5 5	2001/7001286

Sample Matrix	Method	Fortification (mg/kg)	Average recovery (%)	RSD (%)	No	Reference
	GC/MS	0.01 0.02 0.20	121 128 104	NA NA NA	1 1 1	2000/7000136
		0.02	114	14	3	2001/7001286
Grapes	GC/ECD	0.01 0.02 0.20	93 102 101	4 4 7	5 5 5	2000/7000136
		0.02 0.2	100 97	3.3 10	5 5	2001/7001286
	GC/MS	0.01 0.02 0.20	92 98 91	NA NA NA	1 1 1	2000/7000136
		0.02	102	17	3	2001/7001286
Wine	GC/ECD	0.01 0.10	96 97	4 2	5 5	2000/7000136
		0.01 0.1	94 88	3.2 4.7	5 5	2001/7001286
	GC/MS	0.01 0.10	112 105	NA NA	1 1	2000/7000136
		0.1	103	4.4	3	2001/7001286

NA = Not Applicable

RLA 12612V (grapes)

This GC-MS method was described and validated by Smalley, 2000 [Ref: 2000/7000111] as suitable for the analysis of metrafenone residues in grapes with an LOQ of 0.05 mg/kg.

Residues of metrafenone were extracted from grapes with n-heptane and acetone. Metrafenone was cleaned up further using solid phase extraction using silica cartridges. Measurement of metrafenone was carried out by gas chromatography using an electron capture detector. The specificity of the method was determined using GC-MS.

Average recovery rates in samples spiked with 0.05–1.0 mg/kg metrafenone ranged from 93–96% (RSD ≤ 2.0%) and the LOQ was 0.05 mg/kg and this method was independently validated with average recovery rates in samples spiked with 0.05–1.0 mg/kg metrafenone ranged from 79–91% (RSD ≤ 5%).

Table 30 Metrafenone analytical recovery rates for RLA 12612V analytical method

Matrix	Fortification (mg/kg)	Average recovery (%)	RSD (%)	No of tests	Reference
Grapes	0.05 1.0	96 93	1.7 2.0	5 5	2000/7000111
Grapes (ILV)	0.05 1.0	91 79	5.0 4.2		

QuEChERS (plant matrices)

The QuEChERS method (including Amendment 1) was described and reported by Meyer, 2011 [Ref: 2011/7007816] as suitable for as a data-collection method to measure residues of metrafenone in wheat forage, straw and grain, cucumber, lemon, dry bean seed, oilseed rape seed and dried hop cones, with an LOQ of 0.01 mg/kg.

Homogenised samples were extracted with acetonitrile in frozen conditions. After addition of magnesium sulphate, sodium chloride and citrate salts for buffering to pH 5–5.5, the samples were centrifuged for phase separation and an aliquot of the acetonitrile phase was cleaned-up by a

dispersive SPE on PSA (primary secondary amine sorbent). Analysis was by LC-MS/MS, monitoring two parent daughter ion transitions (MRM). The LOQ of the method was 0.01 mg/kg for each matrix.

A matrix effect was noted in the undiluted dry hop cone extracts and matrix-matched standard calibration solutions were therefore used for the evaluation of the recovery rates of these extracts fortified at 0.01 mg/kg and 0.1 mg/kg. The extracts fortified at 20 mg/kg were diluted by a factor of 100 and therefore determined against solvent standard calibration solutions.

Average recovery rates in samples spiked with 0.01–5.0 mg/kg metrafenone (0.01–20 mg/kg for hop cones) ranged from 86–111% (RSD ≤ 5.1%) and the LOQ was 0.01 mg/kg.

This method was independently validated in a study reported by Weber, 2011 [Ref: 2001/7007817] with average recovery rates in samples spiked with 0.01–5.0 mg/kg metrafenone (wheat forage, straw and grain, cucumber, lemon, dry bean seed and oilseed rape seed) or 0.01–20 mg/kg (dried hop cones) ranged from 82–94% (RSD ≤ 11%) except in oilseed rape seed where the average recovery rate was 70% (RSD ≤ 5.7%). In this study, extracts were shown to be stable for up to 3 days when stored in the dark at about 8 °C and up to 7 days at 3 °C.

In a number of the supervised field trials, method validation was also conducted prior to analysis the field samples, and the recovery rates in these studies are also summarized in the following table.

Table 31 Metrafenone analytical recovery rates for QuEChERS analytical method

Matrix	Fortification (mg/kg)	Average recovery (%)	RSD (%)	No of tests	Reference
Wheat forage	0.01 0.10 5.0	100 104 108	2.5 2.5 6.1	5 5 5	2011/7007816
	0.01 0.10 5.0	89 94 76	5.4 9.8 4.5	5 5 4	2001/7007817
Wheat straw	0.01 0.10 5.0	100 101 96	3.4 2.6 3.8	5 5 5	2011/7007816
	0.01 0.10 5.0	94 89 85	7.6 8.9 11	5 5 5	2001/7007817
Wheat grain	0.01 0.10 5.0	104 103 103	1.1 1.7 0.9	5 5 5	2011/7007816
	0.01 0.10 5.0	85 86 85	6.6 8.3 5.7	5 5 5	2001/7007817
Grape	0.01 0.1	89 80	7.2 15.9	2 2	2013/7001430
Cucumber	0.01 0.10 5.0	104 103 109	1.1 2.3 5.0	5 5 5	2011/7007816
	0.01 0.10 5.0	89 90 84	9.4 5.4 8.9	5 5 5	2001/7007817
	0.01 0.1	106 97	17.3 3.7	2 2	2012/7003736
Summer squash	0.01 0.1 1.0	89 96 99	17.1 4.2 1.5	3 3 3	2013/7001798
Melon (cantaloupe)	0.01 0.1 1.0	90 87 96	4.5 3.7 6.0	3 3 3	2013/7001797

Matrix	Fortification (mg/kg)	Average recovery (%)	RSD (%)	No of tests	Reference
Tomato	0.01 0.1 1.0	104 113 107	2.0 1.8 2.0	3 3 3	2013/7001658
Pepper	0.01 0.1 3.0	87 112 97	12.3 1.9 4.9	2 2 3	2013/7000577
Lemon	0.01 0.10 5.0	104 111 110	4.4 1.5 3.7	5 5 5	2011/7007816
	0.01 0.10 5.0	94 94 91	3.0 9.0 9.4	5 5 5	2001/7007817
Beans (dried seed)	0.01 0.10	86 91	5.7 2.8	5 5	2011/7007816
	0.01 0.10	94 90	3.8 5	5 5	2001/7007817
Oilseed rape (seed)	0.01 0.10	97 94	2.0 1.8	5 5	2011/7007816
	0.01 0.10	70 71	8.6 11	5 4	2001/7007817
Hops (green cones)	0.01 0.1 1.0	90 106 96	8.0 4.7 4.7	3 3 3	2013/7001795
Hops (dried cones)	0.01 0.10	99 97 100	1.8 0.9 1.1	5 5 5	2011/7007816
	0.01 0.10 20	85 82 84	13 13 5.5	5 5 5	2001/7007817
	0.01 0.1 1.0 200	91 92 112 100	7.2 6.0 7.7 6.7	3 3 3 3	2013/7001795

BASF Method 535/3 (L0076/03)—hops and beer

The BASF Method 535/3 was described and reported by Lehmann, 2010 [Ref: 2010/1089964] as suitable for as a data-collection method to measure residues of metrafenone in hop cones (green and dried) and in beer, with an LOQ of 0.01 mg/kg.

Metrafenone residues are extracted with a mixture of methanol water and hydrochloric acid. An aliquot of the extract is centrifuged and partitioned at alkaline conditions against cyclohexane. The final determination was performed by HPLC-MS/MS and the LOQ of the method was 0.01 mg/kg for each matrix.

Average recovery rates in samples spiked with 0.01 mg/kg and 0.1 mg/kg metrafenone ranged from 88–100% (RSD ≤ 5.2%) and the LOQ was 0.01 mg/kg.

Table 32 Metrafenone analytical recovery rates for BASF method 535/3 (L0076/3)

Matrix	Fortification (mg/kg)	Average recovery (%)	RSD (%)	No of tests
Hops (green cones)	0.01	99.6	3.9	5
	0.10	96.0	2.4	5
Hops (dried cones)	0.01	87.7	4.6	5
	0.10	92.1	4.9	5
Beer	0.01	95.9	3.6	5
	0.10	93.5	2.6	5

MRM DFG S19 (animal matrices)

The German multi-residue method DFG S19 (extended version) was described and reported by Pelz & Steinhauer, 2001 [Ref: 2001/7000486] as suitable for as a data-collection method to measure residues of metrafenone in milk, meat (muscle) and eggs, with an LOQ of 0.01 mg/kg for milk and 0.05 mg/kg for meat and eggs.

Residues were extracted from the various animal matrices with water:acetone (2:1) as described in module E.1 and partitioned into ethyl acetate:cyclohexane (1:1) and the organic extract was cleaned up using gel permeation chromatography (GPC module). Extracts were analysed for metrafenone using capillary gas chromatography with mass selective detection (module D.4.). The limit of quantitation (LOQ) was 0.01 mg/kg (ppm) for milk and 0.05 mg/kg (ppm) for meat and eggs.

Average recovery rates in samples spiked with 0.01 mg/kg and 0.1 mg/kg metrafenone ranged from 69–89% (RSD ≤ 15%) and the LOQs were 0.01 mg/kg (milk) and 0.05 mg/kg (meat and eggs).

This method was independently validated in a study reported by Class, 2001 [Ref: 2001/7001287] that used matrix-matched calibration standards. Analysis was by GC-MS (module D.4.). Average recovery rates in samples spiked with 0.01 mg/kg and 0.1 mg/kg (milk) or 0.05 mg/kg 0.5 mg/kg (muscle and eggs) ranging from 76–101% (RSD ≤ 14%).

Table 33 Metrafenone analytical recovery rates for analytical method DFG S19

Matrix	Fortification (mg/kg)	Average recovery (%)	RSD (%)	No of tests	Reference
Milk	0.01 0.1	71 69	2.7 2.8	5 5	2001/7000486
	0.01 0.1	101 95	9 14	5 5	2001/7001287
Meat (bovine muscle)	0.05 0.5	97 93	5.1 15	5 5	2001/7000486
	0.05 0.5	101 89	8 9	5 5	2001/7001287
Eggs	0.05 0.5	89 94	3.8 7.7	5 5	2001/7000486
	0.05 0.5	76 97	6 14	5 5	2001/7001287

Enforcement methods

Multi-residue method DFG S19

The German method DFG S19 with GC-ECD or GC-MS analysis is suitable for enforcement of the MRL for metrafenone in plant commodities with a high starch content and high acid content (based on the method validation for wheat and barley grain and in grapes), with an LOQ of 0.01 mg/kg and in muscle, milk and eggs with an LOQ of 0.01 mg/kg for milk and 0.05 mg/kg for meat and eggs.

QuEChERS (plant matrices)

The QuEChERS method (including Amendment 1) is suitable for enforcement of the MRL for metrafenone in plant commodities, based on the method validation for cucumber and wheat forage (representing high water content), lemon (high acid content), wheat grain (high starch content), dry beans (high protein content) and oilseed rape (high oil content).

Analytical (concurrent) recoveries in supervised crop trials

Analytical recovery rates were measured in all the supervised crop field trials, with control samples being fortified with metrafenone at 0.01 mg/kg and at higher levels that generally reflected the range

of expected residues. In the European trials the common analytical method was Method 535/3 and the QuEChERS method was predominantly used in the North American trials. Some of the earlier European cereal trials used method RLA 12619 to measure residues of metrafenone and several metabolites.

For each study, average recoveries per fortification level generally fell within the 70–120% range, with a relative standard deviation of 20% or less. Information on the concurrent recovery rates for individual commodities are summarised in the relevant supervised crop field trial sections.

Stability of residues in stored analytical samples

Plant matrices

The Meeting received information on the stability of residues of metrafenone in various substrates with a high water content (lettuce, tomato, wheat forage and straw), a high starch content (carrot, wheat grain), a high protein content (dry peas), a high oil content (soya beans) and a high acid content (grape) stored at freezer temperatures for 24 months.

In a study by Class, 2001, [Ref: BN-326-010], samples of carrots and lettuce were fortified with 0.5 mg/kg metrafenone and stored in the dark at -18 °C. Samples were taken for extraction (n-heptane:acetone (8:2), partitioning into ethyl acetate and analysis after 0, 3, 8, 12, 18 and 24 months, with the stored control samples being freshly fortified and analysed concurrently to determine the procedural recovery efficiency. The 1-month and 3-month samples were analysed by GC-MS and the remaining samples were cleaned up using gel permeation chromatography before GC-ECD analysis. Mean procedural recovery rates over the study period were 92 ± 13% in carrots and 92 ± 4% in lettuce.

After 24 months storage the measured residues of metrafenone in stored lettuce and carrot samples were greater than 80% of the spiked levels.

Table 34 Stability of metrafenone residues in carrot and lettuce samples spiked at 0.5 mg/kg and stored at -18 °C.

Commodity	Storage interval (months)	Residues remaining [a] (mg/kg)	Residues remaining (%)	Procedural recovery [b] (%)
Carrot	0	0.48	96	99
	3	0.51	102	104
	8	0.4	80	96
	12	0.43	86	71
	18	0.44	88	93
	24	0.47	94	92
Lettuce	0	0.44	88	92
	3	0.47	94	94
	8	0.38	76	90
	12	0.41	82	89
	18	0.45	90	94
	24	0.43	86	95

[a] Mean of three analyses

[b] Mean of two analyses

In a study by Class, 2000, [Ref: 2000/7000144], spiked samples of grapes (fortified with 0.5 mg/kg metrafenone and wine (fortified with 0.1 mg/kg metrafenone) were stored in the dark at –18 °C. Samples were taken for extraction (n-heptane:acetone (8:2), partitioning into ethyl acetate and analysis after 0, 3, 8, 12, 18 and 24 months, with the stored control samples being freshly fortified and analysed concurrently to determine the procedural recovery efficiency. The 1-month, 3-month and 6-month samples were cleaned up and analysed using on line coupled HPLC/GC-MS and the remaining samples were cleaned up using gel permeation chromatography before GC-ECD analysis. Mean procedural recovery rates over the study period were 95% in grapes and 103% in wine.

After 18 months storage the measured residues of metrafenone in stored grape and wine samples were greater than 80% of the spiked levels.

Table 35 Stability of metrafenone residues in grape and wine samples spiked at 0.5 mg/kg and 0.1 mg/kg respectively and stored at –18 °C

Commodity (fortification)	Storage interval (months)	Residues remaining [a] (mg/kg)	Residues remaining [a] (%)	Procedural recovery [b] (%)
Grape (0.5 mg/kg)	0	0.56	112	108
	3	0.43	86	95
	6	0.46	92	101
	12	0.43	86	90
	18	0.42	83	81
Wine (0.1 mg/kg)	0	0.1	100	108
	3	0.101	101	109
	6	0.106	106	108
	12	0.09	90	85
	18	0.083	83	104

[a] % fortified level, mean of three analyses
[b] Recovery in freshly fortified samples, mean of two analyses

In a study by Class, 2002, [Ref: 2002/7004653], spiked samples of wheat grain and wheat straw fortified with 0.5 mg/kg metrafenone were stored in the dark at –18 °C. Samples were taken for extraction (n-heptane:acetone (8:2), partitioning into ethyl acetate and analysis after 0, 11-12, 18, 24 and 29 months (grain only), with the stored control samples being freshly fortified and analysed concurrently to determine the procedural recovery efficiency. The initial (0-month) samples were cleaned up and analysed using on line coupled HPLC/GC-MS and the remaining samples were cleaned up using gel permeation chromatography before GC-ECD analysis. Mean procedural recovery rates over the study period were 101% in wheat grain and 93% in wheat straw.

After 24 months (grain) and 29 months (straw) storage, the measured residues of metrafenone in frozen samples were greater than 97% of the spike level and in wheat straw were greater than 82% of the spike level.

Table 36 Stability of metrafenone residues in wheat grain and straw samples spiked at 0.5 mg/kg and stored at -18 °C

Commodity (fortification)	Storage interval (months)	Residues remaining [a] (mg/kg)	Residues remaining [a] (%)	Procedural recovery [b] (%)
Wheat grain (0.5 mg/kg)	0	0.5	100	99
	12	0.5	100	97
	18	0.46	92	92
	29	0.5	100	116
Wheat straw (0.5 mg/kg)	0	0.41	82	84
	11	0.38	76	93
	18	0.4	80	102
	24	0.35	70	94

[a] % fortified level, mean of three analyses
[b] Recovery in freshly fortified samples, mean of two analyses

In a study by Smalley, 2003, [Ref: 2003/1013928], spiked samples of wheat plants, grain and straw fortified with a combined solution of metrafenone and three metabolites (CL 3000402, CL434223 and CL 376991), each at a concentration of 1.0 mg/kg. Spiked samples were stored in the dark at –20 °C. Samples were taken for extraction and analysis using Method RLA 12619V after 1–3, 7, 15, 19, 24 and 31 months, with the stored control samples being freshly fortified and analysed concurrently to determine the procedural recovery efficiency. Metrafenone procedural recovery rates over the study period ranged from 91–107% in wheat plants, 81–97% in wheat straw and 71–90% in wheat grain.

After 31 months the measured residues of metrafenone in samples of wheat plants and straw were greater than 77% of the spike level and in wheat grain were greater than 74% of the spike level.

Table 37 Stability of residues in wheat matrices spiked at 1.0 mg/kg metrafenone and metabolites CL 3000402, CL434223 and CL 376991 and stored at -18 °C

Commodity (fortification)	Storage interval (months)	Residues remaining [a] (%)	Procedural recovery [b] (%)
Metrafenone			
Wheat plant (1.0 mg/kg)	1	102	107
	7	100	103
	15	106	107
	19	99	99
	24	96	97
	31	83	92
Wheat straw (1.0 mg/kg)	3	100	81
	7	94	97
	15	87	75
	19	92	90
	24	91	93
	31	87	90
Wheat grain (1.0 mg/kg)	2	74	80
	7	79	80
	15	90	90
	19	73	80
	24	87	82
	31	74	71
CL 3000402			
Wheat plant (1.0 mg/kg)	1	95	100
	7	105	103
	15	102	99
	19	96	97
	24	96	96
	31	84	94
Wheat straw (1.0 mg/kg)	3	97	96
	7	96	92
	15	93	83
	19	91	90
	24	94	95
	31	83	82
Wheat grain (1.0 mg/kg)	2	74	77
	7	97	83
	15	88	84
	19	80	88
	24	99	95
	31	83	81
CL434223			
Wheat plant (1.0 mg/kg)	1	93	98
	7	103	104
	15	100	101
	19	93	96
	24	93	95
	31	86	92
Wheat straw (1.0 mg/kg)	3	92	95
	7	97	92
	15	93	89
	19	90	90
	24	92	92
	31	96	89

Commodity (fortification)	Storage interval (months)	Residues remaining [a] (%)	Procedural recovery [b] (%)
Wheat grain (1.0 mg/kg)	2	75	90
	7	94	88
	15	84	80
	19	82	95
	24	99	84
	31	83	79
CL 376991			
Wheat plant (1.0 mg/kg)	1	99	99
	7	103	103
	15	101	105
	19	93	97
	24	91	98
	31	85	92
Wheat straw (1.0 mg/kg)	3	98	91
	7	99	92
	15	89	86
	19	90	91
	24	94	90
	31	93	87
Wheat grain (1.0 mg/kg)	2	77	80
	7	96	87
	15	87	86
	19	82	93
	24	92	89
	31	77	78

[a] % fortified level, mean of three analyses
[b] Recovery in freshly fortified samples, mean of two analyses

In a study by Lehmann & Mackenroth, 2011 [Ref: 2011/1043493], spiked samples of wheat plants, grain and straw, grapes, tomatoes, and dry pea and soya bean seed, fortified with 0.1 mg/kg metrafenone were stored in the dark at –20 °C. Samples were taken for extraction and analysis using BAF Method 535/3 after about 1, 6, 12, 15 and 24 months, with additional soya bean seed samples being analysed after about 2 and 3 month storage. Stored control samples were also freshly fortified and analysed concurrently to determine the procedural recovery efficiency. Mean procedural recovery rates over the study period were greater than 85% in all matrices.

After 24 months the measured residues of metrafenone in samples of wheat plants, grain and straw, grapes, tomato, dried peas and soya bean seeds were greater than 80% of the spike level after correction for procedural recovery.

Table 38 Stability of metrafenone residues in a range of plant matrices spiked at 0.1 mg/kg and stored at -20 °C

Commodity (fortification)	Storage interval (months)	Residues remaining [a] (mg/kg)	Residues remaining [a] (%)	Procedural recovery [b] (%)
Wheat plant (0.1 mg/kg)	0	0.09	86	83
	1	0.07	73	78
	6	0.08	83	86
	12	0.08	80	80
	24	0.085	85	99
Wheat straw (0.1 mg/kg)	0	0.09	91	89
	1	0.09	90	90
	6	0.085	84	89
	12	0.09	91	95
	24	0.08	78	78

Commodity (fortification)	Storage interval (months)	Residues remaining [a] (mg/kg)	Residues remaining [a] (%)	Procedural recovery [b] (%)
Wheat grain (0.1 mg/kg)	0	0.11	107	107
	1	0.08	78	91
	6	0.08	83	97
	12	0.085	85	102
	24	0.08	77	90
Grape (0.1 mg/kg)	0	0.09	89	88
	1	0.075	77	81
	6	0.1	97	99
	12	0.11	106	96
	24	0.085	83	84
Tomato (0.1 mg/kg)	0	0.09	89	85
	1	0.09	88	90
	6	0.1	101	101
	12	0.075	75	97
	15	0.08	76	77
	24	0.095	96	91
Pea (dried seeds)	0	0.1	104	99
	1	0.09	90	96
	6	0.095	96	104
	12	0.09	90	100
	24	0.085	83	96
Soya bean (seeds)	0	0.1	98	100
	1	0.07	72	96
	2	0.08	78	93
	3 (2)	0.09, 0.08	89, 82	106, 102
	6	0.06	60	99
	12	0.07	72	100
	24	0.1	98	103

[a] % fortified level, mean of two analyses
[b] Recovery in freshly fortified samples, mean of three analyses

In summary, metrafenone residues were stable in analytical samples stored frozen, i.e., -18 to -20 °C) for up to 24 months in representative substrates with a high water content (lettuce, tomato), a high starch content (carrot), a high protein content (dry peas), a high oil content (soya bean) and a high acid content (grape, wine) and in wheat grain (high starch), wheat forage and straw (high water content) residues were stable for up to 31 months. In general, residues in the stored samples were greater than 80% of the spiked levels.

USE PATTERNS

Information on GAP in 50 countries in Europe, the Americas, Asia and the Pacific was provided to the Meeting on the use of metrafenone, available as SC formulations, often co-formulated with either epoxiconazole and/or fenpropimorph. Proposed uses were also provided but are not reported.

The following table summarises the representative critical national or regional GAPs for the crops for which supporting residue trials have been provided.

Table 39 Registered uses of metrafenone (300 g ai/L or 500 g ai/L SC formulations)

Crop	Country	Application				Max/season		PHI (days)	Comments
		kg ai/ha	kg ai/hL	water L/ha	RTI (days)	no	kg ai/ha		
Berries and other small fruit (004)									
Grapes									
	Australia		0.01		7–10	4		35	
	Austria Germany	0.04–0.16		100–800	10–14	3		28	Higher rate/ha from BBCH 75
	Bulgaria	0.01	0.01	200–1000	12–14	2		28	
	Canada	0.225			14–21	6	1.35	14	

Crop	Country	Application				Max/season		PHI (days)	Comments
		kg ai/ha	kg ai/hL	water L/ha	RTI (days)	no	kg ai/ha		
	Chile	0.1–0.15	0.075–0.01		15	3		7	
	Czech Republic	0.08–0.16		300–1000	10–14	2			Higher rate/ha from BBCH 61
	France	0.1			10–12	2		28	
	Greece	0.1	0.01	1000	10–14	3		28	
	Hungary	0.05–0.125		600–1000	10–14	4		28	Wine grapes
	Italy	0.1–0.125	0.01–0.0125		8–12	3		28	
	Luxembourg	0.1			10–14	2		28	
	Macedonia	0.1	0.01	600–1000	10–14	3		28	
	Mexico	0.1			7	3		7	
	Portugal	0.1	0.01	600–1000	10–14	3		28	
	Peru	0.125–0.15						28	
	Serbia		0.01	600–1000		3		28	
	Slovakia	0.1		1000	10–14	3		28	
	Slovenia	0.08–0.1			10–12			28	Higher rate/ha from BBCH 79
	South Africa		0.0125		10–14	3		28 (table) 56 (wine)	To BBCH 75
	Spain	0.1	0.01	600–1000	14	3		28	
	Switzerland	0.08–0.16	0.01		10–14	3			To veraison
	Turkey		0.01		10–14			28	
	Ukraine	0.1		500–1000	7–14	3		50	
Strawberries									
	Netherlands	0.15			7	2		3	Indoor crops
	Korea		0.015		7	2		NS	
Fruiting vegetables, Cucurbits (011)									
Cucurbits									
	Australia	0.075–0.15		250–500	7–10	4		7	
Cucumber									
	Bulgaria	0.1	0.01	200–1000	12–14	2		3	Field crops
	France	0.1			7–10	2		3	
	Greece	0.1	0.01	1000	7–10	2		3	
	Korea		0.015		10	2		NS	
Cucumber (indoor)									
	Belarus	0.09		1000	7–10	3		3	
	Bulgaria	0.1	0.01	200–1000	7–10	2		3	
	France	0.1				2		3	
	Turkey		0.01		7–10	2		1	
Melon									
	France	0.1			7–10	2		3	
	Greece	0.1	0.01	1000	7–10	2		3	
	Korea		0.015		10			NS	Also watermelon
Summer squash									
	France	0.1			7–10	2		3	
	Greece	0.1	0.01	1000	7–10	2		3	
Pumpkin									
	Korea		0.015		10			NS	
	New Zealand	0.15			14–21	2		14	
Winter squash									
	New Zealand	0.15			14–21	2		14	
Fruiting Vegetables, other than Cucurbits (012)									
Tomato									
	Bulgaria	0.15	0.015	200–1000	12–14 (F) 7–10 (P)	2		3	F=field crops P=protected crops
	Ecuador		0.01					7	
	France	0.15 (F) 0.225 (P)	0.015		7–10	2		3	F=field crops P=protected crops
	Greece	0.15	0.015		7–10	2		3	
	Spain		0.015			2		3	

Crop	Country	Application				Max/season		PHI (days)	Comments
		kg ai/ha	kg ai/hL	water L/ha	RTI (days)	no	kg ai/ha		
Eggplant									
	France	0.15			7–10	2	3		
Eggplant (indoor)									
	Bulgaria	0.15	0.015	200–1000	7–10	2		3	
	Greece	0.15	0.015		7–10	2		3	
Peppers									
	Korea		0.015		10	2		NS	
Peppers (indoor)									
	Bulgaria	0.15	0.015	200–1000	7–10	2		3	
	France	0.15			7–10	2		3	
	Greece	0.15	0.015		7–10	2		3	
Mushrooms									
	France	0.05 kg ai/100 m^2		15 L/100 m^2		1		10	
Cereal grains (020)									
Barley, oats, rye, triticale, wheat									
	Denmark	0.075–0.15				2			To BBCH 59
	Estonia	0.15			21	2		35	To BBCH 69
	France	0.15				1		35	
	Hungary	0.12			21	2		35	
	Ireland	0.15				2			To BBCH 61
	Latvia	0.15		300–400		2		35	To BBCH 69
	Sweden	0.075–0.15		200–400		2			To BBCH 61
Barley, rye, triticale, wheat									
	Belgium	0.15		200–400	21	2			To BBCH 59
	Czech Republic	0.15				2		35	To BBCH 61
	Germany	0.15		200–400		2			To BBCH 61
	Belarus	0.09				1		71	
Barley, triticale, wheat									
	Netherlands	0.15				2		35	To BBCH 69
	Poland	0.15		300	21	2		35	
Rye, triticale, wheat									
	Switzerland	0.15		300–400		1			To BBCH 61
	UK	0.15		100–400		2			To BBCH 61
Barley, oats									
	Switzerland	0.15		300–400		1			To BBCH 51
	UK	0.15		100–400		2			To BBCH 59

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised field trials involving foliar treatments of metrafenone to the following crops.

Group	Crop	Countries	Table no
Berries and other small fruits	Grape	USA	40–41
	Strawberry	Europe	42
Fruiting vegetables, Cucurbits	Cucumber	Europe, Nth America	43–45
	Summer squash	Europe, Nth America	46–47
	Melon	Europe, Nth America	48–49
Fruiting vegetables, other than Cucurbits	Mushrooms	Europe	50
	Peppers	Europe, Nth America	51–52
	Tomato	Europe, Nth America	53–55
Cereals	Wheat	Europe	56
	Barley	Europe	57

Group	Crop	Countries	Table no
Cereal forage and fodders	Wheat	Europe	58 and 60
	Barley	Europe	59 and 61

The supervised trials were well documented with laboratory and field reports. Laboratory reports included method validation including procedural recoveries with spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analyses or duration of residue sample storage were also provided. Although trials included control plots, no control data are recorded in the tables unless residues in control samples exceeded the LOQ. In such cases, the residues found are noted as "c=nn mg/kg" in the Reference and Comments columns. Residue data are recorded unadjusted for recovery.

Results from replicated field plots are presented as individual values. When residues were not detected they are shown as ND. Residues and application rates have been reported as provided in the study reports, although the results from trials used for the estimation of maximum residue levels (underlined) have been rounded to two significant digits (or if close to the LOQ, rounded to one significant digit) in the Appraisal.

In some trials, samples were taken just before the final application and then, again on the same day after the spray had dried. In the data tables the notation for these two sampling times is '–0' and '0' respectively.

When multiple applications were made to a crop, the application rate, spray concentration and spray volume were not always identical from one application to the next. In most trials, the actual treatment rates were within 10% of the listed 'target' application rates, but if not, the actual treatment rates are listed.

Berries and other small fruits

Grape

Results from supervised trials from the USA on grapes conducted in 2005 and in 2011 were provided to the Meeting. In the 2011 trials, three foliar airblast applications of metrafenone (0.33 kg ai/ha, SC formulation) with added non-ionic surfactant were applied to 12–24 vine plots, 14–15 days apart, using about 1000–1500 L water/ha. Grape samples (min 1 kg and at least 12 bunches or part bunches) were frozen within 3 hours of sampling and stored frozen for up to 20 months before analysis of berries for metrafenone using the QuEChERS method. Procedural recovery rates in grapes fortified at 0.01 to 1.5 mg/kg ranged from 74 to 104% (mean 91 ± 10%, n=10) and the LOQ was 0.01 mg/kg.

Table 40 Residues in grapes from supervised trials in the USA involving three foliar applications of metrafenone (SC formulation).

GRAPE Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2011 Alton, NY (Cayuga White)	3	0.336 0.337 0.337		935 935 935	berries	0DAA1 0DAA2 0 14 15 17 19 21	0.79, 0.84 0.004 [a], 0.007 [b] 0.92, 0.99 0.46, 0.36 0.5, 0.41 0.29, 0.43 0.3, 0.45 0.27, 0.29	0.81 < 0.01 0.95 0.41 0.46 0.36 0.38 0.28	2013/7001430 R110152
USA, 2011 Dundee, NY (Vidal)	3	0.337 0.341 0.337		945 945 945	berries	14	1.1 [c], 0.94 [d]	1.0	2013/7001430 R110153

GRAPE Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2011 Templeton, CA (Marsanne)	3	0.336 0.337 0.335		1496 1422 1468	berries	14	0.28, 0.42 (c=0.015)	0.35	2013/7001430 R110154
USA, 2011 Kingsburg, CA (Crimson)	3	0.337 0.337 0.339		1366 1347 1422	berries	13	0.51, 0.45	0.48	2013/7001430 R110155
USA, 2011 Lindsay, CA (Red Globe)	3	0.336 0.337 0.337		1366 1328 1347	berries	0 DAA1 0 DAA2 0 14 15 17 19 21	0.47, 0.39 0.77, 0.81 0.54, 0.63 0.38, 0.42 0.34, 0.41 0.58, 0.35 0.42, 0.44 0.35, 0.39	0.43 0.79 0.59 0.4 0.38 0.47 0.43 0.37	2013/7001430 R110156
USA, 2011 Dinuba, CA (Ruby Red)	3	0.337 0.337 0.339		1347 1366 1375	berries	13	0.27, 0.4	0.34	2013/7001430 R110157
USA, 2011 Porterville, CA (Thompson Seedless)	3	0.337 0.339 0.34		1394 1375 1337	berries	14	0.25, 0.2	0.22	2013/7001430 R110158
USA, 2011 Ephrata, WA (White Riesling)	3	0.331 0.333 0.333		954 954 954	berries	14	0.4, 0.49	0.45	2013/7001430 R110159

[a] Mean of values 0.005, 0.004, 0.003
[b] Mean of values 0.006, 0.008, 0.006
[c] Mean of 1.2, 0.91, 1.1
[d] Mean of 1.1, 0.84, 0.88

In the 2005 trials, six foliar applications of metrafenone (0.33 kg ai/ha, SC formulation) with no added surfactant were applied 12–15 days apart, with dilute (100–1500 L water/ha) and concentrate (500–700 L water/ha) treatments being applied to separate 40–220 square metre plots.

Grape samples (min 1 kg and at least 12 bunches or part bunches) were frozen within 3 hours of sampling, and stored frozen for up to 6 months before analysis of berries for metrafenone using Method 535/3. Average procedural recoveries of metrafenone from grapes fortified with 0.01–20 mg/kg ranged from 82–127% (mean 99 ± 13%, n=26) and the LOQ was 0.01 mg/kg.

Table 41 Residues in grapes from supervised trials in the USA involving six foliar applications of metrafenone (SC formulation).

GRAPE Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
GAP:Canada	6	0.225				PHI: 14	RTI: 14-21d		1.35 kg ai/ha/season
USA, 2005 Seneca, NY (Catawba)	6	0.33	0.047	700	berries	0 14 28		1.0 3.2 0.64	2006/70070 RCN R05009
	6	0.33	0.024	1440	berries	0 14 28		1.8 1.9 1.1	2006/70070 RCN R05009
USA, 2005 Yates, NY (Vidal Blanc)	6	0.33	0.048	690	berries	0 14 28		1.8 1.5 1.4	2006/70070 RCN R05010

GRAPE Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
	6	0.33	0.024	1440	berries	0 14 28		1.5 1.3 1.0	2006/70070 RCN R05010
USA, 2005 Kern, CA (Ruby Seedless)	6	0.33	0.064	510	berries	0 14 28		0.75 <u>0.62</u> 0.52	2006/70070 RCN R05011
	6	0.34	0.026	1300	berries	0 14 28		0.67 0.55 0.52	2006/70070 RCN R05011
USA, 2005 Tulare, CA (Thompson)	6	0.34	0.065	520	berries	0 7 14 21 28		0.69 0.4 0.2 0.15 0.17	2006/70070 RCN R05012
	6	0.33	0.026	1290	berries	0 7 14 21 28		0.64 0.51 <u>0.32</u> 0.26 0.24	2006/70070 RCN R05012
USA, 2005 Tulare, CA (Thompson)	6	0.35	0.067	530	berries	0 14 28		0.4 <u>0.27</u> 0.16	2006/70070 RCN R05013 (Processing study)
	6	0.34	0.027	1270	berries	0 14 28	0.27, 0.31	0.28 0.17 0.16	2006/70070 RCN R05013 (Processing study)
USA, 2005 Glenn, CA (Centurion)	6	0.34	0.048	700	berries	0 14 28		0.22 <u>0.17</u> 0.07	2006/70070 RCN R05014
	4+	0.34 0.34	0.024 0.032	1450 1060	berries	0 14 28		0.13 0.04 0.02	2006/70070 RCN R05014
USA, 2005 Colusa, CA (Zinfandel)	6	0.33	0.047	700	berries	0 14 28		0.15 0.05 0.08	2006/70070 RCN R05015
	6	0.33	0.031	1050	berries	0 14 28		0.11 <u>0.18</u> 0.13	2006/70070 RCN R05015
USA, 2005 Sacramento, CA (Merlot)	6	0.33	0.047	700	berries	0 14 28		0.04 0.02 0.02	2006/70070 RCN R05016
	6	0.33	0.031	1050	berries	0 14 28		0.11 <u>0.11</u> 0.08	2006/70070 RCN R05016
USA, 2005 Madera, CA (Merlot)	6	0.34	0.048	710	berries	0 14 28		2.6 <u>2.1</u> 1.8	2006/70070 RCN R05017
	6	0.34	0.024	1400	berries	0 14 28		3.3 1.9 2.1	2006/70070 RCN R05017
USA, 2005 Fresno, CA (Not specified)	6	0.34	0.048	710	berries	0 14 28		2.5 <u>2.4</u> 2.0	2006/70070 RCN R05018
	6	0.34	0.024	1400	berries	0 14 28		2.8 2.2 2.3	2006/70070 RCN R05018

GRAPE Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2005 Grant, WA (White Riesling)	6	0.34	0.048	710	berries	0 14		4.0 2.3	2006/70070 RCN R05019
	6	0.34	0.024	1400	berries	0 14		5.6 3.0	2006/70070 RCN R05019
USA, 2005 Benton, OR (Pinot Noir)	6	0.35	0.026	1320	berries	0 14 28		4.1 2.3 1.9	2006/70070 RCN R05020
	6	0.33	0.05	690	berries	0 14 28		1.4 1.3 0.6	2006/70070 RCN R05020 Dilute Spray

Strawberry

Results from supervised trials from Europe on protected strawberries conducted in 2009 were provided to the Meeting. In these trials, two foliar applications of 0.15 kg ai/ha metrafenone (SC formulation) in about 200 L water/ha were applied 7 days apart, using motorized knapsacks or 6-nozzle mini-boom sprayers.

Fruit samples (min 1 kg) were frozen within 12 hours of sampling and stored frozen (–18 °C) for up 15 months before analysis for metrafenone using Method 535/3. Average procedural recoveries of metrafenone from strawberries fortified with 0.01 or 1.0 mg/kg were 101% and 98% respectively and the LOQ was 0.01 mg/kg.

Table 42 Residues in protected strawberries from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation).

STRAWBERRY Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
GAP: Netherlands	2	0.15				3	RTI: 7–10days	
France, 2009 Loiret (Charlotte)	2	0.15	0.08	200	fruit	0 1 3 7	0.16 0.36 0.34 0.18	2010/1201582 S09 00766-01
Germany, 2009 Lower Saxony (Elsanta)	2	0.15	0.08	200	fruit	0 1 4 6	0.23 0.3 0.28 0.25	2010/1201582 S09 00766-02
United Kingdom, 2009 Nottingham (Elsanta)	2	0.15	0.08	200	fruit	0 1 3 7	0.07 0.11 0.08 0.07	2010/1201582 S09 00766-03
Belgium, 2009 Maasmechelen (Florin)	2	0.15	0.08	200	fruit	0 1 2 7	0.15 0.1 0.1 0.1	2010/1201582 S09 00766-04
France, 2009 Tarn-et-Garonne (Guarioutte)	2	0.15	0.08	200	fruit	0 1 3 7	0.06 0.07 0.06 0.04	2010/1201582 S09 00766-05

STRAWBERRY Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
GAP: Netherlands	2	0.15				3	RTI: 7–10days	
Italy, 2009 Bologna (Honey)	2	0.15	0.08	200	fruit	0 1 4 7	0.1 0.13 <u>0.05</u> 0.05	2010/1201582 S09 00766-06
Greece, 2009 Pieria (Karmoroza)	2	0.15	0.08	200	fruit	0 1 2 7	0.13 0.19 <u>0.16</u> 0.11	2010/1201582 S09 00766-07
Spain, 2009 Lucena Del Puerto (Candonga)	2	0.15	0.08	200	fruit	0 1 3 6	0.34 0.32 <u>0.23</u> 0.12	2010/1201582 S09 00766-08

Fruiting vegetables, Cucurbits

Results from supervised trials from Europe and the USA on cucumbers, zucchini (summer squash) and melons (cantaloupes) were provided to the Meeting.

Cucumber

In the European outdoor trials, two foliar applications of 0.1 kg ai/ha metrafenone (SC formulation) in about 300–1000 L water/ha were applied 7 days apart, using motorized knapsacks or 4–8 nozzle mini-boom sprayers. Plot sizes were larger than 30 square metres. In the European indoor cucumber trials, two foliar applications of 0.15 kg ai/ha were applied at 7-day intervals using motorized knapsacks or vertical boom sprayers to apply about 1500 L spray mix/ha to plots of at least 18 square metres.

Fruit samples (min 1 kg) fruit (without stems) were frozen within 12 hours of sampling and stored frozen (-18 °C) for up 16 months before analysis for metrafenone using Method 535/3. Average procedural recoveries of metrafenone from samples fortified with 0.01 mg/kg and 1.0 or 2.0 mg/kg ranged from 90% to 101% and the LOQ was 0.01 mg/kg.

In the North American trials, three foliar applications of 0.34 kg ai/ha metrafenone (SC formulation) with added adjuvant were applied at 6–8 day intervals, using motorized knapsacks or tractor-mounted 4–9 nozzle sprayers to apply about 300–700 L/ha. Plot sizes were larger than 33 square metres.

Duplicate fruit samples (min 2 kg, 12 units) were taken, with the larger cucumber fruit being sub-sampled in the field, frozen within 12 hours of sampling and stored frozen for up 24 months before analysis for metrafenone using the QuEChERS LC-MS/MS method. The average procedural recovery of metrafenone from samples fortified with 0.01 mg/kg or 1.0 mg/kg was 104% and the LOQ was 0.01 mg/kg.

Table 43 Residues in outdoor cucumbers from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

CUCUMBER Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
GAP:France	2	0.1				3	RTI 7-10d	
France (S), 2009 Montauban (Ginial)	2	0.1	0.01	1000	fruit	0 1 3 7	0.04 0.04 <u>0.02</u> 0.01	2010/1033967 BSF 0729-05

CUCUMBER Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
France (S), 2010 Montauban (Raider)	2	0.1	0.033	300	fruit	0 1 3 7	0.08 0.05 <u>0.03</u> < 0.01	2011/1041880 S10-00479-05
Germany, 2009 Nierswalde (Rhinsk Drue)	2	0.1	0.033	300	fruit	0 1 3 7	0.03 0.03 <u>0.02</u> 0.01	2010/1033967 BSF 0729-01
Germany, 2010 Baden-Wurttemberg (Travilo)	2	0.1	0.033	300	fruit	0 1 3 8	0.02 0.01 <u>0.01</u> < 0.01	2011/1041880 S10-00479-02 Knapsack, mid Aug
Germany, 2010 Baden-Wurttemberg (Travilo)	2	0.11	0.033	333	fruit	0 1 2 6	0.03 0.02 <u>0.04</u> 0.01	2011/1041880 S10-00479-09 Boom sprayer, late Aug-Sep
Italy, 2009 Verona (Caman)	2	0.1	0.01	1000	fruit	0 1 3 7	0.07 0.04 <u>0.02</u> < 0.01	2010/1033967 BSF 0729-06
Italy, 2010 Fondi (Caman)	2	0.1	0.033	300	fruit	0 1 3 7	< 0.01 0.03 <u>0.02</u> 0.02	2011/1041880 S10-00479-06
Netherlands, 2009 Ven-Zelderheide (Rhinsk Drue)	2	0.1	0.033	300	fruit	0 1 3 7	0.03 0.02 <u>0.02</u> < 0.01	2010/1033967 BSF 0729-02

Table 44 Residues in outdoor cucumbers from supervised trials in North America involving three foliar applications of metrafenone (SC formulation)

CUCUMBER Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2010 Jeffersonville, GA (Speedway)	3	0.33	0.11	280	fruit	0 1 3 7 10	0.11, 0.09 0.12, 0.05 0.06, 0.04 0.02, 0.02 0.016, < 0.01	0.1 0.09 0.05 0.02 0.01	2012/7003736 R100008
USA, 2010 Chula, GA (Thunder)	3	0.34	0.12	280	fruit	0	0.13, 0.15	0.14	2012/7003736 R100009
USA, 2010 Zellwood, FL (Expedition)	3	0.35	0.12	290	fruit	0	0.09, 0.07	0.08	2012/7003736 R100010
USA, 2010 Richland, IA (Pickle)	3	0.34	0.12	290	fruit	0	0.15, 0.17	0.16	2012/7003736 R100011
USA, 2010 Campbell, MN (Speedway)	3	0.34	0.12	280	fruit	0	0.05, 0.06	0.05	2012/7003736 R100012
USA, 2010 Hinton, OK (Thunder)	3	0.34	0.12	280	fruit	0	0.11, 0.08	0.1	2012/7003736 R100013

Table 45 Residues in indoor cucumbers from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

CUCUMBER Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
GAP: Turkey	2		0.01			1	RTI: 7–10d	
Belgium, 2009 Villers-Perwin (Pepinova)	2	0.15	0.01	1500	fruit	0 1 3 7	0.02 <u>0.02</u> 0.02 0.01	2010/1033969 BSF 0728-03
France (N), 2009 St Genough (Aramon)	2	0.15	0.01	1500	fruit	0 1 3 7	0.05 <u>0.06</u> 0.03 0.02	2010/1033969 BSF 0728-09 Early August treatments
France (N), 2009 St Genouph (Aramon)	2	0.15	0.01	1500	fruit	0 1 3 7	0.06 <u>0.06</u> 0.03 0.03	2010/1033969 BSF 0728-04 Late August treatments
France (S), 2009 Noves (Columbia)	2	0.15	0.01	1500	fruit	0 1 3 7	0.06 <u>0.04</u> 0.03 0.02	2010/1033969 BSF 0728-05
Germany, 2009 Straelen (Proloog)	2	0.15	0.01	1500	fruit	0 1 3 7	0.07 <u>0.07</u> 0.06 0.05	2010/1033969 BSF 0728-01
Greece, 2009 Nea Magnisia (Galileo)	2	0.15	0.01	1500	fruit	0 1 3 7	0.1 <u>0.09</u> 0.06 0.022	2010/1033969 BSF 0728-08
Italy, 2009 Verona (Caman)	2	0.15	0.01	1500	fruit	0 1 3 7	0.08 <u>0.05</u> 0.04 0.02	2010/1033969 BSF 0728-06
Netherlands, 2009 AN Oirlo (Anastasia)	2	0.15	0.01	1500	fruit	0 1 3 7	0.07 <u>0.05</u> 0.03 0.01	2010/1033969 BSF 0728-02
Spain, 2009 Valencia (Dasher)	2	0.15	0.01	1500	fruit	0 1 3 7	0.03 <u>0.04</u> 0.03 0.03	2010/1033969 BSF 0728-07

Summer squash

In the European outdoor trials, two foliar applications of 0.1 kg ai/ha metrafenone (SC formulation) in about 300–1000 L water/ha were applied 7 days apart, using motorized knapsacks or 4–8 nozzle mini-boom sprayers. Plot sizes were larger than 30 square metres.

Fruit samples (min 1 kg) fruit (without stems) were frozen within 12 hours of sampling and stored frozen (-18 °C) for up 14 months before analysis for metrafenone using Method 535/3. The average procedural recovery of metrafenone from samples fortified with 0.01 or 1.0 mg/kg was 96% and the LOQ was 0.01 mg/kg.

In the North American trials, three foliar applications of 0.34 kg ai/ha metrafenone (SC formulation) with added adjuvant were applied at 6–8 day intervals, using motorized knapsacks or

tractor-mounted 4–9 nozzle sprayers to apply about 300–700 L/ha. Plot sizes were larger than 33 square metres.

Duplicate fruit samples (min 2 kg, 12 units) were frozen within 12 hours of sampling and stored frozen for up 28 months before analysis for metrafenone using the QuEChERS LC-MS/MS method. The average procedural recovery of metrafenone from samples fortified with 0.01 mg/kg or 1.0 mg/kg as 100% and the LOQ was 0.01 mg/kg.

Table 46 Residues in outdoor summer squash (zucchini) from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

SUMMER SQUASH Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
GAP: France	2	0.1				3	RTI 7–10d	
Belgium, 2009 Villers-Perwin (Black Beauty)	2	0.1	0.033	300	fruit	0 1 3 7	0.02 0.01 <u>0.01</u> < 0.01	2010/1033967 BSF 0729-03
France (N), 2009 La Poitevine (Quirinal)	2	0.1	0.033	300	fruit	0 1 3 7	0.09 0.05 <u>0.02</u> < 0.01	2010/1033967 BSF 0729-04
Greece, 2009 Nea Magnisia (Ezra)	2	0.1	0.01	1000	fruit	0 1 3 7	0.06 0.05 <u>0.01</u> 0.01	2010/1033967 BSF 0729-07
Spain, 2009 San Antonio de Benageber (Consul)	2	0.1	0.01	1000	fruit	0 1 3 7	0.03 0.04 <u>0.02</u> < 0.01	2010/1033967 BSF 0729-08
France (N), 2010 Essone (Tosca)	2	0.1	0.033	300	fruit	0 1 3 7	0.05 0.04 <u>0.02</u> < 0.01	2011/1041880 S10-00479-03
France (N), 2010 Loiret (Ambassador)	2	0.1	0.033	300	fruit	0 1 3 7	0.04 0.02 <u>0.01</u> < 0.01	2011/1041880 S10-00479-04
Greece, 2010 Thessalonika (Demeter F1)	2	0.1	0.033	300	fruit	0 1 3 6	0.17 0.12 <u>0.04</u> < 0.01	2011/1041880 S10-00479-07
Spain, 2010 Xativa (Nieves)	2	0.11	0.033	330	fruit	0 1 4 7	0.04 0.11 <u>0.01</u> < 0.01	2011/1041880 S10-00479-08

Table 47 Residues in outdoor summer squash from supervised trials in North America involving three foliar applications of metrafenone (SC formulation)

SUMMER SQUASH Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2010 Maricopa, AZ (Sunray Hybrid)	1+ 2	0.35 0.35	0.12 0.08	290 440	Fruit	0	0.25,0.36	0.31	2013/7001798 10478.10-AZ06

SUMMER SQUASH Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
Canada, 2010 Agassiz, BC (Golden Dawn III)	3	0.34	0.09	380	Fruit	0	0.24, 0.35	0.29	2013/7001798 10478.10-BC09
USA, 2010 Holtville, CA (Golden Dawn III)	3	0.34	0.07	480-500	Fruit	0	0.12, 0.13	0.13	2013/7001798 10478.10-CA136
USA, 2010 Citra, FL (Gentry)	3	0.33	0.05	640-650	Fruit	0	0.1, 0.16	0.13	2013/7001798 10478.10-FL40
USA, 2010 Salisbury, MD (Conqueror III)	3	0.33	0.08	390-400	Fruit	0	0.11, 0.09	0.1	2013/7001798 10478.10-MD18
USA, 2010 (Clinton, NC (Multipik)	3	0.34	0.085	400	Fruit	0	0.17, 0.18	0.17	2013/7001798 10478.10-NC29
USA, 2010 Freeville, NY (Multipik)	1+ 2	0.33 0.33	0.12 0.06	270 560	Fruit	0	0.08, 0.07	0.07	2013/7001798 10478.10-NY30
Canada, 2010 Delhi, ON (Leopard)	3	0.33	0.05	690	Fruit	0	0.13, 0.14	0.14	2013/7001798 10478.10-ON21
Canada, 2010 Harrow, ON (Select)	1+ 3	0.14+ 0.34	0.04 0.08	380-410	Fruit	0 1 4 6 9 13	0.25, 0.18 0.07, 0.06 < 0.01, < 0.01 < 0.01, < 0.01 < 0.01, < 0.01 < 0.01, < 0.01	0.22 0.07 < 0.01 < 0.01 < 0.01 < 0.01	2013/7001798 10478.10-ON22 3-d interval between 1st and 2nd applications
Canada, 2010 L'Acadie, QB (Golden Dawn III)	3	0.35	0.06	600-620	Fruit	0	0.1, 0.1	0.11	2013/7001798 10478.10-QC11
USA, 2010 Charleston, SC (Superpik F1)	3	0.34	0.07	500-520	Fruit	0	0.08, 0.12	0.1	2013/7001798 10478.10-SC13
USA, 2010 Weslaco, TX (Anton)	3	0.34	0.09	390-400	Fruit	0	0.14, 0.08	0.11	2013/7001798 10478.10-TX21
USA, 2010 Weslaco, TX (Multipik)	3	0.34	0.07	510	Fruit	0	0.24, 0.31	0.28	2013/7001798 10478.10-TX22
USA, 2010 Moxee, WA (Noche F1)	3	0.34	0.07	500	Fruit	0	0.12, 0.13	0.12	2013/7001798 10478.10-WA36

Melons, except Watermelon

In the European outdoor trials, two foliar applications of 0.1 kg ai/ha metrafenone (SC formulation) in about 300–1000 L water/ha were applied 7 days apart, using motorized knapsacks or 4–8 nozzle mini-boom sprayers. Plot sizes were larger than 30 square metres.

Fruit samples (min 2 kg or 12 units) were subsampled in the field (two opposite quarters/fruit) and frozen within 12 hours and stored at or below -18 °C for up 14 months before analysis for metrafenone using Method 535/3. Average procedural recoveries of metrafenone from samples fortified with 0.01 mg/kg and 1.0 mg/kg ranged from 93% to 98% and the LOQ was 0.01 mg/kg.

In the North American trials, three foliar applications of 0.34 kg ai/ha metrafenone (SC formulation) with added adjuvant were applied at 6–8 day intervals, using motorized knapsacks or

tractor-mounted 4–9 nozzle sprayers to apply about 300–700 L/ha. Plot sizes were larger than 33 square metres.

Duplicate fruit samples (min 2 kg, 12 units) were sub-sampled in the field (two opposite quarters, eighths or sixteenths/fruit), frozen within 12 hours and stored frozen for up 27 months before analysis for metrafenone using the QuEChERS LC-MS/MS method. The average procedural recovery of metrafenone from samples fortified with 0.01 mg/kg or 1.0 mg/kg was 104% and the LOQ was 0.01 mg/kg.

Table 48 Residues in outdoor melons from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

MELON Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
GAP: France	2	0.1				3	RTI: 7–10d	
France (N), 2009 La Roche Clermont (Hugo)	2	0.1	0.033	300	fruit	0 1 3 7	0.04 0.02 <u>0.02</u> 0.02	2010/1033968 BSF 0727-02 Late May planting into sandy clay
France (S), 2009 Cheval Blanc (Anasta)	2	0.1	0.01	1000	fruit	0 1 3 7	0.02 0.01 <u>< 0.01</u> < 0.01	2010/1033968 BSF 0727-03
Italy, 2009 Lupatoto (Macigno)	2	0.1	0.01	1000	fruit	0 1 3 7	0.13 0.07 <u>0.07</u> 0.02	2010/1033968 BSF 0727-04
Spain, 2009 La Llosa (Medellin)	2	0.1	0.01	1000	fruit	0 1 3 8	0.02 0.01 <u>0.01</u> < 0.01	2010/1033968 BSF 0727-05
Greece, 2009 Svoronos, Piera (Lavigal)	2	0.1	0.01	1000	fruit	0 1 3 7	0.06 0.04 <u>0.03</u> 0.02	2010/1033968 BSF 0727-06
France (N), 2009 La Roche Clermont (Hugo)	2	0.1	0.033	300	fruit	0 1 3 7	0.05 0.04 <u>0.02</u> 0.02	2010/1033968 BSF 0727-07 Late June planting into clay loam
Germany, 2010 Goch (Charentais)	2	0.1	0.033	300	fruit	0 1 4 6	0.03 0.04 <u>0.02</u> < 0.01	2011/1041395 S10-00481 -01
Germany, 2010 Baden-Wurttemberg (Charentaise)	1+ 1	0.097 0.094	0.032 0.032	300 290	fruit	0 1 3 6	0.13 0.06 <u>0.06</u> 0.03	2011/1041881 S10-00481 -01
France (N), 2010 Yvelines (Delta)	2	0.1	0.033	300	fruit	0 1 3 7	0.07 0.04 <u>0.05</u> 0.03	2011/1041881 S10-00481 -02
France (S), 2010 Tarn-et-Garonne Hugo)	2	0.1	0.033	300	fruit	0 1 3 7	0.04 0.02 <u>0.01</u> 0.01	2011/1041881 S10-00481 -03

MELON Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
Italy, 2010 Lombardia (Bacir)	2	0.1	0.033	300	fruit	0 1 3 7	0.01 0.01 0.02 0.01	2011/1041881 S10-00481 -04
Spain, 2010 Los Palacios y Villafranca (Nicolas)	2	0.1	0.033	300	fruit	0 1 2 7	0.03 0.03 0.02 0.01	2011/1041881 S10-00481 -05
Greece, 2010 Thessaloniki (Lavigal)	2	0.1	0.033	300	fruit	0 1 3 7	0.05 0.01 0.02 < 0.01	2011/1041881 S10-00481 -06

Table 49 Residues in outdoor melons (cantaloupes) from supervised trials in North America involving three foliar applications of metrafenone (SC formulation)

MELON Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2010 Maricopa, AZ (Primo)	3	0.32	0.07	386–434	fruit	0	0.17, 0.14	0.15	2013/7001797 10477.10-AZ05
USA, 2010 Riverside, CA (Caravelle)	3	0.33	0.07	466–471	fruit	0	0.21, 0.24	0.23	2013/7001797 10477.10-CA133
USA, 2010 Holtville, CA (Navigator)	3	0.33	0.07	488–498	fruit	0	0.12, 0.14	0.13	2013/7001797 10477.10-CA134
USA, 2010 Parlier, CA (Durango)	3	0.35	0.07	466–471	fruit	0	0.07, 0.1	0.09	2013/7001797 10477.10-CA135
USA, 2010 Tifton, GA (Edisto 47)	3	0.33	0.08	392–405	fruit	0	0.23, 0.33	0.28	2013/7001797 10477.10-GA14
USA, 2010 Salisbury, MD (Athena)	3	0.33	0.08	399–405	fruit	0 1 3 7 10 13	0.21, 0.14 0.12, 0.09 0.04, 0.05 0.04, 0.04 0.02, 0.03 0.03, 0.03	0.18 011 0.04 0.04 0.03 0.03	2013/7001797 10477.10-MD17
USA, 2010 Las Cruces, NM (PMR 45)	3	0.34	0.08	409–435	fruit	0	0.15, 0.12	0.13	2013/7001797 10477.10-NM13
USA, 2010 Freemont, OH (Odyssey)	3	0.34	0.08	426–442	fruit	0	0.04 [a], 0.04 [a]	0.04	2013/7001797 10477.10-OH-18
Canada, 2010 Delhi, ON (Jaipur)	3	0.34	0.085	402–404	fruit	0 1 3 7 11 15	0.13, 0.14 0.11, 0.09 0.08, 0.08 0.06, 0.05 0.03, 0.07 0.04, 0.03	0.13 0.1 0.08 0.05 0.05 0.03	2013/7001797 10477.10-ON20
Canada, 2010 L'Acadie, QC (Athena)	3	0.35	0.08	407–423	fruit	0	0.17, 0.24	0.21	2013/7001797 10477.10-QC10

MELON Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2010 Weslaco, TX (Mission)	3	0.34	0.09	391–396	fruit	0	0.19, 0.17	0.18	2013/7001797 10477.10-TX20
USA, 2010 Weslaco, TX (Sarah's Choice)	3	0.34	0.09	393–396	fruit	0	0.08, 0.08	0.08	2013/7001797 10477.10-TX19

[a] Average results from three replicate analyses

Fruiting vegetables, other than Cucurbits

Results from supervised trials from Europe and the USA on peppers and tomatoes and on mushrooms from Europe were provided to the Meeting.

Mushrooms

In a trial conducted in France with mushroom compost sourced from four different suppliers, one drench application equivalent to 0.05 kg ai metrafenone/100 square metres was applied to the mushroom compost in 15–17 litres water, 20 days after inoculation and mushroom samples (min 0.8 kg) were harvested 10 days after treatment and stored frozen for up to 17 months before analysis using the MRM DFG S19 method to measure metrafenone. The LOQ for this method was 0.1 mg/kg and average procedural recovery rates were 86% and 88% in samples spiked with 0.1 mg/kg and 1.0 mg/kg respectively.

Duplicate samples were also analysed at a separate laboratory after a further 9 months frozen storage using Method 535/1 with a lower LOQ of 00.01 mg/kg and with average procedural recovery rates of 101% and 91% in samples spiked with 0.01 mg/kg and 0.2 mg/kg respectively.

One (5 kg) sample was also taken for processing, with the mushrooms being washed 3–4 times in cold running water, stored for 24 hours in sulphured water and blanched for 15 minutes at 98 °C before cooling and placed in cans with added salt, sugar and citric acid. After sealing, the cans were sterilised at 136 °C for 6 minutes.

Table 50 Residues in indoor mushrooms from supervised trials in Europe involving one application of metrafenone (SC formulation) to mushroom compost

MUSHROOMS Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ 100 m^2	kg ai/hL	water (L/100 m^2)			metrafenone	mean	
GAP: France	1	0.05		15		10			
France, 2009 Chace (Amycel Delta)	1	0.056		16.7	fruit	10	0.17, 0.2	0.19	2011/1151102 2011/1144320 RE09001
France, 2009 St Laurent du Lin (Amycel Delta)	1	0.052		15.3	fruit	10	< 0.1, 0.09	0.1	2011/1151102 2011/1144320 RE09002
France, 2009 Roiffe (Amycel Delta)	1	0.053		15.7	fruit	10	< 0.1, 0.11	0.11	2011/1151102 2011/1144320 RE09003
France, 2009 Longue Jumelles (Amycel Delta)	1	0.051		15.3	fruit canned	10 10	0.1, 0.1 < 0.1, 0.02	0.1 0.02	2011/1151102 2011/1144320 RE09004

Results are duplicate analyses by separate laboratories (different analytical methods and LOQs)
Processing factor (residues in processed commodity/residues in RAC) = 0.16

Peppers

In the European trials on indoor sweet peppers, two foliar applications of 0.15 kg ai/ha metrafenone (SC formulation) in about 1000 L water/ha were applied 7 days apart, using motorized knapsack sprayers. Whole fruit samples (min 1 kg) were frozen within 24 hours of sampling and stored frozen (–18 °C) for up 12 months before analysis for metrafenone using Method 535/3. Average procedural recoveries of metrafenone from samples fortified with 0.01–2.0 mg/kg ranged from 73% to 132% with an overall mean of 96% and the LOQ was 0.01 mg/kg.

In the North American trials on outdoor sweet (bell) peppers and chili (non-bell) peppers, three foliar applications of 0.34 kg ai/ha metrafenone (SC formulation) with added adjuvant were applied at 7 day intervals, using pressurised knapsack sprayers (2–6 nozzles) to apply about 200–300 L/ha. Plot sizes were larger than 28 square metres.

Duplicate whole fruit samples (min 2 kg, 12 large or 24 small fruit) were frozen within 2 hours of sampling and stored frozen (–15 °C) for up 25 months before analysis for metrafenone using the QuEChERS LC-MS/MS method. Average procedural recoveries of metrafenone from samples fortified with 0.01–0.1 mg/kg ranged from 109% to 114% with an overall mean of 112% and the LOQ was 0.01 mg/kg.

Table 51 Residues in indoor sweet peppers from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

PEPPER, SWEET Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
GAP: France	2	0.15				3	RTI 7–10 d	
Germany, 2009 Baden-Wuerttemberg (Golden Calwander)	2	0.15	0.015	1000	fruit	0 1 3 7	0.74 0.7 <u>1.3</u> [a] 1.0[a]	2010/1199010 S09-00770-01
Netherlands 2009 Bemmel (Fantasy)	2	0.15	0.015	1000	fruit	0 1 3 7	0.08 0.06 <u>0.07</u> 0.07	2010/1199010 S09-00770-02
Belgium, 2009 Sint-Katelijine-waver (Morraine)	2	0.15	0.015	1000	fruit	0 1 3 7	0.18 0.17 <u>0.12</u> 0.1	2010/1199010 S09-00770-03
France (N), 2009 Loriet (Spartakus)	2	0.15	0.015	1000	fruit	0 1 3 7	0.33 0.31 <u>0.2</u> 0.18	2010/1199010 S09-00770-04
Italy, 2009 Fondi (San Marco)	2	0.15	0.015	1000	fruit	0 1 4 8	0.09 0.11 <u>0.11</u> 0.1	2010/1199010 S09-00770-05
France (N), 2009 Bioule (Mariner)	2	0.15	0.015	1000	fruit	0 1 3 7	0.1 [a] 0.06 [a] 0.08 <u>0.08</u>	2010/1199010 S09-00770-06
Spain, 2009 Valencia (Filon)	2	0.15	0.015	1000	fruit	0 1 3 7	0.17 0.17 <u>0.21</u> 0.2	2010/1199010 S09-00770-07
Greece, 2009 Thessaloniki (Raikon)	2	0.15	0.015	1000	fruit	0 1 3 7	0.08 0.15 <u>0.1</u> 0.06	2010/1199010 S09-00770-08

[a] Mean of two analyses

Table 52 Residues in outdoor peppers (bell and non-bell) from supervised trials in North America involving three foliar applications of metrafenone (SC formulation)

PEPPER Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2010 Madera, CA (Jupiter) Bell pepper	3	0.34	0.12	280	fruit	0 3 7 10 14	0.39, 0.43 0.16, 0.18 0.11, 0.08 0.11, 0.08 0.04, 0.04	0.41 0.17 0.1 0.09 0.04	2013/7000577 R100014
USA, 2010 Chula, GA (Bell) Bell pepper	3	0.34	0.15	230	fruit	0 7	0.47, 0.33 0.17, 0.27	0.4 0.22	2013/7000577 R100015
USA, 2010 Shady Grove, FL (Aristotle) Bell pepper	3	0.33	0.15	220	fruit	0 7	0.18, 0.11 0.13, 0.11	0.15 0.12	2013/7000577 R100016
USA, 2010 Marengo, IL (Lady Bell) Bell pepper	3	0.33	0.15	230	fruit	0 7	0.33, 0.17 0.2, 0.19	0.25 0.19	2013/7000577 R100017
USA, 2010 Hinton, OK (California Wonder) Bell pepper	3	0.34	0.14	250	fruit	0 7	0.33, 0.21 0.1, 0.1	0.27 0.1	2013/7000577 R100018
USA, 2010 Madera, CA (Jupiter) Bell pepper	3	0.36	0.12	280	fruit	0 7	0.51, 0.34 0.2, 0.27	0.43 0.23	2013/7000577 R100019
USA, 2010 Chula,GA (Antillano) Non-bell pepper	3	0.34	0.15	230	fruit	0 7	0.37, 0.34 0.17, 0.12	0.35 0.14	2013/7000577 R100020
USA, 2010 Larned, KS (Jalapeno M) Non-bell pepper	3	0.34	0.16	210	fruit	0 7	0.07, 0.1 0.06, 0.07	0.08 0.07	2013/7000577 R100021
USA, 2010 Madera, CA (Jalapeno RPP7072) Non-bell pepper	3	0.34	0.12	280	fruit	0 7	0.33, 0.67 0.3, 0.29	0.5 0.3	2013/7000577 R100022

Tomato

In the European trials on outdoor and indoor tomatoes, two foliar applications of 0.225 kg ai/ha metrafenone (SC formulation) in about 1500 L water/ha (0.015 kg ai/hL) were applied 7 days apart, using motorized knapsack (1–2 nozzle) or mini-boom (6-nozzle) sprayers. Whole fruit samples (min 1 kg) were frozen within 24 hours of sampling and stored frozen (–18 °C) for up 12 months before analysis for metrafenone using Method 535/3. Average procedural recoveries of metrafenone from samples fortified with 0.01–1.0 mg/kg ranged from 78% to 111% with an overall means of 102% in the outdoor trials and 99% in the indoor trials. The LOQ was 0.01 mg/kg.

In the North American trials on outdoor tomatoes (large and small fruited varieties), three foliar applications of 0.34 kg ai/ha metrafenone (SC formulation) with added adjuvant were applied at 6–8 day intervals, using knapsack or tractor-mounted boom sprayers (3–11 nozzles) to apply about 300–800 L/ha. Plot sizes were larger than 30 square metres.

Duplicate fruit samples (min 2 kg, 12 large or 24 small fruit) were frozen within 3 hours of sampling and stored frozen (–15 °C) for up 24 months before analysis for metrafenone using the QuEChERS LC-MS/MS method. Average procedural recoveries of metrafenone from samples fortified with 0.01–0.1 mg/kg ranged from 91% to 118% with an overall mean of 105% and the LOQ was 0.01 mg/kg.

Table 53 Residues in outdoor tomatoes from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

TOMATO Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
GAP: Spain	2		0.015			3		
France, 2009 Lot et-Garonne (Perfect Peel)	1+ 1	0.23 0.22	0.015 0.015	1540 1480	fruit	0 1 3 7	0.09 0.11 0.08 0.05	2010/1193371 S09-00772-01
Greece, 2009 Thessaloniki (Meteor)	2	0.23	0.015	1500	fruit	0 1 4 7	< 0.01 < 0.01 0.02 0.02	2010/1193371 S09-00772-02
Italy, 2009 Granarola (Guadalete)	1+ 1	0.23 0.21	0.015 0.015	1560 1430	fruit	0 1 4 7	0.14 0.15 0.05 0.05	2010/1193371 S09-00772-03
Spain, 2009 Remolinos (Guadivia)	2	0.23	0.015	1500	fruit	0 1 3 7	0.06 0.06 0.05 0.05	2010/1193371 S09-00772-04
France (S), 2010 Tarn-et-Garonne (Perfect Peel)	2	0.23	0.015	1500	fruit	0 1 3 7	0.31 0.25 0.15 0.07	2011/1041882 S10-00480-01
Greece, 2010 Thessaloniki (Meteor)	2	0.23	0.015	1500	fruit	0 1 4 7	< 0.01 0.06 0.06 0.06	2011/1041882 S10-00480-02
Italy, 2010 Bologna (Gigantico)	2	0.23	0.015	1500	fruit	0 1 3 7	0.14 0.1 0.07 0.05	2011/1041882 S10-00480-03
Spain, 2010 Remolinos (H-9036)	2	0.23	0.015	1500	fruit	0 1 3 7	0.12 0.12 <u>0.06</u> 0.04	2011/1041882 S10-00480-04

Table 54 Residues in indoor tomatoes from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

TOMATO Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)	Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	
GAP: France GAP: Spain	2 2	0.225	0.015 0.015			3 3	RTI: 7–10d	
France (N), 2009 Loiret (Recento)	2	0.22	0.015	1480	fruit	0 1 3 7	0.22 0.21 <u>0.17</u> 0.15	2010/1199009 S09-00769-01
Netherlands, 2009 Huissen (Tourance)	2	0.225	0.015	1500	fruit	0 1 3 7	0.09 0.14 <u>0.1</u> 0.09	2010/1199009 S09-00769-02
Germany, 2009 Heidelburg (Sakura)	2	0.22	0.015	1500	fruit	0 1 3 7	0.14 0.12 <u>0.1</u> 0.11	2010/1199009 S09-00769-03
Belgium, 2009 St-Katelijine-waver (Tricia)	1+ 1	0.22 0.21	0.015	1450 1400	fruit	0 1 3 7	0.19 0.15 0.15 <u>0.16</u>	2010/1199009 S09-00769-04
France (N), 2009 Bouloc (Grourdena)	2	0.225	0.015	1500	fruit	0 1 3 7	0.1 0.13 <u>0.1</u> 0.1	2010/1199009 S09-00769-05
Italy, 2009 Fondi (Caramba)	2	0.225	0.015	1500	fruit	0 1 3 7	0.1 0.17 <u>0.09</u> 0.09	2010/1199009 S09-00769-06
Spain, 2009 Valencia (Rambo)	1+ 1	0.23 0.2	0.015 0.015	1500 1320	fruit	0 1 3 7	0.07 0.07 <u>0.09</u> 0.07	2010/1199009 S09-00769-07
Greece, 2009 Thessaloniki (Optima)	2	0.225	0.015	1500	fruit	0 1 3 7	0.08 0.03 <u>0.06</u> 0.06	2010/1199009 S09-00769-08

Table 55 Residues in outdoor tomatoes from supervised trials in North America involving three foliar applications of metrafenone (SC formulation)

TOMATO Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2010 Tifton, GA (Amelia) large fruited	3	0.34	0.11	300	fruit	0 8	0.09, 0.11 0.01, 0.01	0.1 0.01	2013/7001658 10467.10- GA13
USA, 2010 Davis, CA (Sun 6366) processing	3	0.34	0.11	300	fruit	0 6	0.22, 0.18 0.11, 0.12	0.2 0.12	2013/7001658 10467.10- CA127

TOMATO Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2010 Clinton, NC (Amelia) large, fruited	3	0.34	0.09	380	fruit	0 6	0.08, 0.08 0.05, 0.03	0.08 0.04	2013/7001658 10467.10- NC28
USA, 2010 Las Cruces, NM (Celebrity) large-fruited	3	0.34	0.04	840	fruit	0 6	0.11, 0.11 0.11, 0.08	0.11 0.09	2013/7001658 10467.10- NM12
USA, 2010 Holt, MI (Mountain Spring) large-fruited	3	0.34	0.11	300	fruit	0 6	0.15, 0.19 0.07, 0.11	0.17 0.09	2013/7001658 10467.10- MI42
USA, 2010 Maricopa, AZ (Phoenix) large-fruited	4	0.34	0.09	360	fruit	0 7	0.1, 0.11 0.03, 0.03	0.11 0.03	2013/7001658 10467.10- AZ04
USA, 2010 Davis, CA (Shady Lady) large-fruited	3	0.34	0.11	310	fruit	0 7	0.17, 0.18 0.09, 0.08	0.18 0.09	2013/7001658 10467.10- CA125
USA, 2010 Holtville, CA (Shady Lady) large-fruited	3	0.34	0.11	300	fruit	0 7	0.2, 0.29 0.1, 0.07	0.25 0.09	2013/7001658 10467.10- CA119
USA, 2010 Freemont, OH (Heinz 3402) processing	3	0.34	0.08	430	fruit	0 6	0.09, 0.09 0.04, 0.04	0.09 0.04	2013/7001658 10467.10- OH17 rain over picking
USA, 2010 Freeville, NY (Scarlet Red) processing	3	0.34	0.06	580	fruit	0 8	0.29, 0.28 0.14, 0.19	0.29 0.16	2013/7001658 10467.10- NY27
USA, 2010 Parlier, CA (AB-2) processing	3	0.34	0.09	390	fruit	0 7	0.09, 0.12 0.05, 0.05	0.11 0.05	2013/7001658 10467.10- CA120
USA, 2010 Riverside, CA (Celebrity) large-fruited	3	0.34	0.07	470	fruit	0 6	0.11, 0.08 0.05, 0.06	0.1 0.05	2013/7001658 10467.10- CA122
USA, 2010 Parlier, CA (H 3155) processing	3	0.34	0.07	500	fruit	0 7	0.13, 0.08 0.03, 0.03	0.1 0.03	2013/7001658 10467.10- CA121
USA, 2010 Riverside, CA (Sun 6788) processing	3	0.34	0.07	470	fruit	0 7	0.24, 0.23 0.09, 0.1	0.23 0.09	2013/7001658 10467.10- CA126
USA, 2010 Davis, CA (Sun 6788) processing	3	0.34	0.11	310	fruit	0 7	0.25, 0.26 0.14, 0.12	0.26 0.13	2013/7001658 10467.10- CA123
USA, 2010 Holtville, CA (Naomi) small fruited	3	0.34	0.11	310	fruit	0 7	0.4, 0.45 0.11, 0.18	0.43 0.15	2013/7001658 10467.10- CA128

TOMATO Country, year Location (Variety)	Application				Matrix	DAT	Residues (mg/kg)		Reference & Comments
	no	kg ai/ha	kg ai/hL	water (L/ha)			metrafenone	mean	
USA, 2010 Holtville, CA (Hypeel 45) processing	3	0.34	0.1	340	fruit	0 1 3 6 10 12	0.15 [a], 0.05 [a] 0.04, 0.07 0.06, 0.05 0.03, 0.03 0.02, 0.01 0.02, 0.01	0.1 0.05 0.06 0.03 0.02 0.02	2013/7001658 10467.10- CA124
USA, 2010 Citra, FL (BHN602) large-fruited	3	0.34	0.05	620	fruit	0 1 3 7 9 14	0.1, 0.04 0.09, 0.06 0.07, 0.08 0.07, 0.11 0.07, 0.04 0.02, 0.03	0.07 0.07 0.08 0.09 0.05 0.03	2013/7001658 10467.10- FL38
USA, 2010 Citra, FL (Jolly Elf) small-fruited	3	0.34	0.05	620	fruit	0 7	0.18, 0.26 0.1, 0.17	0.22 0.11	2013/7001658 10467.10- FL39

[a] Sample re-injected in duplicate to confirm initial result.

Cereal grains

Results from supervised trials from Europe on wheat and barley were provided to the Meeting.

Wheat

In the European trials on winter and spring wheat, two foliar applications of 0.15–0.2 kg ai/ha metrafenone were applied by knapsack or plot sprayers with 4–12 nozzle booms to apply 20–400 Litres spray mix/ha to plots larger than 30 square metres. Generally, applications were made during the stem elongation period (BBCH 30–39) and again 4–8 weeks later (towards the end of flowering or later), up to about 5–6 weeks before harvest. In some trials, different formulations (SC, EC, SE) of metrafenone, alone or in combination with other fungicides were applied to separate plots.

Samples of grain (min 1 kg) were taken at maturity, frozen within 24 hours and stored at or below –18 °C for up 29 months before analysis. In the trials conducted before 2004, samples were analysed for metrafenone and the metabolites CL 3000402, CL 434223 and CL 376991 using Method RLA 12619 and in the later trials, Method 535/3 was used to measure only the parent compound. Average procedural recoveries of metrafenone from samples fortified with 0.01 and 0.1 mg/kg ranged from 71% to 104% and the LOQ was 0.01 mg/kg.

Table 56 Residues in wheat grain from supervised trials in Europe involving 1–3 foliar applications of metrafenone

WHEAT Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
GAP: Poland		2	0.15				35		
Netherlands, 2000 Biddinghuizen (Tremie)	300SC (09957)	2	0.16	310	BBCH 76	grain	34	0.04	2001/7000487 00-770-01 RLA 12619.02V
	300SC (10358)	2	0.15	310	BBCH 76	grain	33	0.04	

WHEAT Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
France (N), 2000 Fains (Charger)	300SC (09957)	2	0.14	330	BBCH 77	grain	33	0.03	2001/7001657 00-831-346 RLA 12619.02V
	300SC (10358)	2	0.14	330	BBCH 77	grain	33	0.01	
UK, 2000 Burton-upon-Trent (Aardvark)	300SC (09957)	2	0.15	200	BBCH 79–83	grain	41	0.03	2001/7001658 00-832-01 RLA 12619.02V
	300SC (10358)	2	0.15	200	BBCH 79–83	grain	41	0.04	
Germany, 2000 Schwabenheim (Monopol)	300SC (09957)	2	0.15	300	BBCH 75	grain	35	< 0.01	2002/7004672 00-922-01 RLA 12619.02V
	300SC (10358)	2	0.15	300	BBCH 75	grain	35	< 0.01	
Germany, 1999 Zulpich-Mulheim (Bandit)	300SC (09957)	3	0.2	400	BBCH 65	grain	35 41	< 0.01 < 0.01	2001/7001675 99-106-01 RLA 12619.02V
Germany, 2000 Haimhausen (Tambor)	300SC (09957)	2	0.2	390	BBCH 69	grain	35 41	< 0.01 < 0.01	2001/7001675 99-106-02 RLA 12619.02V
UK, 1999 Newton (Consort)	300SC (09957)	2	0.2	300	BBCH 59–61	grain	41 49	< 0.01 < 0.01	2002/7004680 99-107-01 RLA 12619.02V
Netherlands, 1999 Biddinghuizen (Vivant)	300SC (09957)	2	0.2	270	BBCH 75	grain	35 41	0.01 < 0.01	2002/7004745 99-108-01 RLA 12619.02V
France (N), 2000 Le Plessis Hebert (Isengrain)	300SC (10358)	2	0.15	370	BBCH 73	grain	35	< 0.01	2001/7001660 00-834-347 RLA 12619.02V
Denmark, 2005 Middelfart (Kris)	75SE	2	0.15	200	BBCH 69	grain	35 42	< 0.01 0.01	2005/7004267 ALB/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	grain	35 42	< 0.01 < 0.01	
	300SE	2	0.15	200	BBCH 69	grain	35 42	< 0.01 < 0.01	
Germany, 2005 Wurttenberg (Isengrain)	75SE	2	0.15	200	BBCH 69	grain	27 34 41	< 0.01 0.01 0.02	2005/7004267 DU2/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	grain	27 34 41	< 0.01 < 0.01 0.01	

WHEAT Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
	300SE	2	0.15	200	BBCH 69	grain	27 34 41	0.01 < 0.01 0.01	
France (N), 2005 Villeveque (Royssac)	75SE	2	0.15	200	BBCH 69	grain	35 42	< 0.01 < 0.01	2005/7004267 FBM/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	grain	35 42	< 0.01 < 0.01	
	300SE	2	0.15	200	BBCH 69	grain	35 42	< 0.01 < 0.01	
UK, 2003 Bicester (Malacca)	100EC	2	0.15	300	BBCH 83	grain	34 41	0.01 < 0.01	2004/1010542 OAT/02/03 Method 535/0
	300SC	2	0.15	300	BBCH 83	grain	34 41	0.01 < 0.01	
Denmark, 2002 Fuenen (Vinjett)	300SC	2	0.15	300	BBCH 51	grain	59	< 0.01	2003/1001354 ALB/01/02 Method 993/0 RLA 12619.03V
		1	0.15	300	BBCH 51	grain	59	< 0.01	
Germany, 2002 Baden-Wurttemberg (Transit)	300SC	2	0.15	300	BBCH 49	grain	58	< 0.01	2003/1001354 DU2/03/02 Method 993/0 RLA 12619.03V
	300SC	1	0.15	300	BBCH 49	grain	58	< 0.01	
Denmark, 2003 Fuenen (Triso) spring wheat	100EC	2	0.15	300	BBCH 77	grain	35 41	< 0.01 < 0.01	2004/1010542 ALB/01/03 Method 535/0
	300SC	2	0.15	300	BBCH 77	grain	35 41	< 0.01 0.01	
France S), 2000 Marguet-Meymes (Aztec)	300SC (09957)	2	0.16 0.145	370 350	BBCH 77–83	grain	29	< 0.01	2001/7001656 00-833-290 RLA 12619.02V
	300SC (10358)	2	0.15 0.14	350 340	BBCH 77–83	grain	29	< 0.01	
France (S), 2000 Mormes (Sideral)	300SC (09957)	2	0.15 0.14	360 330	BBCH 77–83	grain	23	< 0.01	2001/7001656 00-833-291 RLA 12619.02V
	300SC (10358)		0.15 0.14	345 338	BBCH 77–83	grain	23	0.01	
France (S), 2000 Pernes les Fontaines (Florence Aurore)	300SC (09957)	2	0.15	400	BBCH 83	grain	34	0.01	2001/7001656 00-833-643 RLA 12619.02V
	300SC (10358)		0.15	400	BBCH 83	grain	34	< 0.01	

WHEAT Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
France (S), 2000 Le Thor (Manital)	300SC (09957)	2	0.15	400	BBCH 83	grain	33	< 0.01	2001/7001656 00-833-644 RLA 12619.02V
	300SC (10358)		0.15 0.16	400 420	BBCH 83	grain	33	0.01 (0.01)	
France (S), 1999 Averon Bergelle (Soissons Real)	300SC (09957)	2	0.2	400	BBCH 65–69	grain	35 42	0.01 < 0.01	2002/7004740 99-109-295 RLA 2619.02V
France (S), 1999 Espas (Soissons)	300SC (09957)	2	0.2	400	BBCH 65–69	grain	35 42	0.01 < 0.01	2002/7004740 99-109-296 RLA 2619.02V
France (S), 1999 Le Thor (Manital)	300SC (09957)	2	0.2	400	BBCH 75–77	grain	35 42	< 0.01 < 0.01	2002/7004740 99-109-631 RLA 2619.02V
France (S), 1999 Orange (Grenat)	300SC (09957)	2	0.2	400	BBCH 75–77	grain	35 42	< 0.01 < 0.01	2002/7004740 99-109-632 RLA 2619.02V
00-923-292 France (S), 2000 Averon-Bergelle (Soissons)	300SC (10358)	2	0.16	350	BBCH 75	grain	33	< 0.01	2001/7001676 00-923-292 RLA 2619.02V
France (S), 2000 Ausonne (Courtaud)	300SC	2	0.14 0.15	280 290	BBCH 75	grain	35	0.03	2002/7004890 FTL/32/01 RLA 12619.02V
France (S), 2005 Rhone-Alpes (Caphorn)	75SE	2	0.15	200	BBCH 69	grain	28 35 42	< 0.01 < 0.01 < 0.01	2005/7004267 FBD/33/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	grain	28 35 42	< 0.01 < 0.01 < 0.01	
	300SE	2	0.15	200	BBCH 69	grain	28 35 42	< 0.01 < 0.01 < 0.01	
Spain, 2003 Salteras (Vitromax) spring wheat	100EC	2	0.15	300	BBCH 69	grain	35 42	< 0.01 < 0.01	2004/1010542 ALO/03/03 Method 535/0
	300SC	2	0.15	300	BBCH 69	grain	35 42	< 0.01 < 0.01	
France (S), 2003 Ausonne (Nefer)	100EC	2	0.15	300	BBCH 73	grain	35 42	< 0.01 < 0.01	2004/1010542 FTL/03/03 Method 535/0
	300SC	2	0.15	300	BBCH 73	grain	35 42	< 0.01 < 0.01	

Values in (brackets) are residues of the CL 3000402 metabolite found above LOQ

Barley

In the European trials on winter and spring barley, two foliar applications of 0.15–0.2 kg ai/ha metrafenone were applied by knapsack or plot sprayers with 5–12 nozzle booms to apply 200–400 Litres spray mix/ha to plots larger than 30 square metres. Generally, applications were made 4–8 weeks apart over the flowering and grain development stages (BBCH 61–83). In some trials, different formulations (SC, EC, SE) of metrafenone, alone or in combination with other fungicides were applied to separate plots.

Samples of grain (min 1 kg) were taken at maturity, frozen within 24 hours and stored at or below –18 °C for up 25 months before analysis. In the trials conducted before 2004, samples were analysed for metrafenone and the metabolites CL 3000402, CL 434223 and CL 376991 using Method RLA 12619 and in the later trials, Method 535/3 was used to measure only the parent compound. Average procedural recoveries of metrafenone from samples fortified with 0.01 and 0.1 mg/kg ranged from 71% to 108% and the LOQ was 0.01 mg/kg.

Table 57 Residues in barley grain from supervised trials in Europe involving 1–3 foliar applications of metrafenone.

BARLEY Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
GAP: Poland		2	0.15				35		
Germany, 2005 Gerolsheim (Scarlett)	75SE	2	0.15	200	BBCH 69	grain	29 36 42	< 0.01 < 0.01 < 0.01	2005/7004267 DU4/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	grain	29 36 42	< 0.01 0.02 < 0.01	
	300SE	2	0.15	200	BBCH 69	grain	29 36 42	0.01 <u>0.02</u> < 0.01	
Sweden, 2005 Bjarred (Prestige)	75SE	2	0.15	200 200	BBCH 69	grain	36 43	<u>0.09</u> 0.06	2005/7004267 HUS/07/05 Method 535/0
	100SC	2	0.15	200 200	BBCH 69	grain	29 36 43	0.94 0.05 0.04	
	300SE	2	0.15	200 200	BBCH 69	grain	36 43	0.04 0.02	
UK, 2005 Bicester (Pearl)	75SE	2	0.15	200 200	BBCH 73	grain	29 36 42	0.05 0.05 0.02	2005/7004267 OAT/16/05 Method 535/0
	100SC	2	0.15	200 200	BBCH 73	grain	28 35 42	0.06 0.04 0.02	
	300SE	2	0.15	200 200	BBCH 73	grain	28 35 42	0.09 <u>0.05</u> 0.04	
France (N), 2002 Alsace (Astoria) spring barley	300SC	2	0.15	300	BBCH 56	grain	34	<u>< 0.01</u>	2003/1001354 FAN/02/02 Method 993/0 RLA 12619.03V
	300SC	1	0.15	300	BBCH 56	grain	39	< 0.01	

BARLEY Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
UK, 2002 Oxfordshire (Siberia)	300SC	2	0.15	300	BBCH 59	grain	39	0.02	2003/1001354 OAT/05/02 Method 993/0 RLA 12619.03V
	300SC	1	0.15	300	BBCH 59	grain	39	0.02	
Germany, 2003 Lentzke (Cadesse)	100EC	2	0.15	300	BBCH 69	grain	35 42	0.01 0.02	2004/1010542 ACK/04/03 Method 535/0
	300SC	2	0.15	300	BBCH 69	grain	35 42	0.06 0.05	
France (N), 2003 Seebach (Astoria) spring barley	100EC	2	0.15	300	BBCH 73	grain	36 42	0.02 0.05	2004/1010542 FAN/05/03 Method 535/0
	300SC	2	0.15	300	BBCH 73	grain	36 42	0.02 0.05	
Germany, 1999 Euskirchen-Oberwichterich (Uschi)	300SC	3	0.2	400	BBCH 65	grain	35 44	0.04 0.04	2001/7001659 99-111-01 RLA 12619.02V
Germany, 1999 Gemarkung (Duet)	300SC	2	0.2	390	BBCH 61	grain	35 42	0.02 0.03	2001/7001659 99-111-02 RLA 12619.02V
Germany, 1999 Ramsen (Angora)	300SC	2	0.2	300	BBCH 69	grain	36 44	0.09 0.07	2001/7001659 99-111-03 RLA 12619.02V
France (N), 2000 Bonnieres Sur Seine (Esterel)	300SC (09957)	1+ 1	0.13 0.14	310 350	BBCH 77	grain	36	0.15 (0.01)	2002/7004445 00/835/355 RLA 12619.02V
	300SC (10358)	2	0.14	340	BBCH 77	grain	36	0.15 (0.01)	
Germany, 2000 Obersteinach (Hanna)	300SC (09957)	1+ 1	0.15 0.14	300 290	BBCH 77	grain	42	0.01 (0.02)	2002/7004463 00/837/01 RLA 12619.02V
	300SC (10358)	2	0.15	300	BBCH 77	grain	42	0.11 (0.01)	
UK 2000 Lichfield (Jewel)	300SC (09957)	2	0.15	200	BBCH 77–79	grain	35	0.14 (0.02)	2002/7004529 00/836/01 RLA 12619.02V
	300SC (10358)	2	0.15	200	BBCH 77–79	grain	35	0.16 (0.01)	
UK, 2000 Bradwall (Jewel)	300SC (09957)	2	0.15	200	BBCH 75–77	grain	35	0.07	2002/7004529 00/836/02 RLA 12619.02V
	300SC (10358)	2	0.15	200	BBCH 75–77	grain	35	0.06	

BARLEY Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
UK, 1999 Newton (Intro)	300SC	2	0.2	300	BBCH 61	grain	43 50	0.02 (0.01) 0.02	2002/7004681 99-110-01 RLA 12619.02V
France (N) 2000 Mousseaux (Majestic)	300SC	2	0.15	370	BBCH 77	grain	36	0.4 (0.02)	2002/7004922 00/840/356 RLA 12619.02V
France (S), 2000 LaGardelle Sur Leze (Nevada)	300 SC	2	0.15 0.14	300 280	BBCH 73	grain	35	0.05	2002/7004890 FTL/31/01 RLA 12619.02V
France (S), 2005 Genissieux (Orelie)	75SE	2	0.15	200 200	BBCH 69	grain	35 41	0.02 0.03	2005/7004267 FBD/34/05 Method 535/0
	100SC	2	0.15	200 200	BBCH 69	grain	29 35 41	0.4 0.02 0.01	
	300SE	2	0.15	200 200	BBCH 69	grain	35 41	0.03 0.03	
France (S), 2003 Rhone-Alpes (Orelie)	100EC	2	0.15	300	BBCH 83	grain	35 42	0.03 0.02	2004/1010542 FBD/02/03 Method 535/0
	300SC	2	0.15	300	BBCH 83	grain	35 42	0.08 0.07	
Italy, 2003 Pozzolo (Prosa) spring barley	100EC	2	0.15	300	BBCH 55	grain	35 42	< 0.01 < 0.01	2004/1010542 ITA/03/03 Method 535/0
	300SC	2	0.15	300	BBCH 55	grain	35 42	0.02 < 0.01	
France (S), 1999 Margouet-Meynes (Sunrise)	300SC	2	0.2	400	BBCH 60–61	grain	34 40	0.08 0.12	2001/7000488 99-112-297 RLA 12619.02V
France (S), 1999 Espas (Systel)	300SC	2	0.2	400	BBCH 65–69	grain	34 40	0.05 0.12	2001/7000488 99-112-298 RLA 12619.02V
France (S), 1999 Courthezon (Baraka)	300SC	2	0.2	400	BBCH 75–77	grain	35 42	0.08 0.06	2001/7000488 99-112-633 RLA 12619.02V
France (S), 1999 Althen des Paluds (Baraka)	300SC	2	0.2	400	BBCH 75–77	grain	35 42	0.04 0.04	2001/7000488 99-112-634 RLA 12619.02V
France (S), 2000 Averon-Bergelle (Plantine)	300SC (09957)	2	0.16	240	BBCH 77–83	grain	34	0.13 (0.01)	2002/7004525 00/839/294 RLA 12619.02V
	300SC (10358)	2	0.16	240	BBCH 77–83	grain	34	0.1 (0.01)	

BARLEY Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
France (S), 2000 Saumane (Baraka)	300SC (09957)	2	0.15	410	BBCH 77–83	grain	36 36	0.06 (0.01)	2002/7004525 00/839/646 RLA 12619.02V
	300SC (10358)	1+1	0.15 0.16	410 420	BBCH 77–83	grain	36	0.05 (0.01)	
France (S), 2000 Althen Des Paluds (Baraka)	300SC (09957)	2	0.15	400	BBCH 83	grain	34	0.04	2002/7004525 00/839/645 RLA 12619.02V
	300SC (10358)	1+1	0.16 0.15	420 410	BBCH 83	grain	34	0.04	
France (S), 2000 Bedarrides (Baraka)	300SC	1+1	0.14 0.15	390 400	BBCH 77–83	grain	35	0.23	2002/7004744 00-841-647 RLA 12619.02V

Values in (brackets) are residues of the CL 3000402 metabolite found above LOQ

Animal feeds

Wheat forage, hay and straw

In some of the above European trials on winter and spring wheat, whole plants (without roots) were sampled 0–14 days after the last application and again 28–35 DALT, with these later samples being separated into ears and the rest-of- the-plant ('foliage'). Samples were frozen within 24 hours and stored at or below -18 °C for up 29 months before analysis. In the trials conducted before 2004, samples were analysed for metrafenone and the metabolites CL 3000402, CL 434223 and CL 376991 using Method RLA 12619 and in the later trials, Method 535/3 was used to measure only the parent compound. Average procedural recoveries of metrafenone from samples fortified with 0.01–20 mg/kg ranged from 71% to 104% and the LOQs were 0.1 mg/kg.

Table 58 Residues in wheat forage from supervised trials in Europe involving 1–3 foliar applications of metrafenone

WHEAT FORAGE Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
GAP: Poland		2	0.15				35		
Germany, 1999 Zulpich-Mulheim (Bandit)	300SC (09957)	3	0.2	400	BBCH 65	plant ears foliage	–0 0 14 28 28	< 0.1 < 0.1 < 0.1 < 0.1 0.15	2001/7001675 99-106-01 RLA 12619.02V
Germany, 2000 Haimhausen (Tambor)	300SC (09957)	2	0.2	390	BBCH 69	plant ears foliage	–0 0 14 28 28	< 0.1 < 0.1 < 0.1 < 0.1 0.13	2001/7001675 99-106-02 RLA 12619.02V

WHEAT FORAGE Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
UK, 1999 Newton (Consort)	300SC (09957)	2	0.2	300	BBCH 59–61	plant ears foliage	–0 0 14 28 35 28 35	0.17 2.6 0.76 < 0.01 1.4 [a] 1.1 0.04 [a]	2002/7004680 99-107-01 RLA 12619.02V
Netherlands, 1999 Biddinghuizen (Vivant)	300SC (09957)	2	0.2	270	BBCH 75	plant ears foliage	–0 0 13 26 26	0.11 3.3 0.58 0.17 0.94	2002/7004745 99-108-01 RLA 12619.02V
France (N), 2000 Le Plessis Hebert (Isengrain)	300SC (10358)	2	0.15	370	BBCH 73	plant ears foliage	–0 0 14 28 28	< 0.1 <u>2.6</u> 1.62 0.25 1.5	2001/7001660 00-834-347 RLA 12619.02V
Denmark, 2005 Middelfart (Kris)	75SE	2	0.15	200	BBCH 69	foliage ear	0 28 0 28	<u>2.6</u> 1.6 1.1 0.04	2005/7004267 ALB/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	foliage ear	0 28 0 28	2.2 0.86 1.4 0.07	
	300SE	2	0.15	200	BBCH 69	foliage ear	0 28 0 28	2.2 2.0 1.4 0.15	
Germany, 2005 Wurttenberg (Isengrain)	75SE	2	0.15	200	BBCH 69	foliage ear	0 0	1.8 1.3	2005/7004267 DU2/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	foliage ear	0 0	2.1 1.4	
	300SE	2	0.15	200	BBCH 69	foliage ear	0 0	<u>2.6</u> 2.1	
France (N), 2005 Villeveque (Royssac)	75SE	2	0.15	200	BBCH 69	foliage ear	0 28 0 28	2.1 0.93 1.6 0.11	2005/7004267 FBM/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	foliage ear	0 28 0 28	<u>2.8</u> 0.33 1.7 0.09	

WHEAT FORAGE Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
	300SE	2	0.15	200	BBCH 69	foliage ear	0 28 0 28	2.5 1.8 3.6 0.09	
UK, 2003 Bicester (Malacca)	100EC	2	0.15	300	BBCH 83	plant ear foliage	0 27 27	2.0 0.16 2.5	2004/1010542 OAT/02/03 Method 535/0
	300SC	2	0.15	300	BBCH 83	plant ear foliage	0 27 27	1.2 0.17 2.8	
Denmark, 2002 Fuenen (Vinjett)	300SC	2	0.15	300	BBCH 51	plant foliage ear	0 36 36	1.8 0.2 < 0.01	2003/1001354 ALB/01/02 Method 993/0 RLA 12619.03V
		1	0.15	300	BBCH 51	plant foliage ear	0 36 36	2.7 0.09 < 0.01	
Germany, 2002 Baden-Wurttemberg (Transit)	300SC	2	0.15	300	BBCH 49	plant foliage ear	0 35 35	2.0 0.62 < 0.01	2003/1001354 DU2/03/02 Method 993/0 RLA 12619.03V
	300SC	1	0.15	300	BBCH 49	plant foliage ear	0 35 35	1.6 0.46 < 0.01	
Denmark, 2003 Fuenen (Triso) spring wheat	100EC	2	0.15	300	BBCH 77	plant ear foliage	0 28 28	2.7 0.09 0.9	2004/1010542 ALB/01/03 Method 535/0
	300SC	2	0.15	300	BBCH 77	plant ear foliage	0 28 28	3.7 0.24 4.9	
France (S), 1999 Averon Bergelle (Soissons Real)	300SC (09957)	2	0.2	400	BBCH 65–69	plant ears foliage	–0 0 13 28 28	0.11 4.1 1.2 0.23 0.23	2002/7004740 99-109-295 RLA 2619.02V
France (S), 1999 Espas (Soissons)	300SC (09957)	2	0.2	400	BBCH 65–69	plant ears foliage	–0 0 13 28 28	0.13 2.9 1.1 0.13 1.1	2002/7004740 99-109-296 RLA 2619.02V
France (S), 1999 Le Thor (Manital)	300SC (09957)	2	0.2	400	BBCH 75–77	plant ears foliage	–0 0 13 28 28	< 0.1 3.7 0.96 0.19 1.11	2002/7004740 99-109-631 RLA 2619.02V

WHEAT FORAGE Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
France (S), 1999 Orange (Grenat)	300SC (09957)	2	0.2	400	BBCH 75–77	plant ears foliage	–0 0 13 28 28	0.1 3.4 (c=0.1) 1.3 (c=0.14) 0.18 1.9	2002/7004740 99-109-632 RLA 2619.02V
France (S), 2000 Averon-Bergelle (Soissons)	300SC (10358)	2	0.16	350	BBCH 75	plant ears foliage	–0 +0 14 28 28	< 0.1 <u>3.3</u> 0.56 0.18 0.7	2001/7001676 00-923-292 RLA 2619.02V
France (S), 2005 Rhone-Alpes (Caphorn)	75SE	2	0.15	200	BBCH 69	foliage ear	0 0	3.6 1.7	2005/7004267 FBD/33/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	foliage ear	0 0	<u>4.8</u> 2.0	
	300SE	2	0.15	200	BBCH 69	foliage ear	0 0	3.9 2.0	
Spain, 2003 Salteras (Vitromax) spring wheat	100EC	2	0.15	300	BBCH 69	plant ear foliage	0 29 29	<u>3.8</u> 0.45 2.0	2004/1010542 ALO/03/03 Method 535/0
	300SC	2	0.15	300	BBCH 69	plant ear foliage	0 29 29	3.6 0.19 3.5	
France (S), 2003 Ausonne (Nefer)	100EC	2	0.15	300	BBCH 73	plant ear foliage	0 29 29	2.3 0.06 1.8	2004/1010542 FTL/03/03 Method 535/0
	300SC	2	0.15	300	BBCH 73	plant ear foliage	0 29 29	<u>4.3</u> 0.28 5.6	

Values in (brackets) are residues of the CL 3000402 metabolite found above LOQ

Foliage = plants without ears. Also described as ‘culm’ in some studies

[a] Samples may have been transposed

Barley forage

In some of the above European trials on winter and spring barley, whole plants (without roots) were sampled just after the last application and again 28–35 DALT, with these later samples being separated into ears and the rest-of- the-plant ('foliage'). In the trials conducted before 2004, samples were analysed for metrafenone and the metabolites CL 3000402, CL 434223 and CL 376991 using Method RLA 12619 and in the later trials, Method 535/3 was used to measure only the parent compound. All samples were frozen within 24 hours and stored at or below –18 °C for up 25 months before analysis. Average procedural recoveries of metrafenone from samples fortified with 0.01–20 mg/kg ranged from 71% to 108% and the LOQs were 0.1 mg/kg.

Table 59 Residues in barley forage from supervised trials in Europe involving 1–3 foliar applications of metrafenone

BARLEY FORAGE Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
GAP: Poland		2	0.15				35		
Germany, 2005 Gerolsheim (Scarlett)	75SE	2	0.15	200	BBCH 69	plant	0	4.4	2005/7004267 DU4/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	plant	0	4.3	
	300SE	2	0.15	200	BBCH 69	plant	0	5.0	
Sweden, 2005 Bjarred (Prestige)	75SE	2	0.15	200 200	BBCH 69	foliage ear	0 29 0 29	3.8 0.79 2.5 0.22	2005/7004267 HUS/07/05 Method 535/0
	100SC	2	0.15	200 200	BBCH 69	foliage ear	0 0	5.8 2.7	
	300SE	2	0.15	200 200	BBCH 69	foliage ear	0 29 0 29	3.5 0.76 0.73 0.12	
UK, 2005 Bicester (Pearl)	75SE	2	0.15	200 200	BBCH 73	foliage ear	0 0	2.3 2.0	2005/7004267 OAT/16/05 Method 535/0
	100SC	2	0.15	200 200	BBCH 73	foliage ear	0 0	2.5 2.0	
	300SE	2	0.15	200 200	BBCH 73	foliage ear	0 0	2.0 1.3	
France (N), 2002 Alsace (Astoria) spring barley	300SC	2	0.15	300	BBCH 56	plant foliage ear	0 34 34	3.4 < 0.01 < 0.01	2003/1001354 FAN/02/02 Method 993/0 RLA 12619.03V
	300SC	1	0.15	300	BBCH 56	plant foliage ear	0 34 34	2.3 < 0.01 < 0.01	
UK, 2002 Oxfordshire (Siberia)	300SC	2	0.15	300	BBCH 59	plant foliage ear	0 35 35	1.8 0.24 0.03	2003/1001354 OAT/05/02 Method 993/0 RLA 12619.03V

BARLEY FORAGE Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
	300SC	1	0.15	300	BBCH 59	plant foliage ear	0 35 35	2.5 0.28 0.05	
Germany, 2003 Lentzke (Cadesse)	100EC	2	0.15	300	BBCH 69	plant ear foliage	0 28 28	<u>3.1</u> 0.03 0.08	2004/1010542 ACK/04/03 Method 535/0
	300SC	2	0.15	300	BBCH 69	plant ear foliage	0 28 28	2.0 0.11 0.84	
France (N), 2003 Seebach (Astoria) spring barley	100EC	2	0.15	300	BBCH 73	plant ear foliage	0 28 28	2.8 0.36 1.5	2004/1010542 FAN/05/03 Method 535/0
	300SC	2	0.15	300	BBCH 73	plant ear foliage	0 28 28	<u>3.8</u> 0.35 3.3	
Germany, 1999 Euskirchen-Oberwichterich (Uschi)	300SC	3	0.2	400	BBCH 65	plant foliage ear	–0 0 14 28 28	1.5 5.1 1.7 2.3 0.51	2001/7001659 99-111-01 RLA 12619.02V
Germany, 1999 Gemarkung (Duet)	300SC	2	0.2	390	BBCH 61	plant ear foliage	–0 0 14 28 28	< 0.1 <u>4.6</u> 0.83 0.29 0.49	2001/7001659 99-111-02 RLA 12619.02V
Germany, 1999 Ramsen (Angora)	300SC	2	0.2	300	BBCH 69	plant ear foliage	–0 0 14 28 28	0.62 6.8 2.0 1.4 1.9	2001/7001659 99-111-03 RLA 12619.02V
UK, 1999 Newton (Intro)	300SC	2	0.2	300	BBCH 61	plant ear foliage	–0 0 15 27 35 43 50	0.12 4.0 0.37 0.26 0.49 0.8 0.1	2002/7004681 99-110-01 RLA 12619.02V
France (N) 2000 Mousseaux (Majestic)	300SC	2	0.15	370	BBCH 77	plant ear foliage	–0 0 14 28 28	0.14 <u>2.3</u> 1.5 0.87 3.1 (0.25)	2002/7004922 00/840/356 RLA 12619.02V

BARLEY FORAGE Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
France (S), 2005 Genissieux (Orelie)	75SE	2	0.15	200 200	BBCH 69	foliage ear foliage ear	0 0 29 29	4.2 4.4 0.39 0.02	2005/7004267 FBD/34/05 Method 535/0
	100SC	2	0.15	200 200	BBCH 69	foliage ear	0 0	<u>4.6</u> 4.8	
	300SE	2	0.15	200 200	BBCH 69	foliage ear foliage ear	0 0 29 29	3.0 3.8 1.4 0.03	
France (S), 2003 Rhone-Alpes (Orelie)	100EC	2	0.15	300	BBCH 83	plant ear foliage	0 29 29	2.7 0.09 0.78	2004/1010542 FBD/02/03 Method 535/0
	300SC	2	0.15	300	BBCH 83	plant ear foliage	0 29 29	<u>3.7</u> 0.37 3.4	
Italy, 2003 Pozzolo (Prosa) spring barley	100EC	2	0.15	300	BBCH 55	plant ear foliage	0 28 28	<u>5.9</u> 0.05 0.94	2004/1010542 ITA/03/03 Method 535/0
	300SC	2	0.15	300	BBCH 55	plant ear foliage	0 28 28	3.6 0.25 2.7	
France (S), 1999 Margouet-Meynes (Sunrise)	300SC	2	0.2	400	BBCH 60–61	plant foliage ear	–0 0 13 26 26	0.1 4.1 0.86 < 0.1 0.22	2001/7000488 99-112-297 RLA 12619.02V
France (S), 1999 Espas (Systel)	300SC	2	0.2	400	BBCH 65–69	plant foliage ear	–0 0 13 26 26	< 0.1 <u>4.6</u> 0.53 0.63 0.13	2001/7000488 99-112-298 RLA 12619.02V
France (S), 1999 Courthezon (Baraka)	300SC	2	0.2	400	BBCH 75–77	plant foliage ear	–0 0 14 28 28	0.29 (0.16) 2.7 0.9 3.7 0.37	2001/7000488 99-112-633 RLA 12619.02V
France (S), 1999 Althen des Paluds (Baraka)	300SC	2	0.2	400	BBCH 75–77	plant foliage ear	–0 0 14 28 28	< 0.1 1.6 0.88 1.6 (0.13) 0.35	2001/7000488 99-112-634 RLA 12619.02V

BARLEY FORAGE Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
France (S), 2000 Bedarrides (Baraka)	300SC	1+ 1	0.14 0.15	390 400	BBCH 77–83	plant foliage ear	–0 0 14 28 28	< 0.1 2.5 0.82 0.61 0.41	2002/7004744 00-841-647 RLA 12619.02V

Values in (brackets) are residues of the CL 3000402 metabolite found above LOQ
Foliage = plants without ears. Also described as 'culm' in some studies

Wheat hay and straw

In the above European trials on winter and spring wheat, samples of straw (min 0.5 kg) were taken at maturity, and in many cases, whole plants (without roots) were sampled 0–14 days after the last application and again 28–35 DALT, with these later samples being separated into ears and the rest-of-the-plant ('foliage').

Frozen within 24 hours and stored at or below –18 °C for up 29 months before analysis. In the trials conducted before 2004, samples were analysed for metrafenone and the metabolites CL 3000402, CL 434223 and CL 376991 using Method RLA 12619 and in the later trials, Method 535/3 was used to measure only the parent compound.

Average procedural recoveries of metrafenone from samples fortified with 0.01–20 mg/kg ranged from 71% to 104% and the LOQs were 0.1 mg/kg.

Table 60 Residues in wheat fodder from supervised trials in Europe involving 1–3 foliar applications of metrafenone

WHEAT FODDER Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
GAP: Poland		2	0.15				35		
Netherlands, 2000 Biddinghuizen (Tremie)	300SC (09957)	2	0.16	310	BBCH 76	straw	34	0.98	2001/7000487 00-770-01 RLA 12619.02V
	300SC (10358)	2	0.15	310	BBCH 76	straw	33	0.61	
France (N), 2000 Fains (Charger)	300SC (09957)	2	0.14	330	BBCH 77	straw	33	2.3 (0.12)	2001/7001657 00-831-346 RLA 12619.02V
	300SC (10358)	2	0.14	330	BBCH 77	straw	33	1.8 (0.11)	
UK, 2000 Burton-upon-Trent (Aardvark)	300SC (09957)	2	0.15	200	BBCH 79–83	straw	41	2.0 (0.16)	2001/7001658 00-832-01 RLA 12619.02V
	300SC (10358)	2	0.15	200	BBCH 79–83	straw	41	1.7 (0.18)	
Germany, 2000 Schwabenheim (Monopol)	300SC (09957)	2	0.15	300	BBCH 75	straw	35	0.4	2002/7004672 00-922-01 RLA 12619.02V

WHEAT FODDER Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
	300SC (10358)	2	0.15	300	BBCH 75	straw	35	0.67	
Germany, 1999 Zulpich-Mulheim (Bandit)	300SC (09957)	3	0.2	400	BBCH 65	straw	35 41	0.11 0.11	2001/7001675 99-106-01 RLA 12619.02V
Germany, 2000 Haimhausen (Tambor)	300SC (09957)	2	0.2	390	BBCH 69	straw	35 41	< 0.1 < 0.1	2001/7001675 99-106-02 RLA 12619.02V
UK, 1999 Newton (Consort)	300SC (09957)	2	0.2	300	BBCH 59–61	straw	41 49	0.59 0.58	2002/7004680 99-107-01 RLA 12619.02V
Netherlands, 1999 Biddinghuizen (Vivant)	300SC (09957)	2	0.2	270	BBCH 75	straw	35 41	1.1 1.9	2002/7004745 99-108-01 RLA 12619.02V
France (N), 2000 Le Plessis Hebert (Isengrain)	300SC (10358)	2	0.15	370	BBCH 73	straw	35	1.4	2001/7001660 00-834-347 RLA 12619.02V
Denmark, 2005 Middelfart (Kris)	75SE	2	0.15	200	BBCH 69	straw	35 42	1.0 1.2	2005/7004267 ALB/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	straw	35 42	1.6 0.86	
	300SE	2	0.15	200	BBCH 69	straw	35 42	3.1 2.8	
Germany, 2005 Wurttenberg (Isengrain)	75SE	2	0.15	200	BBCH 69	straw	27 34 41	0.88 0.68 0.7	2005/7004267 DU2/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	straw	27 34 41	0.76 0.71 0.76	
	300SE	2	0.15	200	BBCH 69	straw	27 34 41	2.3 1.8 1.4	
France (N), 2005 Villeveque (Royssac)	75SE	2	0.15	200	BBCH 69	straw	35 42	0.9 1.3	2005/7004267 FBM/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	straw	35 42	0.81 1.2	
	300SE	2	0.15	200	BBCH 69	straw	35 42	3.0 3.5	
UK, 2003 Bicester (Malacca)	100EC	2	0.15	300	BBCH 83	straw	34 41	2.6 3.4	2004/1010542 OAT/02/03 Method 535/0
	300SC	2	0.15	300	BBCH 83	straw	34 41	3.6 2.9	

WHEAT FODDER Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
Denmark, 2002 Fuenen (Vinjett)	300SC	2	0.15	300	BBCH 51	straw	59	0.11	2003/1001354 ALB/01/02 Method 993/0 RLA 12619.03V
		1	0.15	300	BBCH 51	straw	59	0.1	
Germany, 2002 Baden-Wurttemberg (Transit)	300SC	2	0.15	300	BBCH 49	straw	58	0.23	2003/1001354 DU2/03/02 Method 993/0 RLA 12619.03V
	300SC	1	0.15	300	BBCH 49	straw	58	0.14	
Denmark, 2003 Fuenen (Triso) spring wheat	100EC	2	0.15	300	BBCH 77	straw	35 41	0.49 0.47	2004/1010542 ALB/01/03 Method 535/0
	300SC	2	0.15	300	BBCH 77	straw	35 41	3.6 2.4	
France S), 2000 Marguet-Meymes (Aztec)	300SC (09957)	2	0.16 0.145	370 350	BBCH 77–83	straw	29	1.3 [0.11]	2001/7001656 00-833-290 RLA 12619.02V
	300SC (10358)	2	0.15 0.14	350 340	BBCH 77–83	straw	29	1.1	
France (S), 2000 Mormes (Sideral)	300SC (09957)	2	0.15 0.14	360 330	BBCH 77–83	straw	23	1.6	2001/7001656 00-833-291 RLA 12619.02V
	300SC (10358)		0.15 0.14	345 338	BBCH 77–83	straw	23	1.1	
France (S), 2000 Pernes les Fontaines (Florence Aurore)	300SC (09957)	2	0.15	400	BBCH 83	straw	34	1.1	2001/7001656 00-833-643 RLA 12619.02V
	300SC (10358)		0.15	400	BBCH 83	straw	34	1.1	
France (S), 2000 Le Thor (Manital)	300SC (09957)	2	0.15	400	BBCH 83	straw	33	2.1	2001/7001656 00-833-644 RLA 12619.02V
	300SC (10358)		0.15 0.16	400 420	BBCH 83	straw	33	1.7	
France (S), 1999 Averon Bergelle (Soissons Real)	300SC (09957)	2	0.2	400	BBCH 65–69	straw	35 42	0.89 0.88	2002/7004740 99-109-295 RLA 2619.02V
France (S), 1999 Espas (Soissons)	300SC (09957)	2	0.2	400	BBCH 65–69	straw	35 42	1.1 1.0	2002/7004740 99-109-296 RLA 2619.02V
France (S), 1999 Le Thor (Manital)	300SC (09957)	2	0.2	400	BBCH 75–77	straw	35 42	0.8 1.1	2002/7004740 99-109-631 RLA 2619.02V

WHEAT FODDER Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
France (S), 1999 Orange (Grenat)	300SC (09957)	2	0.2	400	BBCH 75–77	straw	35 42	1.7 1.6	2002/7004740 99-109-632 RLA 2619.02V
France (S), 2000 Averon-Bergelle (Soissons)	300SC (10358)	2	0.16	350	BBCH 75	straw	33	0.67	2001/7001676 00-923-292 RLA 2619.02V
France (S), 2000 Ausonne (Courtaud)	300SC	2	0.14 0.15	280 290	BBCH 75	straw	35	1.6 (0.17) [0.11] {0.07}	2002/7004890 FTL/32/01 RLA 12619.02V
France (S), 2005 Rhone-Alpes (Caphorn)	75SE	2	0.15	200	BBCH 69	straw	28 35 42	3.2 2.1 1.6	2005/7004267 FBD/33/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	straw	28 35 42	4.6 2.6 1.5	
	300SE	2	0.15	200	BBCH 69	straw	28 35 42	4.8 6.7 3.8	
Spain, 2003 Salteras (Vitromax) spring wheat	100EC	2	0.15	300	BBCH 69	straw	35 42	1.7 1.3	2004/1010542 ALO/03/03 Method 535/0
	300SC	2	0.15	300	BBCH 69	straw	35 42	0.96 0.99	
France (S), 2003 Ausonne (Nefer)	100EC	2	0.15	300	BBCH 73	straw	35 42	0.95 1.1	2004/1010542 FTL/03/03 Method 535/0
	300SC	2	0.15	300	BBCH 73	straw	35 42	2.2 3.1	

Values in (brackets) are residues of the CL 3000402 metabolite found above LOQ
Values in [brackets] are residues of the CL 434223 metabolite found above LOQ
Values in {brackets} are residues of the CL376991 metabolite found above LOQ
Foliage = plants without ears. Also described as ‘culm’ in some studies

Barley hay and straw

In the above European trials on winter and spring barley, samples of straw (min 0.5 kg) were taken at maturity, frozen within 24 hours and stored at or below –18 °C for up 25 months before analysis. In the trials conducted before 2004, samples were analysed for metrafenone and the metabolites CL 3000402, CL 434223 and CL 376991 using Method RLA 12619 and in the later trials, Method 535/3 was used to measure only the parent compound. Average procedural recoveries of metrafenone from samples fortified with 0.01–20 mg/kg ranged from 71% to 108% and the LOQs were 0.1 mg/kg.

Table 61 Residues in barley fodder from supervised trials in Europe involving 1–3 foliar applications of metrafenone

BARLEY FODDER Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
GAP: Poland		2	0.15				35		
Germany, 2005 Gerolsheim (Scarlett)	75SE	2	0.15	200	BBCH 69	straw	29 36 42	0.44 0.77 0.67	2005/7004267 DU4/11/05 Method 535/0
	100SC	2	0.15	200	BBCH 69	straw	29 36 42	0.73 0.86 0.54	
	300SE	2	0.15	200	BBCH 69	straw	29 36 42	3.3 3.6 2.9	
Sweden, 2005 Bjarred (Prestige)	75SE	2	0.15	200 200	BBCH 69	straw	36 43	1.2 1.4	2005/7004267 HUS/07/05 Method 535/0
	100SC	2	0.15	200 200	BBCH 69	straw	29 36 43	0.3 1.8 1.2	
	300SE	2	0.15	200 200	BBCH 69	straw	36 43	0.71 0.85	
UK, 2005 Bicester (Pearl)	75SE	2	0.15	200 200	BBCH 73	straw	29 36 42	0.38 1.1 1.2	2005/7004267 OAT/16/05 Method 535/0
	100SC	2	0.15	200 200	BBCH 73	straw	28 35 42	0.69 1.0 1.0	
	300SE	2	0.15	200 200	BBCH 73	straw	28 35 42	1.2 1.3 1.2	
France (N), 2002 Alsace (Astoria) spring barley	300SC	2	0.15	300	BBCH 56	straw	39	< 0.01	2003/1001354 FAN/02/02 Method 993/0 RLA 12619.03V
	300SC	1	0.15	300	BBCH 56	straw	39	< 0.01	
UK, 2002 Oxfordshire (Siberia)	300SC	2	0.15	300	BBCH 59	straw	39	0.24	2003/1001354 OAT/05/02 Method 993/0 RLA 12619.03V
	300SC	1	0.15	300	BBCH 59	straw	39	0.26	

BARLEY FODDER Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
Germany, 2003 Lentzke (Cadesse)	100EC	2	0.15	300	BBCH 69	straw	35 42	0.11 0.07	2004/1010542 ACK/04/03 Method 535/0
	300SC	2	0.15	300	BBCH 69	straw	35 42	0.95 0.83	
France (N), 2003 Seebach (Astoria) spring barley	100EC	2	0.15	300	BBCH 73	straw	36 42	1.1 1.2	2004/1010542 FAN/05/03 Method 535/0
	300SC	2	0.15	300	BBCH 73	straw	36 42	3.9 3.1	
Germany, 1999 Euskirchen-Oberwichterich (Uschi)	300SC	3	0.2	400	BBCH 65	straw	35 44	0.76 1.6	2001/7001659 99-111-01 RLA 12619.02V
Germany, 1999 Gemarkung (Duet)	300SC	2	0.2	390	BBCH 61	straw	35 42	0.39 0.64	2001/7001659 99-111-02 RLA 12619.02V
Germany, 1999 Ramsen (Angora)	300SC	2	0.2	300	BBCH 69	straw	36 44	01.7 (0.1) 0.92	2001/7001659 99-111-03 RLA 12619.02V
France (N), 2000 Bonnieres Sur Seine (Esterel)	300SC (09957)	1+ 1	0.13 0.14	310 350	BBCH 77	straw	36	1.1	2002/7004445 00/835/355 RLA 12619.02V
	300SC (10358)	2	0.14	340	BBCH 77	straw	36	1.2	
Germany, 2000 Obersteinach (Hanna)	300SC (09957)	1+ 1	0.15 0.14	300 290	BBCH 77	straw	42	1.1	2002/7004463 00/837/01 RLA 12619.02V
	300SC (10358)	2	0.15	300	BBCH 77	straw	42	0.78	
UK 2000 Lichfield (Jewel)	300SC (09957)	2	0.15	200	BBCH 77–79	straw	35	1.1 (0.11)	2002/7004529 00/836/01 RLA 12619.02V
	300SC (10358)	2	0.15	200	BBCH 77–79	straw	35	1.3 (0.13)	
UK, 2000 Bradwall (Jewel)	300SC (09957)	2	0.15	200	BBCH 75–77	straw	35	1.1	2002/7004529 00/836/02 RLA 12619.02V
	300SC (10358)	2	0.15	200	BBCH 75–77	straw	35	0.83	

BARLEY FODDER Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
UK, 1999 Newton (Intro)	300SC	2	0.2	300	BBCH 61	plant straw	43 50	0.41 0.54 (0.4)	2002/7004681 99-110-01 RLA 12619.02V
France (N) 2000 Mousseaux (Majestic)	300SC	2	0.15	370	BBCH 77	straw	–36	2.0 (0.14)	2002/7004922 00/840/356 RLA 12619.02V
France (S), 2000 LaGardelle Sur Leze (Nevada)	300 SC	2	0.15 0.14	300 280	BBCH 73	straw	35	2.1 (0.13) [0.04] {0.07}	2002/7004890 FTL/31/01 RLA 12619.02V
France (S), 2005 Genissieux (Orelie)	75SE	2	0.15	200 200	BBCH 69	straw	35 41	0.26 0.21	2005/7004267 FBD/34/05 Method 535/0
	100SC	2	0.15	200 200	BBCH 69	straw	29 35 41	0.02 0.51 0.32	
	300SE	2	0.15	200 200	BBCH 69	straw	35 41	1.1 0.31	
France (S), 2003 Rhone-Alpes (Orelie)	100EC	2	0.15	300	BBCH 83	plant straw	35 42	0.44 0.46	2004/1010542 FBD/02/03 Method 535/0
	300SC	2	0.15	300	BBCH 83	straw	35 42	1.3 1.5	
Italy, 2003 Pozzolo (Prosa) spring barley	100EC	2	0.15	300	BBCH 55	straw	35 42	0.6 0.75	2004/1010542 ITA/03/03 Method 535/0
	300SC	2	0.15	300	BBCH 55	straw	35 42	1.9 1.6	
France (S), 1999 Margouet-Meynes (Sunrise)	300SC	2	0.2	400	BBCH 60–61	straw	34 40	2.8 (0.12) 4.0	2001/7000488 99-112-297 RLA 12619.02V
France (S), 1999 Espas (Systel)	300SC	2	0.2	400	BBCH 65–69	straw	34 40	0.68 0.9	2001/7000488 99-112-298 RLA 12619.02V
France (S), 1999 Courthezon (Baraka)	300SC	2	0.2	400	BBCH 75–77	straw	35 42	2.5 (0.12) 4.3 (0.3)	2001/7000488 99-112-633 RLA 12619.02V
France (S), 1999 Althen des Paluds (Baraka)	300SC	2	0.2	400	BBCH 75–77	straw	35 42	1.2 (0.13) 0.97 (0.12)	2001/7000488 99-112-634 RLA 12619.02V

BARLEY FODDER Country, year Location (Variety)	Application					Matrix	DAT	Residues (mg/kg)	Reference & Comments
	form	no	kg ai/ha	water (L/ha)	GS last application			metrafenone	
France (S), 2000 Averon-Bergelle (Plantine)	300SC (09957)	2	0.16	240	BBCH 77–83	straw	34	1.7 (0.12)	2002/7004525 00/839/294 RLA 12619.02V
	300SC (10358)	2	0.16	240	BBCH 77–83	straw	34	1.6 (0.13)	
France (S), 2000 Saumane (Baraka)	300SC (09957)	2	0.15	410	BBCH 77–83	straw	36	1.9	2002/7004525 00/839/646 RLA 12619.02V
	300SC (10358)	1+ 1	0.15 0.16	410 420	BBCH 77–83	straw	36	1.3	
France (S), 2000 Althen Des Paluds (Baraka)	300SC (09957)	2	0.15	400	BBCH 83	straw	34	1.0	2002/7004525 00/839/645 RLA 12619.02V
	300SC (10358)	1+ 1	0.16 0.15	420 410	BBCH 83	straw	34	0.96	
France (S), 2000 Bedarrides (Baraka)	300SC	1+ 1	0.14 0.15	390 400	BBCH 77–83	straw	35	0.41	2002/7004744 00-841-647 RLA 12619.02V

Values in (brackets) are residues of the CL 3000402 metabolite found above LOQ
Values in [brackets] are residues of the CL 434223 metabolite found above LOQ
Values in {brackets} are residues of the CL376991 metabolite found above LOQ
Foliage = plants without ears. Also described as 'culm' in some studies

FATE OF RESIDUES IN STORAGE AND PROCESSING

High temperature hydrolysis

In a study reported by AN, 2000 [Ref: 2000/7000137], the high-temperature hydrolysis of [bromophenyl-6-^{14}C]-metrafenone in buffered solutions of pH 4, 5, and 6 was investigated to simulate representative processing conditions: pasteurization at 90 °C for 20 minutes in pH 4 solution; baking, brewing, or boiling at 100 °C for 60 minutes in pH 5 solution; and sterilization at 120 °C for 20 minutes in pH 6 solution.

Solutions of buffered [bromophenyl-6-^{14}C]-metrafenone were incubated in the dark at 90, 100, and 120 °C at pH 4, 5, and 6, respectively, and samples were analysed after 20 min. (pH 4 and 6) and 1 h (pH 5) by LSC and HPLC. Examination of the radio-chromatograms showed only one major peak in all samples, identified as the parent compound.

Recoveries of radioactivity at 0-time were 91–92% of the applied radioactivity and after incubation were 96–102% of applied dose. Metrafenone made up about 91% of the radioactivity at 0-time and 95–101% of the applied dose after incubation. The relatively low pre-incubation recovery was attributed to retention on the glass tubes. The results indicate that metrafenone is hydrolytically stable under the simulated processing conditions of pasteurization, baking, brewing, boiling and sterilization.

Table 62 Distribution of radioactivity for [bromophenyl-6-^{14}C]-metrafenone in buffer solutions—high temperature hydrolysis (% radioactivity)

Component	pH 4		pH 5		pH 6	
	Control	90°C	Control	100°C	Control	120°C
Metrafenone (parent)	90.75	100.5	91.24	101.37	90.9	94.8
Others	0.69	1.01	0.81	0.95	1.25	1.42
Total % recovery	91.44	101.15	92.05	102.32	92.15	96.22

Processing

Apples

An apple processing study was reported by Carringer, 2013 [Ref 2012/7004393]. In two field trials in USA, involving three foliar applications of 1.68 kg ai/ha metrafenone (SC formulation), applied at 6–7 day intervals in 750–1000 L water/ha, with added surfactant, bulk samples (36 kg) were taken 6–7 days after the last application and cool-stored for up to 4 days before processing using simulated commercial practices into juice, wet pomace, apple sauce, canned apples, and dried apples).

The bulk apples for processing were quartered, sliced and a portion of these apple slices were set aside for raw juice generation. The remaining portion was ground in a food strainer/sauce maker, producing puree and wet pomace. Apple sauce was prepared by evaporating the puree at 82–93 ºC in a kettle. Apple slices for juice were processed through a juice processor to produce juice and the resulting wet pomace was combined with the wet pomace generated during puree production. Canned apples were prepared from whole apples by peeling, slicing and coring, with the sliced fruit heated with water to about 70 ºF for approximately 45 minutes and stirred to produce slices in syrup. For dried fruit production, whole apples were peeled, cut into 0.3 cm slices, cored and placed one layer deep on dehydrator trays and dried at 65–70 ºC for about 24 hours to achieve a moisture content of approximately 10%.

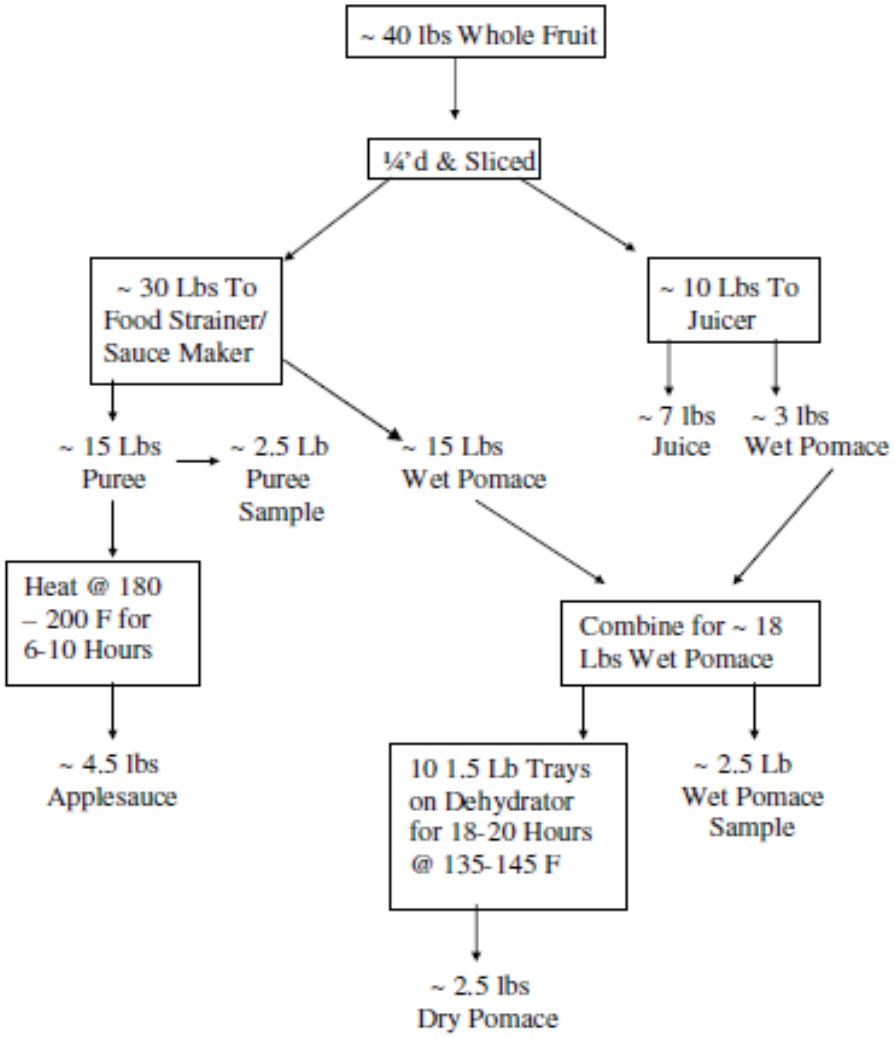


Figure 6 Processing flowchart for apple sauce, juice, and wet pomace

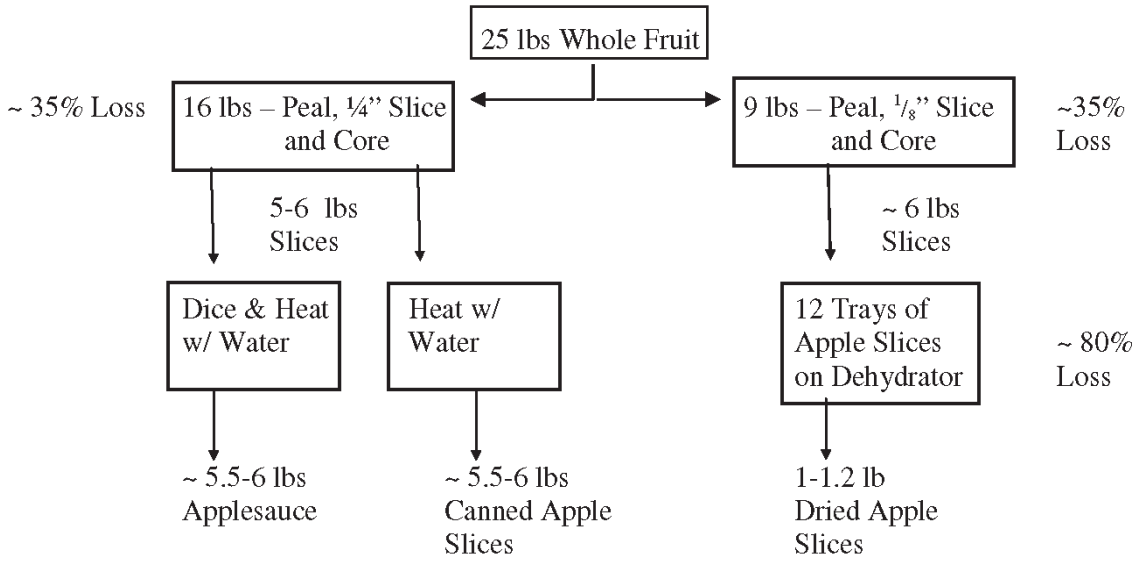


Figure 7 Processing flowchart for canned and dried apple

Representative samples of whole apples (≥ 2 kg), dried apples (approximately 0.5 kg), juice (2 litres) and other processed fractions (≥ 1 kg) were stored at ≤ –16 °C for up to 22 months before analysis for metrafenone using the LC-MS/MS QuEChERS method. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 92–106% in samples spiked with 0.01 to 10.0 mg/kg.

Table 63 Residues in fresh and processed apples from supervised trials in North America involving three foliar applications of metrafenone (SC formulation)

APPLE Study ID	Commodity	Metrafenone (mg/kg)	Processing Factor [a]
R080753 Alton, NY, 2010 3 × 1.7 kg ai/ha PHI: 7 days	Whole Fresh Fruit Juice (raw) Wet Pomace Apple Sauce Canned Apples Dried Apples	1.46 0.28 1.88 7.01 0.2 1.1	– 0.189 1.29 4.80 0.140 0.719
R080754 Weiser, ID, 2010 3 × 1.7 kg ai/ha PHI: 6 days	Whole Fresh Fruit Juice (raw) Wet Pomace Apple Sauce Canned Apples Dried Apples	2.17 0.489 2.37 8.94 0.226 0.851	– 0.225 1.09 4.12 0.104 0.392

[a] The processing factor was calculated by dividing the residue in the apple processed commodity by the residue in the apple RAC sample.

Grapes

One grape processing study conducted in USA was reported by Jordan & Kasiri, 2006 [Ref: 2006/7007012]. In one field trial in the USA, involving six foliar applications of 0.34 kg ai/ha metrafenone (SC formulation) in 1280 Litres water/ha, applied at 12–15 day intervals from BBCH 75 (berries pea-sized), bulk grape samples (170 kg) were taken immediately after the last application and either cool-stored for up to 3 days before processing into juice, red wine, white wine or sun-dried in the field for 28 days before washing.

Grapes were processed into grape juice by crushing and after removing the stems, the pulp was heated to 52–57 °C for 10 minutes and then to 60–66 °C for a further 10 minutes before pressing to separate the juice and pulp. The collected juice was filtered through a U.S. #40 screen to remove course solids and samples were then frozen for analysis.

For wine, the grapes were de-stemmed and crushed, the juice/pulp was heated to approximately 60 °C then cooled to approximately 21 °C (red wine only), and allowed to stand for about an hour after the addition of potassium metabisulfite and pectic enzyme before pressing. The must was allowed to rest overnight and after addition of yeast, primary fermentation was continued at room temperature until the specific gravity reached approximately 1.03. The wine was then racked and stored at approximately 13 °C for 1–2 weeks before the sediment was removed. This 'young wine' was then treated with gelatine as a fining agent and stored for about 3 months before the lees were removed and the finished wine was vacuum filtered over diatomaceous earth.

Representative samples of grapes and processed fractions were stored at ≤ –17 °C for up to 4 months (6 months for grapes) before analysis for metrafenone using the HPLC-MS/MS Method 535/3. The reported LOQ in all matrices was 0.01 mg/kg and average concurrent recoveries were 80–127% in samples spiked with 0.01 to 20.0 mg/kg.

Table 64 Residues in fresh and processed grapes from supervised trials in North America involving three foliar applications of metrafenone (SC formulation)

GRAPE Study ID	Commodity	Metrafenone (mg/kg)	Processing factor
RCN R05013	Unwashed grapes	0.27	–
Tulare, CA	Juice	0.01	0.04
	Must (white wine)	0.04	0.15
6 × 0.35 kg ai/ha	Wet pomace	0.75	2.78
PHI: 0 days	Yeast	0.5	1.85
	Young wine (white)	0.02	0.07
Batch 1	Wine (white)	0.02	0.07
	Unwashed raisins	1.11	4.11
	Washed raisins	0.98	3.63
RCN R05013	Unwashed grapes	0.31	–
Tulare, CA	Juice	0.02	0.06
	Must (red wine)	0.01	0.03
6 × 0.35 kg ai/ha	Wet pomace	1.11	3.58
PHI: 0 days	Yeast	0.18	0.58
	Young wine (red)	0.01	0.03
Batch 2	Wine (red)	0.01	0.03
	Unwashed raisins	0.86	2.77
	Washed raisins	1.22	3.94

In a series of studies conducted in Europe and reported by Smalley, 2002 [Refs: 2002/7004451, 2002/7004455, 2002/7004459, 2002/7004460], grapes from field trials involving eight applications of 0.01–0.033 kg ai/hL metrafenone (0.09–0.13 kg ai/ha), applied at either 7 or 14 day intervals, were taken 27–29 days after the last application and processed into red or white wine or sun-dried to produce raisins.

The wine processing steps were generally as described above, with potassium metabisulphite added as a fermentation inhibitor and gelatin used as a fining agent. For the sparkling wine, sugar and yeasts were added to wine prior to bottling and the bottles stored at 5–10 °C for about 9 months (turned regularly during the last month) before uncapping, disgorging and recapping and frozen for subsequent analysis.

Representative samples of grapes and processed fractions were stored at about –20 °C for up to 6 months before analysis for metrafenone using Method RLA 12612V. The reported LOQ in all matrices was 0.05 mg/kg and average concurrent recoveries were 77–102% in samples spiked with 0.05–0.5 mg/kg.

Table 65 Residues in fresh and processed grapes from supervised trials in Europe involving eight foliar applications of metrafenone (SC formulation)

GRAPE Trial reference	Application details	Commodity	Metrafenone (mg/kg)	Processing factor
Ref: 2002/7004451	8 × 0.01 kg ai/hL	Grapes	0.3	–
Trial:00-845-01 VIN-A	(0.13 kg ai/ha)	Must	0.17	0.57
Italy, 2000	7 day spray interval	Young wine (red)	< 0.05	< 0.17
Castlefranco	DAT: 29 days	Wine (red)	< 0.05	< 0.17
Ref: 2002/7004451	8 × 0.01 kg ai/hL	Grapes	0.24	–
Trial:00-845-01 VIN-B	(0.13 kg ai/ha)	Must	0.28	1.17
Italy, 2000	7 day spray interval	Young wine (red)	< 0.05	< 0.2
Castlefranco	DAT: 29 days	Wine (red)	< 0.05	< 0.2
Ref: 2002/7004451	8 × 0.01 kg ai/hL	Grapes	0.13	–
Trial: 00-845-02 VIN-A	(0.12 kg ai/ha)	Must	0.10	0.77
Italy, 2000	7 day spray interval	Young wine (red)	< 0.05	< 0.38
Toscanella	DAT: 29 days	Wine (red)	< 0.05	< 0.38

GRAPE Trial reference	Application details	Commodity	Metrafenone (mg/kg)	Processing factor
Ref: 2002/7004451 Trial: 00-845-02 VIN-B Italy, 2000 Toscanella	8 × 0.01 kg ai/hL (0.12 kg ai/ha) 7 day spray interval DAT: 29 days	Grapes Must Young wine (red) Wine (red)	0.07 0.09 < 0.05 < 0.05	– 1.29 < 0.71 < 0.71
Ref: 2002/7004455 Trial: 00-843-441-A France (N), 2000 Oger	8 × 0.02 kg ai/hL (0.1 kg ai/ha) 14 day spray interval DAT: 27 days	Grapes Must Still wine (white) Sparkling wine (white)	0.28 < 0.05 < 0.05 < 0.05	– < 0.18 < 0.18 < 0.18
Ref: 2002/7004455 Trial: 00-843-441-B France (N), 2000 Oger	8 × 0.02 kg ai/hL (0.1 kg ai/ha) 14 day spray interval DAT: 27 days	Grapes Must Still wine (white) Sparkling wine (white)	0.19 0.05 < 0.05 < 0.05	– 0.26 < 0.26 < 0.26
Ref: 2002/7004460 Trial: 00-844-648-A France (S), 2000 Jonquerettes	8 × 0.033 kg ai/hL (0.1 kg ai/ha) 7 day spray interval DAT: 29 days	Grapes Must Young wine (red) Wine (red)	0.26 0.21 < 0.05 < 0.05	– 0.81 < 0.19 < 0.19
Ref: 2002/7004460 Trial: 00-844-648-B France (S), 2000 Jonquerettes	8 × 0.033 kg ai/hL (0.1 kg ai/ha) 7 day spray interval DAT: 29 days	Grapes Must Young wine (red) Wine (red)	0.27 0.21 0.08 < 0.05	– 0.78 0.3 < 0.19
Ref: 2002/7004459 Trial: 00-846-11-A Spain, 2000 Malaga	8 × 0.01 kg ai/hL (0.09 kg ai/ha) 7 day spray interval DAT: 28 days	Grapes Raisins	0.07 < 0.05	– < 0.71
Ref: 2002/7004459 Trial: 00-846-11-B Spain, 2000 Malaga	8 × 0.01 kg ai/hL (0.09 kg ai/ha) 7 day spray interval DAT: 28 days	Grapes Raisins	0.08 < 0.05	– < 0.63

Strawberries

In a study reported by Plier, 2011 [Ref: 2011/1041883], bulk samples (min 10 kg) of strawberries were taken from four field trials conducted in Germany (2 × 0.45 kg ai/200 Litres/ha metrafenone, 7 days apart) 3–4 days after the last application and chilled to about 5–8 °C for up to 3 days before processing into jam, preserved fruit and syrup.

Fruit (without stems and crowns) were washed and processed into jam by cooking with sugar and glucose syrup until a dry matter content of about 64% was achieved and after the addition of citric acid and pectin, heated further until a dry matter content reached about 62%. The jam (pH 2.7–3.3) was then cooled and samples frozen for up to 8 months before analysis.

Washed fruit were also preserved by heating with ascorbic acid, citric acid, sugar and water until boiling and immediately pouring the mixture into jars which were topped up with boiled syrup, sealed and pasteurized for one minute at 90–95 °C. Cooled samples (pH 3–4) were then frozen for up to 8 months before analysis.

The analytical method 535/1 was used to measure residues of metrafenone, with an LOQ of 0.01 mg/kg and concurrent recoveries from samples spiked with 0.01, 0.1 or 1.0 mg/kg ranged from 82-94%, with an average recovery of 89%.

Table 66 Residues in fresh and processed strawberries from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

STRAWBERRY Trial reference	Application details	Commodity	Metrafenone (mg/kg)	Processing factor
Ref: 2011/1041883 Trial:L100269 Germany, 2010 Leisnig	2 × 0.45 kg ai/ha (200 L water/ha) 7 day spray interval DAT: 3 days	Strawberries Washed fruit wash water Preserved fruit Jam after cooking Jam before cooking Syrup	0.41 0.166 0.543 0.344 0.087 0.077 0.064	– 0.4 1.3 0.84 0.2 0.19 0.16
Ref: 2011/1041883 Trial:L100270 Germany, 2010 Coswig	2 × 0.45 kg ai/ha (200 L water/ha) 7 day spray interval DAT: 3 days	Strawberries Washed fruit wash water Preserved fruit Jam after cooking Jam before cooking Syrup	0.157 0.078 0.221 0.155 0.038 0.045 0.028	– 0.5 1.4 0.99 0.24 0.29 0.18
Ref: 2011/1041883 Trial:L100271 Germany, 2010 Pillnitz	2 × 0.47 kg ai/ha (210 L water/ha) 7 day spray interval DAT: 4 days	Strawberries Washed fruit wash water Preserved fruit Jam after cooking Jam before cooking Syrup	0.284 0.148 0.28 0.225 0.061 0.066 0.053	– 0.52 0.99 0.79 0.21 0.23 0.19
Ref: 2011/1041883 Trial:L100272 Germany, 2010 Alitzheim	2 × 0.45 kg ai/ha (200 L water/ha) 7 day spray interval DAT: 3 days	Strawberries Washed fruit wash water Preserved fruit Jam after cooking Jam before cooking Syrup	0.195 0.088 0.261 0.222 0.055 0.055 0.03	– 0.45 1.34 1.14 0.28 0.28 0.15

Tomatoes

In a study reported by Plier, 2011 [Ref: 2011/1041884], tomatoes were taken for processing from four field trials conducted in Germany. In these field trials, two applications of 0.6–0.7 kg ai/ha were applied 6–8 days apart using 450–550 Litres spray mix/ha. Bulk samples of 13–21 kg ripe tomatoes were taken 3–4 days after the last application and chilled to about 5–8 °C for 1–12 days before processing into preserve, juice, paste, ketchup and puree.

Tomatoes (without stems) were washed, blanched (1 minute at 75–85 °C), cooled and peeled manually. The peeled tomatoes were placed in jars, topped up with water, sealed and autoclave sterilised (5–12 minutes at 118–125 °C) before cooling and sampling for subsequent analysis.

For juice, puree and ketchup, washed tomatoes were crushed and heated for 30 minutes at 80–87 °C, then pressed and sieved to separate the juice and pomace. Samples of the raw juice were concentrated to achieve a dry matter content of 7–14% (for paste) and 18–24% (for puree). Ketchup was prepared by adding vinegar (0.4%), sugar (42%) and salt (15%) to the paste. The paste, ketchup and puree were pasteurised at 90–95 °C for 1–20 minutes, cooled and samples were stored frozen for up to 6 months before analysis for metrafenone using Method 535/1, with a limit of quantification of 0.01 mg/kg. Concurrent recoveries from samples spiked with 0.01–5.0 mg/kg ranged from 80–109%, with an average recovery of 93%.

Table 67 Residues in fresh and processed tomatoes from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

TOMATO Trial reference	Application details	Commodity	Metrafenone (mg/kg)	Processing factor
Ref: 2011/1041884 Trial: L100261 Germany, 2010 Motterwitz	2 × 0.71 kg ai/ha (530 L water/ha) 7 day spray interval DAT: 3 days	Tomatoes	0.423	–
		Blanched fruit	0.535	1.26
		Blanching water	< 0.01	< 0.02
		Preserved fruit	< 0.01	< 0.02
		Peeled fruit	< 0.01	< 0.02
		Wash water	0.066	0.16
		Tomato peel	3.184	7.5
		Wet pomace	2.034	4.8
		Washed fruit	0.382	0.9
		Raw juice	0.168	0.4
		Ketchup (pasteurised)	0.177	0.42
		Tomato paste	0.225	0.53
		Tomato puree	0.335	0.79
		Preserving stock	< 0.01	< 0.02
Ref: 2011/1041884 Trial: L100262 Germany, 2010 Gerichshain	2 × 0.73 kg ai/ha (540 L water/ha) 7 day spray interval DAT: 3 days	Tomatoes	0.775	–
		Blanched fruit	0.352	0.45
		Blanching water	0.013	0.02
		Preserved fruit	0.015	0.02
		Peeled fruit	< 0.01	< 0.01
		Wash water	0.507	0.65
		Tomato peel	4.807	6.2
		Wet pomace	2.567	3.31
		Washed fruit	0.477	0.62
		Raw juice	0.198	0.26
		Ketchup (pasteurised)	0.327	0.42
		Tomato paste	0.207	0.27
		Tomato puree	0.501	0.65
		Preserving stock	< 0.01	< 0.01
Ref: 2011/1041884 Trial: L100263 Germany, 2010 Dupow	2 × 0.71–0.61 kg ai/ha (530–450 L water/ha) 6 day spray interval DAT: 4 days	Tomatoes	0.583	–
		Blanched fruit	0.528	0.91
		Blanching water	0.017	0.03
		Preserved fruit	< 0.01	< 0.02
		Peeled fruit	0.031	0.05
		Wash water	0.218	0.37
		Tomato peel	4.585	7.9
		Wet pomace	3.592	6.2
		Washed fruit	0.488	0.84
		Raw juice	0.194	0.33
		Ketchup (pasteurised)	0.219	0.38
		Tomato paste	0.174	0.3
		Tomato puree	0.485	0.84
		Preserving stock	< 0.01	< 0.02
Ref: 2011/1041884 Trial: L100264 Germany, 2010 Oderberg	2 × 0.69–0.63 kg ai/ha (510–460 L water/ha) 8 day spray interval DAT: 3 days	Tomatoes	0.425	–
		Blanched fruit	0.398	0.94
		Blanching water	0.012	0.03
		Preserved fruit	< 0.01	< 0.02
		Peeled fruit	0.01	0.02
		Wash water	0.152	0.36
		Tomato peel	1.588	3.7
		Wet pomace	2.679	6.3
		Washed fruit	0.242	0.57
		Raw juice	0.149	0.35
		Ketchup (pasteurised)	0.211	0.5
		Tomato paste	0.201	0.47
		Tomato puree	0.478	1.12
		Preserving stock	< 0.01	< 0.02

Barley

In a study reported by Pollmann, 2002 [Ref: 2002/1004080], samples of summer barley grain were taken for processing from four field trials conducted in Germany. In these field trials, two applications of about 0.5 kg ai/ha were applied 10–15 days apart using about 300 Litres spray mix/ha. Bulk samples of at least 25 kg grain were taken 35 days after the last application and stored at ambient temperature for 2–3 months before processing into pearl barley and beer.

Pearl barley was prepared by mechanical de-awning and cleaning (< 2.5 mm slotted screen) to separate husks and other impurities, conditioning to 14% moisture content and decortications to achieve an abrasion rate of 20–30%. Samples were frozen within 4 hours for subsequent analysis

The malting and brewing process involved steeping the barley (2 × 3hours at 14 °C), sprouting over 7 days at about 12 °C and kilning (7 hours at 55 °C and 1.5 hours at 85 °C) before the sprouts were separated over a wire mesh and the malt was conditioned for 8–21 days at 12–15 °C before being ground for brewing. Mash was produced using the infusion method and wort was removed during the lautering process. Hops were added to the wort during the 1 hour boiling period and after cooling, yeast was added to initiate fermentation. Primary fermentation proceeded for 7–8 days at 8–14 °C and after bottling, secondary fermentation continued for 21–32 days (8–14 °C) when samples were frozen for subsequent analysis.

Samples were stored frozen (about -18 °C) for up to 7 months before analysis for metrafenone using Method RLA 12619.03V (993/0), with a limit of quantification of 0.01 mg/kg. Concurrent recoveries from samples spiked with 0.01–0.1 mg/kg ranged from 73–93% (except malt sprouts, where the recovery was 47%), with an average recovery of 85%.

Table 68 Residues in barley and processed barley fractions from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

BARLEY Trial reference	Application details	Commodity	Metrafenone (mg/kg)	Processing factor
Ref: 2002/1004080 Trial: G01N055R Germany, 2001 Mulsum	2 × 0.47 kg ai/ha (310 L water/ha) 14 day spray interval DAT: 35 days	Stored barley Beer Stored barley Pearl barley	0.06 < 0.01 0.08 < 0.01	– < 0.17 – < 0.13
Ref: 2002/1004080 Trial: G01N056R Germany, 2001 Mulsum	2 × 0.45–0.46 kg ai/ha (310 L water/ha) 13 day spray interval DAT: 35 days	Stored barley Beer Stored barley Pearl barley	0.03 < 0.01 0.05 < 0.01	– < 0.33 – < 0.2
Ref: 2002/1004080 Trial: G01N057R Germany, 2001 Kleinsachsenheim	2 × 0.44–0.46 kg ai/ha (300 L water/ha) 10 day spray interval DAT: 35 days	Stored barley Malt Malt sprouts Brewer's grain Spent hops Brewer's yeast Beer Stored barley Pearl barley Pearl barley abrasion	0.1 0.04 0.08 0.03 < 0.01 < 0.01 < 0.01 0.08 0.01 0.2	– 0.4 0.8 0.3 < 0.1 < 0.1 < 0.1 – 0.13 2.5
Ref: 2002/1004080 Trial: G01N058R Germany, 2001 Gemmrigheim	2 × 0.44–0.45 kg ai/ha (310 L water/ha) 10 day spray interval DAT: 35 days	Stored barley Beer Stored barley Pearl barley	0.08 < 0.01 0.09 0.02	– < 0.13 – 0.22

Wheat

In a study reported by Pollmann, 2002 [Ref: 2002/1006302], samples of summer wheat grain were taken for processing from four field trials conducted in Germany. In these field trials, two applications of about 1.5 kg ai/ha were applied 27 or 38 days apart using about 300 Litres spray mix/ha. Bulk samples of at least 7 kg grain were taken 35 days after the last application and stored frozen for up to 2 months before processing into flour, bran and bread.

After cleaning to remove dust and plant fragments, 6–10 kg samples of wheat grain were conditioned to a moisture content of about 17% and milled by passing through a series of corrugated and smooth rollers (0.5 mm down to 0.01 mm apertures) to obtain flour and bran + adhesive flour, the latter being centrifuged to separate the coarse bran, fine bran and the bran flour. Samples were frozen within 9 hours for subsequent analysis.

A sample of the whole meal flour was kneaded with water, ascorbic acid, yeast, salt, sugar and peanut fat to produce dough, which was allowed to ferment at about 27 °C for 30 minutes before being formed into a loaf and given a further 60 minute fermentation period (32 °C) before baking at 210 °C for 50 minutes. The loaves were then cooled and samples were immediately frozen for subsequent analysis.

Samples were stored frozen (about –18 °C) for up to 7 months before analysis for metrafenone using Method RLA 12619.03V (993/0), with a limit of quantification of 0.01 mg/kg. Concurrent recoveries from samples spiked with 0.01–0.1 mg/kg ranged from 76–104% with an average recovery of 89%.

Table 69 Residues in wheat and processed wheat fractions from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

WHEAT Trial reference	Application details	Commodity	Metrafenone (mg/kg)	Processing factor
Ref: 2002/1006302	2 × 1.5 kg ai/ha	Grain [a]	0.28	–
Trial: G01N051R	(300 L water/ha)	Wholemeal flour	0.31	1.1
Germany, 2001	38 day spray interval	Flour type 550	0.06	0.21
Ladekop	DAT: 36 days	Bran flour	0.45	1.6
		Coarse bran	0.08	0.29
		Fine bran	0.97	3.5
		Whole grain bread	0.18	0.64
Ref: 2002/1006302	2 × 1.5 kg ai/ha	Grain [a]	0.14	–
Trial: G01N052R	(300 L water/ha)	Wholemeal flour	0.27	1.9
Germany, 2001	38 day spray interval	Flour type 550	0.04	0.29
Ladekop	DAT: 36 days	Bran flour	0.37	2.6
		Coarse bran	0.06	0.43
		Fine bran	0.69	4.9
		Whole grain bread	0.14	1.0
Ref: 2002/1006302	2 × 1.5–1.6 kg ai/ha	Grain [b]	0.18	–
Trial: G01N053R	(300 L water/ha)	Wholemeal flour	0.17	0.94
Germany, 2001	27 day spray interval	Flour type 550	0.03	0.17
Ludwigsburg-Ossweil	DAT: 35 days	Bran flour	0.24	1.3
		Coarse bran	0.06	0.33
		Fine bran	0.47	2.6
		Whole grain bread	0.11	0.61
Ref: 2002/1006302	2 × 1.4–1.5 kg ai/ha	Grain [b]	0.07	–
Trial: G01N054R	(280–310 L water/ha)	Wholemeal flour	0.12	1.7
Germany, 2001	27 day spray interval	Flour type 550	0.01	0.14
Affalterbach	DAT: 35 days	Bran flour	0.18	2.6
		Coarse bran	0.04	0.57
		Fine bran	0.37	5.3
		Whole grain bread	0.05	0.71

[a] Conditioned to approximately 17% by drying
[b] Conditioned to about 17% by addition of water

Hops

In two studies reported by Braun, 2011 [Ref: 2011/1041879] and Plier, 2011 [Ref: 2011/1041886], hops from field trials conducted in Germany were taken for drying or processing into beer. In these field trials, two applications of about 0.33–0.35 kg ai/ha were applied 6–8 days apart using about 3300 Litres spray mix/ha.

Samples of green cones were taken 3–4 days after the last application and kiln-dried for about 7–8 hours at approximately 58 °C to produce dried cones. The green and dried cone samples were frozen within 12 hours and stored below –18 °C for subsequent analysis (up to 8 months after sampling). In addition, bulk dried cone samples (min 1.8 kg) were stored at ambient temperatures for about 1 month prior to processing.

Dried cones were milled and added to the separated wort and after boiling for about 90 minutes, the flocs (hops draff) were separated in a whirlpool and after cooling, yeast was added to initiate fermentation. Primary fermentation proceeded for 9–11 days at about 9 °C and secondary (cask) fermentation continued for a further 2 days at 20 °C and under pressure for a further 24 days at 2 °C before being filtered and sampled for subsequent analysis.

Dried cones were also processed into Extracted Hops by dissolving with ethanol using a soxhlet extractor for 3–4 hours, with the miscella being filtered and concentrated twice using a vacuum evaporator (above 50 °C and 0.5–1.0 bar) before cooling and sampling for subsequent analysis.

Samples were stored frozen (about -18 °C) for up to 4 months before analysis for metrafenone using Method 535/3, with a limit of quantification of 0.01 mg/kg. Concurrent recoveries from samples spiked with 0.01–1.0 mg/kg (and 10 mg/kg in extracted hops and 50–100 mg/kg in dried cones) ranged from 73–111% (except in extracted hops, where recovery rates were 65–68%) with an average recovery of 87%.

Table 70 Residues in hops and processed hop fractions from supervised trials in Europe involving two foliar applications of metrafenone (SC formulation)

HOPS Trial reference	Application details	Commodity	Metrafenone (mg/kg)	Processing factor
Ref: 2011/1041879 Trial: L090302 Germany, 2009 Golzern	2 × 0.31–0.34 kg ai/ha (3200–3400 L water/ha) 8 day spray interval DAT: 2 days	Green cones Dried cones Dried cones Extracted hops Beer Brewer's yeast Hops Draff	3.74 21.3 17.7 31.1 < 0.01 0.2 4.17	– 5.7 – 1.76 < 0.0006 0.01 0.24
Ref: 2011/1041879 Trial: L090303 Germany, 2009 Hohenebra	2 × 0.33–0.35 kg ai/ha (3300–3600 L water/ha) 7 day spray interval DAT: 3 days	Green cones Dried cones Dried cones Extracted hops Beer Brewer's yeast Hops Draff	3.4 22.8 21.1 37.9 < 0.01 0.24 5.17	– 6.7 – 1.8 < 0.0005 0.01 0.25
Ref: 2011/1041879 Trial: L090304 Germany, 2009 Kleinbadegast	2 × 0.31–0.34 kg ai/ha (3100–3300 L water/ha) 6 day spray interval DAT: 3 days	Green cones Dried cones Dried cones Extracted hops Beer Brewer's yeast Hops Draff	1.78 13.3 18.3 32.7 < 0.01 0.15 4.39	– 7.5 – 1.79 < 0.0005 0.008 0.24

HOPS Trial reference	Application details	Commodity	Metrafenone (mg/kg)	Processing factor
Ref: 2011/1041879 Trial: L090305 Germany, 2009 Simonshofen	2 × 0.35–0.34 kg ai/ha (3500–3400 L water/ha) 7 day spray interval DAT: 4 days	Green cones Dried cones	3.05 19.7	– 6.5
Ref: 2011/1041886 Trial: L100073 Germany, 2010 Weddegast	2 × 0.33 kg ai/ha (3300 L water/ha) 8 day spray interval DAT: 3 days	Green cones Dried cones	4.5 34	7.6
Ref: 2011/1041886 Trial: L10074 Germany, 2010 Golzern	2 × 0.33 kg ai/ha (3300 L water/ha) 7 day spray interval DAT: 3 days	Green cones Dried cones	8.5 33	3.9

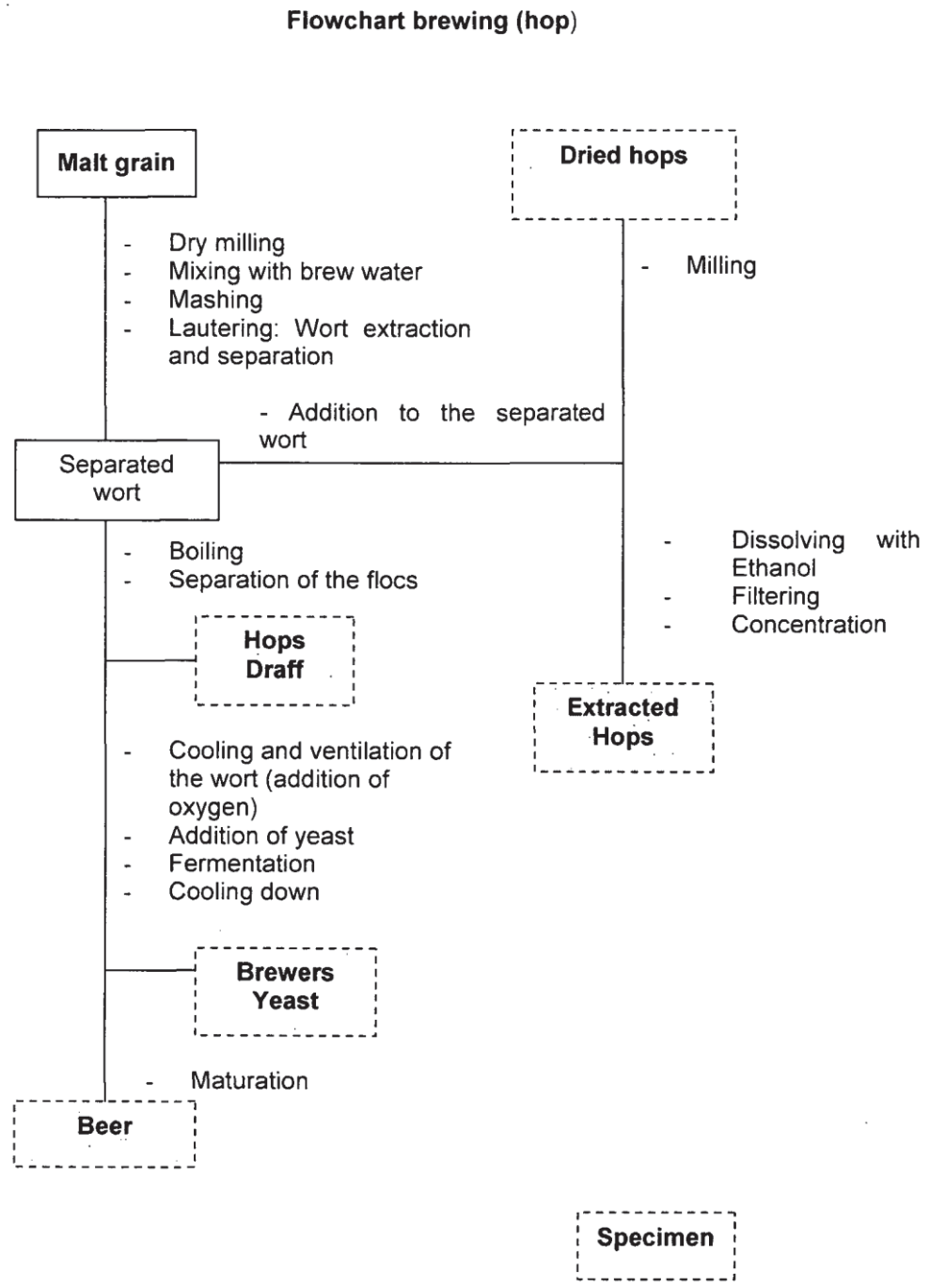


Figure 8 Processing Flowchart for Hops

Table 71 Summary of processing factors for metrafenone

RAC	Matrix	Metrafenone [a]	
		Calculated processing factors	PF median or best estimate
Apple	fruit		
	canned	0.1, 0.14	0.12
	juice	0.19, 0.23	0.21
	wet pomace	1.1, 1.3	1.2
	dried slices	0.39, 0.72	0.56
	sauce	4.1, 4.8	4.45
Grape	grapes		

RAC	Matrix	Metrafenone [a]	
		Calculated processing factors	PF median or best estimate
	must (red wine)	0.03, 0.57, 0.77, 0.78, 0.81, 1.2, 1.3	0.78
	must (white wine)	0.15, < 0.18, 0.26	0.18
	wet pomace	2.8, 3.6	3.2
	young wine (white)	0.07	< 0.2
	young wine (red)	0.03, < 0.17, < 0.19, < 0.21, 0.3, < 0.38, < 0.71	
	wine (white)	0.07, < 0.18, < 0.26	< 0.19
	wine (red)	0.03, < 0.17, < 0.19, < 0.19, < 0.21, < 0.38, < 0.71	
	juice	0.04, 0.06	0.05
	raisins	0.63, < 0.71, 3.6, 3.9	3.75
Strawberry	fruit		
	washed fruit	0.4, 0.45, 0.5, 0.52	0.475
	preserved fruit	0.79, 0.84, 0.99, 1.1	0.915
	jam	0.21, 0.21, 0.24, 0.28	0.225
	syrup	0.15, 0.16, 0.18, 0.19	0.17
Tomato	fresh		
	washed	0.57, 0.62, 0.84, 0.9	0.73
	blanched	0.45, 0.91, 1.3, 0.94	1.1
	peeled	< 0.01, < 0.02, 0.02, 0.05	0.02
	preserved	< 0.02, < 0.02, < 0.02, 0.02	< 0.02
	juice (raw)	0.26, 0.33, 0.35, 0.4	0.34
	wet pomace	3.3, 4.8, 6.2, 6.3	5.5
	peel	3.7, 6.2, 7.5, 7.9	6.85
	paste	0.27, 0.3, 0.47, 0.53	0.385
	ketchup	0.38, 0.42, 0.42, 0.5	0.42
	puree	0.65, 0.79, 0.83, 1.1	0.81
Mushroom	fresh		
	canned [b]	0.16	0.16
Barley	grain		
	pearl barley	< 0.13, 0.13, < 0.2, 0.22	0.165
	pearl barley abrasion	2.5	2.5
	malt	0.4	0.4
	Brewer's grain	0.3	0.3
	spent hops	< 0.1	< 0.1
	Brewer's yeast	< 0.1	< 0.1
	beer	< 0.1, < 0.13, < 0.17, < 0.33,	< 0.15
Wheat	grain		
	wholemeal flour	0.94, 1.1, 1.7, 1.9	1.4
	flour type 550	0.14, 0.17, 0.21, 0.29	0.19
	bran flour	1.3, 1.6, 2.6, 2.6	2.1
	coarse bran	0.29, 0.33, 0.43, 0.57	0.38
	fine bran	2.6, 3.5, 4.9, 5.3	4.2
	whole grain bread	0.6, 0.64, 0.71, 1.0	0.675
Hops	dried cones		
	extracted hops	1.8, 1.8, 1.8	1.8
	Brewer's yeast	0.008, 0.01, 0.01	0.01
	hops draff	0.24, 0.24, 0.25	0.24
	beer	< 0.0005, < 0.0005, < 0.0006	< 0.0005

[a] Each value represents a separate study where residues were above the LOQ in the RAC. The factor is the ratio of metrafenone residues in the processed item divided by the residue of metrafenone in the RAC.
[b] See Table 50

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

No livestock feeding studies were provided.

NATIONAL RESIDUE DEFINITIONS

Table 72 Metrafenone: National residue definitions for MRL-compliance and dietary intake estimation

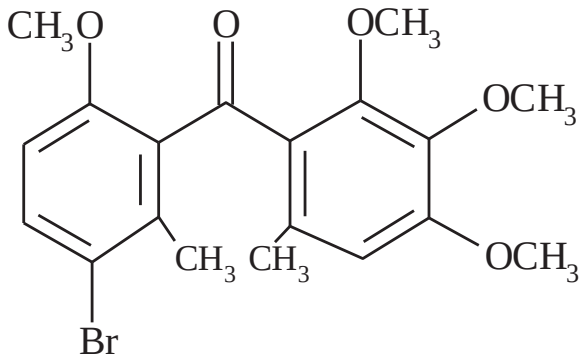
Country	MRL-compliance	Dietary intake estimation
Australia	metrafenone	metrafenone
Canada	metrafenone	metrafenone
Europe	metrafenone	metrafenone
Korea	metrafenone	metrafenone
New Zealand	metrafenone	metrafenone
USA	metrafenone	metrafenone

APPRAISAL

Metrafenone is a benzophenone fungicide, active mainly against powdery mildews and eyespot, inhibiting mycelium growth, leaf penetration, haustoria formation and sporulation.

It was scheduled by the Forty-fifth Session of the CCPR as a new compound for consideration by the 2014 JMPR. The manufacturer submitted studies on metabolism, analytical methods, supervised field trials, processing, freezer storage stability, environmental fate in soil and rotational crop residues.

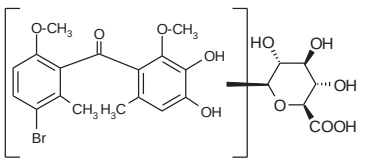
Authorisations exist for the use of metrafenone on cereals, grapes, strawberries and fruiting vegetables in over 50 countries in Europe, the Americas, Asia and the Pacific.

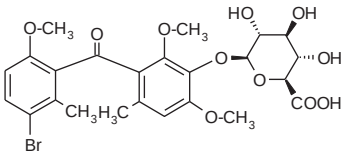
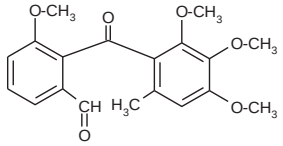
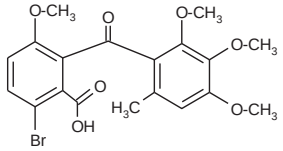
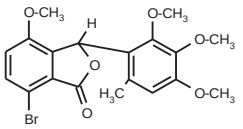
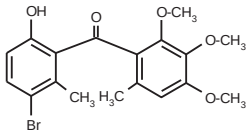
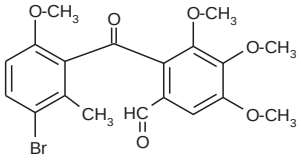
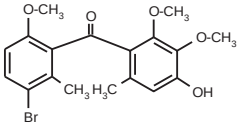
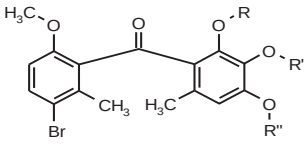


Metrafenone
(MW 409.3)

The following abbreviations are used for the major metabolites discussed below:

Major metrafenone metabolites identified in plant, animal and soil matrices

Code	Structure	Chemical Name	Occurrence
CL 1023363		3-(3-bromo-6-methoxy-2-methylbenzoyl)-6-hydroxy-2-methoxy-4-methylphenyl β-D-glucopyranosiduronic acid Mono-O-glucuronide of Methanone, (3-bromo-6-hydroxy-2-methylphenyl)(3,4-dihydroxy-2-methoxy-6-methylphenyl-	goat

Code	Structure	Chemical Name	Occurrence
CL 1500698		3-(3-bromo-6-methoxy-2-methylbenzoyl)-2,6-dimethoxy-4-methylphenyl β-D-glucopyranosiduronic acid Methanone, (3-bromo-6-methoxy-2-methylphenyl)[3-beta-D-glucopyranuronosyloxyl)-2,4-dimethoxy-6-methylphenyl-	rat, goat
CL 1500836		3-methoxy-2-(2,3,4-trimethoxy-6- methylbenzoyl) benzaldehyde	wheat grape
CL 197675		Methanone, (3-bromo-6-methoxy-2-carboxyl)(2,3,4-trimethoxy-6-methylphenyl)-	grape
CL 3000402		7-bromo-4-methoxy-3-(2,3,4-trimethoxy-6-methylphenyl)-2-benzofuran-1(3H)-one	rat wheat grape
CL 376991		Methanone, (3-bromo-6-methoxy-2-methylphenyl)(2,3,4-trimethoxy-6-methylphenyl)-	rat wheat
CL 379395		2-(3-bromo-6-methoxy-2-methylbenzoyl)- 3,4,5-trimethoxybenzaldehyde	grape
CL 434223		Methanone, (3-bromo-6-methoxy-2-methylphenyl)(4-hydroxy-2,3-dimethoxy-6-methylphenyl)-	rat wheat
M560F06	 R = H, R' and R" = CH_3 or R' = H, R and R" = CH_3 or R" = H, R and R' = CH_3	Methanone, (3-bromo-6-methoxy-2-methylphenyl)(2-hydroxy-3,4-dimethoxy-6-methylphenyl)- or Methanone, (3-bromo-6-methoxy-2-methylphenyl)(3-hydroxy-2,4-dimethoxy-6-methylphenyl)- or Methanone, (3-bromo-6-methoxy-2-methylphenyl)(4-hydroxy-2,3-dimethoxy-6-methylphenyl)-	hen

Animal metabolism

The Meeting received information on the metabolism of ^{14}C-metrafenone, separately labelled at the bromophenyl and the trimethoxyphenyl groups, in rats, lactating goats and laying hens. As no cleavage of the molecule was observed in these metabolism studies, the results for both radiolabels are reported together.

The metabolism of metrafenone in rats was evaluated by the WHO Core Assessment Group of the 2014 JMPR. Absorption of metrafenone is rapid and complete (> 88%) at the low dose of 10 mg/kg bw, limited to 15–20% at the high dose of 1000 mg/kg bw suggesting saturation of the

absorption processes. Metrafenone is widely distributed in the body, with highest residue levels mainly found in the gastro-intestinal (GI) tract, liver and fat. There is no evidence of accumulation. The labelled material is relatively rapidly excreted into the GI tract via the bile (85–90%) resulting in extensive excretion via faeces. Excretion via urine is relatively low (5–6% depending on radiolabel position), and even lower at the high dose level (*ca.* 1%). Metrafenone is extensively metabolised, with most of the radioactivity (approximately 80%) not identified, consisting of many (11–26) different components and totalling < 0.1 ppm at the low dose and < 1 ppm at the high dose. The identified metabolites, mostly < 1.0 mg eq./kg, included metrafenone and glucuronic acid conjugates in fat, liver and kidney.

Lactating goats

Lactating goats were orally dosed with ^{14}C-metrafenone at doses equivalent to about 10 ppm (8–13 ppm) and 70 ppm (60–87 ppm) in the feed for 5 consecutive days and sacrificed 23 hours after the last dose.

The majority of the radioactivity (76–86% AR) was excreted, mainly through the faeces. The highest residue levels were found in liver (0.21–0.23 mg eq./kg at the lower dose and 0.72–1.3 mg eq./kg at the higher dose) and kidney (0.05–0.06 mg eq./kg at the low dose and 0.16–0.33 mg eq./kg at the higher dose). Residues were significantly lower in fat (0.015–0.022 mg eq./kg at the high dose rate) and were ≤ 0.01 mg eq./kg in muscle and milk regardless of the dose rate. Residues reached a plateau in milk (0.01 mg eq./kg) within 3 days.

Residue characterization and identification was conducted on samples from the high dose groups with more than 95% TRR could be extracted from liver, kidney, milk and fat. Muscle samples were not investigated further because of the low TRR levels (< 0.01 mg eq./kg).

In fat, the predominant residue was metrafenone (0.01–0.02 mg/kg), making up 60–85% TRR and no other residues above 0.005 mg eq./kg (9% TRR) were found.

In liver and kidney, metrafenone made up about 3-4% TRR. The predominant residues were the glucuronide metabolites CL 1500698 and CL 1023363, not measured individually but together represented up to 15-21% TRR (0.27 mg eq./kg) in liver and up to 26–28% TRR (max 0.09 mg eq./kg) in kidney. An additional radiolabel fraction that included the glucuronide metabolites CL 1023361, CL1023362 and CL 1500702 totalled about 9–14% of TRR (max 0.17 mg eq./kg in liver and 0.03 mg.kg in kidney). About half the TRR was made up of a number of other unidentified metabolites, each present at < 5% TRR.

In milk, residues of metrafenone (24% TRR) and numerous metabolites, including one radiolabel fraction containing CL 1500698 and CL 1023363 (11% TRR), were all < 0.005 mg eq./kg.

Laying hens

In a poultry study laying hens were orally dosed with ^{14}C-metrafenone at doses equivalent to about 14 ppm in the feed for 12 consecutive days and sacrificed 22 hours after the last dose.

The majority (86-95%) of the administered dose was excreted, with about 0.25% AR (0.1 mg eq./kg) remaining in eggs, up to 0.09% AR (0.3-0.5 mg eq./kg) found in liver, < 0.01 % AR (0.06–0.08 mg eq./kg) present skin+fat and 0.003% AR (0.01 mg eq./kg) in muscle. Residues reached a plateau in eggs after 9 days.

Extraction was able to retrieve about 80% TRR from eggs, 60% TRR from skin+fat and about 30% TRR in liver and muscle. Characterisation and identification of residues in solvent-extracted samples indicated the presence of numerous polar and non-polar components. The one identified metabolite M560F06 was found in poultry skin+fat (6-11% TRR, < 0.01 mg eq,/kg) and was identified but not quantified in eggs.

Metrafenone was found only in eggs and skin+fat, making up about 2% TRR (0.001-0.002 mg/kg) and the metabolite M560F06 was also measured in skin+fat (6–11% TRR) and

identified in eggs. With the exception of one unknown component in eggs (about 14% TRR, 0.015 mg eq./kg) all other metabolites were < 10% TRR (< 0.01 mg eq./kg) in all tissues and eggs.

In summary, residues were rapidly eliminated in the excreta (76–95% of the dose) with up to 0.5% of the total administered dose remaining in liver, 0.25% remaining in eggs, and TRRs were up to 0.02 mg eq./kg in fat and ≤0.01 mg eq./kg in muscle, poultry skin+fat and in milk.

The proposed metabolic pathways include hydroxylation and demethylation of the methyl groups and the phase II glucuronidation of the hydroxylated metabolites to various mono-O-glucuronides, qualitatively similar to the metabolic pathway in the rat.

Metrafenone made up about 2–4% of the TRR in liver, kidney, eggs and poultry skin+fat, was the main component in fat and was about 24% TRR in milk, but at very low levels (< 0.005 mg eq./kg). Most of the residues in liver and kidney were the glucuronide conjugates of metrafenone (CL 1500698, CL 1023363) which together made up 15–30% TRR, and numerous unidentified components, each present at < 10% TRR.

Plant metabolism

The Meeting received information on the metabolism of ^{14}C-metrafenone, separately labelled at the bromophenyl and the trimethoxyphenyl groups, in grapes, cucumber and wheat.

Grape

In outdoor grapevines treated with five foliar applications of ^{14}C-metrafenone at a rate equivalent to 0.2 kg ai/ha, 10-11 days apart, TRRs in grapes immediately after the last application were 0.6–0.77 mg eq./kg, reducing to 0.28–0.44 mg eq./kg at maturity, 35 days later. In leaves sampled immediately after the last application, TRRs were 40–42 mg eq./kg, reducing to 25–38 mg eq./kg after 35 days.

In grape juice, pomace and in leaves, 77–100% TRR was able to be sequentially extracted with acetone, methanol:water and water, with about 39–45% of the TRR in leaves being present in the acetone surface wash. Whole grapes were not analysed.

Metrafenone was not found in juice, but was the major residue in pomace (23–25% TRR, 0.06–0.11 mg/kg), and made up about 11–15% TRR in mature leave (35 days after the last application).

Characterisation of the residues in grape juice and pomace indicated the presence of several chromatographic fractions more polar than the parent, not exceeding 0.05 mg eq./kg and not more than 17% TRR. These were not identified further except for CL197675, found in juice at about 9% TRR (0.006 mg eq./kg).

Cucumber

In cucumber plants (confined) treated with two foliar applications of ^{14}C-metrafenone, applied 17 and 3 days before harvest, at a rate equivalent to 0.2 kg ai/ha, TRR in mature fruit, sampled 3 days after the second application were about 0.05 mg eq./kg (TRR), with 0.013 mg eq./kg present in pulp and 0.26 mg eq./kg in peel. More than 89% TRR was able to be extracted with methanol.

Metrafenone was the only identified residue component, making up 42% of the TRR in the mature fruit (0.02 mg/kg), and mostly in the peel (61% TRR, 0.16 mg/kg). Metrafenone also made up about 80% TRR in vines (without roots and fruit) at harvest.

Numerous polar and medium polar metabolites, characterized by their HPLC retention times and elution profiles, were present in fruit and vines at low concentrations (each less than 9% TRR).

Wheat

In outdoor wheat plants treated with 3 foliar applications of ^{14}C-metrafenone at rates equivalent to 0.3, 0.3 and 0.2 kg ai/ha, applied at 13–14 day intervals and with the last application being 35 days before

harvest, highest radioactive residues (up to 9 mg eq./kg) were found in hay and straw, with the lowest residues found in the grain (0.2–0.4 mg eq./kg). The TRR in foliage, 3 days after the first application were 5–8 mg eq./kg. Methanol:water extraction was able to release about 95% TRR in foliage, 78% TRR in hay, 61% TRR in straw and 35% TRR in grain. Additional extraction with hexane and acidified methanol was able to release a further 12–14% TRR in grain.

Metrafenone was the major component in all matrices, about 59–64% TRR in foliage, 13–26% TRR in hay, 8–14% in straw and 3–8% TRR in grain.

Other characterized or identified metabolites in foliage, hay and straw each represented less than 10% TRR. In grain, no identified metabolites were found above 0.004 mg eq./kg and although only about 50% of the radioactivity was extracted, further investigation showed that residues in the PES were made up of multiple minor components.

The proposed metabolic pathway involves oxidation of the methyl groups on the bromophenyl and trimethoxyphenyl rings to yield the corresponding aldehydes. In the case of the bromophenyl ring, the aldehyde can undergo further oxidation to the carboxylic acid, cyclization to form the lactone, and/or dehalogenation to form the des-bromo aldehyde.

In summary, metrafenone is the predominant residue in crops, with numerous minor metabolites or fractions present at low concentrations and generally more polar than the parent. While these were not all identified or quantified, individual peaks were < 10% TRR or < 0.01 mg eq./kg.

Environmental fate

The Meeting received information the environmental fate and behaviour of metrafenone, including hydrolytic stability, photolysis in aqueous solutions, aerobic metabolism and rotational crop metabolism studies.

Metrafenone was stable in sterile buffered solutions at pH 4, 7, and 9 but rapidly degraded in aqueous pH 7 solutions by photolysis (DT_{50} values of 2.6–3.1 days) with the formation of multiple degradation products, all found at < 10% of the applied radioactivity. DT_{90} values were 8.5 days (natural water) and 10.2 days (sterile water).

Aerobic soil metabolism

Metrafenone degraded slowly in loamy sand, sandy loam and clay loam soils treated with the equivalent of about 0.1 kg ai/ha [bromophenyl-label]-metrafenone or [trimethoxy-label]-metrafenone and incubated for up to 210 days under aerobic laboratory conditions. Metrafenone made up about 82% AR after 120-days and 66–69% AR after 210 days. Calculated half-lives (1st order kinetics) ranged from 182–365 days.

Residues in succeeding crops

In one outdoor rotational crop metabolism study, a leafy vegetable crop (lettuce), root crop (radish) and oil crop (canola) were planted back at various time intervals (30, 60, 90 and 365 days) after a single application of [trimethoxy-label]-metrafenone or [bromophenyl-label]-metrafenone to bare soil at a rate equivalent to 0.625 kg ai/ha.

The uptake of residues in these representative rotational crops (lettuce, radish, canola) was low, with TRRs at all plant-back intervals ranging from < 0.004 to 0.048 mg eq./kg (in canola pods), generally highest in the samples from the 30-day plant back interval. In soil, radioactive residues declined by about 50% after 90 days, and were mostly found in the top 10 cm of soil samples.

Total extractable residues ranged from 64% to 88% TRR in the majority of the samples (42–86% TRR in canola seed) and comprised mostly of multiple unidentified polar components, all present at < 0.02 mg eq./kg. Metrafenone accounted for 0.004 mg/kg of the TRR in lettuce (90 DAT) and radish roots (30 DAT) and was not found in canola or radish tops.

In summary, metrafenone is stable to hydrolysis, rapidly degraded by photolysis, slowly degraded in soil under aerobic conditions (remaining mostly in the top 10 cm) and not found at

significant levels in rotational crops. The Meeting concluded that residues are not expected in rotational crops following treatments according to the GAPs under consideration.

Analytical methods

Several analytical methods have been reported and validated for the analysis of metrafenone in plant and animal commodities. One method has also been validated for measuring residues of the CL 300402, CL 434223 and CL 376991 metabolites. The basic approach employs extraction with methanol/water, aqueous acetone or n-heptane/acetone, SPE or GPC clean-up and analysis by GC-ECD, GC-MS, or LC-MS/MS. In some methods, an additional partition step is included, using dichloromethane, cyclohexane, acetone, ethyl acetate, singly or sequentially.

For plant and processed plant commodities, the DFG S19 (GC-ECD or GC-MS) or the QuEChERS (LC-MS/MS) methods were used in most of the supervised residue field trials, with the RLA 12619 (LC-MS/MS) method used to measure parent and metabolites in some cereal trials. These methods were validated in a range of matrices (wheat, barley, grapes, cucumber, summer squash, melon, tomato, pepper, lemon, dry bean, oilseed rape and hops). The LOQ is 0.1 mg/kg for mushrooms and cereal forage and straws and 0.01 mg/kg for all other matrices.

For animal commodities, the DFG S19 (GC-MS) method was validated for the analysis of metrafenone in muscle, milk and eggs. After extraction with aqueous acetone, extracts are partitioned into ethyl acetate/cyclohexane before SPE clean-up and analysis. The LOQ is 0.01 mg/kg for milk and 0.05 mg/kg for muscle and eggs.

Stability of pesticide residues in stored analytical samples

Metrafenone residues were stable in analytical samples stored frozen (-18 to -20 °C) for up to 24 months in representative substrates with a high water content (lettuce, tomato), a high starch content (carrot, wheat grain), a high protein content (dry peas), a high oil content (soya bean) (grape, wine) and in , wheat forage and straw residues were stable for at least 31 months. In general, residues in the stored samples were greater than 80% of the spiked levels.

Definition of the residue

In animal commodities, metrafenone was the main identified component in goat fat (60–85% TRR) and poultry eggs and skin+fat (2% TRR) but made up about only 3–4% of the TRR in goat liver and kidney. Most of the identified residues in goat liver and kidney were in the radiolabel fraction that included CL 1500698 and CL 1023363 (totalling 15-30% TRR), with numerous unidentified minor fractions found at lower levels, each generally < 5% TRR. In muscle, TRRs were not found above 0.01 mg eq./kg in the highest dose groups of 65–87 ppm (goat) and 14 ppm (hen) and the TRR in milk was also < 0.01 mg eq./kg.

Based on the metabolism studies, a residue definition for animal commodities that includes metrafenone and the CL 1500698 and the CL 1023363 glucuronides could be considered. However the Meeting noted that these metabolites were not found in hens and only present in goats at low levels (totalling up to 0.27 mg eq./kg in liver and 0.09 mg eq./kg in kidney) following dosing at levels more than 7 times higher than the anticipated maximum livestock dietary burdens. CL 1023363 is structurally similar to rat metabolites and CL 1500698 was found in the rat metabolism study. Both metabolites are accommodated in the ADI. The Meeting therefore concluded that they need not be included in the residue definitions.

Based on the anticipated dietary exposure, the Meeting concluded that significant residues of the CL 1500698 and CL 1023363 metabolites are not expected in animal commodities and as a multi-residue method existed to measure the parent compound in animal commodities, a suitable residue definition for MRL-compliance and dietary intake estimation was metrafenone. Based on the Log P_{ow} of 4.3 and since residues of metrafenone were only found in fat and milk, the Meeting concluded that metrafenone is fat-soluble.

In plant commodities from treated crops, the metabolism studies indicated that metrafenone was the major residue in grape (up to 25% TRR in grape pomace), cucumber (up to 42% TRR) and wheat matrices (up to 8% TRR in grain and 14-64% TRR in foliage and straw), with numerous minor metabolites or radiolabel fractions present at low concentrations and generally more polar than the parent. While these were not all identified or quantified, individual peaks were < 10% TRR or < 0.01 mg eq./kg.

Metabolite CL 3000402 was occasionally found in grain at levels up to about 10% of the parent concentration but were < 0.02 mg/kg. Metabolites CL 3000402, CL 434223 and CL 376991, found in the wheat metabolism study at up to 7% TRR in foliage and straw, were also measured in the foliage, straw and hay from a number of wheat and barley field trials, generally at levels less than 10% of the parent residue. These three metabolites were also found in the rat metabolism study and are accommodated in the ADI.

The Meeting noted that multiresidue methods exists to measure parent residues and agreed that for MRL-compliance and dietary intake estimation, the residue definition for plant commodities should be metrafenone.

Proposed definition of the residue (for compliance with the MRL and estimation of dietary intake for plant commodities): *metrafenone.*

Proposed definition of the residue (for compliance with the MRL and estimation of dietary intake for animal commodities: *metrafenone.*

Metrafenone is fat-soluble.

Results of supervised residue trials on crops

The Meeting received supervised trial data for foliar applications of metrafenone on a range of berries and other small fruits, fruiting vegetables, cereals and hops. These trials were conducted mainly in Europe and/or North America.

Where residues have been reported as ND (< LOD) the values have been considered as < LOQ (< 0.01 mg/kg) for the purposes of MRL setting. If a higher residue level was observed at a longer PHI than the GAP, the higher value has been used in MRL setting.

The Meeting noted that GAP has been authorised for the use of metrafenone in more than 50 countries in Europe, the Americas, Asia and the Pacific and that product labels were available from many of these countries. Supervised trial data were also provided for pome fruit, stone fruit and hops, but no GAP information was available to support maximum residue level estimations for these commodities.

Berries and small fruit

Results from supervised trials on grapes conducted in USA and strawberries conducted in Europe were provided to the Meeting.

Grape

The critical GAP for metrafenone on grapes is in Canada, up to 6 foliar applications of 0.225 kg ai/ha applied at least 14–21 days apart with a PHI of 14 days and with a total of 1.35 kg ai/ha/season. In trials from USA conducted at about 1.5 time higher rate than the Canadian GAP, metrafenone residues in grapes were: 0.11, 0.17, 0.18, 0.27, 0.32, 0.62, 2.1, 2.3, 2.4, 3.0, and 3.2 mg/kg. When proportionally adjusted to the Canadian GAP (scaling factors (S_f) of 0.64–0.68), metrafenone residues in these trials are: 0.08, 0.11, 0.12, 0.17, 0.22, 0.42, 1.1, 1.4, 1.5, 1.6, 2.0 and 2.2 mg/kg (n=12).

The Meeting estimated an STMR of 0.74 mg/kg and a maximum residue level of 5 mg/kg for metrafenone on grapes.

Strawberry

The critical GAP for metrafenone on strawberries is on protected crops in the Netherlands, up to 2 foliar applications of 0.15 kg ai/ha, applied at least 7 days apart with a PHI of 3 days. In trials on protected strawberries matching this GAP in Netherlands, metrafenone residues in fruit were: 0.05, 0.06, 0.08, 0.1, 0.16, 0.23, 0.28 and 0.34 mg/kg (n=8).

The Meeting estimated an STMR of 0.13 mg/kg and a maximum residue level of 0.6 mg/kg for metrafenone on strawberries.

Fruiting vegetables, Cucurbits

Results from supervised trials on cucumbers, summer squash (zucchini) and melons (cantaloupes) conducted in Europe and North America were provided to the Meeting. However no GAP information was available from North America

Cucumber

The critical GAP for metrafenone on cucumbers is in France, up to 2 foliar applications of 0.1 kg ai/ha, applied at least 7–10 days apart with a PHI of 3 days. This GAP applies to both outdoor and protected crops.

In trials on outdoor cucumbers in Europe matching this GAP in France, metrafenone residues in cucumbers were: 0.01, 0.02, 0.02, 0.02, 0.02, 0.02, 0.03 and 0.04 mg/kg (n=8).

In trials on protected cucumbers matching this GAP in France, metrafenone residues in cucumbers were: 0.02, 0.04, 0.04, 0.05, 0.05, 0.06, 0.06, 0.07 and 0.09 mg/kg (n=9).

Based on the data set for protected cucumbers, the Meeting estimated an STMR of 0.05 mg/kg and a maximum residue level of 0.2 mg/kg for metrafenone on cucumber.

The Meeting also agreed to extrapolate these estimations to gherkins.

Summer squash

The critical GAP for metrafenone on summer squash is in France, up to 2 foliar applications of 0.1 kg ai/ha, applied at least 7–10 days apart with a PHI of 3 days. In trials on summer squash in Europe matching this GAP in France, metrafenone residues in summer squash were: 0.01, 0.01, 0.01, 0.01, 0.02, 0.02, 0.02 and 0.04 mg/kg (n=8).

The Meeting estimated an STMR of 0.015 mg/kg and a maximum residue level of 0.06 mg/kg for metrafenone on summer squash.

Melons (except watermelon)

The critical GAP for metrafenone on melons is in France, up to 2 foliar applications of 0.1 kg ai/ha, applied at least 7–10 days apart with a PHI of 3 days. In trials on melons in Europe matching this GAP in France, metrafenone residues in melons were: < 0.01, 0.01, 0.01, 0.02, 0.02, 0.02, 0.02, 0.02, 0.02, 0.03, 0.05, 0.06 and 0.07 mg/kg (n=13).

However the Meeting noted that in these trials, the melons had been quartered in the field and although the subsamples had been frozen within 12 hours after sampling, no information was available on residue stability in chopped or sliced samples.

The Meeting was unable to estimate a maximum residue level for metrafenone on melons.

Fruiting vegetables, other than Cucurbits

Results from supervised trials on tomatoes and peppers (sweet, bell and non-bell) conducted in Europe and North America and from trials on mushrooms in Europe were provided to the Meeting.

Mushrooms

The critical GAP for metrafenone on mushrooms is in France, one broadcast treatment of 0.05 kg ai/15 litres water/100 square metres of compost, applied up to 10 days before harvest. In trials on mushrooms in Europe matching this GAP in France, metrafenone residues in mushrooms were: 0.1, 0.1, 0.11 and 0.19 mg/kg (n=4)

The Meeting estimated an STMR of 0.105 mg/kg and a maximum residue level of 0.5 mg/kg for metrafenone on mushrooms.

The Meeting noted that the OECD MRL-calculator proposed a maximum residue level of 0.4 mg/kg, but agreed that a higher value on 0.5 mg/kg was more appropriate due to the small data set and because the relatively close spread of results may not reflect the residue variability arising from different composts used in mushroom production.

Pepper, Sweet

The critical GAP for metrafenone on peppers is in France for protected crops, up to 2 foliar applications of 0.15 kg ai/ha, applied at least 7–10 days apart with a PHI of 3 days. In trials on protected sweet peppers matching this GAP in France, metrafenone residues in peppers were: 0.07, 0.08, 0.1, 0.11, 0.12, 0.2, 0.21 and 1.3 mg/kg (n=8).

The Meeting estimated an STMR of 0.115 mg/kg and a maximum residue level of 2.0 mg/kg for metrafenone on peppers, sweet and agreed to extrapolate these estimations to chili pepper.

For dried chili peppers, applying the default processing factor of 10 to the STMR and the maximum residue level estimated for peppers, the Meeting estimated an STMR-P of 1.15 mg/kg and a maximum residue level of 20 mg/kg for metrafenone on dried chili peppers.

Tomato

The critical GAP for metrafenone on tomatoes is in Spain, up to 2 foliar applications of 0.015 kg ai/hL with a PHI of 3 days. This GAP applies to both outdoor and protected crops.

In trials on outdoor tomatoes in Europe matching this GAP in Spain, metrafenone residues in tomatoes were: 0.02, 0.05, 0.05, 0.06, 0.06, 0.07, 0.08 and 0.15 mg/kg (n=8).

In trials on protected tomatoes matching this GAP in Spain, metrafenone residues in tomatoes were: 0.06, 0.09, 0.09, 0.1, 0.1, 0.1, 0.16 and 0.17 mg/kg (n=8).

Based on the data set for protected tomatoes, the Meeting estimated an STMR of 0.1 mg/kg and a maximum residue level of 0.4 mg/kg for metrafenone on tomato.

Cereal grains

Results from supervised trials on wheat and barley conducted in Europe were provided to the Meeting.

Wheat

The critical GAP for metrafenone on wheat is in Poland, up to 2 foliar applications of 0.15 kg ai/ha with a PHI of 35 days. In trials in Europe matching this GAP in Poland, metrafenone residues in wheat grain were: < 0.01 (9), 0.01 (4), 0.02, 0.03, 0.03, 0.04 and 0.04 mg/kg (n=18).

The Meeting estimated an STMR of 0.01 mg/kg and a maximum residue level of 0.06 mg/kg for metrafenone on wheat.

The Meeting also agreed to extrapolate these estimations to rye and triticale.

Barley

The critical GAP for metrafenone on barley is in Poland, up to 2 foliar applications of 0.15 kg ai/ha with a PHI of 35 days. In trials in Europe matching this GAP in Poland, metrafenone residues in

barley grain were: < 0.01, 0.02 (3), 0.03, 0.04, 0.05 (3), 0.06, 0.06, 0.07, 0.08, 0.09, 0.11, 0.13, 0.15, 0.16, 0.23 and 0.4 mg/kg (n=20).

The Meeting estimated an STMR of 0.06 mg/kg and a maximum residue level of 0.5 mg/kg for metrafenone on barley.

The Meeting also agreed to extrapolate these estimations to oats.

Animal feeds

Cereal forages

Wheat and barley plant or foliage samples were collected in many of the European trials matching the GAP in Hungary/Poland (up to 2 foliar applications of 0.15 kg ai/ha).

Wheat forage

In wheat trials matching the GAP in Poland, metrafenone residues in plant (forage) samples taken 0-days after the last application were: 1.8, 2.0, 2.0, 2.6, 2.6, 2.6, 2.8, 3.3, 3.7, 3.8, 4.3 and 4.8 mg/kg (fresh weight).

The Meeting estimated a median residue of 2.7 mg/kg (fresh weight) and a highest residue of 4.8 mg/kg (fresh weight) for wheat forage and agreed to extrapolate these estimations to rye and triticale.

Barley forage

In barley trials matching the GAP in Poland, metrafenone residues in plant (forage) samples taken 0-days after the last application were: 1.8, 2.3, 2.5, 2.5, 3.1, 3.4, 3.7, 3.8, 4.6, 5.0, 5.8 and 5.9 mg/kg (fresh weight).

The Meeting estimated a median residue of 3.75 mg/kg (fresh weight) and a highest residue of 5.9 mg/kg (fresh weight) for barley forage and agreed to extrapolate these estimations to oats.

Cereal and grass straws and hays

Wheat and barley straw samples were collected in many of the European trials matching the GAP in Poland (up to 2 foliar applications of 0.15 kg ai/ha).

Wheat straw

In trials in Europe matching this GAP in Poland, metrafenone residues in wheat straw (fresh weight) were: 0.67, 0.67, 0.98, 1.1, 1.3, 1.4, 1.6, 1.7, 1.8, 2.0, 2.1, 2.3, 3.1, 3.1, 3.5, 3.6, 3.6 and 6.7 mg/kg (n=18). After correction for an average 88% dry matter content, residues (dry weight) were: 0.76, 0.76, 1.1, 1.3, 1.5, 1.6, 1.8, 1.9, 2.1, 2.3, 2.4, 2.6, 3.5, 3.5, 4.0, 4.1, 4.1 and 7.6 mg/kg.

The Meeting estimated a median residue of 1.9 mg/kg (fresh weight), a highest residue of 6.7 mg/kg (fresh weight) and a maximum residue level of 10 mg/kg (dry weight) for metrafenone in wheat straw.

The Meeting also agreed to extrapolate these estimations to rye and triticale.

Barley straw

In trials in Europe matching the GAP in Poland, metrafenone residues in barley straw (fresh weight) were: < 0.01, 0.24, 0.41, 0.95, 1.0, 1.1, 1.1, 1.1, 1.2, 1.3, 1.3, 1.5, 1.7, 1.8, 1.9, 1.9, 2.0, 2.1, 3.6 and 3.9 mg/kg (n=20). After correction for an average 89% dry matter content, residues (dry weight) were: < 0.01, 0.29, 0.46, 1.1, 1.1, 1.2, 1.2, 1.24 1.4, 1.5, 1.5, 1.5, 1.9, 2.0, 2.1, 2.1, 2.3, 2.4, 4.0 and 4.4 mg/kg.

The Meeting estimated a median residue of 1.3 mg/kg (fresh weight), a highest residue of 3.9 mg/kg (fresh weight) and a maximum residue level of 6 mg/kg (dry weight) for metrafenone in barley straw.

The Meeting also agreed to extrapolate these estimations to oats.

Fate of residues during processing

The effect of processing on the nature of residues was investigated using radiolabelled metrafenone in buffer solutions incubated under conditions simulating pasteurisation (in pH 4 buffer at 90 °C for 20 minutes); baking, brewing, or boiling (in pH 5 buffer at 100 °C for 60 minutes); and sterilization (in pH 6 buffer at 120 °C for 20 minutes). Metrafenone was stable under these processing conditions with no significant changes in the radio-chromatograms.

The fate of metrafenone residues has been examined in a number of studies simulating household and commercial processing of apples, grapes, strawberries, tomatoes, barley, wheat and hops. Estimated processing factors and STMR-Ps for the commodities considered at this Meeting are summarised below.

Summary of selected processing factors and STMR-P values for metrafenone

RAC	Matrix	Metrafenone [a] Calculated processing factors	PF best estimate	STMR (mg/kg)	STMR-P (mg/kg)
Grape	grapes			0.76	
	must (red wine)	0.03, 0.15, < 0.18, 0.26, 0.57, 0.77, 0.78, 0.81, 1.17, 1.29	0.67		0.51
	wet pomace	2.8, 3.6	3.2		2.4
	wine	0.03, 0.07, < 0.17, < 0.18, < 0.19, < 0.19, < 0.21, < 0.26, < 0.38, < 0.71	0.19		0.14
	juice	0.04, 0.06	0.05		0.038
	raisins	< 0.63, < 0.71, 3.63, 3.94	3.75		2.85
Tomato	fresh			0.1	
	preserved	< 0.02, < 0.02, < 0.02, 0.02	< 0.02		< 0.002
	juice (raw)	0.26, 0.33, 0.35, 0.4	0.34		0.034
	wet pomace	3.3, 4.8, 6.2, 6.3	5.5		0.55
	paste	0.27, 0.3, 0.47, 0.53	0.385		0.039
	puree	0.65, 0.79, 0.83, 1.1	0.81		0.081
Mushroom	fresh			0.105	
	canned	0.16	0.16		0.017
Barley	grain			0.06	
	pearl barley	< 0.13, 0.13, < 0.2, 0.22	0.165		0.01
	abraded fraction	2.5	2.5		0.15
	malt	0.4	0.4		0.024
	brewers grain	0.3	0.3		0.018
	beer	< 0.1, < 0.13, < 0.17, < 0.33,	< 0.15		< 0.009
Wheat	grain			0.01	
	wholemeal flour	0.94, 1.1, 1.7, 1.9	1.4		0.014
	flour type 550	0.14, 0.17, 0.21, 0.29	0.19		0.002
	fine bran	2.6, 3.5, 4.9, 5.3	4.2		0.042
	whole grain bread	0.6, 0.64, 0.71, 1.0	0.675		0.007

[a] Each PF value represents a separate study where residues were above the LOQ in the RAC and is the ratio of the metrafenone residues in the processed item divided by the residues in the RAC.

The Meeting noted that in the studies available, metrafenone residues did not concentrate in food commodities during processing, except in dehydrated commodities such as raisins, bran and flour. Residues also increased in wet pomace (grape and tomato), tomato peel and barley abrasion fractions.

The Meeting estimated a maximum residue level for dried grapes of 20 mg/kg based on the maximum residue level estimated for grapes (5.0 mg/kg) and the median processing factor (3.75) from the USA processing studies.

The Meeting estimated a maximum residue level for wheat bran (processed) of 0.25 mg/kg based on the maximum residue level estimated for wheat (0.06 mg/kg) and a median processing factor of 4.2.

The Meeting estimated a maximum residue level for wheat wholemeal of 0.08 mg/kg based on the maximum residue level estimated for wheat (0.06 mg/kg) and a median processing factor of 1.4.

Residues in animal commodities

Farm animal dietary burden

The Meeting estimated the dietary burden of metrafenone in farm animals on the basis of the diets listed in Appendix IX of the 2009 edition of the JMPR Manual. Noting that fresh forage commodities are not significant in international trade, the Meeting only included the burden contributions from the cereal forages in the European dietary burden calculation, as metrafenone is not authorised for use on cereals in US-Canada, Australia or Japan.

Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are presented in Annex 6 of the 2014 Report and are summarized below:

Estimated maximum and mean dietary burdens of farm animals

	Animal dietary burden, metrafenone, ppm of dry matter diet							
	US-Canada		EU		Australia		Japan	
	max	mean	max	mean	max	mean	max	mean
Beef cattle	0.8	0.26	5.9	3.8	9.3 [a]	4.9 [c]	0.07	0.07
Dairy cattle	0.8	0.25	5.9	3.8	9.2 [b]	4.9 [d]	0.42	0.14
Poultry – broiler	0.05	0.05	0.05	0.05	0.02	0.02	0.007	0.007
Poultry – layer	0.05	0.05	2.0 [e g]	1.3 [f h]	0.015	0.015	0.008	0.008

[a] Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian tissues
[b] Highest maximum dairy cattle dietary burden suitable for MRL estimates for mammalian milk
[c] Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian tissues.
[d] Highest mean dairy cattle dietary burden suitable for STMR estimates for milk.
[e] Highest maximum poultry dietary burden suitable for MRL estimates for poultry tissues.
[f] Highest mean poultry dietary burden suitable for STMR estimates for poultry tissues.
[g] Highest maximum poultry dietary burden suitable for MRL estimates for poultry eggs.
[h] Highest mean poultry dietary burden suitable for STMR estimates for poultry eggs.

For beef and dairy cattle, the calculated maximum dietary burden is 9.3 ppm dry weight of feed and for poultry, noting that in some countries, laying hens may also be consumed, the calculated maximum dietary burden suitable is 2.0 ppm dry weight of feed.

Farm animal feeding studies

No livestock feeding studies were provided.

Animal commodity maximum residue levels

The Meeting noted that in the goat metabolism study, up to 0.014 mg/kg metrafenone was found in the kidney from the high (87 ppm) dose group animals and by extrapolation, this would equate to a maximum level of 0.0015 mg/kg in kidney from animals exposed to the calculated maximum dietary burden of 9.3 ppm.

In liver, metrafenone residues were up to 0.025 mg/kg in the high (60 ppm) dose group animals and by extrapolation, this would equate to a maximum level of 0.004 mg/kg in liver from animals exposed to the calculated maximum dietary burden of 9.3 ppm.

In animals dosed with 10 ppm in the diet (approximating the maximum calculated dietary burden for beef and dairy cattle, radiolabel residues were < 0.005 mg eq/kg in muscle, milk and fat.

The Meeting estimated maximum residue levels of 0.01* mg/kg for metrafenone in meat (from mammals other than marine mammals), 0.01 mg/kg for edible offal (mammalian), 0.01* mg/kg for mammalian fat and 0.01* mg/kg for milks. Estimated STMRs for dietary intake estimation are 0 mg/kg for meat, 0.01 mg/kg for edible offal, 0 mg/kg for fat and 0 mg/kg for milk.

In the hen metabolism study, residues of metrafenone were up to 0.002 mg/kg in eggs and up to 0.001 mg/kg in skin+fat in hens dosed with 14 ppm in the diet (about 7-fold higher than the maximum calculated dietary burden for poultry). In muscle and liver, metrafenone residues were not detected.

The Meeting estimated maximum residue levels of 0.01* mg/kg for metrafenone in poultry meat, 0.01* mg/kg for poultry offal, 0.01* mg/kg for poultry fat and 0.01* mg/kg for eggs. Estimated STMRs for dietary intake estimation are 0 mg/kg for poultry fat, 0 mg/kg for poultry meat, 0 mg/kg for poultry offal and 0 mg/kg for eggs.

RECOMMENDATIONS

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

Definition of the residue (for MRL-compliance and estimation of dietary intake, plant commodities): *metrafenone.*

Definition of the residue (for MRL-compliance and estimation of dietary intake, animal commodities): *metrafenone.*

The residue is fat soluble.

	Commodity	MRL	STMR or
CCN	Name	New	STMR-P
FB 0269	Grapes	5.0	0.76
DF 0269	Dried grapes	20	2.85
FB 0275	Strawberry	0.6	0.13
VC 0424	Cucumber	0.2	0.05
VC 0245	Gherkin	0.2	0.05
VC 0431	Squash, Summer	0.06	0.015
VO 0488	Tomato	0.4	0.1
VO 0445	Pepper, Sweet	2.0	0.115
VO 0444	Peppers, Chili	2.0	0.115
HS 0444	Peppers, Chili, dried	20	1.15
VO 0450	Mushroom	0.5	0.105
GC 0640	Barley	0.5	0.06
GC 0647	Oats	0.5	0.06
GC 0654	Wheat	0.06	0.01
GC 0650	Rye	0.06	0.01
GC 0653	Triticale	0.06	0.01
AS 0654	Wheat straw and fodder, Dry	10 (dw)	1.9 (fw) (hi-res 6.7)

	Commodity	MRL	STMR or
CCN	Name	New	STMR-P
AS 0650	Rye straw and fodder, Dry	10 (dw)	1.9 (fw) (hi-res 6.7)
AS 0653	Triticale straw and fodder, Dry	10 (dw)	1.9 (fw) (hi-res 6.7 fw)
AS 0640	Barley hay and straw	6 (dw)	1.3 (fw) (hi-res 3.9 fw)
AS 0647	Oat straw and fodder, Dry	6 (dw)	1.3 (fw) (hi-res 3.9 fw)
MM 0095	Meat (from mammals other than marine mammals)	0.01 (*)	0
MM 0100	Mammalian fats (except milk fats)	0.01 (*)	0
MO 0105	Edible offal (Mammalian)	0.01	0.01
ML 0106	Milks	0.01 (*)	0
PM 0110	Poultry meat	0.01 (*)	0
PF 0111	Poultry fat	0.01 (*)	0
PO 0111	Poultry, Edible offal of	0.01 (*)	0
PE 0112	Eggs	0.01 (*)	0
	Grape must		0.51
	Wine		0.14
JF 0269	Grape juice		0.04
JF 00488	Tomato juice		0.03
VW 0488	Tomato paste		0.04
	Tomato puree		0.08
	Tomato (canned)		0.002
	Mushrooms (canned)		0.017
CF 0654	Wheat bran, Processed	0.25	0.042
CF 1212	Wheat wholemeal	0.08	0.014
	Pearl barley		0.01
	Malt		0.024
	Beer		0.009
	Flour		0.002
	Bread (wholegrain)		0.007
	Tomato pomace (wet)		0.55
	Grape pomace (wet)		2.4
	Barley bran fractions		0.15
	Brewers grain		0.018
	Wheat forage		2.7 (fw) hi res 4.8 fw)
AF 0650	Rye forage (green)		2.7 (fw) hi res 4.8 fw)
	Triticale forage		2.7 (fw) hi res 4.8 fw)
	Barley forage		3.75 (fw) hi res 5.9 fw)
AF 0647	Oat forage (green)		3.75 (fw) hi res 5.9 fw)

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intake (IEDI) for metrafenone 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.

The International Estimated Daily Intakes of metrafenone for the 17 GEMS/Food cluster diets, based on estimated STMRs were 0% of the maximum ADI of 0.3 mg/kg bw (Annex 3). The Meeting concluded that the long-term intake of residues of metrafenone from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The 2014 JMPR decided that an ARfD was unnecessary. The Meeting therefore concluded that the short-term intake of metrafenone residues is unlikely to present a public health concern.

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7000150	Steinfuehrer, T and Weis, D	2000	^{14}C-AC 375839 (CL 375839): Rate of degradation in soil under aerobic conditions at 10°C. Cyanamid Forschung GmbH, Schwabenheim, Germany Fed.Rep. 2000/7000150. GLP/GEP: Yes. Unpublished
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1129562	Anonymous	2009	Foods of plant origin—Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE-QuEChERS-method—English version of DIN EN 15662:2009-02. DIN Deutsches Institut fuer Normung e. V. Berlin, Berlin, Germany Fed.Rep. 2009/1129562. GLP/GEP: No. Unpublished
7000136	Hausmann, S and Class, T	2000	AC 375839 (CL 375839): Validation of the multi-residue method DFG S19 with modified extraction for the determination of AC 375839 residues in barley grain, grapes, and wine. Cyanamid Forschung GmbH, Schwabenheim, Germany Fed.Rep. 2000/7000136. GLP/GEP: Yes. Unpublished
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7001286	Steinhauer, S and Pelz, S	2001	BAS 560 F (AC 375839): Independent laboratory validation of multi-residue method DFG S 19 with modified extraction for the determination of BAS 560 F residues in barley grain, grapes, and wine. Dr. Specht & Partner Chemische Laboratorien GmbH, Hamburg, Germany Fed.Rep.. 2001/7001286. GLP/GEP: Yes. Unpublished
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7001287	Class, T	2001	BAS 560 F: Independent laboratory validation (ILV) of the multi-residue enforcement method DFG S19 for the determination of BAS 560 F in foodstuff of animal origin (milk, muscle, egg). PTRL Europe GmbH, Ulm, Germany Fed.Rep. 2001/7001287. GLP/GEP: Yes. Unpublished
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7000247	Smalley, R	2001	Method Validation of RLA 12618.00 “LC-MS determination of CL 375839 (BAS 560 F) and CL 377160 residues in soil. BASF Agro Research Gosport, Hampshire, UK. 2001/7000247. GLP/GEP: Yes. Unpublished
7004636	Travis, D	2002	BAS 560 F (CL 375839): Laboratory Validation of LC/MS Determinative and LC/MS/MS Confirmatory Method M 3441 for the Determination of BAS 560 F and CL 377160 Residues in Soil. BASF Agro Research Princeton, New Jersey, USA. 2002/7004636. GLP/GEP: Yes. Unpublished
7005048	Xing, J	2002	BAS 560 F (CL 375839) Laboratory validation of LC/MS determinative and LC/MS/MS confirmatory method M 3503 for the Determination of BAS 560 F and CL 375816 residues in drinking and surface water. BASF Agro Research, Princeton, NJ USA. 2002/7005048. GLP/GEP: Yes. Unpublished
7004394	Carringer, SJ	2013	Magnitude and decline of the residue of Metrafenone in or on pome fruit raw agricultural commodities following three foliar applications of BAS 560 03 F fungicide. The Carringers Inc., Apex NC, United States of America. 2012/7004394. GLP/GEP: Yes. Unpublished
7000577	Greenland, RG	2013	Magnitude of the residue of BAS 560 F in peppers after applications with BAS 560 03 F. Stewart Agricultural Research Services Inc., Clarence MO, United States of America. 2013/7000577. GLP/GEP: Yes. Unpublished
7004672	Greenstreet, CA and Deutsch, E	2002	BAS 560 F (AC 375839) 300 g as/L SC (SF10358) and BAS 560 F 300 g as/L SC (SF09957): At harvest residue study on BAS 560 F in winter wheat, Germany, 2000. CEMAS–CEM Analytical Services Ltd., North Ascot Berkshire SL5 8JB, United Kingdom. 2002/7004672. GLP/GEP: Yes. Unpublished
7001794	Homa, K	2013	Metrafenone: Magnitude of the residue on cherry. IR-4 Project Headquarters, Princeton NJ, United States of America. 2013/7001794. GLP/GEP: Yes. Unpublished
7001835	Homa, K	2013	Metrafenone: Magnitude of the residue on peach. IR-4 Project Headquarters, Princeton NJ, United States of America. 2013/7001835. GLP/GEP: Yes. Unpublished
7001797	Homa, K	2013	Metrafenone: Magnitude of the residue on cantaloupe. IR-4 Project Headquarters, Princeton NJ, United States of America. 2013/7001797. GLP/GEP: Yes. Unpublished
7001798	Homa, K	2013	Metrafenone: Magnitude of the residue on squash (summer). IR-4 Project Headquarters, Princeton NJ, United States of America. 2013/7001798. GLP/GEP: Yes. Unpublished
7001658	Homa, K	2013	Metrafenone: Magnitude of the residue on tomato. IR-4 Project Headquarters, Princeton NJ, United States of America. 2013/7001658. GLP/GEP: Yes. Unpublished

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7004890	Jones, S	2002	Study on the residue behaviour of BAS 560 F in cereals after application of BAS 560 00 F under field conditions in France (S), 2001. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004890. GLP/GEP: Yes. Unpublished
7007012	Jordan, JM and Kasiri, A	2006	Magnitude of BAS 560 F residues in grapes and grape processed fractions following applications of BAS 560 00 F (amended final report). BASF Agro Research RTP, Research Triangle Park NC, United States of America. 2006/7007012. GLP/GEP: Yes. Unpublished
1151102	Malet, JC	2011	Residue of Metrafenone, after one application of Vivando on growing substrat for cultivated mushroom in support of the registration. Ministere de l Alimentation de l Agriculture de la Peche de la Ruralite et de l Amenagement du Territoire, Paris, France. 2011/1151102. GLP/GEP: Yes. Unpublished
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1201582	Oxspring, S	2010	Study on the residue behaviour of Metrafenone in strawberry after treatment with BAS 560 02 F under protected conditions in Northern and Southern Europe during 2009. Eurofins Agroscience Services, Melbourne Derbyshire DE73 8AG, United Kingdom. 2010/1201582. GLP/GEP: Yes. Unpublished
1193371	Oxspring, S	2010	Study on the residue behaviour of Metrafenone in tomato after treatment with BAS 560 02 F under field conditions in Southern Europe during 2009. Eurofins Agroscience Services, Melbourne Derbyshire DE73 8AG, United Kingdom. 2010/1193371. GLP/GEP: Yes. Unpublished
1041880	Oxspring, S	2011	Study on the residue behaviour of Metrafenone in cucumber or zucchini (outdoor) after treatment with BAS 560 02 F in Northern and Southern Europe during 2010. Eurofins Agroscience Services, Melbourne Derbyshire DE73 8AG, United Kingdom. 2011/1041880. GLP/GEP: Yes. Unpublished
1041881	Oxspring, S	2011	Study on the residue behaviour of Metrafenone in melon (outdoor) after treatment with BAS 560 02 F in Northern and Southern Europe during 2010. Eurofins Agroscience Services, Melbourne Derbyshire DE73 8AG, United Kingdom. 2011/1041881. GLP/GEP: Yes. Unpublished
1199010	Oxspring, S	2011	Study on the residue behaviour of Metrafenone in pepper after treatment with BAS 560 02 F under protected conditions in Northern and Southern Europe during 2009. Eurofins Agroscience Services, Melbourne Derbyshire DE73 8AG, United Kingdom. 2010/1199010. GLP/GEP: Yes. Unpublished
1199009	Oxspring, S	2011	Study on the residue behaviour of Metrafenone in tomato after treatment with BAS 560 02 F under protected conditions in Northern and Southern Europe during 2009. Eurofins Agroscience Services, Melbourne Derbyshire DE73 8AG, United Kingdom. 2010/1199009. GLP/GEP: Yes. Unpublished
1041882	Oxspring, S	2011	Study on the residue behaviour of Metrafenone in tomato (outdoor) after treatment with BAS 560 02 F in Southern Europe during 2010. Eurofins Agroscience Services, Melbourne Derbyshire DE73 8AG, United Kingdom. 2011/1041882. GLP/GEP: Yes. Unpublished
1041886	Plier, S	2011	Determination of residues of BAS 560 F (Metrafenone) in hops after two applications of BAS 560 02 F in Germany. BioChem agrar Labor fuer biologische und chemische Analytik GmbH, Gerichshain, Germany Fed.Rep. 2011/1041886. GLP/GEP: Yes. Unpublished
1001354	Raunft, E *et al.*	2004	Study on the residue behaviour of BAS 560 F in cereals after application of BAS 560 00 F under field conditions in Germany, Denmark, France (N) and United Kingdom, 2002. BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed.Rep. 2003/1001354. GLP/GEP: Yes. Unpublished

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1144320	Richter, M	2011	Determination of residues of BAS 560 F (Reg.No. 4037710) in cultivated mushrooms after treatment with Vivando. BASF SE, Limburgerhof, Germany Fed.Rep.. 2011/1144320. GLP/GEP: Yes. Unpublished
7003736	Riley, M	2013	Magnitude and decline of the residue following application of BAS 560 03 F cucumbers. Eurofins Agroscience Services Inc., Forsyth GA, United States of America. 2012/7003736. GLP/GEP: Yes. Unpublished
1033967	Schaeufele, M	2010	Residue study (decline) with BAS 560 02 F applied to cucumber (field) and zucchini (field) in Germany, the Netherlands, Belgium, Northern France, Southern France, Italy, Greece and Spain in 2009. Huntingdon Life Sciences Ltd., Eye Suffolk IP23 7PX, United Kingdom. 2010/1033967. GLP/GEP: Yes. Unpublished
1033968	Schaeufele, M	2010	Residue study (decline) with BAS 560 02 F applied to melons (field) in Northern France, Southern France, Italy, Greece and Spain in 2009. Huntingdon Life Sciences Ltd., Eye Suffolk IP23 7PX, United Kingdom. 2010/1033968. GLP/GEP: Yes. Unpublished
1033969	Schaeufele, M	2010	Residue study (decline) with BAS 560 02 F applied to cucumber (greenhouse) in Germany, the Netherlands, Belgium, Northern France, Southern France, Italy, Greece and Spain in 2009. Huntingdon Life Sciences Ltd., Eye Suffolk IP23 7PX, United Kingdom. 2010/1033969. GLP/GEP: Yes. Unpublished
1041395	Schaeufele, M	2011	Residue study (decline) with BAS 560 02 F applied to melons (field) in Germany in 2010. Huntingdon Life Sciences Ltd., Eye Suffolk IP23 7PX, United Kingdom. 2011/1041395. GLP/GEP: Yes. Unpublished
7001657	Smalley, R	2001	BAS 560 F (AC 375839) 300 g as/L SC (SF10358) and BAS 560 F (AC 375839) 300 g as/L SC (SF09957): At harvest residue study on BAS 560 F in winter wheat–North France 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2001/7001657. GLP/GEP: Yes. Unpublished
7001658	Smalley, R	2001	BAS 560 F (AC 375839) 300 g as/L SC (SF10358) and BAS 560 F (AC 375839) 300 g as/L SC (SF09957): At harvest residue study on BAS 560 F in winter wheat–United Kingdom 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2001/7001658. GLP/GEP: Yes. Unpublished
7001675	Smalley, R	2001	AC 375839 300 g as/L SC (SF 09957): Decline curve residue study on AC 375839 in winter wheat—Germany 1999. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2001/7001675. GLP/GEP: Yes. Unpublished
7001660	Smalley, R	2001	BAS 560 F (AC 375839) 300 g as/L SC (SF 10358): Decline curve residue study on BAS 560 F in winter wheat–North France 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2001/7001660. GLP/GEP: Yes. Unpublished
7001656	Smalley, R	2001	BAS 560 F (AC 375839) 300 g as/L SC (SF10358) and BAS 560 F (AC 375839) 300 g as/L SC (SF09957): At harvest residue study on BAS 560 F in winter wheat—South France 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2001/7001656. GLP/GEP: Yes. Unpublished
7001676	Smalley, R	2001	BAS 560 F (AC 375839) 300 g as/L SC (SF 10358): Decline curve residue study on BAS 560 F in winter wheat—South France 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2001/7001676. GLP/GEP: Yes. Unpublished
7001659	Smalley, R	2001	AC 375839 300 g as/L SC (SF 09957): Decline curve residue study on AC 375839 in winter barley—Germany 1999. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2001/7001659. GLP/GEP: Yes. Unpublished
7004680	Smalley, R	2002	AC 375839 300 g as/L SC (SF 09957): Decline curve residue study on AC 375839 in winter wheat—United Kingdom 1999. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004680. GLP/GEP: Yes. Unpublished
7004745	Smalley, R	2002	AC 375839 300 g as/L SC (SF 09957): Decline curve residue study on AC 375839 in winter wheat—Netherlands 1999. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004745. GLP/GEP: Yes. Unpublished

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7004740	Smalley, R	2002	AC 375839 300 g as/L SC (SF 09957): Decline curve residue study on AC 375839 in winter wheat—France South 1999. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004740. GLP/GEP: Yes. Unpublished
7004445	Smalley, R	2002	BAS 560 F (AC 375839) 300 g as/L SC (SF10358) and BAS 560 F (AC 375839) 300 g as/L SC (SF09957): At harvest residue study on BAS 560 F in winter barley—North France 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004445. GLP/GEP: Yes. Unpublished
7004463	Smalley, R	2002	BAS 560 F (AC 375839) 300 g as/L SC (SF10358) and BAS 560 F (AC 375839) 300 g as/L SC (SF09957): At harvest residue study on AC 375839 in winter barley—Germany 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004463. GLP/GEP: Yes. Unpublished
7004525	Smalley, R	2002	BAS 560 F (AC 375839) 300 g as/L SC (SF10358) and BAS 560 F (AC 375839) 300 g as/L SC (SF09957): At harvest residue study on BAS 560 F in winter barley—South France 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004525. GLP/GEP: Yes. Unpublished
7004529	Smalley, R	2002	BAS 560 F (AC 375839) 300 g as/L SC (SF10358) and BAS 560 F (AC 375839) 300 g as/L SC (SF09957): At harvest residue study on BAS 560 F in winter barley—United Kingdom 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004529. GLP/GEP: Yes. Unpublished
7004744	Smalley, R	2002	BAS 560 F (AC 375839) 300 g as/L SC (SF 10358): Decline curve residue study on BAS 560 F in winter barley—South France 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004744. GLP/GEP: Yes. Unpublished
7004922	Smalley, R	2002	BAS 560 F (AC 375839) 300 g as/L SC (SF 10358): Decline curve residue study on BAS 560 F in winter barley—North France 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004922. GLP/GEP: Yes. Unpublished
7000487	Trewhitt, JA	2001	AC 375839 300 g as/L SC (SF10358 (BAS 560 00 F) and SF09957): At harvest residues study on AC 375839 (BAS 560 F) in winter wheat—The Netherlands, 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2001/7000487. GLP/GEP: Yes. Unpublished
7000488	Trewhitt, JA	2001	AC 375839 300 g as/L SC (SF09957): Decline curve residue study on AC 375839 (BAS 560 F) in winter barley, South France, 1999. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2001/7000488. GLP/GEP: Yes. Unpublished
7004681	Trewhitt, JA	2002	AC 375839 300 g as/L SC (SF09957): Decline curve residue study on AC 375839 (BAS 560 F) in winter barley—UK, 1999. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004681. GLP/GEP: Yes. Unpublished
7004267	White, MT and Stewart, J	2006	Residue of Metrafenone (BAS 560 F) Fenpropimorph, (BAS 421 F) Epoxiconazol (BAS 480 F) in formulation bridging on wheat, barley after BAS 565 00 F BAS 562 00 F BAS 560 00 F BAS 421 12 F BAS 480 31 F field, in DE, DK, N-FR, S-FR, SE, UK 2005. BASF Agro Research RTP, Research Triangle Park NC, United States of America. 2005/7004267. GLP/GEP: Yes. Unpublished
7001430	Wyatt, DR	2013	Magnitude and decline of the residues of Metrafenone in or on grape raw agricultural commodities following three foliar applications of BAS 560 03 F fungicide. The Carringers Inc., Apex NC, United States of America. 2013/7001430. GLP/GEP: Yes. Unpublished
7000144	Class, T	2000	AC 375839 (CL 375839): Storage stability of AC 375839 residues at < –18 °C in grapes and wine. PTRL Europe GmbH, Ulm, Germany Fed.Rep. 2000/7000144. GLP/GEP: Yes. Unpublished
BN-326-010	Class, T	2001	BAS 560 F (AC 375839): Storage stability of BAS 560 F residues at less than or equal to –18 °C in carrots and lettuce. PTRL Europe GmbH. BN-326-010. GLP/GEP: Yes. Unpublished
7004653	Class, T	2002	BAS 560 F (AC 375839): Storage stability of BAS 560 F residues at less than or equal to –18 °C in cereal grain and straw. PTRL Europe GmbH, Ulm, Germany Fed.Rep. 2002/7004653. GLP/GEP: Yes. Unpublished

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1043493	Lehmann, A and Mackenroth, C	2011	Investigation of the storage stability of BAS 560 F in plant matrices. BASF SE, Limburgerhof, Germany Fed.Rep. 2011/1043493. GLP/GEP: Yes. Unpublished
1166088	Lehmann, A and Mackenroth, C	2012	Investigation of the storage stability of BAS 560 F in plant matrices. BASF SE, Limburgerhof, Germany Fed.Rep. 2012/1166088. GLP/GEP: Yes. Unpublished
1187284	Mackenroth, C and Radzom, M	2011	Metrafenone (BAS 560 F)—Statement to request of Chemical Regulation Directorate on Metrafenone storage stability. BASF SE, Limburgerhof, Germany Fed.Rep. 2011/1187284. GLP/GEP: No. Unpublished
1013928	Smalley, R	2003	AC 375839 and metabolites—Freezer storage stability in wheat (whole plant, straw and grain). BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2003/1013928. GLP/GEP: Yes. Unpublished
7000137	An, D	2000	AC 375839: Effects of processing on the nature of the residues due to hydrolysis. BASF Corp., Ewing NJ, United States of America. 2000/7000137. GLP/GEP: Yes. Unpublished
1041879	Braun, D	2011	Determination of residues of BAS 560 F in hops and its processed products after two applications of BAS 560 02 F in Germany. BioChem agrar Labor fuer biologische und chemische Analytik GmbH, Gerichshain, Germany Fed.Rep. 2011/1041879. GLP/GEP: Yes. Unpublished
7004393	Carringer, SJ	2013	Magnitude of the residue of Metrafenone in or on apple processed commodities following three foliar applications of BAS 560 03 F fungicide. The Carringers Inc., Apex NC, United States of America. 2012/7004393. GLP/GEP: Yes. Unpublished
7007012	Jordan, JM and Kasiri, A	2006	Magnitude of BAS 560 F residues in grapes and grape processed fractions following applications of BAS 560 00 F (amended final report). BASF Agro Research RTP, Research Triangle Park NC, United States of America. 2006/7007012. GLP/GEP: Yes. Unpublished
1041884	Plier, S	2011	Determination of residues of BAS 560 F (Metrafenone) in tomatoes and their processed products after two applications of BAS 560 02 F in Germany. BioChem agrar Labor fuer biologische und chemische Analytik GmbH, Gerichshain, Germany Fed.Rep. 2011/1041884. GLP/GEP: Yes. Unpublished
1041883	Plier, S	2011	Determination of residues of BAS 560 F (Metrafenone) in strawberries and their processed products after two applications of BAS 560 02 F in Germany. BioChem agrar Labor fuer biologische und chemische Analytik GmbH, Gerichshain, Germany Fed.Rep. 2011/1041883. GLP/GEP: Yes. Unpublished
1004080	Pollmann, B	2002	Determination of residues of BAS 560 F in field samples and in processed goods after application of BAS 560 00 F in summer barley at 4 sites in Germany in 2001. GAB Biotechnologie GmbH & IFU Umweltanalytik GmbH, Niefern-Oeschelbronn, Germany Fed.Rep. 2002/1004080. GLP/GEP: Yes. Unpublished
1006302	Pollmann, B	2002	Determination of residues of BAS 560 F in field samples and processed goods after application of BAS 560 00 F in summer wheat at 4 sites in Germany in 2001. GAB Biotechnologie GmbH & IFU Umweltanalytik GmbH, Niefern-Oeschelbronn, Germany Fed.Rep.. 2002/1006302. GLP/GEP: Yes. Unpublished
7004451	Smalley, R	2002	BAS 560 01 F (AC 375839) 500 g as/L SC (SF 09955): At harvest residue and processing study on BAS 560 F in vines—Italy, 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004451. GLP/GEP: Yes. Unpublished
7004455	Smalley, R	2002	BAS 560 01 F (AC 375839) 500 g as/L SC (SF 09955): At harvest residue and processing study on BAS 560 F in vines—North France, 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004455. GLP/GEP: Yes. Unpublished
7004459	Smalley, R	2002	BAS 560 01 F (AC 375839) 500 g as/L SC (SF 09955): At harvest residue and processing study on BAS 560 F in vines—Spain, 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004459. GLP/GEP: Yes. Unpublished

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7004460	Smalley, R	2002	BAS 560 01 F (AC 375839) 500 g as/L SC (SF 09955): At harvest residue and processing study on BAS 560 F in vines—South France, 2000. BASF plc, Gosport Hampshire PO13 0AU, United Kingdom. 2002/7004460. GLP/GEP: Yes. Unpublished
7001048	Smalley, R	2001	Method Validation of RLA 12619.00 "Determination of CL 375839, CL 3000402, CL434223 and CL 376991 Residues in Cereals (whole plant and straw) using LC-MS". BASF Agro Research, BASF plc. Gosport Hampshire PO13 0AU, United Kingdom. 2001/70001048. GLP/GEP: Yes. Unpublished
7001770	Kang, J	2001	Validation of RLA 12619.02V for CL 375839 in Wheat Grain to a Limit of Quantification of 0.01 mg/kg. BASF Agro Research, BASF plc. Gosport Hampshire PO13 0AU, United Kingdom. 2001/70001770. GLP/GEP: Yes. Unpublished
1004080	Pollmann, B	2002	Determination of residues of BAS 560 F in field samples and in processed goods after application of BAS 560 00 F in summer barley at four sites in Germany in 2001. GAB Biotechnologie GmbH & IFU Umweltanalytik GmbH, Niefern-Oeschelbronn, Germany Fed.Rep. 2002/1004080. GLP/GEP: Yes. Unpublished
7000111	Smalley, R	2000	Validation of a gas chromatography method for the determination of CL 375839 residues in grapes. BASF Agro Research, BASF plc. Gosport Hampshire PO13 0AU, United Kingdom. 2000/7000111. GLP/GEP: Yes. Unpublished