MESOTRIONE (277)

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EXPLANATION

Mesotrione is a systemic pre-emergence and post-emergence herbicide for the selective contact and residual control of broadleaf weeds. It is rapidly absorbed by green plant tissue or taken up through the soil during emergence. It acts by inhibiting the enzyme 4-hydroxyphenolpyruvate dioxygenase (HPPD), leading to a reduction of carotenoids causing bleaching symptoms in the plant. Mesotrione was scheduled for the evaluation as a new compound by the 2014 JMPR at the 45th Session of the CCPR (2013). Metabolism studies on animal and plants, environmental fate studies, analytical methods and residue trials on berries, okra, sweet corn, soya bean and tolerant soya bean, asparagus, rhubarb maize, millet, oat, rice, sorghum, sugarcane and linseed were submitted for evaluation.

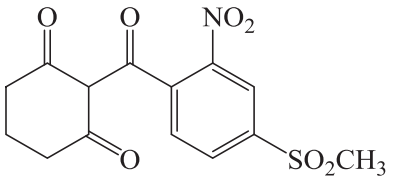
IDENTITY

ISO Common Name: Mesotrione

Chemical name: IUPAC: 2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1.3-dione

CAS (104206-8): 2-[4-(methylsulfonyl)-2-nitrobenzoyl]-1.3-cyclohexanedione

Structural formula



Molecular formula: $C_{14}H_{13}NO_7S$

Molecular mass: 339.3

PHYSICAL AND CHEMICAL PROPERTIES

Mesotrione pure material (> 99%) was used for colour, physical state, odour, melting point, pH and spectroscopic characterisation, and also for density, aqueous solubility, dissociation constant, octanol/water partition coefficient and vapour pressure determinations. Colour, odour, solubility in organic solvents, density, pH and surface tension determinations for mesotrione technical material were conducted with material containing 96.7% mesotrione.

Properties of pure mesotrione

Property	Results	Reference; Report
Melting point	165.3 °C with decomposition	Goodman, 1996; RR95-077B
Density at 20 ºC	1.49 g/cm^3	
Vapour pressure at 20 ºC	< 5.7 × 10^{-6} Pa	
Volatility at 20 ºC	Henry's law constant: < 5.1 × 10^{-7} Pa/m^3/mol.	
Physical state, colour, odour	Odourless pale yellow solid (room temperature)	
Solubility in water at 20 ºC	0.16 g/L (unbuffered water) 2.2 g/L at pH 4.8 (buffered water) 15 g/L at pH 6.9 (buffered water) 22 g/L at pH 9 (buffered water)	
Partition coefficient n-octanol/ water at 20 ºC	log P_{OW}: 0.11 in unbuffered water 0.90 at pH 5 < –1.0 at pH 7 and 9	
pH at 20 ºC	3.38 at 25.4 °C in 1% aqueous solution	

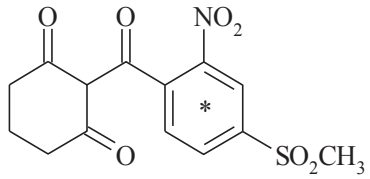
Property	Results	Reference; Report
Hydrolysis in water at 25 ºC	Less than l0% degradation of mesotrione (1 µg/ml) occurred during the test period of 30 days in the pH of 4–9 at both 25 and 50 °C.	Miles & Powell, 1995; RJ1776B
Photochemical stability in water	The photolysis half-life and rate constant in sterile aqueous buffer solutions at pH 7 at 25 °C were 83.7 days and 8.40 × $l0^{-3}$/day, respectively at 37°56' latitude local sunlight, or 92 days at 50°N. No degradates exceeding 10% of the applied radioactivity were observed during the photolysis of [^{14}C-phenyl] mesotrione. The major degradation product was carbon dioxide ($^{14}CO_2$), the others were present at levels < 5% of the applied radioactivity. Recovery ranged from 92.2 to 101.8%. Recovery of 92.2% was only observed prior to trapping volatiles formed during photolysis of [^{14}C-cyc1ohexane] mesotrione. The average recovery of applied radioactivity after trapping volatiles was 95.4%.	Eya, 1995; RR94-071B
Dissociation constant at 20 ºC	pK_a=3.12	Goodman, 1996; RR95-077B

Technical grade material (Goodman, 1996; RR96-004B)

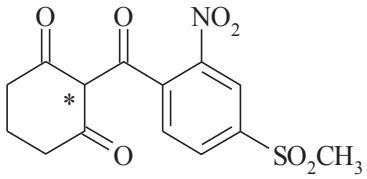
Property	Results
Physical state, colour, odour	Light tan or sand coloured opaque solid with slight odour. sweet (not pungent)
Solubility in organic solvents at 20 ºC	Acetone 76.4 g/L Acetonitrile 96.1 g/L 1.2-Dichloroethane 82.7 g/L Ethyl acetate 16.6 g/L Heptane < 0.3 g/L Methanol 3.6 g/L Toluene 2.7 g/L Xylenes 1.4 g/L
Density	The density at 20 °C: 1.46 g/ml; bulk density at 23.3 °C: 0.56 g/mL
pH	The pH of a 1% solution: 3.42 at 24.8 °C
Surface tension at 20 ºC	Aqueous solution,90% saturated: 72.5 mN/m (without indication of surface activity)

METABOLISM AND ENVIRONMENTAL FATE

The fate and behaviour of mesotrione in animals, plants, and soils were investigated using the following [^{14}C] labelled test materials:



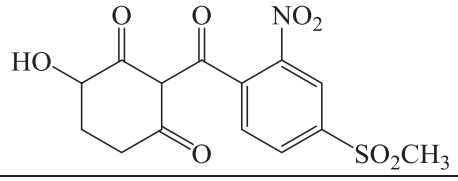
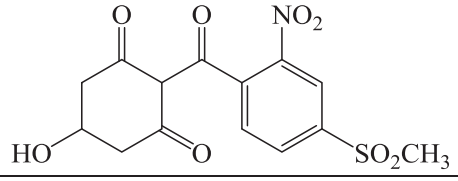
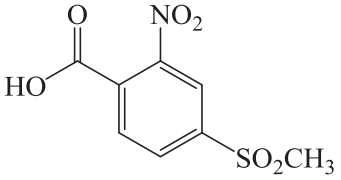
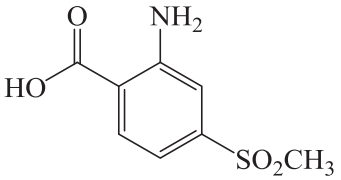
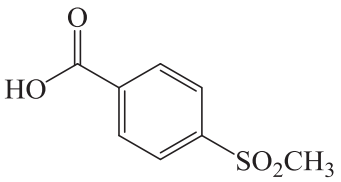
[Phenyl-U-^{14}C]-mesotrione



[Cyclohexane-2-^{14}C]-mesotrione

Concentrations of radioactivity are expressed as mg mesotrione equivalents/kg throughout. The chemical structures of the major degradation compounds arising from the metabolism of mesotrione are presented in the following table.

Degradation compounds from metabolism of mesotrione in plants and animals

Compound Name	Structure	Found in:
4-Hydroxy-mesotrione 4-hydroxy-2-[4-(methylsulphonyl-2-nitrobenzoyl]-1,3-cyclohexanedione		Livestock, plant
5-Hydroxy-mesotrione 5-hydroxy-2-[4-(methylsulphonyl-2-nitrobenzoyl]-1,3-cyclohexanedione		Livestock, plant
MNBA 4-(methylsulphonyl)-2-nitrobenzoic acid		Livestock, plant
AMBA (2-amino-4-(methylsulphonyl)-benzoic acid)		Livestock, plant
MBA 4-(methylsulphonyl) benzoic acid		Livestock, plant

Animal metabolism

Cow

Two metabolism studies were conducted in lactating cows, one with [phenyl-U-^{14}C]-mesotrione (Powell & Marples, 1996; RJ 1890B) and one with [cyclohexane-2-^{14}C]-mesotrione (Hand, 1995; RJ 1830B). The studies used similar dosing regimens, sampling protocol and analysis. In each study, one lactating cow was dosed orally with [^{14}C]mesotrione for 7 consecutive days at a nominal rate of 10 ppm in the diet (450–650 kg cow, 20 kg feed intake per day). Milk and excreta were collected daily; the cows sacrificed 16 hours after the final dose and tissues taken for analysis. Milk production was around 20 L per day.

Tissue samples were homogenised in sequence in the presence of solvents such as hexane, acetonitrile/hexane, dichloromethane, acetonitrile, acetonitrile/water (1:9) and 2% sodium dodecyl sulphate (SDS). Each of the extracts was radioassayed. Extracts were partitioned in diethyl ether and water, ethyl acetate and water, hexane and water or hexane and acetonitrile. Solubilised protein was denatured with acetone. Hydrolyses of proteins and extracts were conducted to characterise the bound and/or conjugated residues, using a variety of enzymes, including papain (to hydrolyse ester and peptide bonds) and β-glucuronidase (to hydrolyse glucuronides). Subsamples of the milk extract were submitted to chemical hydrolysis using either 1 M HCl or 1 M NaOH. Protein hydrolysate samples

were derivatized with isobutyl chloroformate to facilitate the chromatography. Residues in tissues were determined by combustion analysis. Normal or reserve phase TLC and HPLC radiochromatograms were used to characterise the components.

Table 1 shows the total radioactive residues found in tissues, milk and excreta (Hand, 1995, Powell & Marples, 1996). Over 90% of the administered dose was found in excreta, mostly in faeces. Liver and kidney contained the highest residues (about 0.1 mg/kg eq.). Residues in muscle were below 0.01 mg/kg eq and reached 0.08 mg/kg eq in milk, with a plateau at day 5 in the cyclohexane experiment (Table 2).

Table 1 Radioactive residues in lactating cow tissues, milk and excreta after oral administration of [^{14}C]mesotrione

	[phenyl-U-^{14}C]-mesotrione		[Cyclohexane-2-^{14}C]-mesotrione	
Matrix	mg/kg eq.	% Total administered	mg/kg eq.	% Total administered
Liver	0.077	–	0.110	–
Kidney	0.067	–	0.110	–
Muscle (fore)	0.002	–	0.007	–
Muscle (hind)	0.002	–	0.007	–
Peritoneal Fat	≤ 0.004	–	0.008	–
Perirenal Fat	0.007	–	0.005	–
Subcutaneous Fat	≤ 0.004	–	0.013	–
Milk	0.01 to 0.04 (day 5)	0.29	0.06 to 0.08 (day 5–8)	–
Urine		9.65d		13.1
Faeces		80.9		79.4
Total in excreta		90.6		92.5

Table 2 Mean daily radioactive residues in milk (mg/kg mesotrione equivalents)

Study	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8 [a]
[phenyl-U-^{14}C]	0.006	0.052	0.065	0.067	0.074	0.078	0.079	0.072
[Cyclohexane-2-^{14}C]-	0.01	0.03	0.03	0.03	0.04	0.03	0.03	0.03

[a] AM collection only

Table 3 (Powell & Marples, 1996) and Table 4 (Hand, 1995) show the results of the characterization of radioactive residues in liver and kidney. Mesotrione accounted for up to 12.3%TRR in liver and 18%TRR in kidney (< 0.02 mg/kg eq.), while AMBA was only identified in kidney.

Table 3 Summary of the identification and characterisation of radioactive residues of mesotrione in liver and kidney of cows treated with [phenyl-U-^{14}C]-mesotrione

Commodity		Liver		Kidney	
TRR mg/kg		0.085		0.065	
Origin of component	Component	%TRR	mg/kg	%TRR	mg/kg
Solvent extracts [a]	Mesotrione	10.3	0.009	18.0	0.012
	AMBA	ND	ND	15.0	0.010
	Unknowns	24.1 [b]	0.020	35.8 [c]	0.023
	Remainder [d]	6.9	0.006	5.7	0.004
Protein associated fractions	Acetone precipitate	8.7	0.007	1.7	0.001
	Acetone precipitate/Papain hydrolysis debris	9.9	0.008	2.9	0.002
Uncharacterised organosoluble fractions	Acetone [e]	3.0	0.002	4.5	0.003
	Methanol [f]	8.3	0.007	4.0	0.003
	Acidified methanol [f]	13.2	0.011	–	–

Commodity		Liver		Kidney	
Uncharacterised aqueous soluble fractions	H_2O extract	3.7	0.003	2.5	0.002
Unextracted		1.7	0.001	4.1	0.003
Losses/gains		10.2	0.009	5.8	0.004
Total		100	0.083 [g]	100	0.066 [g]

[a] Values are based on the mean values obtained from three different TLC systems
[b] Containing at least eight individual components
[c] Components, none of which were > 7.9% TRR, 0.007 mg/kg
[d] Containing at least seven individual components, none of which were > 6.4% TRR, 0.004 mg/kg
[e] Area corresponding to quantifiable radioactivity containing no discrete bands
[f] Originates from the de-proteination of a subsample of the SDS tissue fraction
[g] Originates from the C_{18} fractionation of the solubilised material from the papain hydrolysis

Table 4 Summary of the identification and characterisation of radioactive residues of mesotrione in liver and kidney of cows treated with [cyclohexane-2-^{14}C]-mesotrione

Matrix	Liver		Kidney	
TRR [a]	0.101 mg/kg		0.107 mg/kg	
Component/Fraction	%TRR [a]	mg/kg	%TRR [a]	mg/kg
Mesotrione	12.5	0.013	14.4	0.015
Neutral organosoluble unknowns [b]	4.2	0.004	6.0	0.006
Aqueous unknowns [c]	1.8	0.002	–	–
Acidic organosoluble unknowns [d]	–	–	2.5	0.003
Acidic unknowns from debris [e]	–	–	0.7	0.01
Remainder [f]	21.3	0.022	13.6	0.015
Uncharacterised soluble fractions. organosoluble [g]	3.4	0.003	8.2	0.009
Aqueous soluble [h]	12.1	0.012	11.9	0.013
Aqueous soluble (eluted from anion ex. resin) [i]	–	–	19.0	0.020
Acid soluble [j]	10.0	0.010	–	–
Base soluble	7.5	0.008	–	–
Proteinaceous solids [k]	29.3	0.030	7.1	0.008
Unextracted	5.4	0.005	–	–
Ion exchange resin-bound	–	–	10.1	0.011
Losses During Fractionation	4.9	0.005	6.5	0.005
Total	100.0	0.101	100	0.106 [l]

[a] TRRs was calculated from the summation of fractions obtained from various complex extraction schemes required to determine the nature of this type of residue
[b] Consists of three components, the largest represents 2% (0.002 mg/kg) liver and 2.6% (0.003 mg/kg) kidney
[c] Consists of two components, largest represents 0.9% (< 0.001 mg/kg)
[d] Consists of two components, largest represents 1.4% (0.001 mg/kg)
[e] Consists of five components resulting from 6 N HCl and subsequent derivatization (largest 0.2%, < 0.001 mg/kg)
[f] Derives from chromatography of multiple extracts. Includes baseline material and non-discrete areas of ^{14}C
[g] Acetonitrile wash of debris (liver), SDS extraction of debris (kidney), which consists of two extracts (max 6.2% TRR. 0.007 mg/kg)
[h] Consists of two extracts, largest represents 7.4% (0.007 mg/kg) in liver and 7.1% (0.008 mg/kg) in kidney
[i] Consists of three extracts, largest representing 11.0% TRR (0.012 mg/kg) of the which could not be chromatographed due to the high concentration of acid present. These extracts were considered to chemical distinct in terms of their ionic nature
[j] Consists of two extracts, largest represents 6.3% TRR (0.006 mg/kg) liver
[k] Consists of two precipitates, largest represents 22.7% (0.023 mg/kg) liver |TRR. This was hydrolysed with 6 N HCl and derivatized with isobutyl chloroformate. The resulting acidic organosoluble fraction consisted of five components, the largest representing 4.0% (0.004 mg/kg)
[l] The slight discrepancy is due to rounding of the calculated values.

Tables 5 shows the results of the characterization study of residues in milk collected from the phenyl labelled experiment (Powell & Marples, 1996). Most of the radioactivity was found in the skimmed milk (97.3% TRR), which was deproteinated using acetone. The resultant aqueous acetone fraction (78.2% TRR) showed to contain at least three polar components, not hydrolysed with enzymes but degraded to up to seven components under harsh acid and basic conditions.

Table 5 Summary of the identification and characterisation of radioactive residues of mesotrione in milk [phenyl-U-^{14}C]-mesotrione

Total [a]			0.036 mg/kg	
Component/Fraction			%TRR	mg/kg
Whole milk	Centrifugation	Butterfat Skim milk [b]	0.6 1.8	0.000 0.001
Skimmed milk (following centrifugation)	Partition	Dichloromethane soluble [c]	3.6	0.001
	SDS precipitation	Protein Aqueous acetone fraction [d]	4.6 3.9	0.002 0.001
	Chromatography of aqueous fraction (following SDS precipitation)	Unknown 1	50.0	0.018
		Unknown 2	2.2	< 0.001
		Unknown 3	21.9	0.008
		Remainder [e]	4.1	0.001
Losses During Fractionation			7.3	0.005
Total			100.0	0.036

Based on the extraction of the Day 6 (initial) milk sample. Further characterisation of additional samples was carried out following derivatization or acid/base hydrolysis but as this did not lead to the identification of discrete components the data is not reported in the table above

[a] Total concentration taken from sum of extractions and combustion analyses

[b] Consists of one sample, skim milk removed from the butterfat samples

[c] Consists of one sample from the partition of skimmed milk with dichloromethane

[d] Consists of two samples obtained from the aqueous wash of the protein fraction

[e] Area corresponding to quantifiable radioactivity containing no discrete bands

TRR in milk from the cyclohexanedione experiment (Hand, 1995) was 0.07 mg/kg eq., 90% of which was associated with the skimmed milk fraction. Lactose accounted for 35.1% TRR in whole milk (Table 6), with the remainder of the extracted radioactivity comprised several unknown components, the largest of which was aqueous soluble and represented 14.7% TRR (0.010 mg/kg). Low levels of radioactivity were found to be associated with the proteinaceous solids and the butterfat.

The radioactive residues in subcutaneous fat were 0.012 mg/kg, with 37% extracted with acetonitrile, leaving 63.3% associated with the debris, from which 46.7% was not extracted (Hand, 1995).

Table 6 Summary of the identification and characterisation of radioactive residues of mesotrione in milk [cyclohexane-2-^{14}C]-mesotrione

Total [a]	0.070 mg/kg	
Component/Fraction	%TRR [a]	mg/kg
Lactose	35.1	0.025
Aqueous Fractions [b]	24.4	0.017
Organosoluble Fractions [c]	10.5	0.007
Remainder [d]	10.5	0.007
Proteinaceous material	7.6	0.005
Butterfat	10.2	0.007
Losses During Fractionation	1.7	0.001
Total	100.0	0.069 [e]

[a] Total concentration taken from sum of skimmed milk and butterfat

[b] Consists of five unknowns, largest of which represents 14.7% TRR (0.01 mg/kg)

[c] Consists of nine unknowns, largest of which represents 5.3% TRR (0.004 mg/kg)

[d] Remainder derives from the chromatography of four extracts. No discrete peaks

[e] Slight difference due to rounding.

Swine

One female Hampshire swine (30 kg) was dosed orally with [phenyl-U-^{14}C]-mesotrione for 5 consecutive days at 6 ppm (Brown, 2006; T020371-04). Excreta were collected daily, the animal sacrificed 23 hours after the final dose, and tissues taken for analysis. Tissue samples were extracted twice with acetonitrile/water (80:20), and further extraction with water was performed on the solids

obtained from the kidney and liver sub-samples. Liquid-liquid partitions were carried out with ethyl acetate after adjustment to pH 2 with acetic acid. C_{18} SPE columns were used to purify the isolated metabolites. Protein was precipitated with either ammonium sulphate or acetone. To extract ionic material and membrane-bound proteins from cell walls, liver PES was extracted with 2% SDS solution, and the solids obtained were submitted to enzymatic hydrolysis. Analytes were separated using 1 and 2-D TLC on silica gel plates. The metabolites were characterised and isolated using HPLC coupled to a UV detector, radioisotope flow monitor and a fraction collector. Additional confirmation and identification was undertaken using tandem mass spectrometry and ^{1}H-NMR.

The radioactivity detected in the excreta accounted for 89.4% of the administered dose. In tissues, highest residues were found in liver (1.75 mg/kg eq) and kidney (0.12 mg/kg eq); residues in muscle reached 0.01 mg/kg eq. (Table 7). Residues in the tissues were readily extracted with solvents, and showed to be mainly mesotrione (up to 90% TRR in liver; Table 8). Residues AMBA accounted for up to 2% TRR in kidney. MNBA was only found in liver (0.3% TRR). The major identified residue in urine collected on day 5 was AMBA which accounted for approximately 36.5% TRR.

Table 7 Radioactive residues in swine tissues and excreta after oral administration of [phenyl-U-^{14}C]-mesotrione

Matrix	Radioactive residue phenyl-U-^{14}C mesotrione equivalents		
	% of the applied dose	mg/kg eq. [a]	mg/kg eq. [b]
Liver	4.2	1.748	1.630
Kidney	0.05	0.117	0.118
Muscle	0.26	0.0096	0.011
Fat	0.06	0.006	n/d
Urine	36.5	–	–
Faeces	51.1	–	–
Total in excreta	89.4 (includes cage washings)	–	–
Total recovered	94.2	–	–

[a] Based on the initial combustion values

[b] Based on dpm from extracted sample. These values were used for calculation in the study. Fat and the remaining tissues were not analysed further

Table 8 Summary of the identification and characterisation of radioactive residues of mesotrione in tissues of swine dosed with [phenyl-U-^{14}C]-mesotrione

Matrix	Liver		Kidney		Muscle	
TRR (mg/kg eq.):	1.630		0.118		0.011	
Extracted (%)	98.7 [b]		90.2		90.7	
Component/Fraction	%TRR [a]	mg/kg eq. [a]	%TRR [a]	mg/kg eq. [a]	%TRR [a]	mg/kg eq. [a]
Mesotrione	89.9	1.465	72.8	0.086	77.9	0.009
AMBA	1.8 [d]	0.029 [d]	2.0	0.002	0.7	< 0.001
MNBA	0.3	0.005	–	–	–	–
Unknown 1	1.0	0.016	–	–	–	–
Unknown 2	–	–	0.3	< 0.001	–	–
Unknown 4	0.2	0.003	0.3	< 0.001	–	–
Unknown 5	< 0.2 [c]	0.003	0.5	0.001	–	–
Unknown 6	1.2	0.020	0.2	< 0.001	–	–
Unknown 7	0.9	0.015	0.3	< 0.001	–	–
Unknown 8	0.7	0.011	1.1	0.001	–	–
Unknown 9	0.2	0.004	0.9	0.001	–	–
Baseline	9.3	0.152	11.5	0.014	6.9	0.001
PES	2.8 [e]	0.046 [e]	9.7	0.011	9.3	0.001
Total [g]	108	1.760 [f]	99.6	0.118 [f]	94.8	0.010 [f]

[a] These calculations include values obtained from HPLC fraction collecting. Components in the HPLC fractograms, as % of the chromatogram, were calculated from the total radioactivity in specific fractions divided by the total radioactivity injected. The total radioactivity recovered from the HPLC fractions ranged from 97–112%, compared to the amount injected. These recoveries were not taken into account in the calculation and thus contributed to the slight losses or gains in the total accountability compared to the initial residues. Small discrepancies between the % and mg/kg values are due to rounding

[b] Includes 2% SDS and protease extraction values

[c] < Value not included in summation
[d] Portions not identified (0.2% TRR AMBA)
[e] Solids remaining after protease and 2% SDS extractions of original PES (16.5% TRR. 0.269 mg/kg)
[f] Calculated by % TRR total × total residue mg/kg

Poultry

Two metabolism studies were conducted in poultry, one with [phenyl-U-^{14}C]-mesotrione (Young & Skidmore, 1995; RJ 177778B) and one with [cyclohexane-2-^{14}C]-mesotrione (Grout, 1996; RJ 12071B). The studies used the same dosing regimen, sampling protocol and analysis. In each study, hens were dosed by gelatine capsule with [^{14}C]- mesotrione for 10 consecutive days at 11 ppm, assuming a daily dietary intake of 150 g and average body weight of 2 kg. Each experiment used 10 hens (*Gallus gallus domesticus*). Excreta and eggs were collected daily.

Eggs were separated into yolks and whites and stored frozen for analysis. The hens were sacrificed approximately 16 hours after the final dose, and tissues stored frozen until analysis. Once thawed, liver, kidney and peritoneal fat samples were chopped, muscle samples were minced whilst partly frozen using a food processor. The skin and subcutaneous fat samples were ground with solid CO_2.

The amount of radioactivity in excreta, edible tissues and eggs was determined in 2–3 hens and samples from the remaining hens were retained for analysis if required. TRR were determined using LSC/combustion or tissue solubilisation/LSC. Tissue samples and egg yolk were homogenised and sequentially extracted with methylene chloride, acetonitrile and acetonitrile/water. Fat samples from the cyclohexane experiment were first extracted with hexane. Between each extraction, the organic phase was separated from the solids (post extraction solids, PES) by centrifugation and analysed for radioactivity. Liquid phases were concentrated and extracted with either ethyl acetate and water or hexane and acetonitrile. SDS was used to extract ionic material and membrane-bound proteins from cell walls; proteins were precipitated out with acetone. Samples of edible tissues and eggs that contained a radioactive residue greater than 0.01 mg/kg were analysed further for residue characterisation. Components were separated using 2-D normal and reverse phase TLC, HPLC-UV or a radioisotope flow monitor and a fraction collector.

The radioactivity in excreta accounted for 90 to 98.7% of the administered dose in both experiments. TRR in edible tissues and egg samples are summarised in Table 9. Highest residues were found in liver and kidney (0.06–1.2 mg/kg eq.) Residues in muscle were below 0.02 mg/kg eq in eggs, residues were higher in the yolk compared to whites, reaching 0.094 mg/kg eq. in yolk in the cyclohexanedione label experiment.

Table 9 Radioactive residues (mg/kg eq.) in eggs and tissues following oral administration of [^{14}C]mesotrione to hens for 10 consecutive days at 11 ppm

	[Phenyl-U-^{14}C]-mesotrione	[^{14}C-cyclohexanedione]-mesotrione
Matrix	Mean TRR (n=3)	Mean TRR (n=2)
Liver	1.121	1.245
Kidney	0.063	0.068
Thigh muscle	< 0.004	0.011
Breast muscle	0.004	0.012
Skin/subcutaneous fat	0.042	0.048
Peritoneal fat	< 0.003	0.010
Egg white	< 0.004 at all days	0.012 (day 1) to 0.025 (day 4); mean=0.019
Egg yolk	< 0.003 (day 1) to 0.024 (day 10); mean=0.015	0.002 (day 1) to 0.094 (day 9/10), mean=0.056

Summaries of the radioactivity extracted sequentially using a range of solvents in each study are present in Tables 10 and 11. In the phenyl label experiment (Table 10), most of radioactivity was extracted from liver and egg yolk with ACN/water, and about 70% TRR extracted from fat with methylene chloride (Young & Skidmore, 1995). Radioactivity in PES ranged from 0.6 to 4.5% TRR in egg yolk.

Table 10 Radioactivity levels extracted from hen tissues and egg samples after oral administration of [phenyl-U-^{14}C]-mesotrione using a range of different solvents

Matrix (TRR, mg/kg eq.)	Extraction solvent (% TRR)					PES (%)
	Methylene chloride	ACN:water (9:1)	ACN:water (1:1)	Water	SDS solution	
Liver (1.234)	–	52.8	22.0	10.3	14.3	0.6
Skin/subc. fat (0.037)	69.2	23.1	1.4	2.7	–	3.6
Egg yolk (0.021)	37.2	53.1	5.3	0	–	4.5

PES Post extraction solids
– Not applicable

In the ^{14}C-cyclohexanedione experiment (Table 11), the majority of the radioactive residue in skin and subcutaneous fat and egg white was extracted with acetonitrile and acetonitrile/water, while peritoneal fat residues were mostly extracted with hexane (Grout, 1996). Half of residues present in muscle were extracted with acetonitrile, with the remaining staying in PES. Residues from egg yolk were mostly extracted with methylene chloride.

Table 11 Radioactivity levels extracted from hen tissues and egg samples after oral administration of [^{14}C-cyclohexanedione]-mesotrione using a range of different solvents

Matrix	Extract (% TRR)						**PES (%)**
	Hexane	Methylene chloride	ACN	ACN/water (1:1)	Water	SDS	
Liver	–	–	19.2	23.5	36.6	18.9	1.8
Skin/subc. fat (n=2)	4.4	–	72.6	11.4	0.0	–	11.6
Peritoneal fat	64.0	–	–	–	–	–	36.0
Thigh muscle	–	–	49.9	–	–	–	50.1
Breast muscle (n=2)	–	–	50	–	–	–	50
Egg white	–		32.3	38.5	5.5	–	23.7
Egg yolk	8.1	59.1	12.4	–	7.1	11.0	2.4

DCM: dichloromethane
ACN= acetonitrile
PES: Post extraction solids
– Not applicable

Mesotrione was detected in both experiments, accounting for over 85% TRR (1.1 mg/kg) in liver (Table 12). Mesotrione was not detected in muscle. The lipid fraction present in the combined yolk sample from the [^{14}C-cyclohexanedione] experiment was extracted with acetone which released 51.7% TRR (0.041 mg/kg), and found to contain mesotrione (0.019 mg/kg). The second acetone fraction was saponified, fractionated and showed to contain palmitic/oleic acid (Table 12). Excreta were shown to contain mesotrione (19.7–55%TRR) and AMBA (18% TRR).

Table 12 Mesotrione residues extracted from hen liver, skin, fat and egg yolk after oral administration

	Liver				Subcutaneous Fat and Skin				Egg Yolk			
	[^{14}C-phenyl]		[^{14}C-cyclo]		[^{14}C-phenyl]		[^{14}C-cyclo]		[^{14}C-phenyl]		[^{14}C-cyclo]	
	mg/kg eq.	%TRR	mg/kg eq.	%TRR	mg/kg eq.	%TRR	mg/kg eq.	%TRR	mg/kg eq.	%TRR	mg/kg eq.	%TRR
Mesotrione	1.051	85.2	1.097	90.7	0.032	85.3	0.033	59.0-71.2	0.017	80.9	0.019	19.5
Palmitic/ oleic acid											0.015	15.0

Metabolism of AMBA in cow

AMBA is a metabolite found in maize forage and fodder when the plant is treated with mesotrione. A lactating cow was orally administered [phenyl-U-^{14}C]-AMBA using gelatine capsule for 7 consecutive days at a rate of 12.2 ppm in the diet, equivalent to 200 mg ai/day (Hand, 1997; RJ

2309B). Milk and excreta were collected daily. The cow was sacrificed approximately 23 hours after the final dose and tissues were taken for analysis.

Samples were sequentially homogenised in the presence of a variety of solvents including hexane, ethyl acetate, acetonitrile/water (1:1) and water. Liquid-liquid partitions were carried out between ethyl acetate and water. Metabolites were separated using normal or reserve phase TLC with visualisation of the radiochromatograms undertaken by phosphor image analysis.

The total recovery was found to be 88.7% of the administered dose, with the majority of the radioactivity recovered in the excreta (Table 13). Highest residues were found in kidney (0.053 mg/kg eq.) and fat (0.018 mg/kg eq.), with no detected residues in muscle or in omental fat. Residues in milk reached a maximum of 0.009 mg/kg eq. (Day 6), decreasing to 0.003 mg/kg eq. on Day 8 after the initial dose.

Table 13 Radioactive residues in lactating cow after oral administration of [^{14}C]AMBA

Matrix	Radioactive residue	
	[^{14}C]AMBA equivalents (mg/kg)	% Total administered
Liver	0.005	
Kidney	0.053	
Fat (perirenal)	0.018	
Fat (omental)	0.000	
Fat (subcutaneous)	0.003	
Milk (peak daily concentration)	0.009 (day 6)	0.06
Urine		32.0
Faeces		56.7
Total in excreta		88.7

Residues in the kidney and perirenal fat were readily extracted with solvents. AMBA represented 79.0 and 61.6% TRR, equivalent to 0.038 and 0.013 mg/kg in the kidney and perirenal fat respectively. Unknown components did not account for more than 0.001 mg/kg (Table 14).

Table 14 Nature of the residues of AMBA in kidney and perirenal fat

	Kidney		Perirenal fat	
TRR, mg/kg (% chromatographed)	0.048 (87.9)		0.021 (81.7)	
Component/Fraction	%TRR	mg/kg	%TRR	mg/kg
AMBA	79.0 [a]	0.038	61.6	0.013
Unknown	0.5	0.000	3.2	0.001
Unidentified	8.4	0.004	16.9	0.004
Aqueous fractions [b]	5.9	0.003	21.3	0.004
Organic fractions	2.5	0.001	–	–
Unextracted	3.1	0.001	9.7	0.002
Gains/Losses	0.6	0.000	–12.7	0.003
Total	100.0	0.047	100.0	0.021

[a] Summation of the % AMBA in two major fractions

[b] Two fractions, the largest of which represents 12.6% TRR (0.003 mg/kg) in the perirenal fat and 3.0% TRR (0.001 mg/kg) in the kidney;

Based on the metabolism studies conducted with [cyclohexane-2-^{14}C]-mesotrione, [phenyl-U-^{14}C]-mesotrione and [^{14}C]AMBA with poultry, cow and swine, the proposed biotransformation of mesotrione in livestock involves the oxidative cleavage of the parent molecule to yield MNBA and the reduction of the nitro group in MNBA giving AMBA (Figure 1).

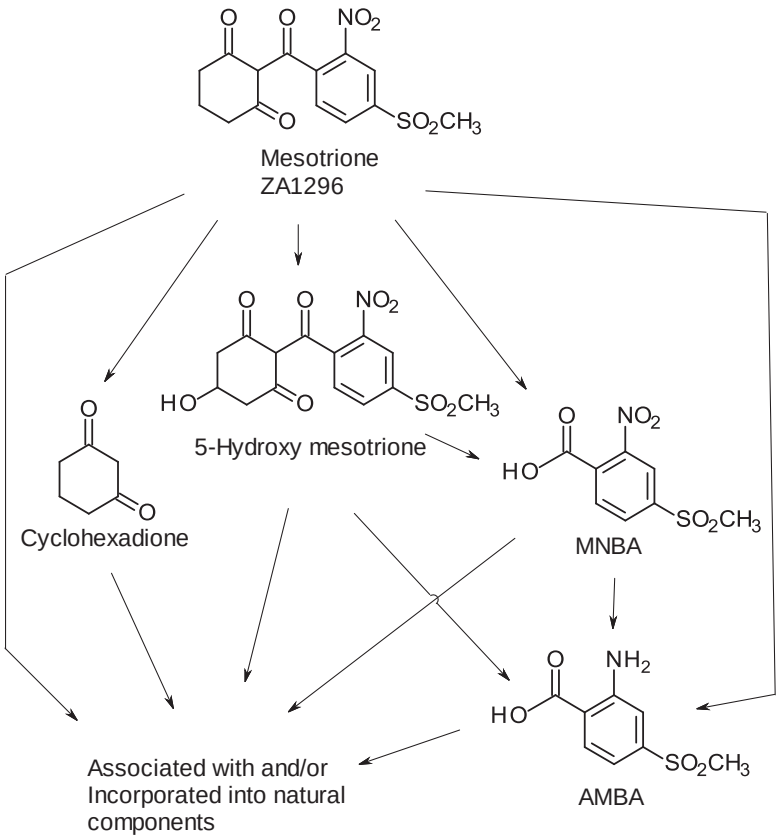


Figure 1 Proposed metabolism of mesotrione in livestock

Plant metabolism

Cranberries

[Phenyl-U-^{14}C]-mesotrione was applied (diluted with aqueous formulation) twice to pollinated cranberry plants (*Vaccinium spp.* var. Howe), 4 to 5 years in age, in the greenhouse, under two dose regimes (Ray 2005). The first application at 0.331 or 0.919 kg ai/ha, and the second application, 14 days later, at 0.242 or 0.642 kg ai/ha. Total application at 1× rate was 0.573 kg ai/ha and at 3× rate 1.561 kg ai/ha. The radioactive residues in samples of mature cranberry foliage and fruit, harvested 46 days after the second foliar application, were quantified and characterized. A subsample of each commodity type was homogenised in dry ice and the radioactive residue determined by combustion/LSC. Mature fruit samples that were found to have a radioactive residue greater than 0.01 mg/kg were subject to additional analysis. Samples were extracted with acetonitrile/water and fractionated. Further treatment comprised of hydrolysis with dilute acid under reflux conditions. Extracted radioactivity was analysed by 2D TLC and reverse-phase HPLC. Additional confirmation and identification was undertaken using tandem mass spectrometry and ^{1}H-NMR.

About 100% of the total restudies were extracted from cranberry fruits from both treatments, with about 2.2 to 2.5% corresponding to PES. TRR in the mature foliage were 16.8 mg/kg and 31.8 mg/kg, for the 1× and 3× treatments, respectively. The extracted TRRs in the mature cranberry fruit were 2.64 mg/kg eq. and 4.94 mg/kg eq., respectively. Only the fruits samples were used for the characterisation and identification of metabolites (Table 15). The extracted residues identified in cranberry fruits were mostly mesotrione and AMBA, accounting for 60.2% TRR and 34.8% at the 1× rate, respectively, with MBNA accounting for 3.0% TRR.

Table 15 Summary of radioactive residues in mature cranberry fruit samples following treatment with [phenyl-U-^{14}C]-mesotrione

Application Rate:	0.573 kg ai/ha		1.561 kg ai/ha	
Total extracted:	2.637 mg/kg eq.		4.936 mg/kg eq.	
Component	mg/kg eq.	%TRR	mg/kg eq.	%TRR
Mesotrione	1.548	60.2	3.257	67.1
AMBA	0.895	34.8	1.178	24.3
MBNA	0.076	3.0	0.078	1.6
Unknown baseline	0.042	1.6	0.057	1.2
Unextracted (PES)	0.064	2.5	0.107	2.2
Losses/gains	0.075	2.9	0.364	7.5
Total recovered	2.701	105.0	5.043	103.9

Mesotrione tolerant (HT) soya beans

HT soya bean seeds (*Glycine max* var. Jack) were grown under greenhouse conditions in containers filled with a sandy loam soil (Dohn & Chu. 2012). [Phenyl-U-^{14}C]- and [cyclohexane-2-^{14}C]-mesotrione were applied separately using three separate treatment regimes. The first application was a single pre-emergence treatment at a nominal rate of 0.225 kg ai/ha, the second was a combined pre-emergence treatment at 0.225 kg ai/ha followed by a post-emergence treatment at 0.125 kg ai/ha and the third was a single post-emergence treatment at a nominal 0.225 kg ai/ha. [^{14}C]Mesotrione was applied to the plots as a suspension concentrate using a plastic hand held sprayer.

The radioactive residues in the soya bean foliage and hay samples were extracted twice with a mixture of acetonitrile and water (1:1). Soya bean seed samples were sequentially extracted with acetone/hexane (1:4), acetonitrile/water (1:1) and acetonitrile. Characterisation of the PES samples with residues ≥ 10% TRR or ≥ 0.05 mg/kg was attempted using with hydrolytic enzymes, 1 N hydrochloric acid at room temperature and/or 60 °C. One and 2D normal phase TLC, reverse-phase HPLC-UV, radioisotope flow monitor and a fraction collector was used for sample analyses. Additional identification was undertaken using LS-MS.

The TRR (extracted plus PES) for soy commodities from each application regime and labels are summarised in the Table 16. In the phenyl label experiment, PES accounted for 41%TRR in pre-emergence forage to 57.7%TRR in post-emergence seed. In the cyclohexane label experiment, the values ranged from 21.9%TRR in pre-/post-emergence hay to 53.3%TRR in post-emergence seed.

Table 16 Total radioactive residues in soya bean RACs

Soya bean RAC	Application Stage	DAA (days)	TRR (mg/kg) Phenyl label	TRR (mg/kg) Cyclohexane label
Forage	Pre-emergence	28	0.212	0.077
	Pre- and post-emergence	28	0.162	0.055
	Post-emergence	22	0.499	0.260
Hay	Pre-emergence	42	0.142	0.076
	Pre- and post-emergence	42 (1st app.); 9 (2nd app.)	2.015	1.632
	Post-emergence	40	0.370	0.082
Seed	Pre-emergence	123	0.063	0.039
	Pre- and post-emergence	123 (1st app.); 90 (2nd app.)	0.104	0.093
	Post-emergence	110/118 [a]	0.052	0.015

[a] [Phenyl-U-^{14}C]-mesotrione: 110 days. [Cyclohexane-2-^{14}C]-mesotrione: 118 days. DAA=days after application

A summary of radioactive residues from [phenyl-U-^{14}C]-mesotrione treated soya bean forage extract is detailed in Table 17. MNBA was the most abundant residue present in the single pre-emergence and combined pre- and post-emergence forage samples and 4 or 5-hydroxy-mesotrione the most abundant residues in the post-emergence sample (0.073 mg/kg). Mesotrione residues were in the range of 0.021–0.03 mg/kg eq.). Extraction and acid hydrolysis released about 30% TRR found in pre-emergence forage PES, and lignin extraction released about 50% TRR in post-emergence forage

PES. Results from the [cyclohexane-2-^{14}C]-mesotrione experiment showed mesotrione and 4 or 5-hydroxy-mesotrione as the major residues in forage (8.5 to 19.2% TRR), while MNBA and AMBA were not detected. Most of the radioactivity found in PES was released by enzyme, acid extraction and lignin extraction.

Table 17 Summary of radioactive residues in soya bean forage samples following pre- and post-emergence application of [^{14}C]mesotrione

Treatment regime:	Pre-emergence [a]		Pre-+ post-emergence		Post-emergence	
Experiment	[phenyl-^{14}C]	[Cyclo -^{4}C]-	[phenyl-^{14}C]	[Cyclo -^{4}C]-	[phenyl-^{14}C]	[Cyclo -^{4}C]-
TRR, mg/kg eq.	0.212	0.077	0.162	0.055	0.499	0.260
Component	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)
MNBA	0.052 (24.5)		0.039 (24.1)		0.065 (13.0)	
AMBA	0.003 (1.4)		0.001 (0.6)		0.004 (0.8)	
4/5-Hydroxy-mesotrione	0.017 (8.0)	0.011 (14.3)	0.011 [b] (6.8)	0.007 (12.7)	0.073 (14.6)	0.050 (19.2)
Mesotrione	0.030 (14.2)	0.013 (16.9)	0.021 (13.0)	0.010 (18.2)	0.028 (5.6)	0.022 (8.5)
Polar unknowns [c]	0.005 (2.4)	0.009 (11.7)	0.006 (3.7)	0.005 (9.1)	0.008 (1.6)	0.034 13.1)
Unassigned (< 10% TRR)	–		–		0.032 (6.4)	
Unassigned (each < 0.01 mg/kg)	0.018 (8.5)	0.010 (13.0)	0.010 (6.2)	0.08 (14.5)	0.044 (8.8)	0.057 (21.9)
Total characterised	0.125 (59.0)	0.043 (55.8)	0.088 (54.3)	0.030 (54.5)	0.254 (50.9)	0.163 (62.7)
PES	0.087 (41.0)	0.034 (44.2)	0.074 (45.7)	0.025 (45.5)	0.245 (49.1)	0.097 (37.3)
Total	0.212 (100)	0.077 (100)	0.162 (100)	0.055 (100)	0.499 (100)	0.260 (100)

[a] Forage harvested prior to second application
[b] Confirmed by TLC
[c] Acetonitrile/water combined extracts
–=Not applicable

The metabolites MNBA and 4/5 hydroxy-mesotrione were the major residues found in hay of soya-treated with [phenyl-U-^{14}C]-mesotrione in the three application regimes ranging from 9 to 20%TRR (Table 18). Mesotrione accounted for 6.2 to 8.8%TRR (up to 0.178 mg/kg eq.). Treatment of PES with enzymes, 1 N HCl and lignin digestion released 15.5%TRR in plants from the pre-emergence trial and 13.2% TRR in post-emergence. 4/5-hydroxyl-mesotrione was the major identified residue in hay of soya treated with [cyclohexane-2-^{14}C] mesotrione, accounting for 15 to 25% TRR (0.409 mg/kg eq). Mesotrione accounted for 6.6 to 7.3%TRR, and the metabolites AMBA and MNBA were not detected. PES treatment released a total of 16.8% TRR in the pre-and post-emergence plants.

Table 18Summary of radioactive residues in soya bean hay samples following pre- and post-emergence application of [phenyl-U-^{14}C]-mesotrione

Treatment regime:	Pre-emergence		Pre- and post-emergence		Post-emergence	
Experiment	[phenyl-^{14}C]	[Cyclo -^{4}C]-	[phenyl-^{14}C]	[Cyclo -^{4}C]-	[phenyl-^{14}C]	[Cyclo -^{4}C]-
TRR, mg/kg	0.142	0.076	2.015	1.632	0.370	0.082
Component	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)
Mesotrione	0.009 (6.3)	0.005 (6.6)	0.178 (8.8)	0.134 (8.2)	0.023 (6.2)	0.006 (7.3)
MNBA	0.015 (10.6)	ND	0.410 (20.3)	ND	0.042 (11.4)	ND
AMBA	ND	ND	0.055 (2.7)	ND	ND	ND
4/5-Hydroxy-mesotrione	0.013 (9.2)	0.012 (15.8)	0.331 (16.4)	0.407 (24.9)	0.054 (14.6)	0.016 (19.5)
Polar unknowns	0.006 (4.2)	0.012 (15.8)	0.026 (1.3)	0.243 (14.9)	0.006 (1.6)	0.012 (14.6)
Unassigned (each < 6%TRR)	0.012 (8.5)	–	0.335 (16.6)	0.491 (30.1)	–	–
Non-defined (each < 0.01 mg/kg)	0.013 (9.2)	0.010 (13.2)	ND	ND	0.05 (13.5)	0.015 (18.3)
Total characterised	0.068 (47.9)	0.039 (51.3)	1.34 (66.3)	1.275 (78.1)	0.175 (47.3)	0.049 (59.8)
PES	0.074 (52.1)	0.037 (48.7)	0.680 (33.7)	0.357 (21.9)	0.195 (52.7)	0.033 (40.2)
Total	0.142 (100)	0.073 (100)	2.015 (100)	1.632 (100)	0.370 (100)	0.082 (100

None of the identified residues in soya bean seeds from the experiment with [phenyl-U-^{14}C]-mesotrione accounted for more than 10% TRR in any treatment or at levels higher than 0.007 mg/kg eq. (Table 19). Mesotrione accounted for up to 9.5% TRR%, or 0.006 mg/kg eq. AMBA was detected only in the pre-and post-emergence regime (1.9%TRR). Enzyme extracts of PES contained multiple components up to ≤ 0.007 mg/kg. Only mesotrione and 4/5-hydroxy-mesotrione were detected in soya bean seeds from the [cyclohexane-2-^{14}C] mesotrione experiment. The PES Viscozyme extracts from the combined pre- and post-emergence sample mainly contained unknown polar peak components (0.011 mg/kg, 11.8% TRR).

Table 19 Summary of radioactive residues in soya bean seed samples following use of [phenyl-U-^{14}C]-mesotrione

Treatment regime:	Pre-emergence		Pre- and post-emergence		Post-emergence	
Experiment	[phenyl-^{14}C]	[Cyclo -^{4}C]	[phenyl-^{14}C]	[Cyclo -^{4}C]	[phenyl-^{14}C]	[Cyclo -^{4}C]
TRR, mg/kg	0.063	0.039	0.104	0.093	0.052	0.015
Component	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)
Mesotrione	0.006 (9.5)	0.02 (5.1)	0.003 (2.9)	0.003 (3.2)	0.002 (3.8)	
MNBA	0.001 (1.6)	ND	0.005 (4.8)	ND	ND	
AMBA	ND	ND	0.002 (1.9)	ND	ND	
4/5-Hydroxy-mesotrione	0.003 (4.8)	0.01 (2.6)	0.007 (6.7)	0.003 (3.2)	0.004 (7.7)	
Polar unknowns	0.004 (6.3)	0.07 (17.9)	0.010 (9.6)	0.029 (31.2)	0.008 (15.4)	
Unassigned peaks	–		0.010 (9.6)		–	
Non-defined (each < 0.01 mg/kg)	0.008 (12.8)	0.02 (5.1)	0.007 (6.7)	0.007 (7.5)	0.003 (5.8)	
Total characterised	0.022 (34.9)	0.012 (30.8)	0.044 (42.3)	0.042 (45.2)	0.017 (32.7)	
PES	0.035 (55.6)	0.020 (51.3)	0.052 (50.0)	0.039 (41.9)	0.030 (57.7)	0.008 (53.3)
Acetone/Hexane extractions	0.006 (9.5)	0.007 (17.9)	0.008 (7.7)	0.012 (12.9)	0.005 (9.6)	0.002 (13.3)
Totals	0.063 (100)	0.039 (100)	0.104 (100)	0.093 (100)	0.052 (100	0.015 (110)

Maize

[Phenyl-U-^{14}C]-mesotrione was applied to the soil surface after planting the seeds of maize (*Zea mays*) (pre-emergence) at a rate of 0.28 kg ai/ha and post-emergence by application to surfaces of plants and soil 28 days after planting at a rate of 0.164 kg ai/ha (Tarr & van Neste, 1997; RR 96-007B). The radioactive residues in plant samples of forage (55 days after planting) and of grain and straw from mature crops (125 days after post-emergence treatment) were characterised.

Samples were extracted with water and acetonitrile (1:1) and fractionated by partition with ethyl acetate and/or with Amberlite XAD7 resin. Acid hydrolysis (micro-wave or reflux) followed by base hydrolysis or treatment with enzymes (porcine carboxylic acid esterase, papain, pancreatin, pectolyase and driselase) of the extracted residues and PES was attempted for characterisation and further solubilisation of residues. The PES from post-emergence fodder was also treated with a solution of potassium permanganate to solubilise bound residues by oxidation. Residue characterization was performed using normal and reversed-phase TLC and/or reversed-phase HPLC with radio-detector or fraction collecting, and LSC.

Table 20 summarises the TRRs found in maize matrices after pre- or post-emergence application. Total residues were higher in fodder and forage, and similar in both treatments in seed (0.013–0.014 mg/kg eq.). Using acetonitrile/water (1:1 v/v), most of the residues were extracted from forage and seed, but unextracted residues accounted for over 60% TRR in fodder. No additional analysis was conducted in seed due to the low radioactivity found.

Table 20 Total radioactive residues (TRRs) in maize after pre- and post-emergence application of [phenyl-U-^{14}C]-mesotrione

Sample. DAT	TRR by initial combustion	Extracted residues (acetonitrile/water 1:1 v/v)		Unextracted residues		Sum of extracted and unextracted residues	
	mg/kg eq.	% TRR [a]	mg/kg eq.	% TRR	mg/kg eq.	% TRR	mg/kg eq.
Pre-emergence application							
Forage. 27	0.356	84.6	0.301	26.2	0.093	110.8	0.394
Fodder. 153	0.795	43.9	0.349	61.8	0.491	105.7	0.840
Grain. 153	0.013	69.6	0.009	26.8	0.004	96.7	0.013
Post-emergence application							
Forage. 28	0.244	72.7	0.177	23.9	0.058	96.6	0.235
Fodder. 125	1.066	48.1	0.513	67.4	0.719	115.5	1.232
Grain. 125	0.014	61.5	0.008	23.2	0.003	84.7	0.011

DAT: Days after treatment

[a] Based on residue values derived from initial combustion

Table 21 shows the characterization of the residues found in forage and fodder from both treatments. Mesotrione was a minor component of the residue, present at a higher level in pre-emergence forage samples (2.2% TRR, 0.008 mg/kg eq.). MNBA was the major identified compound in forage from the pre-emergence treatment (19.7%TRR) and a minor component in post-emergence and in fodder. AMBA was a major compound mostly presented in conjugated form accounting for 12–28%TRR in forage and fodder. The predominant AMBA conjugates isolated were α- and β-anomers of the 2-acylglucosides. Acid or base hydrolysis and enzyme treatment did not release additional AMBA from fodder extracts.

Table 21 Summary of radioactive residues in maize forage and fodder samples following pre- and post-emergence application of ^{14}C-phenyl labelled mesotrione

Component	Pre-emergence application		Post-emergence application	
	Forage	Fodder	Forage	Fodder
	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)
TRR by combustion	0.356 (100)	0.795 (100)	0.244 (100)	1.066 (100)
Mesotrione	0.008 (2.2)	< 0.003 (< 0.4)	0.001 (0.4)	< 0.003 (< 0.3)
4-OH-mesotrione (total/glucose Conjugate)	0.027/0.013 (7.6/3.8)	0.007/< 0.01 (0.9/< 1.2)	0.016/0.009 (6.6/3.6)	0.007/< 0.01 (0.7/< 0.1)
MNBA	0.070 (19.7)	0.008 (1.0)	0.008 (3.4)	0.019 (1.9
AMBA (total/conjugates)	0.043/0.031 (12.2/8.9)	0.108/0.104 (13.6/13.0)	0.032/0.029 (13.2/11.5)	0.301/0.295 (28.2/27.6)
Minor components extracted with water/acetonitrile	0.164 (46.0)	0.280 (35.2)	0.128 (52.4) (each < 0.03 mg/kg)	0.320 (30.0) (each < 0.03 mg/kg)
Minor components extracted with 0.1 M HCl /microwave heating	0.049 (13.6)	0.229 (28.8)	0.033 (13.7) (each < 0.03 mg/kg)	0.378 (35.4) (each < 0.03 mg/kg)
Minor components extracted with 1 M NaOH/40 °C		0.030 (3.8)		0.044 (4.1)
Not extracted	0.028 (7.9)	0.033 (4.2)	0.017 (7.0)	0.063 (5.9)

In another study conducted in maize, [phenyl-U-^{14}C]-mesotrione was applied to the bare sandy loam soil surface one day after planting the seeds (pre-emergence) at a rate of 0.302 kg ai/ha and post-emergence (31 days after planting) by application to surfaces of plants at the true eight leaf stage at a rate of 0.179 kg ai/ha (Vispetto & Smith, 1999; RR 99-006B). Samples of forage (78 days after first pre-emergence treatment) and of stover and grain from mature crops, 121 days after pre-emergence treatment were taken for analysis.

Samples were extracted with a mixture of water and acetonitrile (1:1), extracts fractionated by hydrolysis with HCl or partitioned with ethyl acetate. PES which exceeded 10% TRR or 0.05 mg/kg were hydrolysed by microwave extraction with HCl, and the hydrolysates cleaned up by C_{18} SPE. HPLC radiochromatograms were obtained by fraction collecting and LSC. TLC was conducted using silica plates.

Highest residues were detected in the stover (0.57 mg/kg), with lower residues in the forage (0.27 mg/kg) and grain (0.03 mg/kg) (Table 22). Over 60% of the radioactivity was extracted and contained a large number of components, all at ≤ 0.01 mg/kg and predominantly water soluble. Mesotrione was not detected in any sample. AMBA, MNBA and their conjugates, and 4-hydroxy-mesotrione were the major compounds identified in forage. 4-hydroxy mesotrione was not detected in grain and stover.

Table 22 Total radioactive residues (TRRs) in maize after pre- and post-emergence application of [phenyl-U-^{14}C]-mesotrione

		Forage		Stover		Grain	
		% TRR	mg/kg eq.	% TRR	mg/kg eq.	% TRR	mg/kg eq.
Total Residue (by combustion)		100	0.27	100	0.57	100	0.03
Acetonitrile/water		69.6	0.19	70.3	0.40	60.6	0.02
2 M/4 M HCl Hydrolysis of extract	Organosoluble	–	–	9.5	0.05	–	–
	Aqueous soluble	–	–	45.8	0.26	–	–
	Precipitate	–	–	10.7	0.06	–	–
Non-extracted (PES)		29.9	0.08	32.9	0.19	46.9	0.01
2 M/4 M HCl PES Hydrolysis		9.8	0.03	7.0	0.04	–	–
Post–hydrolysed solids (PHS)		22.6	0.06	23.5	0.13		
AMBA/ conjugate		2.4/4.6	0.01/0.01	1.7/2.3	0.01/0.01	–	–
MNBA/ conjugate		3.3/2.2	0.01/< 0.01	2.2/1.0	0.01/0.01	–	–
4-hydroxy-mesotrione		5.4	0.01	–	–	–	–
Unidentified		5.7	0.14	7.7	0.34	6.9	0.02

[a] Fraction comprises a number of small components all < 4.6% TRR (≤ 0.02 mg/kg)

In the third study conducted in maize, [cyclohexane-2-^{14}C]–mesotrione was applied to the soil surface after planting the seeds (pre-emergence) at a rate of 0.307 kg ai/ha and post-emergence 28 days after planting at a rate of 0.161 kg ai/ha (Wei & Dohn, 1997; RR 96-026B). Samples of forage (27 or 28 days after planting) and of grain and straw from mature crops (125 days after post-emergence treatment) were extracted three times with either a mixture of water and acetonitrile (1:1). Acid hydrolysis of the extracted residues and PES from post-emergence fodder samples was attempted for characterization of residues and enzyme digestion was used in pre- and post-emergence forage samples. HPLC radiochromatograms were obtained using a flow through radio-detector or by fraction collecting and LSC. All critical analyses were confirmed by use of at least two TLC and or HPLC methods.

Total radioactive residues in maize were 0.067, 0.001 and 0.015 mg/kg in pre-emergence forage, grain and fodder respectively. Corresponding values for post-emergence treatments were 0.098, 0.011 and 0.330 mg/kg (Table 23). Much of the radioactivity in forage was readily extracted (78–84% TRR). Remaining solids after extraction were not analysed further. About 60% TRR in pre-emergence fodder and post-emergence grain were not extracted with solvents.

Table 23 Total radioactive residues (TRRs) in maize after pre- and post-emergence application of [cyclohexane-2-^{14}C]–mesotrione

Sample	TRR by initial combustion	Extracted residues		Unextracted residues	
	mg/kg	% TRR [a]	mg/kg eq.	% TRR	mg/kg eq.
Pre-emergence application					
Forage	0.067	78.3	0.053	20.9	0.014
Fodder [b]	0.015 (0.025 in leaves)	38.1.	0.006 (0.010 in leaves)	60.8	0.010 (0.015 in leaves)
Grain	0.001	–	–	–	–
Post-emergence application					
Forage [b]	0.098 (0.190 in leaves)	84.0	0.082 (0.159 in leaves)	19.6	0.018 (0.037 in leaves)
Fodder	0.330 [b] (0.649 in leaves)	67.5 [c]	0.223	9.4	0.031
Grain	0.011	35.1	0.004	60.7	0.007

[a] % TRR's are based on residue values derived from initial combustion

[b] The extractions were performed on the leaf sample, but the mg/kg values are corrected for the total (leaves + stalks) sample mass
[c] Includes material released by acid hydrolysis and lignin and cellulose fractions

The major identified residue in forage was 4-dydroxy-mesotrione, accounting for up to 10.4%TRR in pre-emergence samples (0.007 mg/kg) (Table 24). Mesotrione was found at low levels (up to 0.002 mg/kg). In fodder, mesotrione was detected only in trace amounts (< 0.0005 mg/kg) and no other compound was identified (Table 24). The solubilised material from PES accounted for 13.6% TRR (0.045 mg/kg) and showed to contain glucose. Treatment of remaining solids gave evidence for the incorporation of ^{14}C into lignin and cellulose.

Table 24 Summary of radioactive residues in maize forage and fodder following pre- and post-emergence application of [cyclohexane-2-^{14}C]-mesotrione

Component	Forage		Fodder (leaves and stalks)
	Pre-emergence	Post-emergence [a]	post-emergence
	mg/kg (% TRR)	% of TRR [b]	mg/kg eq.
TRR combustion value	0.067 (100)	0.098 (100)	0.330 (100)
Mesotrione	0.002 (3.0)	0.001 (1.0)	< 0.0005
4-Hydroxy-mesotrione	0.007 (10.4)	0.006 (6.1)	
Components extractable with water/acetonitrile (including neutral carbohydrates formed by acid hydrolysis of the extract) [c]			0.123 (37.3) (each < 0.012 mg/kg)
Components solubilised by refluxing 6 M HCl. majority were neutral carbohydrates, including glucose [c]			0.045 (13.6) (each < 0.029)
Intractable solids from neutralisation of 6 M HCl reflux			0.016 (4.8)
Lignin [c]			0.044 (13.3)
Cellulose [c]	0.006 (9.0)	0.002 (2.0)	0.011 (3.4)
Minor components including carbohydrates	0.038 (56.7)	0.067 (each ≤ 0.012 mg/kg)	
Post-extracted solids (PES)	0.014 (20.9)	0.018 (18.4)	0.031 (9.4)
Not analysed [b]	–	0.007 (7.1)	0.024 (7.3)

[a] Leaves and the woody stalks, the leaves contained over 90% of the residue
[b] The characterisation experiments were performed on the leaf sample, but the values are corrected for the total (leaves + stalks) sample
[c] The order of the extractions was water/acetonitrile. 6 M HCl, hot dimethylsulphoxide (for lignin), and Schweizer's reagent (for cellulose)

Rice

Rice plants (*Oryza sativa* spp. *japonica cv* Kirana 397) at the 2–3 leaf stage in a flooded paddy greenhouse system were treated with [phenyl-U-^{14}C]-mesotrione added directly to the paddy water at either 0.090 kg ai/ha or 0.225 kg ai/ha (Humphries & Evans. 2005; RJ 3738B). The day 14 and 27 days after treatment (DAT) samples were whole tops, the 40 DAT samples were separated into ears and stalks, the 109 DAT samples were separated into grain, husk and straw. The paddy was maintained flooded to a depth of 3–5 cm until 7 days before final harvest, when irrigation was stopped allowing the paddy system to dry. Natural daytime sunlight was supplemented with artificial light with a fixed 13 hour day period. Samples were extracted with acetonitrile/water mixture and water and PES were further extracted with microwave assisted extractions and acid hydrolysis. Liquid partitions were carried out between ethyl acetate/water (1:1). Extracted radioactivity was analysed by normal and reversed-phase TLC and reverse-phase HPLC.

Extracted radioactivity in the whole tops up to 27 DAT accounted for at least 60%TRR (Table 25). Total residues in grain were 0.01 and 0.02 mg/kg eq. at 0.09 and 0.225 kg ai/ha, respectively, with extracted residues accounting for up to 0.003 mg/kg eq., which were not further characterized. Residues in straw were higher (0.032 and 0.066 mg/kg eq.), from which 43–45%TRR was extracted.

Table 25 Total radioactive residues (TRRs) in rice after treatment of paddy water with [phenyl-U-^{14}C]-mesotrione

Treatment. kg ai/ha	DAA		Acetonitrile/water		Non-extracted residues		Total Residue mg/kg eq.
		Commodity	% TRR [a]	mg/kg	% TRR	mg/kg	
0.090	14	Whole tops [b)]	70.7	0.0461	29.3	0.0191	0.0652
	27	Whole tops	59.9	0.0198	40.1	0.0133	0.0331
	40	Ears	n/a	n/a	n/a	n/a	0.0057
		Stalks	48.1	0.0092	51.9	0.0099	0.0191
	109	Grain	12.4	0.0011	87.7	0.0087	0.0099
		Husk	22.7	0.0022	77.3	0.0077	0.0099
		Straw	43.1	0.0139	56.9	0.0183	0.0321
0.225	14	Whole tops	76.2	0.1934	23.8	0.0604	0.2538
	27	Whole tops	60.7	0.0416	39.3	0.0270	0.0686
	40	Ears	27.0	0.0032	73.0	0.0085	0.0117
		Stalks	46.4	0.0175	53.6	0.0202	0.0377
	109	Grain	17.2	0.0033	82.8	0.0158	0.0191
		Husk	33.1	0.0108	66.8	0.0217	0.0325
		Straw	45.3	0.0298	54.7	0.0360	0.0659

[a] %TRR's are based on residue values derived initial combustion
[b] Immature plants harvested by cutting the plant 2 cm above the paddy rice water

Tables 26 shows the residues identified in immature whole tops (14 and 27 DAT) and stalks (40 DAT). All commodities analysed contained parent mesotrione, 5-hydroxy-mesotrione, AMBA and MNBA. At early stage, mesotrione comprised the majority of the residues, accounting for 28% TRR for the 0.225 g ai/ha treatment.

Table 26 Summary of radioactive residues in immature rice samples following treatment of paddy water with phenyl-U-^{14}C labelled mesotrione

Component	0.090 kg ai/ha						0.225 kg ai/ha	
	14 Whole Tops [a]		27 Whole Tops [a]		40 Stalks		14 Whole Tops	
	% TRR	mg/kg	% TRR	mg/kg eq.	% TRR	mg/kg	% TRR	mg/kg
Mesotrione	15.0	0.0098	5.9	0.0020	5.0	0.0010	27.9	0.0708
5-HO-mesotrione [b]	11.4	0.0074	7.5	0.0025	11.1	0.0021	14.1	0.0359
MNBA	4.6	0.0030	4.8	0.0016				
AMBA	2.0	0.0013	3.0	0.0010	1.7	0.0003	2.2	0.0055
Total	33.0	0.0215	21.2	0.0071	17.8	0.0034	44.2	0.1122
Unknowns	4.9	0.0032						
Baseline	16.2	0.0105	30.1	0.0100	16.5	0.0032	16.0	0.0406
Remainder	18.5	0.0120	6.8	0.0021	15.4	0.0030	15.2	0.0386
Unextracted [c]	29.3	0.0191	40.1	0.0133	51.9	0.0099	23.8	0.0604
Loss/gain on fractionation [c]	–1.8	–0.0012	1.8	0.0006	–1.7	–0.0003	0.8	0.0020
Total	100.1	0.0651	100.0	0.0331	99.9	0.0192	100.0	0.2538

Unknowns: unidentified discrete components; Baseline: Polar residue components, which are retained on the baseline after elution
Remainder: diffuse unassigned radioactivity comprising minor indiscrete components and areas of streaking of radioactivity
[a] Immature plants harvested by cutting the plant 2 cm above the paddy rice water
[b] 5-Hydroxy-mesotrione was assigned based on TLC data from later samples where reference standards were available
[c] Not chromatographed

Residues in straw extracts showed the similar pattern as seen in whole tops and stalk samples (Table 27). Baseline polar extract was acidified to 0.1 M with HCl, heated to 80 °C for two hours to released 5-hydroxy-mesotrione (3.2% TRR, 0.001 mg/kg) and MNBA (2.4% TRR, 0.0008 mg/kg), mesotrione (1.5% TRR, 0.0005 mg/kg) and AMBA (1.1% TRR, 0.0004 mg/kg). The 56.9% TRR

(0.0183 mg/kg) in the PES was further extracted showing mesotrione and AMBA present at < 1% TRR (0.0002 mg/kg), MNBA and 5-hydroxy-mesotrione (0.4% TRR).

Table 27 Summary of radioactive residues in mature rice straw (109 DAT) following treatment of paddy water with phenyl-U-^{14}C labelled mesotrione at 90 g ai/ha

Component	Solvent extraction		Acid hydrolysis of solvent extract		Acid hydrolysis of debris sample	
	% TRR	Residue	% TRR	Residue	% TRR	Residue
Mesotrione	1.8	0.0006	1.5	0.0005	0.7	0.0002
5-HO-mesotrione [a]	5.0	0.0016	3.2	0.0010	0.4	0.0001
MNBA			2.4	0.0008		
AMBA	1.2	0.0004	1.1	0.0004	0.6	0.0002
Baseline	24.6	0.0079	13.8	0.0044	13.3	0.0042
Remainder	7.6	0.0024	9.0	0.0029	3.5	0.0012
Extracted	n/a	n/a	n/a	n/a	53.7	0.0173
Unextracted [b]	56.9	0.0183	56.9	0.0183	26.1	0.0084
Loss/gain on fractionation [b]	2.8	0.0009	12.0	0.0038	1.6	0.0005
Total	99.9	0.0321	99.9	0.0321	99.9	0.0321

Unknowns: unidentified discrete components; Baseline: Polar residue components which are retained on the baseline after elution; Remainder: diffuse unassigned radioactivity comprising minor indiscrete components and areas of streaking of radioactivity

[a] 5-hydroxy-mesotrione was assigned on basis of comparison with TLC data from later samples where reference standards were available

[b] Not chromatographed

Peanuts

[Phenyl-U-^{14}C]-mesotrione was solubilised in acetonitrile, diluted with aqueous blank formulation and applied to peanuts (*Arachis hypogaea* var. NCV 11) planted in silt loam soil in three outdoor subplots (Brown, 2003; Report 1286-01). [^{14}C]mesotrione was applied to the soil surface after planting the seeds (pre-emergence) at 0.305 and 0.796 kg ai/ha. Peanut foliage was harvested 90 DAT (50% maturity), mature peanuts and peanut hay were harvested 153 DAT.

Samples were extracted four times with water:acetonitrile (8:2) and nutmeat was extracted twice with hexane and twice with acetonitrile:water (8:2). Aliquots of the extracts were partitioned with hexane, dichloromethane or chloroform. Cellulase and amyloglucosidase enzymes were added to sodium acetate buffered subsamples of aqueous and hexane fractions (pH 4.6). Esterase, lipase, and/or pancreatin were added to TRIS-hydrochloric acid buffered subsamples of aqueous and hexane fractions (pH 7.8–8). Samples were incubated for approximately 24 hours at 42 or 47 °C. Aqueous and hexane fractions and PES were hydrolysed with 6 N hydrochloric acid under reflux followed by XAD-7 separation and/or dichloromethane partitioning. Hexane fractions were hydrolysed with 1 N potassium hydroxide in water under reflux for approximately 6 or 24 hours. Aminolysis using diethylamine was attempted. PES was refluxed over night with water to extract various complex sugars. Plant extracts cleaned up with C_{18} or NH_2 SPE. Components were separated using 2-D normal phase TLC. Reversed-phase HPLC coupled to UV detector, radioisotope flow monitor and a fraction collector was also used. Additional separation was performed by ion exchange chromatography where necessary.

Table 28 shows the residues found in peanut foliage and hay after both treatments. From 30 to 42% TRR was extracted from foliage and hay, with MNBA being the major residue. AMBA residues were released from PES after basic hydrolysis. MBA was found in trace amount only in hay treated at the highest rate.

Table 28 Summary of radioactive residues in peanut foliage and hay samples following pre-emergence treatment with [phenyl-U-^{14}C]-mesotrione

Application Rate:		0.305 kg ai/ha		0.796 kg ai/ha	
Commodity		Foliage	Hay	Foliage	Hay
Total Radioactive Residue (%TRR):		0.028 (100)	0.012 (100)	0.064 (100)	0.028 (100)
Extracted residues (%TRR) [a]		0.012 (42.2)	0.004 (31.5)	0.026 (40.5)	0.010 (34.2)
Component		mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)
Aqueous following partition (%TRR)		0.007 (23.6)	0.002 (16.0)	0.012 (19.2)	0.007 (24.8)
MNBA		0.003 (10.9)	0.001 (4.0)	0.007 (10.7)	0.002 (5.8)
AMBA		0.001 (2.1)	–	< 0.001 (0.5)	< 0.001 (1.1)
MBA					< 0.001 (1.1)
Unknown 1		0.001 (4.5)	0.001 (4.0)	0.003 (4.4)	0.002 (7.6)
Unknown 2		0.001 (1.9)	< 0.001 (1.0)	–	0.001 (3.4)
Unknown 4			–		0.001 (3.3)
Others		[b]	[d]	[c]	
Organic following partition (%TRR):		0.004 (15.8)	0.002 (13.3)	0.010 (15.6)	0.003 (8.8)
Organic after 6 N HCl hydrolysis		0.003 (12.3)	0.001 (10.3)	0.009 (14.1)	0.002 (6.7)
AMBA		0.001 (4.9)	< 0.001 (2.2)	0.003 (4.3)	< 0.001 (1.5)
Unextracted (PES)		0.014 (48.7)	0.008 (62.8)	0.038 (59.6)	0.019 (67.7)
PES treated with NaOH	MNBA	< 0.001 (1.4)	< 0.001 (1.1)	–	< 0.001 (0.6)
	MBA	–	< 0.001 (3.2)	< 0.001 (0.6)	0.001 (1.7)
	AMBA	0.003 (9.7)	< 0.001 (4.7)	0.002 (2.3)	0.001 (2.0)

[a] Extract was separated into aqueous and organic fraction
[b] At least seven components ranging from 0.2% to 1.4% TRR
[c] At least eight components ranging from 0.1% to 1.2% TRR
[d] At least five components ranging from 0.3% to 0.7% TRR

The TRRs in hulls and nutmeat for plots treated with the higher rate were 0.025 and 0.037 mg/kg, respectively (Table 29). Extracted residues were higher from nutmeat samples (35–40%TRR) than hulls (20–23% TRR). Low levels of MNBA residues were detected in hull samples treated at both application rates (≤ 0.002 mg/kg) including residues released from PES. Traces of AMBA, 4-hydroxy-mesotrione and MBA were detected only after hydrolysis of hull PES.

Table 29 Summary of radioactive residues in peanut hulls and nutmeat samples following treatment with [phenyl-U-^{14}C]-mesotrione

Application Rate:		0.305 kg ai/ha		0.796 kg ai/ha	
Commodity		Hulls	Nutmeat	Hulls	Nutmeat
Total Radioactive Residue, mg/kg eq.		0.011	0.013	0.025	0.037
Extracted residues		0.003 (23.0) [a]	0.005 (40.0)	0.005 (19.6) [a]	0.013 (35.9)
Aqueous following partition (%TRR):		0.002 (15.5)		0.005 (18.2)	
Acetonitrile fraction from nutmeat extract [b]			< 0.001 (3.8)		0.001 (3.9)
Hexane fraction from nutmeat extract [c]			0.005 (36.2)		0.013 (35.9)
	Component	mg/kg	%TRR	mg/kg	%TRR
Chromatography of aqueous partition for hulls	MNBA	< 0.001 (2.4)		< 0.001	1.7
	Unknown 1	< 0.001 (5.4)		0.002	6.7
	Unknown 2	< 0.001 (3.0)			
	Unknown 3	–	–	< 0.001	1.7
	Others	[d]		[e]	
Organic following partition of hull extract (%TRR):		< 0.001 (5.3)		< 0.001	2.2
Unextracted (PES)		0.007 (60.1)	0.008 (60.7)	0.017 (68.5)	0.023 (61.5)
PES treated using NaOH	MNBA	< 0.001 (1.2)		0.002 (7.9)	< 0.001 (2.4)
	MBA	0.001 (6.7)		–	–

Application Rate:		0.305 kg ai/ha		0.796 kg ai/ha	
	AMBA	< 0.001 (1.6)	0.002 (15.0)	< 0.001 (1.4)	< 0.001 (1.4)
	4-hydroxy-mesotrione	0.001 (6.9)		–	–

[a] Extract was separated into aqueous and organic fraction
[b] Low residues in the aqueous fraction and its concentrated matrices prevented TLC and HPLC analyses of samples
[c] The hexane fraction was further characterised by treatment with base partition treatment with acid and further partition or with a mixture of enzymes which afforded several unknowns none greater than 0.002 mg/kg
[d] At least three components ranging from 0.2% to 1.2% TRR
[e] At least four components ranging from 0.2% to 1.4% TRR

In another study conducted with peanuts, [cyclohexane-2-^{14}C]-mesotrione was applied to the soil surface after planting the seeds (pre-emergence) at rates of 0.327 kg ai/ha and 0.836 kg ai/ha (Brumback, 2003; Report 1287-01). Peanut foliage was harvested 90 DAT (50% maturity), and mature peanuts and peanut hay harvested 154 DAT. Auxiliary in vitro experiments with peanut cell culture and excised peanut shoots were performed to generate metabolites for identification. Peanut cells were dosed at 50 mg/L [cyclohexane-2-^{14}C]-mesotrione, diluted in dimethyl sulfoxide (DMSO) and harvested 7 and 14 days after dosing. Peanut shoots were dosed at 100 mg/L and harvested after 2 days. Plant samples having radioactive residues ≥ 0.010 mg/kg were extracted with water:acetonitrile (8:2). Nutmeat was sequentially extracted with hexane, hexane/ethyl acetate and acetonitrile:water (8:2). Aliquots of the extracts were partitioned between aqueous and organic phases. An aqueous buffer mixture of 0.1 M sodium acetate buffer and 0.1 M acetic acid (1:1) was added to subsample extracts, following addition of cellulase and amyloglucosidase enzymes and incubation for 16 hours at 37 to 47 °C. Nutmeat extracts were acidified to pH 1 after microwave treatment and partitioning between water and hexane. Components in extracts were separated using 2-D normal phase TLC and/or reversed-phase or anion exchange. The components were detected with HPLC-UV detector; radioisotope flow monitor and a fraction collector were also used. Additional confirmation was undertaken using tandem mass spectrometry and 1H-NMR for the metabolites isolated from the in vitro experiments.

Samples of peanuts treated at 0.327 kg ai/ha resulted in TRR < 0.01 mg/kg eq and no further analysis in the samples was performed. Table 30 shows the radioactive residues found in peanut samples from the higher rate plots. TRR was higher in foliage and nutmeat (0.02 mg/kg eq.), with about 40–50%% being extracted. Characterisation of extracts from foliage, hay and hull samples from the 0.836 mg/kg rate showed only one significant metabolite, identified as 4-hydroxy-mesotrione, which was also generated in vitro. The peanut oil fraction was shown to be composed primarily of ^{14}C-labelled neutral lipids resulting from metabolism of mesotrione to single carbon units that entered the carbon pool.

Table 30 Summary of radioactive residues in peanut samples following treatment with [cyclohexane-2-^{14}C]-mesotrione at 0.836 kg ai/ha

Crop and Commodity:	Peanut foliage	Peanut hay	Peanut hulls	Peanut nutmeat
TRR, mg/kg eq.:	0.020	0.011	0.015	0.022
Initial extraction (%TRR):	0.008 (38.9%)	0.003 (28.2%)		
Aqueous acetonitrile extract (%TRR):			0.003 (19.9%)	0.001 (4.7%)
Non polar solubles (%TRR)			–	0.011 (51.4%)
Component	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)	mg/kg (%TRR)
Neutral/base components	0.003 (11.7)	0.001 (6.7)	< 0.001 (4.4)	–
Acidic components	0.003 [a] (17.3)	0.002 [c, d] (16.0)	0.003 [a, c] (12.6)	–
Organic wash	< 0.001 (1.2)	< 0.001 (1.4)	< 0.001 (1.8)	–
Lipids				0.008 (37.8)
Fatty acids				0.001 (5.7)
Phospholipids				0.001 (4.1)
Unextracted (PES)	0.013 (65.9)	0.008 (71.6)	0.013 (84.5)	0.011 (50.8)

[a] Three separate regions
[b] Two separate regions
[c] Contained a component characterised as 4-hydroxy-mesotrione (1.4% TRR)

Based on the metabolism studies conducted in cranberries, soya bean, maize, rice and peanut with labelled mesotrione, a metabolism pathway of mesotrione in plants is proposed in Figure 2. The process involves hydroxylation, hydrolysis to form MNBA, which is reduced to AMBA followed by de-amination to form MBA.

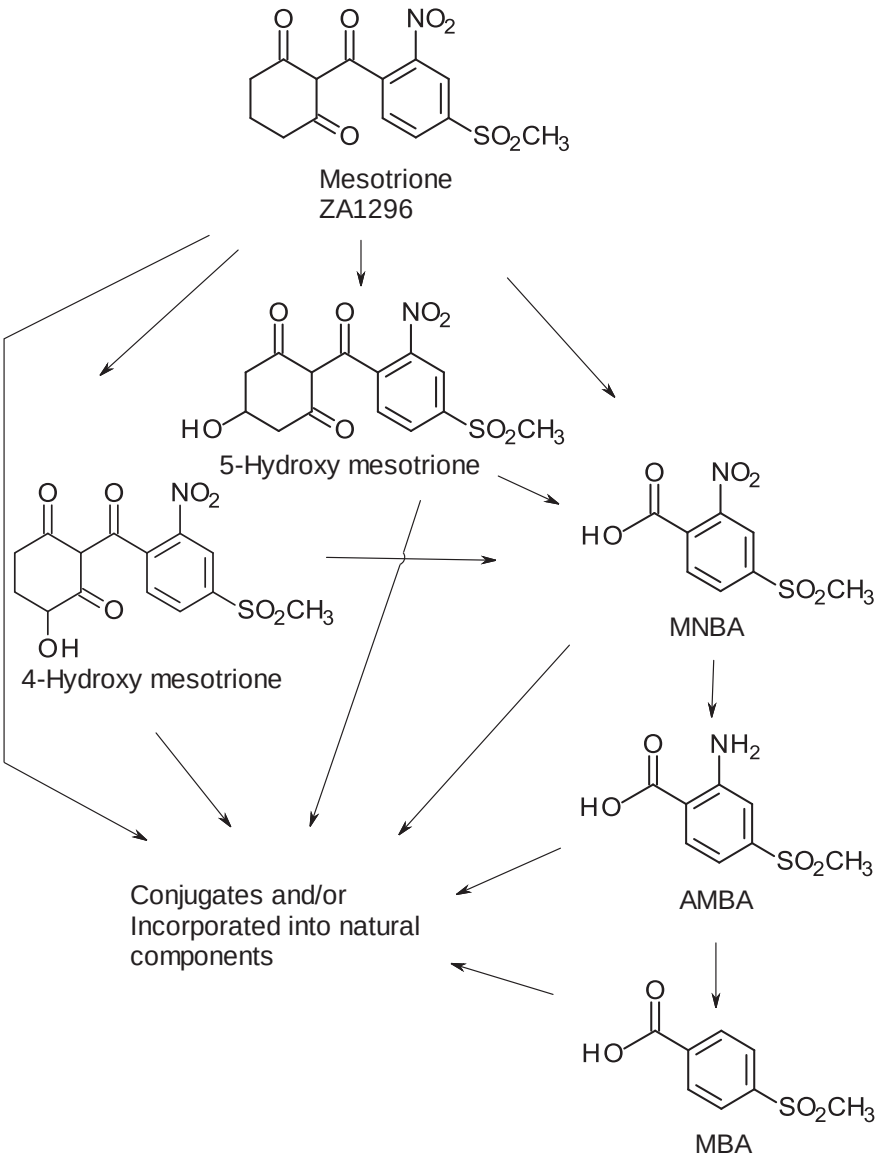


Figure 2 Proposed metabolism of mesotrione in plants

Environmental Fate in Soil

Two soil photolysis studies and five aerobic and anaerobic degradation studies of mesotrione in soil were conducted, using soils collected in 1994 and 1995 in Richmond, Wisconsin (USA). The soil characteristics are shown in Table 31.

Table 31 Silt loam soils used to investigate the metabolism of mesotrione under aerobic conditions

	Studies	Studies
Soil properties	RR95-082B, RR95-047B, RR96-033B, RR96-060B	RR97-033B
% Sand	17.1	16.4

	Studies	Studies
Soil properties	RR95-082B, RR95-047B, RR96-033B, RR96-060B	RR97-033B
% Silt	57.7	58.9
% Clay	25.2	24.8
% Organic Matter	2.72	2.16
pH	6.2	6.1
Cation exchange capacity (meq/100 g)	12.0	10.5
% Moisture holding capacity (saturation)	–	47.2
% Moisture holding capacity (1/3 Bar)	27.4	–
Moisture holding capacity (15 Bar)	7.90	–
Microbial biomass, mg C/kg (zero to end of incubation)	[a]	230 to 182–191

[a] Biological activity of soil was monitored by measuring the soil respiration for 11 days soil pre-incubation. The soil was active as indicated by the formation of 0.6 mg of CO_2 per gram of soil during 11 days of incubation.

Soil photolysis

The photolysis of [phenyl-^{14}C] mesotrione and [cyclohexane-^{l4}C] mesotrione was studied silt loam soil (Table 31) (Van Nest *et al.,* 1996; RR 96-060B). Mesotrione was applied at a nominal rate of 0.30 kg ai/ha, the soil incubated for 31 to 36 days in local sunlight (latitude 37° 56') at 20 to 24 °C. Dark control plates were maintained at 20 to 24 °C. Photolysis of mesotrione was studied under experimental conditions specified by EPA and EEC guidelines. In the EPA protocol, the soil disks were air-dried overnight before the treatment, whereas in the EEC conditions, they were further oven-dried at 35 °C for 7 hours prior to treatment. One day of xenon irradiation corresponded to 2.42 days of irradiation by sunlight in the phenyl EPA study, 2.17 days in the phenyl EEC study and 2.20 days in the cyclohexane study.

The percentage of mesotrione recovered at each sampling interval is shown in Tables 32 and 43. Over 90% AR was recovered immediately after application from the photolysed samples and 88.6% from the control samples. In general, CO_2 was the major photodegradation product from the irradiated samples of [phenyl-^{14}C]- and [cyclohexane-^{14}C] mesotrione. The total $^{14}CO_2$ produced after 31–36 sunlight equivalent days of photolysis was approximately 12% AR for the [phenyl-^{14}C] mesotrione and 32% AR for the [cyclohexane-^{14}C] mesotrione. MNBA and AMBA residues accounted for less than 12% AR each. The calculated half-lives of [phenyl-^{14}C] mesotrione (EEC study), [cyclohexane-^{14}C] mesotrione and [phenyl-^{14}C] mesotrione (EPA study) were 15, 19 and 21 days, respectively, with a mean of 18.5 ± 3.6 days (equivalent to 20.3 days at 50°N; Eya, 1997).

Table 32 Mesotrione soil photolysis treated with [phenyl-^{14}C] and [cyclohexyl-^{14}C] mesotrione (EEC guideline; Van Nest *et al.,* 1996; RR 96-060B), in % of applied ^{14}C in soil extracts

		Equivalent days of summer sunlight at latitude 37° 56' North [phenyl-^{14}C] / [cyclohexyl-^{14}C]						
		0 / 0	4.7 / 4.5	13 / 13	17 / 18	21 / 22	28 / 29	33 / 31
% of applied ^{14}C, [phenyl/ [cyclohexyl]	Mesotrione [a]	94.4 / 95.5	71.5 / 68.8	46.5 / 47.6	42.1 / 41.2	39.2 / 72.8	33.3 / 46.8	32.4 / 54.3
	MNBA	0.4	7.6	11.5	10	8.7	9	8.5
	AMBA	0.4	3.4	6.6	7.5	6.7	7.8	7.3
	$^{14}CO_2$	–	1.78 / 14.9	6.23 / 25.4	8.33 / 28.3	9.74 / 29.9	11.2 / 31.4	11.8 / 31.8

[a] Mean of replicate analysis

Table 33 Mesotrione silt loam soil photolysis treated with [phenyl-^{14}C] mesotrione (EPA protocol, Van Nest *et al.,* 1996; RR 96-060B), in % of applied ^{14}C

	Equivalent days of summer sunlight at latitude 37° 56' North									
	0.0	4.9	12	19	36	0.0 D	2.0 D	8.0 D	14 D	30 D
Mesotrione [a]	92.4	70.8	52.2	44.3	41.0	88.6	90.1	88.7	87.0	84.5
MNBA	0.1	5.4	6.8	7.6	6.5					

	Equivalent days of summer sunlight at latitude 37° 56' North									
	0.0	4.9	12	19	36	0.0 D	2.0 D	8.0 D	14 D	30 D
AMBA	0.3	2.4	5.2	6.0	5.5					
$^{14}CO_2$			12.4	14.4	14.4					

[a] Mean of replicate analysis
D=dark control. Sunlight equivalent days calculated for dark control assuming 24 h of darkness equivalent to 2 days of photolysis

Aerobic and anaerobic degradation in soil

The metabolism of [phenyl-2-^{14}C]-mesotrione (Subba-Rao, 1996; RR 95-082B) and [cyclohexane-2-^{14}C]-mesotrione (Vispetto & Tovshteyn, 1997; RR 95-047B) was investigated in a silt loam soil under aerobic conditions at a rate equivalent to 0.313 and 0.348 kg ai/ha, respectively. The treated soil was incubated in the dark at 25 ± 1 °C and the moisture content was maintained at 20.6% for 58–63 days under conditions which allowed $^{14}CO_2$ and any other volatilised degradates to be trapped. In addition, the metabolism of [phenyl-^{14}C] mesotrione was further investigated at a rate of 0.233 kg ai/ha in a soil incubated in the dark at 20 ± 2 °C and 23.6% moisture content (Miller, 1997; RR 97-033B). $^{14}CO_2$ was collected in NaOH traps over the course of the study. Polyurethane foam plugs inserted in the sidearm of the flasks were analysed for any other volatile radioactive degradates. Soil was extracted with 0.05 M NH_4OH and acetone or acetonitrile. Unextracted radioactivity was further extracted from soil with 0.5 N NaOH or 0.1 N NaOH and microwave extraction.

Average recoveries ranged from 89.8 to 111% AR in the three studies. The percentages of mesotrione and resultant degradates recovered at each sampling interval are presented in Tables 34–36. Levels of radioactivity bound to the soil (unextracted) in the cyclohexane study ranged from 1.5 to 15.2% AR, with no correlation with incubation time; CO_2 accounted for 75% AR by the end of the study (Table 34). In both phenyl- labelled studies (Table 35 and 36), bound residues in soil (unextracted with 0.5 M NaOH) increased throughout the incubation period, when accounted for 34.1 to 37.0% AR. DT_{50} and DT_{90} values for the three studies calculated using first order kinetic ranged from 12 to 14 days and from 45 to 54 days, respectively.

Table 34 Mesotrione and degradates under aerobic conditions in silt loam soil treated with [cyclohexane-^{14}C] mesotrione at 0.313 kg/ai/ha, in % AR

Distribution of residues	Incubation period, days									
	0	1	3	6	9	13	15	21	30	58
Mesotrione	91.0	86.7	73.6	61.5	55.7	47.7	39.5	29.8	19.6	5.67
Reminder—NH_4OH/acetone [a]	2.40	4.30	4.10	4.40	1.10	0.00	6.40	0.70	1.6	1.17
Unidentified [b]	– [e]	– [e]	9.07	– [e]	– [e]	9.84	– [e]	– [e]	11.4	8.59
Reminder—0.1 N NaOH [c]	– [e]	– [e]	0.83	– [e]	– [e]	1.63	– [e]	– [e]	– [e]	0.71
$^{14}CO_2$	0.04	2.08	7.83	17.1	25.4	34.6	38.9	50.1	60.3	75.2
Trapped volatiles [d]	0.00	0.00	0.27	0.05	0.45	0.00	0.00	0.00	0.00	0.02
Unextracted	2.70 [d]	3.00 [d]	1.50	6.80 [d]	11.2 [d]	4.43	12.5 [d]	15.2 [d]	3.63	3.10
Total Recovered	96.1	96.1	96.4	89.8	93.9	96.6	97.3	95.8	96.5	93.8

[a] Radioactivity remaining in the NH_4OH/acetone extracts after accounting for parent from the total via reverse-phase HPLC quantification of the residue
[b] Unidentified; represents two metabolites extracted from 0.1 N NaOH microwave extractions of soil which had been previously extracted with NH_4OH, neither metabolite exceeded 10% of the applied radioactivity
[c] Radioactivity remaining in the 0.1 N NaOH extract after accounting for the unidentified metabolites
[d] Average of two flasks at each interval
[e] NaOH extractions were not completed on these sampling points

MNBA reached a maximum level of 7.6% of the [phenyl-^{14}C] applied radioactivity after six days and declined rapidly, with less than 1% remaining after 63 days (Table 35). The calculated DT_{50} for MNBA in the soil was 1.1 days (Subba-Rao, 1996, RR 95-082B).

Table 35 Mesotrione degradates under aerobic conditions silt loam soil treated with [phenyl-U-^{14}C]-mesotrione at 0.348 kg ai/ha, in % AR

Distribution of residues	Incubation period. Days									
	0	1	3	6	9	13	16	23	30	63
Mesotrione	97.9	96.4	89.1	74.4	57.4	46.3	35.5	27.2	19.1	6.5
MNBA	0.0	4.1	6.8	7.6	5.7	5.5	4.1	1.8	1.8	0.7
AMBA	0.0	2.2	3.7	5.5	7.4	8.7	9.4	9.7	7.3	4.5
$^{14}CO_2$	0.0	0.1	0.8	0.2	5.0	7.4	10.9	15.7	17.8	27.5
NaOH extract [a]	6.1	5.8	6.5	8.9	14.6	13.7	15.2	16.2	23.7	21.1
Unextracted	1.6	2.3	4.4	9.8	8.5	16.4	22.8	24.8	26.9	34.1
Total Recovered	106	111	111	106	98	98	98	95	97	94

[a] The radioactivity not extracted by ammonium hydroxide and acetone was further extracted from soils with 0.5 N NaOH. The alkali extracts humic and fulvic acid components of soil organic matter. This is the overall total for the NaOH fraction before additional clean-up and analysis steps

In the study conducted by Miller (1997; RR 97-033B).MNBA reached a maximum level of 5.8% of the [phenyl-^{14}C] applied radioactivity after 10 days and declined rapidly to non-detectable levels at 56 days (Table 36). In this study the DT_{50} of MNBA, calculated using a first order metabolite model was 0.7 day.

Table 36 Mesotrione degradates under aerobic conditions silt loam soil treated with [phenyl-U-^{14}C]-mesotrione at 0.233 kg ai/ha, in % AR

Distribution of residues	Incubation period. Days							
	0	3	7	10	14	21	28	56
Mesotrione	94.6	82.4	71.2	53.1	48.5	33.4	24.2	11.9
MNBA	1.4	4.5	5.0	5.8	5.1	1.0	0.9	nd
AMBA	nd	2.3	1.8	3.2	3.0	2.3	4.9	7.9
$^{14}CO_2$	na	1.1	3.1	4.9	6.9	10.9	14.7	24.5
Unidentified	nd	nd	nd	7.0	3.2	7.5	2.5	8.1
Water soluble radioactivity	na	1.7	2.9	3.9	4.0	3.5	4.0	6.1
Reminder [a]	3.0	0.7	1.0	1.1	1.3	1.7	1.8	2.0
Unextracted	0.8	5.9	11.7	16.0	22.7	33.0	37.6	37.0
Total Recovered	99.8	98.6	96.8	95	94.6	93.1	90.6	97.5

nd=not detected
na=not applicable
[a] Radioactivity associated with the flocculate which precipitated after acidification of the 0.05 M NH_4OH extract

In two studies to investigate the degradation of mesotrione under anaerobic conditions, [cyclohexane-2-^{14}C] (Vispetto & Tovshteyn, 1996; RR 95-048B) and [phenyl-U-^{14}C]-mesotrione (Carley, 1996; RR 96-033B) were applied to a silt loam soil at 0.280 and 0.340 kg ai/ha, respectively. The soil was incubated in the dark at 25±2 °C and anaerobic conditions were produced by flooding the soil under nitrogen for 30 days prior to treatment.

Average total recoveries ranged from 86.2 to 105% AR throughout the incubation period, with the exception of day 59 of the phenyl-labelled experiment (Tables 36 and 37). Using the [cyclohexane-2-^{14}C]-mesotrione, the amount of unextracted radioactivity increased to a maximum of 23.4% AR after 30 days of incubation (Table 36), while it reached 17% AR after 59 days of incubation using [phenyl-U-^{14}C]-mesotrione (Table 37). AMBA was found to be the only degradation product (Table 37).

Table 36 Mesotrione and degradates under anaerobic conditions in silt loam soil treated with [cyclohexyl-2-^{14}C]-mesotrione, in % AR

Distribution of residues	Incubation period. Days					
	0	1	3	7	14	30
Mesotrione (s + w)	102	77.6	74.5	39.4	9.32	< 0.01
$^{14}CO_2$	0.05	0.09	0.48	1.96	4.83	16.1
Trapped volatiles	0.01	0.00	0.00	0.04	0.93	0.00
Unidentified [a] (s + w)	–	–	4.48	8.19	9.18	10.4

Distribution of residues	Incubation period. Days					
	0	1	3	7	14	30
Remaining ^{14}C from microwave hydrolysis	1.13	3.21	3.97	3.91	9.12	8.0
0.1 N NaOH precipitate (fulvic and humic acids)	0.47	1.57	3.95	7.90	11.4	12.2
Reminder (s + w)	0.21	11.4	4.95	14.4	28.5	16.2
Unextracted (soil after base and microwave)	1.13	4.43	8.70	17.7	14.3	23.4
Total Recovered	105	98.3	101	93.5	87.6	86.3

(s)=Detected in soil extracts
(w)=Detected in flood water
[a] Up to two compounds detected at any sampling interval, with no individual compound exceeding 9.7%

Table 37 Mesotrione and degradates under anaerobic conditions in silt loam soil treated with [phenyl-U-^{14}C]-mesotrione, in % AR

Distribution of residues	Incubation period. Days						
	0	1	3	7	14	30	59
Mesotrione (w)	90	80	47	18	2.7	0	0
Mesotrione (s)	0	3.2	16	18	3.5	0	0
AMBA (w)	0	0	1.5	1.8	9.2	2.7	7.9
AMBA (s)	0	0	1.8	15	28	38	14
$^{14}CO_2$	< 0.1	< 0.5	< 0.1	< 0.1	< 0.1	< 0.3	< 0.5
Reminder [a] (w)	2.5	6.4	5.1	7.9	8.1	5.9	4.9
Reminder [a] (s)	0	2.6	3.9	18	32.9	24.8	12.4
Unextracted	1.5	5.1	11.7	7.4	8.4	14.5	17
Total Recovered	93.7	97.1	87.6	86.3	92.8	86.2	56

(s)=Detected in soil extracts
(w)=Detected in flood water
[a] Unresolved and background radioactivity in chromatograms

Table 38 summarizes the degradation rates of mesotrione in silt loam soil estimated under aerobic and anaerobic conditions.

Table 38 Mesotrione DT_{50} and DT_{90} in silt loam soil under aerobic and anaerobic conditions

Labels (ref)	Conditions	DT_{50} (days)	DT_{90} (days)
[Cyclohexane-^{14}C] mesotrione (Vispetto &Tovshteyn, 1995)	Aerobic	14	45
[Phenyl-^{14}C] mesotrione (Subba-Rao,1996)	Aerobic	12	54
[Phenyl-^{14}C] mesotrione (Miller, 1997)	Aerobic	14	47
[Cyclohexane-^{14}C] mesotrione (Vispetto & Tovshteyn, 1996)	Anaerobic	4.1	14
[Phenyl-^{14}C] mesotrione (Carley, 1996)	Anaerobic	3.6	12

The rate of aerobic degradation of mesotrione was studied in sandy loam, loam and clay loam soils with the characteristics summarised in Table 39 (Miller & Wilson, 1997; RR 96-090B). with [phenyl-U-^{14}C]-mesotrione applied at a nominal rate of 0.165 kg ai/ha and the soils incubated for up to 56 days in the dark at 20 ± 2 °C. Moisture content was 50% of the maximum holding capacity and under conditions which allowed $^{14}CO_2$ to be trapped.

Table 39 Soils used to investigate mesotrione rate of degradation under aerobic laboratory conditions

Soil Property	ERTC [a]	GARRONNE [b]	Pickett Piece [c]
% Sand	73.2	43.5	41.3
% Silt	19.2	34.9	25.5
% Clay	7.6	21.6	33.2
% Organic Matter	0.98	1.46	5.70
pH	6.4	7.7	7.1
Cation exchange capacity (meq/100 g)	2.44	8.60	22.90
% Moisture holding capacity (zero saturation)	23.2	44.9	60.5
% Moisture holding capacity (1/3 Bar)	13.1	23.6	32.6
Moisture holding capacity (15 Bar)	–	–	–

Soil Property	ERTC [a]	GARRONNE [b]	Pickett Piece [c]
Microbial biomass. mg C/kg (zero time)	160	180	604
Microbial biomass. mg C/kg (end of incubation)	109	171	667
Soil classification	silt loam	Loam	clay loam

[a] Zeneca Eastern Research Technical Centre (ERTC), North Carolina, USA
[b] Zeneca Toulouse Field Station, Garomie field, Grisolles, France
[c] Pickett Piece, Oxfordshire, England

Degradation of mesotrione in sandy soils was slower, with a DT_{50} of 12 days. In loam and clay soils the DT_{50} were 5.9 and 4.5 days, respectively Table 40.

Table 40 Mesotrione degradation rate (Miller & Wilson, 1997) in % AR

Sampling Interval (days)	Residue of mesotrione detected (% of applied ^{14}C)		
	Sandy loam	Loam	Clay loam
0	99.9	96.8	102
3	80.0	63.3	73.7
7	42.1	22.3	35.5
10	50.1	16.6	31.8
14	28.4	16.1	18.0
21	39.8	17.2	3.7
28	29.9	1.8	na
56	2.5	na	na
DT_{50} (days) mesotrione	12	5.9	4.5
DT_{90} (days) mesotrione	39	20	15
DT_{50} (days) MNBA	1.3	1.7	-

Na: not analysed as DT_{90} already achieved

[Phenyl-U-^{14}C]-mesotrione was applied at rates ranging from 0.60 to 0.85 mg/kg soil, equivalent to approximately 0.600 to 0.850 kg ai/ha, to 13 soils (characteristics summarised in Table 41) (Tarr, 1997, RR 93-092B).The soils were incubated in the dark, under aerobic conditions at 25 ± 2 °C, maintaining a moisture content of 100% of 1/3 bar moisture capacity and evolved $^{14}CO_2$ was trapped. The soils were incubated for up to 28 days, and samples were extracted with 0.05 M NH4OH and acetone, acidified and portioned with ethyl acetate.

Table 41 Soils used to investigate mesotrione rate of aerobic degradation

	Clay loam	Silt loam		Loam	Loamy sand	loam sandy	Clay loam		Silty clay loam				
Soil Property	721	729	723	725	724	728	727	730	722	731	732	741	742
% Sand	26.2	18.9	7.2	35.0	86.6	52.2	29.0	19.3	5.8	10.8	8.2	13.8	12.0
% Silt	36.8	58.7	69.5	37.7	9.2	29.5	42.8	48.5	63.0	57.0	57.4	52.6	48.8
% Clay	36.9	22.4	23.3	27.3	4.2	18.3	28.2	32.2	31.2	32.3	34.3	33.7	39.2
% Organic Matter	5.4	1.9	2.1	2.3	1.0	1.6	2.5	1.7	3.2	2.0	5.2	3.2	4.5
pH	5.8	5.6	5.8	6.2	5.0	6.4	5.6	6.1	6.0	7.2	5.7	5.5	§
Cation exchange capacity (meq/100 g)	26.2	9.4	8.3	11.9	4.0	6.2	13.9	10.9	16.4	18.2	20.5	16.1	25.5
% Moisture holding capacity (1/3 Bar/15 Bar	35.0/ 16.9	28.0/ 7.3	31.2/ 6.4	24.2/ 8.8	5.2/ 2.4	19.5/ 5.4	27.0/ 10.2	27.4/ 10.4	34.8/ 12.6	31.9/ 13.2	36.8/ 13.9	28.6/ 13.2	34.4/ 13.9

Average total recoveries immediately after treatment ranged from 86.4 to 92.7% of the applied radioactivity and decreased below 90% for six of the soils after 14 days of incubation (Tarr, 1997). Mesotrione degraded rapidly with DT_{50} and DT_{90} values ranging from 8–32 days and 27–105 days, respectively (Table 42). In most soils (10 out of 13), levels of MNBA represented less than 4% AR at any sampling day (DT_{50} < 2 days).

Table 42 Mesotrione degradation rate (aerobic), in % AR

	721	729	723	725	724	728	727	730	722	731	732	741	742
DT_{50} (days)	22	13	17	8	26	8.5	24	19	11	14	16	32	8.2
DT_{90} (days)	73	43	55	27	86	28	80	63	35	48	53	105	27

The aerobic degradation of [phenyl-U-^{14}C]-mesotrione was studied in subsamples of two soils from Michigan (Table 43) treated at a rate of about 1/10 the rate of application to surface soils, or 0.03 mg/kg (Tarr & Tovshteyn, 1997; RR 97-053B). The soils were incubated for up to 42 days in the dark at 20 ± 1 °C, maintaining moisture contents of 100% to 600% of 1/3 bar moisture capacity (about 5 to 10% of the dry soil weight). The higher percentage moisture content was necessary because the soil was very sandy and appeared too dry at < 100% of 1/3 bar. Mesotrione was degraded in soils collected from all depths, at a slower rate in subsoil collected from 1.8–4.8 m below the surface (Table 43).

Table 43 Properties of soils from two locations in Michigan, the USA

	Three Rivers				White Pigeon			
Soil	Loamy sand	Sand	Sand	Sand	Sand	Sand	Sand	Sand
Depth (meters)	0–0.15	1.2–1.8	1.8–2.4	4.2–4.8	0–0.15	1.2–1.8	1.8–2.4	4.2–4.8
Acidity (pH)	6.8	6.6	7.5	8.6	6.4	6.6	7.4	8.4
WHC at Saturation (%)	12.8	12.2	22.2	14.0	14.2	28.8	22.1	18.3
WHC at 1/3 bar (%)	8.1	4.2	3.3	1.5	5.0	4.0	2.6	1.7
WHC at 15 bars (%)	3.6	2.5	1.8	0.8	3.4	2.2	1.3	0.7
Organic Matter (%)	1.4	0.4	0.2	0.1	1.3	0.5	0.2	0.2
CEC (meq/100 g)	6.9	3.0	2.2	1.3	3.6	2.5	2.1	1.2
Sand (%)	79.1	91.9	93.7	96.3	89.5	93.3	96.3	96.8
Silt (%)	12.1	3.4	3.6	1.0	3.8	2.0	0.9	1.3
Clay (%)	8.8	4.8	2.8	2.8	6.8	4.8	2.8	2.0
Dry Bulk Density (g/cm^3)	1.35	1.34	1.43	1.66	1.45	1.46	1.52	1.65
DT_{50} (aerobic)	6	24	105	63	13	12	68	98

Aerobic soil degradation of MNBA

One study was conducted with the purpose to determine the rate of degradation of MNBA in four soils collected from agricultural fields in England and the United States (Lay & Peyton, 2000; RR 99-098B). MNBA was applied to the incubated soil at 0.22 µg/g soil (equivalent to 0.220 kg ai/ha). Immediately after treatment of the soil, eight soil samples were taken for analysis and the remaining soil samples were incubated in the dark under aerobic conditions at 20 °C±2 °C. Samples were collected 0.3, 1, 2, 3, 4, 7, 14, 21, 45 and 60 days after treatment, and extracted with 0.05 N NH_4OH. The MNBA in the extract was chemically reduced to AMBA, which was analysed by a reversed-phase HPLC system using fluorescence detection. DT_{50}s ranged from 0.6 days to 10.6 days (Table 44).

Table 44 DT_{50} and DT_{90} values for MNBA in soils under laboratory aerobic conditions

Soil Origin	Spinks Soil (Three Rivers, Michigan. USA)	Delavan Soil (Wisconsin, USA)	Wisborough Green Soil (West Sussex, England)	East Anglia Soil (Suffolk. England)
	Loamy Sand	Silt Loam	Loam	Sand
pH	6.7	6	5.5	7.9
% Organic Matter	1.4	2.4	5.1	2.2
DT_{50}. days	8.6	1 0. 1	0.6	10.6
DT_{90}. days	28.5	33.6	2.0	35.1

Aerobic soil degradation of AMBA

One study was conducted with the purpose to determine the rate of degradation of MNBA in four soils collected from agricultural fields in England and the United States (Lay & Peyton, 2000; RR 99-

098B). MNBA was applied to the incubated soil at 0.22 µg/g soil (equivalent to 0.220 kg ai/ha). Immediately after treatment of the soil, 8 soil samples were taken for analysis and the remaining soil samples were incubated in the dark under aerobic conditions at 20 °C±2°C. Samples were collected 0.3, 1, 2, 3, 4, 7, 14, 21, 45 and 60 days after treatment, and extracted with 0.05 N NH_4OH. The MNBA in the extract was chemically reduced to AMBA, which was analysed by a reversed-phase HPLC system using fluorescence detection. DT_{50}'s ranged from 0.6 days to 10.6 days (Table 45).

Table 45 DT_{50} and DT_{90} values for MNBA in soils under laboratory aerobic conditions

Soil Origin	Spinks Soil (Three Rivers, Michigan. USA)	Delavan Soil (Wisconsin, USA)	Wisborough Green Soil (West Sussex, England)	East Anglia Soil (Suffolk. England)
	Loamy Sand	Silt Loam	Loam	Sand
pH	6.7	6	5.5	7.9
% Organic Matter	1.4	2.4	5.1	2.2
DT50. days	8.6	1 0. 1	0.6	10.6
DT90. days	28.5	33.6	2.0	35.1

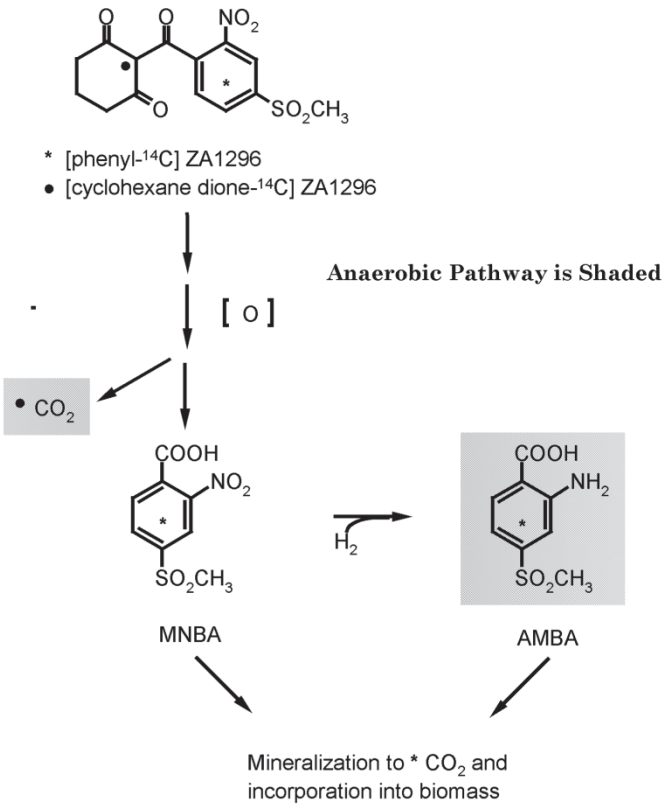


Figure 3 Proposed metabolism of mesotrione in soil

Water sediment study

Mesotrione labelled in either the cyclohexane or phenyl rings was applied to two water sediment systems at a rate equivalent to 0.200 kg ai/ha, evenly distributed throughout a 30 cm deep water body (Cary, 1999; RR 96 033B). The physico-chemical characteristics of the systems are shown in Table 48. The systems were incubated up to 101 days in the dark at 20 °C.

Radioactivity recovered from the water/sediment systems immediately after application ranged from 93% and 102% of the applied dose. The mean recovery from all the samples taken throughout the remainder of the 101 days incubation period was 100% AR. DT_{50} were 3–6 days (Table 46). The level of mesotrione in the sediment did not exceed 4% AR at any time point, and DT_{50} and DT_{90} values in the water-sediment were equivalent to the ones in the water phase.

Table 46 Physico-chemical characteristics of the sediments and water prior to the study start

Sediment			Water		
Property	Old Basing	Virginia Water	Properties	Old Basing	Virginia Water
Soil classification	Sandy loam	Sand	Dissolved oxygen	82	77
Sand (%)	57	96	pH (at collection)	7.2	6.8
Silt (%)	26	2	Suspended solids mg/L	72.0	122
Clay (%)	18	3	Organic carbon, mg/L	64.9	37.1
Organic Matter (%)	7.5	0.5	Total oxidised nitrogen mg/L	5.5	2.0
pH	7.8	7.5	Nitrite mg N/L	< 0.1	< 0.1
Cation exchange capacity, eq/100 g	16.3	1.3	Nitrate mg N/L	5.5	2.0
Phosphorus, mg/kg	19.8	16.9	Ammonia mg N/L	< 0.1	< 0.1
Total nitrogen (%)	0.708	0.033	Orthophosphate mg P/L	< 0.50	< 0.50
			Calcium mg/kg Ca/L	115	37.2
			Magnesium mg/L	1.8	11.4
			Total hardness mg $CaCO_3$/L	294	140
			Conductivity µS/cm	503	379
			Alkalinity	310	52.7
Old Basing	DT_{50}: 3 days; DT_{90}: 10 days				
Virginia Water	DT_{50}: 6 days; DT_{90}: 30 days				

[Phenyl-^{14}C] mesotrione was degraded to MNBA and AMBA (Tables 49 and 50). MNBA was only detected in the Virginia Water system. It reached a maximum of 8% AR on Day 3 and was almost entirely present in the water phase. AMBA was distributed in both the water and the sediment and reached up to 18% at Day 28 in the 'Old Basing' system and up to 19% in 'Virginia Water' system at Day 14.

Table 47 Distribution of radioactivity in 'Old Basing' sediment treated with [Phenyl-^{14}C] mesotrione, in % of applied radioactivity

		Days after treatment									
		0	3	6	10	14	28	42	56	69	101
	$^{14}CO_2$	nd	0.0	0.0	0.0	0.0	0.4	1.0	1.8	2.9	5.5
Surface Water	Mesotrione	73.2	39.2	16.6	9.9	1.4	0.0	0.0	0.0	0.0	0.0
	MNBA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	AMBA	0.0	2.6	5.0	7.2	7.1	9.6	9.2	6.6	8.1	7.1
	Baseline	8.3	7.9	5.9	7.4	6.5	3.6	4.5	3.7	3.6	3.9
	Others	6.0	6.2	11.3	12.8	7.1	3.2	4.4	3.3	2.1	2.3
Sediment	Mesotrione	nd	0.5	0.9	0.9	0.3	0.0	0.0	0.0	0.0	0.0
	MNBA	nd	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	AMBA	nd	2.0	4.7	5.2	5.8	7.9	6.1	7.9	7.0	6.6
	Baseline	nd	1.9	3.2	2.8	4.0	3.2	3.4	2.9	3.6	4.0
	Others	2.9	6.6	6.9	7.6	8.0	7.4	5.2	6.4	6.8	6.0
	Unextracted	2.3	21.3	48.1	55.5	64.7	70.8	67.3	73.8	75.0	73.7
Surface Water + Sediment	Mesotrione	73.2	39.6	17.6	10.8	1.7	0.0	0.0	0.0	0.0	0.0
	MNBA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	AMBA	0.0	4.5	9.7	12.4	12.9	17.5	15.3	14.5	15.1	13.8
	Unidentified [a]	17.3	22.6	27.3	30.6	25.7	17.4	17.5	16.3	16.1	16.1
	Unextracted	2.3	21.3	48.1	55.5	64.7	70.8	67.3	73.8	75.0	73.7
	Total	92.7	88.1	102.7	109.3	105.0	106.1	101.1	106.4	109.1	109.1

[a] Unidentified is Baseline+ Others (from TLC of extracts). 0= < 0.05%
nd=Not determined

Table 48 Distribution of radioactivity in 'Virginia Water' sediment treated with [Phenyl-^{14}C] mesotrione, in % of applied radioactivity

		Days after treatment									
		0	3	6	10	14	28	42	56	69	101
$^{14}CO_2$		nd	0.0	0.0	0.0	0.1	2.6	6.6	9.9	12.1	15.6
Surface Water	Mesotrione	71.2	53.5	41.0	34.8	10.7	3.0	0.5	0.0	Nd	nd
	MNBA	0.0	7.4	4.9	0.8	1.3	2.5	0.9	0.0	Nd	nd
	AMBA	0.0	2.5	4.8	3.0	11.5	9.0	2.9	0.8	Nd	nd
	Baseline	11.4	12.3	7.7	8.5	8.8	4.9	2.9	2.4	Nd	nd
	Others	7.8	6.2	11.6	8.1	8.3	6.4	3.8	2.2	4.3	2.2
Sediment	Mesotrione	nd	3.8	1.3	1.9	0.3	0.0	0.0	0.0	0.0	0.0
	MNBA	nd	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	AMBA	nd	1.2	2.7	6.4	7.7	6.1	6.2	3.0	4.3	3.1
	Baseline	nd	2.5	4.6	9.2	11.5	10.4	11.3	12.5	12.0	12.1
	Others	5.3	4.4	7.7	9.0	12.6	12.6	11.5	14.7	13.0	9.9
	Unextracted	0.2	3.7	12.4	20.0	27.5	42.1	47.7	56.5	54.8	64.5
Surface Water.+ Sediment	Mesotrione	71.2	57.3	42.2	36.6	10.9	3.0	0.5	0.0	0.0	0.0
	MNBA	0.0	7.9	4.9	0.8	1.3	2.5	0.9	0.0	0.0	0.0
	AMBA	0.0	3.7	7.5	9.4	19.2	15.1	9.1	3.8	4.3	3.1
	Unidentified [a]	24.4	25.4	31.6	34.8	41.2	34.3	29.6	31.8	29.4	24.2
	Unextracted	0.2	3.7	12.4	20.0	27.5	42.1	47.7	56.5	54.8	64.5
Total		95.8	98.0	98.6	101.7	100.3	99.6	94.3	102.0	100.6	107.4

[a] Unidentified is Baseline+ Others (from TLC of extracts)
0.0= < 0.05%
nd=Not determined

[Cyclohexane-^{14}C] mesotrione degraded into CO_2, which accounted for approximately 27% of the applied radioactivity at Day 101 in both the 'Virginia Water' and 'Old Basing' systems respectively (Tables 49–50).

Table 49 Distribution of radioactivity in 'Old Basing' sediment treated with [Cyclohexane-^{14}C] mesotrione, in % of applied radioactivity

		Days after treatment									
		0	3	6	10	14	28	42	56	69	101
$^{14}CO_2$		nd	0.1	0.2	0.9	3.0	12.5	18.5	22.1	24.7	27.8
Surface Water	Mesotrione	86.0	74.7	31.7	16.3	12.7	0.0	0.4	nd	Nd	nd
	Baseline	8.7	10.4	8.1	8.7	8.2	4.6	2.6	nd	Nd	nd
	Others	5.6	8.2	17.6	14.0	12.4	5.1	1.6	3.8	3.0	2.5
Sediment	Mesotrione	nd	nd	0.0	0.0	0.0	0.0	0.0	nd	Nd	nd
	Baseline	nd	nd	2.5	2.9	3.6	2.8	2.7	2.4	Nd	nd
	Others	0.8	1.8	8.2	9.5	11.2	8.8	3.4	7.0	8.8	7.6
	Unextracted	0.9	3.2	28.8	39.2	43.8	57.6	58.4	60.6	58.0	63.8
Surface water + Sediment	Mesotrione	86.0	74.7	31.7	16.3	12.7	0.0	0.4	nd	Nd	nd
	Unidentified [b]	15.1	20.4	36.4	35.1	35.5	21.3	10.3	13.2	11.8	10.1
	Unextracted	0.9	3.2	28.8	39.2	43.8	57.6	58.4	60.6	58.0	63.8
	Total	102.0	98.4	97.1	91.5	95.0	91.4	87.6	95.9	94.5	101.7

[a] Any summation differences in values within the table result from rounding of numbers within individual calculations
[b] Unidentified is Baseline + Others (from TLC of extracts)
0.0= < 0.05%
nd=Not determined

Table 50 Distribution of radioactivity in 'Virginia Water' sediment treated with [Cyclohexane-^{14}C] mesotrione, in % of applied radioactivity

		Days after treatment									
		0	3	6	10	14	28	42	56	69	101
$^{14}CO_2$		nd	0.3	0.7	2.1	3.6	8.6	16.5	21.0	23.6	26.8
Surface	Mesotrione	80.0	na	59.7	26.4	33.0	4.8	0.8	0.0	nd	nd

		Days after treatment									
		0	3	6	10	14	28	42	56	69	101
Water	Baseline	9.5	na	9.1	6.0	7.0	2.1	2.4	0.0	nd	nd
	Others	6.8	na	18.4	10.5	7.6	4.1	3.6	4.4	4.2	4.8
Sediment	Mesotrione	nd	nd	1.4	0.7	1.9	0.0	0.0	0.0	0.0	0.0
	Baseline	nd	nd	3.3	11.5	9.0	9.6	14.9	12.0	8.7	8.2
	Others	3.1	1.1	5.4	17.1	18.3	20.3	20.4	17.2	16.9	14.7
	Unextracted	0.1	0.4	5.7	24.6	19.8	48.4	42.9	48.0	43.9	44.7
Surface water + Sediment	Mesotrione	80.0	na	61.2	27.1	34.9	4.8	0.8	0.0	0.0	0.0
	Unidentified [a]	19.5	na	36.2	45.1	41.8	36.1	41.3	33.6	29.8	27.7
	Unextracted	0.1	na	5.7	24.6	19.8	48.4	42.4	48.0	43.9	44.7
Total		99.6	103.0	103.8	98.9	100.1	97.4	101.0	102.6	97.3	99.2

[a] Unidentified is Baseline+ Others (from TLC of extracts)
0.0= < 0.05%
nd=Not determined
na=Not available

Degradation in soil–field studies

Six field studies were conducted to evaluate the rate of degradation of mesotrione in soil. A single application of a 0.100 kg ai/L suspension concentrate of mesotrione was applied to bare soil at rates of 0.150 and 0.200 g ai/ha in 1995/96 and 1996/97 seasons, respectively (Table 51). Soil samples were collected up to 30 cm depth, prepared in 10 cm horizons and analysed for mesotrione, MNBA and AMBA. Calculated DT_{50} and DT_{90} for mesotrione are also shown in Table 51.

In the 1996-1997 Italian trial, MNBA was detected at up to 0.031 mg/kg in 0–10 cm horizon, six days after application and declined to < 0.005 mg/kg by 89 days after treatment. AMBA was detected only in the 0-10 cm horizon six days after application (0.006 mg/kg). In one 1996–1997 German trial, MNBA reached a maximum of 0.016 mg/kg in the 0–10 cm horizon eight days after application and decreased to <0.005 mg/kg 89 days after treatment. No measurable residues of mesotrione or metabolites were detected in the soil below 10 cm.

Table 51 Field dissipation of mesotrione in Europe

				Soil Property		DT_{50}	DT_{90}	Reference
Year	Location	Application Rate (kg ai/ha)	Soil Type	Organic Carbon (%)	pH			
1995-1996	France (south)	0.150	0 - 10 cm (clay loam) 10 - 20 cm (clay loam) 20 - 30 cm (clay)	2.1 1.7 0.4	6.0 6.3 7.1	7	73	Grahan *et al.*, 1997a
	Italy	0.150	0 - 10 cm (clay loam) 10 - 20 cm (silt loam) 20 - 30 cm (silt clay)	2.7 1.9 0.4	6.1 6.6 7.1	7	36	Grahan *et al.*, 1997b
	Germany	0.150	0 - 10 cm (sandy clay loam) 10 - 20 cm (sandy clay) 20 - 30 cm (sandy loam)	2.6 0.7 0.4	6.2 6.5 7.2	3	59	Grahan *et al.*, 1997c
1996-1997	Italy	0.200	0 - 10 cm (sandy loam) 10 - 20 cm (sandy loam) 20 - 30 cm (loamy sand)	0.8 0.6 0.2	8.0 8.3 8.5	8	26	Grahan *et al.*, 1998a
	Germany 1	0.200	0 - 10 cm (loam) 10 - 20 cm (silt loam) 20 - 30 cm (silt loam)	2.5 1.6 1.0	7.0 7.4 7.6	8	26	Grahan *et al.*, 1997b
	Germany 2	0.200	0 - 10 cm (sandy clay loam) 10 - 20 cm (sandy loam) 20 - 30 cm (sandy loam)	2.8 1.6 0.5	6.9 7.1 7.4	2	21	Wiebe, 1999

Aerobic soil degradation of AMBA

In another study, [phenyl-U-14C]-AMBA was applied at 0.213 kg ai/ha (Marth, 1997; RR 97-032B) or 0.225 kg ai/ha (Lay, 2000; RR 99-096B). Soil characteristics are shown in Table 52. The soils were incubated for up to 60 days in the dark under aerobic conditions at a temperature of 20 ± 2°C,

maintaining a moisture content of 40% of water holding capacity. Average total recoveries ranged from 92.7–98.6% AR at Day 0. AMBA DT50 ranged from 2 to 6 days and no AMBA degradates exceeded 10% AR in any of the three soils (Table 52).

Table 52 AMBA rate of degradation in various soils under aerobic conditions

	Marth, 1997			Lay, 2000	
	Wisborough Green, England	Delevan, USA	East Anglia, England	Spinks, USA	
Soil Property	Clay	Silt loam	Sandy loam	Loamy sand	
% organic matter	3.1	2.4	2.46	1.4	
pH	4.9	6.4	7.9	6.7	
Cation exchange capacity, meq/100 g	10.52	12.11	8.47	6.1	
Sampling days	% of AR			Sampling days	% of AR
0	98.6	98.6	98.1	0	92.7
0.1	72.2	82.8	90.8	0.3	84.1
3	40.1	55.2	45.6	1	71.4
7	30.3	45.7	28.4	2	54.1
10	25.4	41.5	19.3	3	43.6
14	19.2	37.4	18.1	4	39.1
21	13.4	26.6	17.1	7	24.5
28	7.8	23.7	15.1	14	13.2
56	7.8	20.2	11.1	21	11.4
				45	14.1
				60	11.8
DT_{50} (days)	3	6	2	1.8	
DT_{90} (days)	39	>56	63	56	

Confined rotational crops

This study was designed to provide information on the uptake and metabolism of [phenyl-U-^{14}C]-mesotrione in rotational crops following a single application onto the bare surface of a sandy loam soil at a rate of 0.165 kg ai/ha (Gorder *et al.,* 1997; RR 96-084B). At intervals of 120 and 300 days after treatment (DAT), three representative rotational crops (endive, radish and wheat) were sown into the treated soil. Crops planted in the 120 DAT soils were harvested: endive at 78 days after planting (DAP), radish roots and leaves at 56 DAP, wheat forage at 22 DAP, wheat hay at 57 DAP and wheat grain and straw at 134 DAP. The 300 DAT crops were not harvested due to low residues found in 120 DAT crops. Crops with residues ≥ 0.01 mg/kg were extracted with acetonitrile/water and the extracted residues (> 0.01 mg/kg) were analysed by HPLC-radiodetector.

Analysis of soil cores showed that the residue had declined to 34% of the applied radioactivity (AR) after 120 days and to 15% AR after 300 days. In soil, mesotrione accounted for 0.1% AR after 120, MNBA for 8% and AMBA for 2% AR.

Total radioactive residues in crop commodities from the 120 DAT are shown in Table 53. Residue levels were ≤ 0.035 mg/kg for feed commodities and ≤ 0.014 mg/kg eq. for food commodities. Untreated soil and pots contained low levels of radioactivity (≤ 0.004 mg/kg eq.), resulting from mineralisation of [^{14}C]mesotrione in the soil. Unextracted residues represented ≤ 0.015 mg/kg eq. and were not further analysed.

Commodities with residues > 0.01 mg/kg eq. were extracted with acetonitrile/water. From 46 to 59% TRRs were extracted. The major metabolite in wheat commodities was MNBA accounting for 36%TRR in forage (Table 53). AMBA was present mostly in conjugated form.

Table 53 Summary of total radioactive residues in rotational crop samples grown in soil treated at 0.165 kg/ai/ha with [phenyl-2-^{14}C]-mesotrione–120 DAT

Crop	TRR, mg/kg eq.	Extracted, mg/kg (%TRR)	PES, mg/kg (%TRR)	Losses in sample work-up, mg/kg (%TRR)
Wheat forage, 22 DAP	0.031	0.018 (58)	0.006 (21)	0.007 (21)
Wheat hay, 57 DAP	0.019	0.011 (59)	0.007 (36)	0.001 (5)
Wheat straw, 134 DAP	0.035	0.016 (46)	0.015 (43)	0.004 (11)
Wheat grain, 134 DAP	0.006	–	–	–
Endive, 78 DAP	0.014	0.007 (51)	0.007 (51)	(+2)
Radish root, 56 DAP	0.004	–	–	–
Radish leaves, 56 DAP	0.004	–	–	–

Table 54 Summary of total radioactive residues in 120 DAT wheat feed commodities

	Forage		Hay		Straw	
Metabolite[1)]	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
MNBA	0.011	36	0.003	16	0.003	9
AMBA Sulphate conjugate	0.002	6	0.002	11	0.004	10
AMBA Conjugate	0.002	5	–	–	–	–
AMBA	–		0.001	5	0.001	3
Others (each < 0.001) [a]	0.004	11	0.005	26	0.009	24

[a] All radioactivity that did not form discrete HPLC peaks

In another study, [phenyl-U-^{14}C]-mesotrione was applied at 0.308 kg ai/ha and 0.462 kg ai/ha, the lower rate representative of the pre-emergence use and the higher rate being representative of a pre-emergent followed by post-emergent use (Gorder *et at.,* 1996; RR 96-035B). Each application was sprayed onto the bare surface of a sandy loam soil contained in 51 cm diameter pots. The pots were sown with combinations of wheat, soy, endive and radish at intervals of 30, 120 and 300 DAT. Leaf and root crops could not be planted at 30 DAT due to crop sensitivity

Samples having radioactive residues greater than or equal to 0.01 mg/kg were extracted 2–3 times with acetonitrile/water. The 30-DAT wheat grain sample was extracted by refluxing with 2 M HCl. Solids with residues > 0.05 mg/kg (> 10% TRR) were subjected to further extraction with 1 M/10M ammonium hydroxide and 6 M HCl at ambient temperature and/or under reflux. HPLC and TLC were used for the characterisation of residues.

Radioactive residues in soil declined to 27% AR at 300 DAT. Mesotrione levels were < 1% AR between 28 and 300 DAT, forming MNBA and to a lesser extent AMBA present at the 120 and 300 day sowing intervals.

Radioactive residues in wheat feed commodities declined with increasing sowing intervals, being highest in wheat straw (2.58 mg/kg eq. at 30 DAT). In wheat grain, it was 0.038 mg/kg at 30 DAT and < 0.02 mg/kg at all other planting intervals. Soya bean residues were 0.145 mg/kg at DAT with feed commodities containing 0.462 and 0.645 mg/kg for hay and forage respectively. Residues in endive and radish root declined to 0.019 and 0.005 mg/kg respectively after 300 DAT (Table 55). Residues in control did not exceed 0.007 mg/kg eq.

Table 55 Total Radioactive Residues (mg/kg eq.) in rotational crop samples grown in soil treated with [phenyl-U-^{14}C]-mesotrione

Crop	30 DAT (0.308 kg ai/ha)		120 DAT (0.462 kg ai/ha)		300 DAT (0.462 kg ai/ha)	
	Treated	Control	Treated	Control	Treated	Control
Wheat straw	2.58	0.005	0.233	0.003	0.197	0.001
Wheat forage	1.011	0.001	0.303	0.001	0.100	0.000
Wheat hay	0.756	0.003	0.127	0.001	0.044	0.000
Wheat grain	0.038	0.004	0.014	0.004	0.015	0.001

Crop	30 DAT (0.308 kg ai/ha)		120 DAT (0.462 kg ai/ha)		300 DAT (0.462 kg ai/ha)	
	Treated	Control	Treated	Control	Treated	Control
Soy forage	0.645	0.001	Not planted	Not planted	Not planted	Not planted
Soy hay	0.462	0.003	Not planted	Not planted	Not planted	Not planted
Soya bean	0.145	0.007	Not planted	Not planted	Not planted	Not planted
Endive	Not planted	Not planted	0.053	0.000	0.019	0.000
Radish root	Not planted	Not planted	0.037	0.000	0.005	0.005
Radish leaves	Not planted	Not planted	0.048	0.000	0.009	0.000

The major identified metabolite in all wheat samples was MNBA, reaching 0.63 mg/kg in 30 DAT wheat forage (Tables 56 and 57). AMBA was mostly present as sulphate conjugate. Wheat grain samples from 30 DAT contained MNBA at 0.003 mg/kg and an unidentified glucose conjugate (0.013 mg/kg). About 70% TRR of grain samples from 120 and 300 DAT were retained in PES, but no further work was conducted in the samples.

Table 56 Radioactive residues in wheat RACs following treatment of soil with [phenyl-U-^{14}C]-mesotrione

	0.308 kg ai/ha /30 DAT				0.462 kg ai/ha /120 DAT			
Commodity	Forage	Hay	Straw	Grain*	Forage	Hay	Straw	Grain
Component	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)
MNBA	0.625 (62)	0.172 (23)	0.458 (18)	0.003 (8)	0.165 (54)	0.023 (18)	0.018 (8)	
AMBA	0.086 (9)	0.083 (11)	0.330 (13)	–	0.019 (6)	0.020 (16)	0.012 (5)	
AMBA sulphate	0.088 (9)	0.131 (17)	0.317 (12)	–	0.028 (9)	0.015 (12)	0.018 (8)	
AMBA conj.	0.036 (4)	0.021 (3)	0.021 (1)	–	0.021 (7)	0.001 (1)	0.002 (1)	
4-OH mesotrione	0.014 (1)	–	–	–	–	–	–	
Mesotrione	0.012 (1)	–	–	–	–	–	–	
Unknown M2	–	0.012 (2)	0.022 (1)	–	–	–	–	
Unknown M12	–	0.011 (1)	–	–	–	0.001 (1)	–	
Unknown M13	–	0.009 (1)	0.017 (1)	–	–	–	–	
Unknown M18	–	0.018 (2)	–	–	–	–	–	
Unknown M19	–	0.017 (2)	–	–	–	–	–	
Unknown M22	–	–	0.015 (1)	–	–	–	–	
Glucose conj.	–	–	–	0.013 (34)	–	–	–	
Others (each < 0.01)	0.118 (12)	0.184 (24)	1.01 (39)	0.009 (24)	0.035 (12)	0.032 (25)	0.119 (51)	
PES	0.051 (5)	0.073 (10)	0.35 (14)	0.011 (29)	0.014 (5)	0.012 (9)	0.034 (15)	0.001 (72)
Losses on workup	0.02 (–2)	0.03 (3)	0.04 (2)	< 0.01 (5)	0.02 (7)	0.02 (18)	0.03 (13)	< 0.01 (12)
Total	1.011 (100)	0.756 (100)	2.58 (100)	0.038 (100)	0.303 (100)	0.127 (100)	0.233 (100)	0.014 (100)

Table 57 Radioactive residues in wheat RACs following treatment of soil with [phenyl-U-^{14}C]-mesotrione

	0.462 kg ai/ha / 300 DAT			
Commodity	Forage	Hay	Straw	Grain [a]
Component	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)
Mesotrione	–	0.001 (2)	–	–
MNBA	0.043 (43)	0.007 (17)	0.015 (8)	–
AMBA	0.007 (7)	0.003 (7)	0.014 (7)	–
AMBA conj.	0.005 (5)	0.002 (4)	0.003 (1)	–
AMBA sulphate conj.	0.011 (11)	0.009 (21)	0.026 (13)	–
Unknown	–	0.002 (4)	0.005 (3)	–
Others (each < 0.01 mg/kg)	0.016 (16)	0.011 (24)	0.072 (37)	–
PES	0.015 (15)	0.013 (30)	0.029 (15)	0.001 (71)
Loss on Partitioning	0 (0)	< 0.01 (–7)	0.03 (15)	0 (0)
Total	0.100 (100)	0.044 (100)	0.197 (100)	0.015 (100)

[a] The aqueous fraction for the wheat grain sample was a hydrolysate

Radioactive residues in soy forage represented 0.645 mg/kg, of which 61% TRR was extracted (Table 58). The PES containing 38% TRR was hydrolysed releasing a further 20% TRR (0.129 mg/kg). MNBA was the major metabolite in soy forage and hay (up to 48% TRR). Over 40%TRR in the soya beans was extracted. The PES containing 54% TRR (0.078 mg/kg) was further extracted with base, acid with hexane, which solubilised a further 24% TRR (0.036 mg/kg). AMBA was the major compound in soya bean (0.024 mg/kg), in addition to a unknown glucose metabolite (0.003 mg/kg). A number of unknown metabolites were observed in all commodities, no one representing > 0.011 mg/kg.

Table 58 Radioactive residues in soya bean RACs following treatment of soil with [phenyl-U-^{14}C]-mesotrione 0.308 kg ai/ha / 30 DAT

Commodity	Forage		Hay		Bean	
Component	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
MNBA	0.312	48	0.166	35	0.014	10
AMBA	0.069	11	0.034	7	0.024	17
Unknown M1	0.004	1	0.003	1	0.01	7
Unknown M2	0.011	2	0.013	3	–	–
Unknown M18	0.009	1	0.009	2	0.005	4
Unknown M20	0.005	1	–	–	–	–
Unknown M14	–	–	0.004	1	–	–
Unknown M15	–	–	0.005	2	–	–
Glucose	–	–	–	–	0.004	3
Others (each < 0.01 mg/kg)	0.112	17	0.096	21	0.033	23
PES	0.104	16	0.124	27	0.026	18
Loss on Partitioning	0.02	3	< 0.01	2	0.03	19
Total	0.645	100	0.462	100	0.145	100

Not applicable

The major residue in endive was MNBA, accounting for up to 38% TRR (0.02 mg/kg) at 120 DAT (Table 59). Traces of AMBA were detected at 300 DAT. A number of minor unknowns were seen, each at ≤ 0.002 mg/kg. Residue levels in radish were low (≤ 0.05 mg/kg), and distributed with slightly more radioactivity in tops than roots, with MNBA accounting for to up to 53%TRR (Table 59).

Table 59 Summary of radioactive residues in endive and radish RACs following treatment of soil with [phenyl-U-^{14}C]-mesotrione at 0.462 kg ai/ha

Rotation Period	Endive		Radish Top	Radish Root
	120 DAT	300 DAT	120 DAT	
Component	mg/kg (% TRR)	mg/kg (%TRR)	mg/kg (% TRR)	mg/kg (%TRR)
MNBA	0.02 (38)	0.007 (35)	0.025 (53)	0.013 (36)
AMBA	–	0.001 (6)		
AMBA conj.	–	–		0.003 (8)
Unknown M1	0.001 (3)	0.002 (13)		
Unknown M5	0.001 (3)	–		
Others (each < 0.001 mg/kg)	0.005 (9)	0.005 (25)	0.010 (20)	0.004 (10)
PES	0.023 (43)	0.007 (37)	0.012 (25)	0.017 (45)
Total	0.053 (100)	0.019 (100)	0.048 (100)	0.037 (100)

[Cyclohexane-2-^{14}C]-mesotrione at a nominal rate of 0.165 kg ai/ha was sprayed once onto the bare surface of a sandy loam soil contained in pots in greenhouse (Spillner *et al.,* 1997; RR 95-042B). Endive, radish and wheat were sown into the treated soil (120 DAT). Soil cores were taken immediately after sowing and at 273 and 300 DAT. Endive was harvested 63 DAP, radish roots and leaves at 56 DAP, forage wheat at 22 DAP, forage hay at 57 DAP and wheat grain and straw at 131 DAP. Total radioactive residues in all samples ranged from < 0.001 mg/kg eq. in endive and radish to 0.004 mg/kg eq. in wheat straw. Residues in control reached 0.002 mg/kg in wheat grain and straw.

Radioactive residues in soil declined to 4% of the applied radioactivity by 120 DAT. No further analysis was conducted since the radioactive residues were < 0.01 mg/kg.

In another rotational study, [cyclohexane-2-^{14}C]-mesotrione was sprayed once at 0.308 kg ai/ha or 0.462 kg ai/ha to sandy loam soil pots (Spillner *et al.,* 1996; RR 96-005B). Wheat was planted at 30, 120 and 300 DAT, soy at 30 DAT and endive and radish at 120 DAT. Samples with residues ≥ 0.01 mg/kg were extracted with acetonitrile:water. Soya beans were first extracted with hexane to remove the oil. The 30-DAT wheat grain sample was hydrolysed using 2 N hydrochloric acid; the hydrolysate partitioned with ethyl acetate to remove the organosoluble residues, and the aqueous phase was analysed for ^{14}C-glucose. Reverse-phase HPLC was used for the characterisation mesotrione and its metabolites.

Radioactive residues in the soil declined to 10, 5 and 4% AR after 30, 120 and 300 DAT, respectively. Radioactive residues in wheat commodities declined over time, with the highest residues found in feed (Table 60). Residues in the soy ranged from 0.017 in beans to 0.026 mg/kg in forage at 30 DAT. In root crops at 120 DAT they reached 0.004 mg/kg in radish leaves and were not further investigated.

Table 60 Summary of total radioactive residues in rotational crop samples grown in soil treated with [cyclohexane-2-^{14}C]-mesotrione

Crop	30 DAT (0.308 kg/ha)		120 DAT (0.462 kg/ha)		300 DAT (0.462 kg/ha)	
	Treated (mg/kg)	Control (mg/kg)	Treated (mg/kg)	Control (mg/kg)	Treated (mg/kg)	Control (mg/kg)
Wheat straw	0.059	0.002	0.043	0.002	0.006	< 0.001
Wheat forage	0.054	0.001	0.017	< 0.001	0.002	< 0.001
Wheat hay	0.048	0.001	0.013	< 0.001	0.002	< 0.001
Wheat grain	0.010	0.002	0.008	0.002	0.001	< 0.001
Soy forage	0.026	0.001	–	–	–	–
Soy hay	0.021	0.001	–	–	–	–
Soya bean	0.017	0.003	–	–	–	–
Endive	–	–	0.003	< 0.001	–	–
Radish root	–	–	0.002	< 0.001	–	–
Radish leaves	–	–	0.004	< 0.001	–	–

Mesotrione was a major residue in feed wheat commodities, but was not detected in grain, in which the only identified residue was a glucose conjugate (Table 61). Residues in wheat grain was 0.01 mg/kg at 30 DAT. 4-hydroxy mesotrione was the major metabolite identified, accounting for up to 15% TRR in forage (0.008 mg/kg). Over 70% of the residues were extracted from all matrices, and PES was not analysed further.

Table 61 Radioactive residues in wheat RACs following treatment with [cyclohexane-2-^{14}C]-mesotrione

	0.308 kg ai/ha/ 30 DAT				0.462 kg ai/ha/120 DAT		
Commodity	Forage	Hay	Straw	Grain [a]	Forage	Hay	Straw
Component	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)	mg/kg (% TRR)
mesotrione	0.009 (17)	0.003 (7)	0.0034 (5.7)	–	0.001 (5)	–	0.001 (3)
4-OH	0.008 (15)	0.004 (8)	0.0021 (3.6)	–	0.002 (12)	–	0.003 (6)
Unknown 1	–	–	0.0021 (3.6)	–	–	–	< 0.001 (1)
Unknown 2	0.002 (4)	0.003 (6)	–	–	0.001 (8)	–	0.002 (5)
XanH4	0.001 (2)	0.001 (2)	0.0021 (3.6)	–	< 0.001 (3)	–	0.002 (4)
Unknown 3	0.002 (3)	0.002 (4)	0.0025 (4.3)	–	–	–	0.001 (3)
4-OGlu	0.002 (4)	0.003 (6)	0.0017 (2.8)	–	0.001 (6)	–	0.002 (4)
5-OH	0.001 (1)	0.002 (4)	0.0025 (4.3)	–	< 0.001 (2)	–	0.001 (2)
Unknown 4	0.001 (1)	0.001 (3)	0.0029 (5.0)	–	< 0.001 (2)	–	0.001 (2)
Unretained	0.007 (12)	0.009 (20)	0.0147 (24.9)	–	0.002 (10)	–	0.010 (23)
Remainder	0.006 (10)	0.005 (10)	0.0080 (13.5)	–	0.001 (8)	–	0.006 (13)
Glucose				0.007 (69)			

	0.308 kg ai/ha/ 30 DAT				0.462 kg ai/ha/120 DAT		
Commodity	Forage	Hay	Straw	Grain [a]	Forage	Hay	Straw
acetone rinse + acetonitrile	0.009 (16)	0.004 (8)	< 0.001 (1)	< 0.001 (5)	0.003 (20)	0.0026 (20)	0.001 (2)
PES	0.008 (15)	0.011 (22)	0.017 (28%)	0.003 (26)	0.004 (24)	0.0027 (21)	0.014 (32)
Total	0.056 (100)	0.048 (100)	0.059 (100)	0.010 (100)	0.017 (100)	0.013 (100)	0.043 (100)

[a] The aqueous fraction for the wheat grain sample was a hydrolysate. not an extract; 4-OH: 4-hydroxy-mesotrione; 4-OGlu: 4-hydroxy-mesotrione glucoside conjugate; 5-OH:5-hydroxy-mesotrione; XanH4: 6-(methylsulfonyl)-1-oxo-1.2.3.4-tetrahydro-9H-xanthen-9-one

About 70% of radioactivity was extracted from soy forage and hay, and PES was not analysed further. 13% TRR was extracted from soya beans with hexane and 20% TRR with acetonitrile/water mixtures (< 0.01 mg/kg); PES accounted for 64% TRR (0.01 mg/kg). Neither the soya bean extracts nor PES were analysed further. Mesotrione was the major residue in soy forage and hay (up to 11% TRR, 0.003 mg/kg), while 5-hydroxy-mesotrione and 4-hydroxy-mesotrione represented 4 to 6% TRR (Table 62).

Table 62 Radioactive residues in soy samples following treatment with [cyclohexane-2-^{14}C]-mesotrione (0.308 kg ai/ha/30DAT)

Commodity:		Forage		Hay		Bean	
	Component	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
	Mesotrione	0.003	11	0.002	10	–	–
	5- hydroxy-mesotrione	0.001	6	0.001	5	–	–
	4-hydroxy-mesotrione	0.001	4	–	–	–	–
	4-OH—glucose conjugate	–	–	0.001	5	–	–
	XanH4	0.001	3	0.001	4	–	–
	Unretained	0.005	20	0.005	22	–	–
	Unknown 1	–	–	< 0.001	3	–	–
	Unknown 3	–	–	0.001	5	–	–
	Remainder	0.005	19	0.003	13	–	–
Acetone rinse + acetonitrile		0.002	7	0.001	6	0.004 [a]	23 [a]
PES		0.08	29	0.006	27	0.011	64
Total		0.026	100	0.021	100	0.017	100

[a] Organic extract also included value obtained from the hexane extraction step; XanH4: 6-(methylsulfonyl)-1-oxo-1.2.3.4-tetrahydro-9H-xanthen-9-one

The proposed pathways of mesotrione in rotated crops obtained from studies using the mesotrione labelled in phenyl and the cyclohexane are shown in Figure 4.

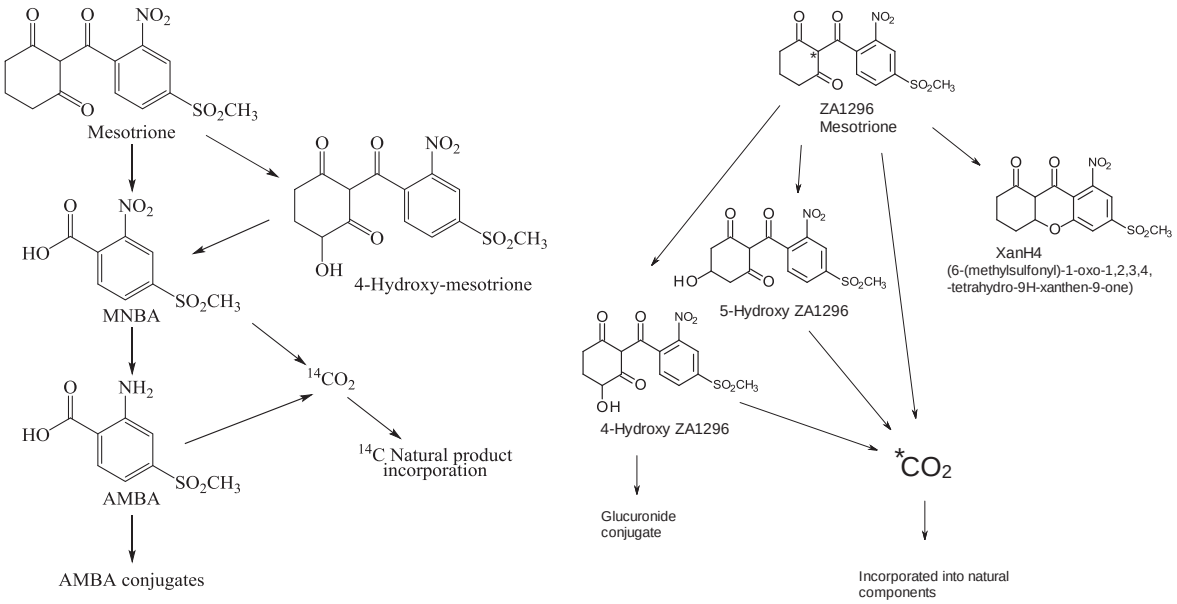


Figure 4 Proposed metabolic pathway of mesotrione in rotational crops

Analytical Methods

Vegetable crops

In Method RAM 366/01, residues of mesotrione and MNBA were extracted from crop samples with acetonitrile/water containing 10 g/L sodium chloride (50:50), an aliquot diluted with water and formic acid and cleaned up by Oasis® HLB SPE. The extract is partitioned into methylene chloride, evaporated to dryness, taken up with acetonitrile/water and analysed by HPLC-MS/MS, in negative ion mode, 290.9 m/z ion for quantification and no confirmation ion included. LOQ was 0.01 mg/kg in all crop matrices. Recovery data for mesotrione in corn (Hill, 2001; Report 2704 and Crook, 2001; RJ3253B), and cranberry (Salzman, 2005; 08903) are summarised in Table 63. The method was also successfully validated for MNBA.

Table 63 Recovery data for mesotrione by LC-MS/MS (negative ion mode; m/z=338 → 291)

Matrix	Fortification Level (mg/kg)	N	Mean (%)	RSD (%)	Report
Corn/maize (whole plant)	0.01	5	95	5	2704 and RJ3253B
	0.10	5	100	3	
	1.0	5	91	9	
	10	5	105	4	
Corn/maize (grain)	0.01	5	86	12	
	0.10	5	84	7	
	1.0	5	96	5	
Cranberries	0.01	6	100	21	08903
	0.10	3	99	7	
	1.0	5	114	11	

Results of the recovery experiments conducted as part of the residue studies in which method RAM 366/01 was used are summarised in Table 64.

Table 64 Mesotrione procedural recovery data obtained during residue analysis

Matrix	Fortification Level (mg/kg)	n	Mean (%)	RSD (%)	Report
Cranberries	0.01	3	113	5	08903
	0.10	5	93	9	
Blueberries	0.01	9	84	7	T010288-04
	1.0	5	93	16	
Raspberries	0.01	6	90	11	
	1.0	3	94	10	
Blackberries	0.01	1	87	–	
Okra	0.01	13	80	11	T021571-04
	0.10	7	91	6	
	1.0	6	100	9	
Sweet corn (kernel)	0.01	1	80	–	04-7012
	0.02	1	81	–	
Sweet corn (cob)	0.01	1	103	–	
	0.02	1	90	–	
Field corn (kernel)	0.01	1	96	–	T000921-09-REG
	0.10	1	83	–	
Field corn (cob)	0.01	1	100	–	
	0.10	1	85	–	
Field corn (whole cob)	0.01	1	84	–	
	0.10	1	62	–	
Field corn (rest plant)	0.01	2	98	–	
	0.10	2	89	–	
Field corn (kernel)	0.01	1	97	–	T000920-09-REG
	0.10	1	98	–	
Field corn (cob)	0.01	1	115	–	
	0.10	1	78	–	
Field corn (whole cob)	0.01	1	91	–	
	0.10	1	85	–	
Field corn (rest plant)	0.01	2	104	–	
	0.10	2	88	–	
Sweet corn (forage w/o ears)	0.01	2	97	–	T001589-08
	0.50	2	90	–	
Sweet corn (ears)	0.01	1	99	–	
	0.50	1	96	–	
Sweet corn (stover)	0.01	1	105	–	
	0.50	1	81	–	
Soya bean (seed)	0.01	6	114	10	T005595-06
	0.10	6	108	13	
Soya bean (meal)	0.01	1	114	–	
	0.10	1	113	–	
Soya bean (hulls)	0.01	1	107	–	
	0.10	1	122	–	
Soya bean (oil)	0.01	1	134	–	
	0.10	1	100	–	
Soya bean (seed)	0.01	21	83	15	T000908-07
	0.10	21	87	11	
Soya bean (meal)	0.01	1	76	–	
	1.0	1	118	–	
Soya bean (hulls)	0.01	1	82	–	
	1.0	1	90	–	
Soya bean (crude oil)	0.01	1	86	–	
	1.0	1	104	–	
Soya bean (refined oil)	0.01	1	96	–	
	1.0	1	96	–	
Soya bean (AGF)	0.01	1	71	–	
	1.0	1	85	–	
Soya bean (flour)	0.01	1	87	–	
	1.0	1	95	–	
Soya bean	0.01	1	77	–	

Matrix	Fortification Level (mg/kg)	n	Mean (%)	RSD (%)	Report
(milk)	1.0	1	101	–	
Soya bean (tofu)	0.01	1	70	–	
	1.0	1	97	–	
Soya bean (soy sauce)	0.01	1	70	–	
	1.0	1	84	–	
Soya bean (miso)	0.01	1	86	–	
	1.0	1	90	–	
Asparagus	0.01	14	84	15	T021572-04
	0.05	1	82	–	
	0.10	2	88	–	
	0.50	1	97	–	
	1.0	2	94	–	
	10	1	93	–	
Rhubarb (petioles)	0.01	7	88	10	T014372-05
	0.10	5	86	8	
	1.0	2	95	–	
Millet (forage)	0.01	7	81	10	T010289-04
	1.0	7	91	7	
Millet (hay)	0.01	7	78	13	
	1.0	7	86	9	
Millet (straw)	0.01	6	95	19	
	1.0	5	93	13	
Millet (grain)	0.01	7	88	18	
	1.0	6	90	10	
Oat (forage)	0.01	14	77	8	T004407-05
	0.02	1	74	–	
	0.05	6	85	6	
	0.10	1	86	–	
	0.50	1	70	–	
	1.0	1	94	–	
Oat (hay)	0.01	12	73	7	
	0.02	3	71	6	
	0.05	4	76	4	
	0.10	3	84	2	
	0.20	1	83	–	
	0.50	1	74	–	
Oat (straw)	0.01	11	77	11	
	0.02	2	83	–	
	0.10	1	78	–	
	0.50	3	85	4	
Oat (grain)	0.01	10	75	11	
	0.02	1	70	–	
	0.05	5	80	3	
	0.20	1	84	–	
Sorghum (forage)	0.01	12	86	12	T020419-04
	0.05	3	87	11	
	0.10	2	91	–	
	0.20	2	94	–	
	0.50	1	80	–	
	1.0	1	94	–	
	2.0	1	119	–	
	20	2	99	–	
Sorghum (stover)	0.01	13	84	10	
	0.02	1	75	–	
	0.05	1	83	–	
	0.10	1	112	–	
	0.20	1	95	–	
	0.50	1	91	–	
	1.0	2	92	–	
	2.0	1	96	–	

Matrix	Fortification Level (mg/kg)	n	Mean (%)	RSD (%)	Report
Sorghum (grain)	0.01	12	90	11	
	0.05	4	78	6	
	0.10	3	92	1	
	0.20	3	101	14	
	0.50	3	98	12	
	1.0	1	94	–	
	2.0	1	105	–	
Sorghum (AGF)	0.01	2	82	–	
	0.10	2	88	–	
Sugarcane	0.01	16	71	6	T020420-04
	0.05	2	70	–	
	0.10	9	77	4	
	0.20	2	83	–	
	0.50	1	87	–	
	1.0	1	82	–	
	10	1	90	–	
Flax / Linseed (seed)	0.01	6	97	17	T010290-04
	1.0	6	98	10	
Flax / Linseed (meal)	0.01	1	85	–	
	1.0	1	102	–	

In Methods TMR0643B and TMR0882B, mesotrione and MNBA residues are extracted with acetonitrile/water (1:1). An aliquot is diluted with water, acidified, partitioned with ethyl acetate and subjected to silica SPE clean-up. Further clean-up is done by reversed phase HPLC. The MNBA, isolated in the first fraction, is chemically reduced to AMBA with $SnCl_2$ in HCl. The mesotrione residue, isolated in the second fraction, is oxidised to MNBA using hydrogen peroxide, which is reduced to AMBA using acidic $SnCl_2$. After clean-up by C18 SPE, mesotrione and MNBA fractions are each analysed for the AMBA conversion product by a reversed-phase HPLC-fluorescence detection (ex 227 nm; em 424 nm). Mesotrione and MNBA standards were converted to AMBA concurrent with the samples. The method was validated for corn with a LOQ of 0.01 mg/kg for both mesotrione and MNBA. Independent validation was also provided. The recovery data for mesotrione are shown in Table 65.

Table 65 Mesotrione recovery data of methods TMR0643B and TMR0882B (HPLC-FL)

Matrix	Fortification Level (mg/kg)	N	Mean (%)	RSD (%)	Report
Corn (forage)	0.01	13	82	16	Method TMR0643B ADD Alferness, 1996, 1997
	0.10	11	85	15	
Corn (fodder)	0.01	9	78	10	
	0.10	5	67	15	
Corn (grain)	0.01	2	109	–	
	0.10	2	86	–	
Corn (forage)	0.01	2	85	–	Bolygo, 1996 RJ2149B Independent laboratory validation
	0.05	2	94	–	
Corn (grain)	0.01	2	76	–	
	0.05	2	81	–	
Corn (fodder)	0.01	2	108	–	
	0.05	2	104	–	
Field corn (forage)	0.01	11	85	12	RR 96-018B Residue trials
	0.10	7	86	17	
Field corn (fodder)	0.01	11	78	10	
	0.10	3	82	11	
Field corn (grain)	0.01	13	95	13	
	0.10	3	100	12	
Corn (forage)	0.01	4	77	6	Method TMR0882B Alfeness, 1999
	0.10	4	79	7	
Corn (fodder)	0.01	8	78	4	
	0.10	5	81	4	

Matrix	Fortification Level (mg/kg)	N	Mean (%)	RSD (%)	Report
Corn (grain)	0.01	4	85	14	
	0.10	4	81	2	
Sugar cane	0.01	4	75	5	
	0.10	4	73	2	
Corn (fodder)	0.01	2	99	–	James, 1999; RR 99-062B Independent validation
	0.02	2	79	–	
Sweet corn (ears)	0.01	5	67	10	487-01 residue trial
	0.10	5	74	8	
	1.0	1	74	–	
Sweet corn (forage w/o ears)	0.01	6	88	20	
	0.10	6	84	11	
	1.0	3	90	15	
Sweet corn (forage with ears)	0.01	6	76	19	
	0.10	6	76	6	
	1.0	1	93	–	
Sweet corn (stover)	0.01	4	73	15	
	0.10	5	75	7	
	1.0	1	83	–	
	2.0	1	83	–	
Field corn (forage)	0.01	3	89	13	1847-01 residue trial
	0.10	5	78	5	
Field corn (stover)	0.01	4	87	22	
	0.10	4	80	5	
Field corn (grain)	0.01	4	80	10	
	0.10	4	84	9	
Sugarcane	0.05	2	80	–	RJ3076B; Residue trial

Method TMR0643B was radio-validated using incurred radioactive residues in a forage sample treated pre-emergence (Tarr & van Neste, 1997). An aliquot of the forage sample was extracted once with an acetonitrile:water mixture (1:1) using a high speed homogeniser, an aliquot of the supernatant partitioned three times into ethyl acetate, the combined fractions evaporated and reconstituted in acetonitrile. Residues of mesotrione and MNBA were quantified by TLC with storage-phosphor autoradiography. Levels of mesotrione and MNBA in forage were 0.008 and 0.073 mg/kg, respectively. Residues of mesotrione and MNBA obtained by exhaustive extraction within this metabolism study were 0.008 mg/kg and 0.070 mg/kg, respectively.

In Method TMR0689B (Meyers, 1996), mesotrione and MNBA residues are extracted from corn commodities with acetonitrile/water (1:1), an aliquot diluted with a sodium sulphate solution, acidified and partitioned with methylene chloride. The methylene chloride extract is evaporated and the residue heated with Jones Reagent (chromium^{VI} oxide acid solution) to convert mesotrione to MNBA. The total MNBA is extracted with ethyl acetate, evaporated to dryness, the residue dissolved in methyl ethyl ketone and the isopropyl ester of MNBA is formed by heating the mixture with 2-iodopropane and potassium carbonate. The methyl ethyl ketone is evaporated, the residue extracted with acetone, evaporated to dryness and the isopropyl-MNBA residue dissolved in toluene containing 0.05% (w/v) 5-nitrovanillin for analyse by GC-MS (monitoring ion: m/z 246). The method determines the sum of mesotrione and MNBA at a combined LOQ of 0.01 mg/kg (Table 66).

Table 66 Mesotrione procedural recovery data obtained during residue analysis by GC-MS

Matrix	Fortification Level (mg/kg)	N	Mean (%)	RSD (%)	Report
Field corn (grain)	0.1	1	85	–	RR 97-043B
	0.3	2	98	–	
Field corn (silage)	0.01	1	94	–	
	0.03	3	93	8	
Field corn (grain)	0.01	3	80	5	RR 98-035B
Field corn (silage)	0.01	2	83	–	

Samples were analysed based on the QuEChERS multi-residue method (Watson, 2013). The method involves extraction with acetonitrile, addition of magnesium sulphate, sodium chloride and buffering citrate salts, centrifugation, an aliquot of the acetonitrile phase transferred to the freezer overnight (oilseed rape seed only) and cleaned up with magnesium sulphate prior to analysis by LC-MS/MS. Primary secondary amine (PSA) used in the original QuEChERS was not included due to low procedural recoveries for mesotrione. The LOQ was 0.01 mg/kg in all matrices. Recovery data in orange, maize and oilseed rape are summarised in Table 67.

Table 67 Mesotrione recovery data for method based on QuEChERS by LC-MS/MS (negative mode)

Matrix	Fortification Level (mg/kg)	n	Transition m/z=338 → 291		Transition m/z=338 → 212		Report
			Mean (%)	RSD (%)	Mean (%)	RSD (%)	
Orange (whole fruit)	0.01	5	77	14	81	15	Watson, 2013; Report S12-03251
	0.10	5	74	5.0	74	4.9	
Maize (grain)	0.01	5	89	2.0	87	5.2	
	0.10	5	89	2.7	90	3.8	
Maize (forage)	0.01	5	97	6.2	99	5.3	
	0.10	5	84	6.9	84	8.8	
Oilseed Rape (seeds)	0.01	5	80	2.5	88	14	
	0.10	5	81	4.2	82	4.2	
Maize (forage)	0.01	5	92	9	101	10	Independent validation (report S12-04607)
	0.10	4	72	5	71	8	
Maize (grain)	0.01	5	85	3	83	5	
	0.10	5	77	4	76	5	

Food of animal origin

In method TMR0914B, mesotrione and MNBA residues are extracted from milk and eggs with acetone and from animal tissues with an acetone/water (60:40). An aliquot is diluted with acidified water, partitioned twice into methylene chloride, and residues of mesotrione are converted to MNBA using hydrogen peroxide. After elimination of excess peroxide with catalase enzyme, MNBA is reduced to AMBA by heating with $SnCl_2$ and HCl and AMBA determined by reversed phase HPLC-fluorescence detection. The LOQ was 0.01 mg/kg in all matrices. Recovery data for mesotrione is summarised in Table 68.

Table 68 Mesotrione recovery data for Method TMR0914B

Matrix	Fortification Level (mg/kg)	n	Mean (%)	RSD (%)	Report
Meat (bovine)	0.01	6	88	4	Meyers, 1999 TMR0914B
	0.10	6	84	2	
Liver (bovine)	0.01	6	79	6	
	0.10	6	74	6	
Milk (cow)	0.01	6	90	4	
	0.10	6	93	3	
Egg (hen)	0.01	6	88	5	
	0.10	6	88	3	
Meat (bovine)	0.01	2	78	–	Brookey, 2000 RR 96-005B independent laboratory validation
	0.02	2	79	–	
Milk (cow)	0.01	2	88	–	
	0.02	2	86	—	

Mesotrione was determined in animal matrices using the modified QuEChERS, excluding PSA (Watson, 2013; Report no. S12-03250). LOQ was 0.01 mg/kg. The same procedure was independently validated (Bernal, 2013; Report no. S12-04608). The results are shown in Table 69.

Table 69 Mesotrione validation data (n=5 at each level)

Matrix	Fortification level (mg/kg)	Report no. S12-03250				Report no. S12-04608			
		m/z=338 → 291		m/z=338 → 212		m/z=338 → 291		m/z=338 → 212	
		Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)
Milk	0.01	92	1.8	93	3.9	84	3	82	4
	0.10	87	1.1	88	104	83	4	80	2
Eggs	0.01	77	3.1	77	3.0	90	6	97	5
	0.10	71	2.2	71	2.3	92	4	93	3
Muscle	0.01	92	2.6	93	3.5				
	0.10	86	2.7	88	2.9				
Fat	0.01	102	1.4	103	2.0				
	0.10	97	1.8	99	2.7				
Liver	0.01	86	2.7	88	3.9	79	5	71	9
	0.10	84	0.7	83	1.6	75	3	75	2
Kidney	0.01	99	2.0	92	3.0				
	0.10	91	0.9	87	2.2				

Storage stability under frozen conditions

Samples of maize grain, maize forage, maize fodder, radish root, and soya bean seed were homogenized and fortified at 0.1 mg/kg with either mesotrione or MNBA (Wiebe & Peyton, 1999). Duplicate samples were stored under frozen conditions (-18 °C ± 5 °C) and analysed at intervals up to 44 months. Mesotrione and MNBA were quantified as AMBA by HPLC fluorescence detection (Method TMR0643B). The limit of quantification for mesotrione and MNBA in all matrices was 0.01 mg/kg. The results are shown in Table 70.

Table 70 Stability of residues in crop commodities during frozen storage, in % remaining (not corrected for analytical recovery). Mean of duplicate samples fortified at 0.1 mg/kg

Month of storage	Maize grain		Maize forage		Maize fodder		Radish root		Soya bean seed	
	mesotrione	MNBA	mesotrione	MNBA	mesotrione	MNBA	mesotrione	MNBA	mesotrione	MNBA
0	72	79	79	78	53 [a]	76	86	95	89	92
0.5					58	87				
1	89	88	70	89	61	85	79	83		
2									80	81
3			75	86	77	92			78	84
4	86	86								
5							94	89		
6									79	101
7					86	100	80	90		
8	81	80	75	84						
13							87	91 [a]		
14									102	114
15							77	80		
17	86	103			78	107				
18			74	105						
29		89				87			129	94
30					110	81				
31	109		81	85					97	
32							104	81		
40									91 [a]	92
42	86	100	65 [a]	85 [a]	73 [a]	91				
44							85	93		

[a] Single value reported; duplicate sample lost during sample clean-up

Samples of blueberry, asparagus, sugarcane and okra were grounded in dry ice and fortified with mesotrione at 1.0 mg/kg (Link, 2007). Duplicate samples were prepared and stored under frozen conditions (-20 °C) and analysed at intervals over 13 months for sugarcane and okra and over 22

months for blueberry and asparagus. Mesotrione was quantified by HPLC-MS/MS (LOQ of 0.01 mg/kg). The results shown in Table 71 are not corrected for procedural recovery.

Table 71 Stability of residues, in crop commodities, during frozen storage. Samples were fortified at 1.0 mg/kg of mesotrione

Commodity	Month of storage	% remaining individuals	% remaining, mean	Normalised to day 0 (%)
Blueberry	0	92; 93	93	100
	1	83; 81	82	89
	3	90; 89	90	97
	6	82; 90	86	93
	13	98; 101	100	108
	22	78; 79	79	85
Asparagus	0	92; 104	98	100
	1	97; 92	95	96
	3	92; 96	94	96
	6	94; 90	92	94
	13	98; 99	99	101
	22	93; 93	93	95
Sugarcane	0	77; 74	76	100
	1	89; 87	88	117
	3	81; 83	82	109
	6	83; 84	84	111
	13	80; 86	83	110
Okra	0	102; 101	102	100
	1	98; 96	97	96
	3	87; 91	89	88
	6	94; 99	97	95
	13	98; 97	98	96

USE PATTERNS

Mesotrione is an herbicide used pre-emergence and post-emergence for selective control of annual broad-leaved weeds, which cease growth soon after application (high or low volume sprayers). Mesotrione is registered in many countries, but only the relevant GAP information for this evaluation is given in Table 72. DAT means days after treatment.

Table 72 Registered uses of mesotrione relevant for the evaluation

Crop	Country	Formulation		Application			PHI (days)
		kg ai/L kg	Type	Method	Rate kg ai/ha	No	
Asparagus	USA	0.480	SC	Pre-emergence prior to spear emergence	0.270	1	–
Asparagus	USA	0.480	SC	Post-emergence after completion of harvesting	0.105	1	–
Asparagus	USA	0.480	SC	Pre-+ post-emergence	0.165 + 0.105	2	–
Bush and Cane berries	USA	0.480	SC	Pre-emergence	0.210	1	
		0.480	SC	Direct spray to the base of the plant, before bloom	0.105	2	GS
Cranberries	USA	0.480	SC	Broadcast foliar	0.280	2	45
Flax/Linseed	USA	0.480	SC	Post-emergence	0.210	1	NS
Maize	Canada	0.480	SC	Pre-or early post-emergence	0.14	1	GS
Maize	Canada	0.480	SC	Late post-emergence	0.10	1	GS
Maize	Germany	0.100	SC	Broadcast	0.150	1	GS
Maize	USA	0.480	SC	Pre-emergence	0.270	1	
Maize	USA	0.480	SC	Pre-+ post-emergence (up to 8 leaf stage)	0.165 + 0.105	2	GS
Millet	USA	0.480	SC	Pre-emergence	0.210	1	–
Oat	USA	0.480	SC	Pre-emergence	0.210	1	
Oat	USA	0.480	SC	Post-emergence	0.105	1	50

Crop	Country	Formulation		Application			PHI (days)
		kg ai/L kg	Type	Method	Rate kg ai/ha	No	
Okra	USA	0.480	SC	Pre-emergence	0.210	1	28
		0.480	SC	Post-emergence, directed to the weed	0.105	1	
Rhubarb	USA	0.480	SC	Pre-emergence	0.210	1	21
Rice	Republic of Korea	0.006	GR	Post planting into the water, 5–7 days after transplanting	0.09	1	Ns
Soy	USA	0.480	SC	Pre-emergence	0.210	1	Ns
Soy HT	Canada	0.480	SC	Pre-emergence	0.144	1	45
Soy HT	Canada	0.480	SC	Early Post-emergence	0.144	1	45
Soy HT	Canada	0.480	SC	Post-emergence	0.100	1	45
Soy HT	USA	0.480	SC	Pre-emergence	0.225	1	Ns
Soy HT	USA	0.480	SC	Early post-emergence, up to BBCH 13	0.225	1	Ns
Soy HT	USA	0.480	SC	Pre-+ post-emergence (BBCH 14 to 60)	0.225 + 0.125	2	GS
Sorghum	USA	0.480	SC	Pre-emergence	0.224	1	–
Sugar Cane	South Africa	0.480	SC	Broadcast	0.150	1	181
Sugar Cane	USA	0.480	SC	Pre-emergence	0.270	1	–
Sugar Cane	USA	0.480	SC	Post-emergence	0.105	2	114
Sugar Cane	USA	0.480	SC	Pre-+ post-emergence	0.36	1	114
Sweet corn	Germany	0.100	SC	Post-emergence (BBCH 12–18)	0.150	1	GS
Sweet corn	USA	0.480	SC	Pre-emergence	0.270	1	45
Sweet corn	USA	0.480	SC	Pre-+ post-emergence (up to 8 leaf stage)	0.165 + 0.105	2	45

NS= not specified
GS= growth stage

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

Supervised residue trials conducted with mesotrione on a variety of crops in Europe, Canada and USA were submitted to the Meeting. Studies were conducted according to GLP, and specified concurrent determination of residues in untreated crops gave residues < LOQ, unless specified. Residues of mesotrione arising from use patterns where rate or days after treatment (DAT) ± 25% of GAP are underlined and considered for estimation of maximum residue levels and STMRs. When residues in samples harvested at a later stage were higher than those found at the critical PHI, they were used for the estimations. In trials conducted in the USA, duplicate or multiple field samples from replicate plots were taken for analysis at each sampling time and the mean was selected for the estimations. In total, 373 supervised trials were submitted and food commodities analysed for residues; in 193 cereal trials, feed commodities were also analysed. The data are summarized in Table 73.

Table 73 Summary of the supervised trials conducted with mesotrione

Codex group	Commodity	Region	No. of trials	Table No.
Berries and other small fruits	Blueberries, Raspberries, blackberries and cranberries	USA	25	74
Fruiting vegetables, other than Cucurbits	Okra	USA	20	75
	Sweet corn	France/USA	8/15	76
Pulses	Soy	USA	23	77
	HT Soy	USA	49	78
Stalk and stem vegetables	Asparagus	USA	24	79
	Rhubarb	USA	8	80
Cereal grains	Maize	EU/CAN/USA	3/24/24	81
	Millet	USA	15	82
	Oats	USA	34	83
	Rice	Japan/Korea	8/2	84
	Sorghum	USA	28	85
Grasses, for sugar or syrup production	Sugarcane	USA/South Africa	26/4	86

Codex group	Commodity	Region	No. of trials	Table No.
Oilseeds	Flax/Linseed	USA	17	87
Feed commodities	Corn/maize	EU/CAN/USA	101	88
	Millet	USA	15	89
	Oat	USA	34	90
	Rice	Japan/Korea	16	91
	Sorghum	USA	28	92

Berries and other small fruits

Twenty five supervised residue trials were conducted on berries in the USA using broadcast application during 2004 and 2005. Five trials were conducted on cranberries and ten trials were conducted on bush and cane berries. The results are shown in Table 74. Samples were stored deep-frozen for a maximum of 16.4 months and analysed for residues of mesotrione using method RAM 366/01 (LC-MS/MS).

Table 74 Summary of residue trials conducted with mesotrione (SC formulation) in USA on berries in 2004/2005

State	Crop (Variety)	Application rate, kg ai/ha	Growth Stage at Application	DAT (days)	Residue (mg/kg)	Report, trial
Massachusetts	Cranberry (Early Black)	0.341+ 0.224 (+ NIS)	Fruit development Fruit sizing—Early colour	43	< 0.01 (2)	08903.05-CAR20, MA01
New Jersey	Cranberry (Early Black)	0.346 + 0.226 (+ NIS)	fruiting fruiting	44	< 0.01 (2)	08903.05-CAR20, NJ26
Oregon	Cranberry (McFarlin)	0.388 + 0.240	small green berry White fruit—Pink fruit	48	< 0.01 (2)	08903.05-CAR20, OR18
Wisconsin [a]	Cranberry (McFarlin)	0.343 + 0.220 (+ NIS)	fruiting	43	< 0.01 (2)	08903.05-CAR20, WI18
Wisconsin [a]	Cranberry (Stevens)	0.354 + 0.220 (+ NIS)	fruiting	43	< 0.01 (2)	08903.05-CAR20, WI19
New York	Blueberry (Blue Ray)	0.102	BBCH 59	77	< 0.01 (2)	T010288-04, 5A-HR04-5630
		0.211	BBCH 59	77	< 0.01 (2)	
North Caroline [b]	Blueberry (Reveille)	0.107	Early Fruit set	32	< 0.01 (2)	T010288-04, SJ-HR04-5631
				35	< 0.01 (2)	
				39	< 0.01 (2)	
				43	< 0.01 (2)	
	Blueberry (Reveille)	0.216	Early Fruit set	32	< 0.01 (2)	
				35	< 0.01 (2)	
				39	< 0.01 (2)	
				43	< 0.01 (2)	
North Caroline [b]	Blueberry (Reveille)	0.109	Early Fruit set	34	< 0.01 (2)	T010288-04, SJ-HR04-5632
		0.214	Early Fruit set	34	< 0.01 (2)	
Michigan (Freemont)	Blueberry (Blue Crop)	0.106	Early pink bud	72	< 0.01 (2)	T010288-04, NL-HR04-5633
		0.209	Early pink bud	72	< 0.01 (2)	
Michigan (Conklin	Blueberry (Blue Ray)	0.105	Pink bud	64	< 0.01 (2)	T010288-04, NL-HR04-5634
		0.212	Pink bud	64	< 0.01 (2)	
Washington	Blueberry (Nelson and lliot)	0.104	Fruit present—Blooming	88	< 0.01 (2)	T010288-04, WF- HR04-5635
		0.210		88	< 0.01 (2)	
Michigan (Belding)	Raspberry (K81-6)	0.106	Pre-bloom—Leaves present	64	< 0.01 (2)	T010288-04, NL-HR04-5636
				70	< 0.01 (2)	
				74	< 0.01 (2)	
				78	< 0.01 (2)	
	Raspberry (K81-6)	0.208	Pre-bloom—Leaves present	64	< 0.01 (2)	
				70	< 0.01 (2)	
				74	< 0.01 (2)	
				78	< 0.01 (2)	

State	Crop (Variety)	Application rate, kg ai/ha	Growth Stage at Application	DAT (days)	Residue (mg/kg)	Report, trial
Oregon (Corvallis) [c]	Raspberry (Caroline)	0.105	BBCH 51	52	< 0.01 (2)	T010288-04, WG-WG-HR04-5637
	Raspberry (Caroline)	0.209	BBCH 51	52	≤ 0.01 (2)	
Oregon (Hullsboro)	Blackberry (Kotata)	0.107	Pre-bloom	62	< 0.01 (2)	T010288-04, WG-HR04-5638
	Blackberry (Kotata)	0.218	Pre-bloom	62	≤ 0.01 (2)	
Oregon (Corvallis) [c]	Raspberry (Caroline)	0.109	BBCH 51	83	< 0.01 (2)	T010288-04, WG-HR05-6370
	Raspberry (Caroline)	0.208	BBCH 51	83	≤ 0.01 (2)	

NIS=Non-ionic surfactant
[a] Trials conducted at the same location and dates, different variety
[b] Trials conducted at the same location and dates, one value was considered
[c] Trials conducted at the same location, but in different periods.

Okra

Twenty supervised residue trials were conducted on okra in the USA (Report T021571-04) during 2005 using either one pre-emergence application or one post-emergence application directed to the weed. A suspension concentrate (SC) formulation containing mesotrione was applied using soil surface spray pre-emergence (SS), post-emergence broadcast application over-the-top of the weed (POT) and or post-emergence directed application (PD). Samples were analysed for mesotrione residues using the method RAM 366. The results are summarized in Table 75.

Table 75 Summary of residue trials of mesotrione on okra (pods) using SC formulation in USA

State, trial	Okra variety	Application rate, kg)	Growth stage	DAT (days)	Residues (mg/kg)
North Carolina, SJ-HR05-6260	Clemson Spineless	0.225 (SS)	00	73	< 0.01 (2)
		0.106 (POT)	2-3 leaf	45	< 0.01 (2)
		0.105 (PD)	(38) 10 leaf stage	28	< 0.01 (2)
		0.229 (SS) + 0.105 (POT)	00 + 2-3 leaf	45	< 0.01 (2)
		0.228 (SS) +10.05 (PD)	00 + (36) 9 leaf stage	28	≤ 0.01 (2)
Florida, VQ-HR05-6261	Clemson Spineless	0.105 (POT)	12 to 13	45	< 0.01 (2)
Mississippi, 3A-HR2005-6262	Perkins Long	0.109 (POT)	13	45	< 0.01 (2)
		0.106 (PD)	pre-bloom	28	≤ 0.01 (2)
		0.232 (SS) + 0.105 (POT)	00 + 13	45	< 0.01 (2)
		0.233 (SS) + 0.103 (PD)	00 + pre-bloom	28	< 0.01 (2)
Texas, 3A-HR2005-6262	Louisiana Green Velvet	0.228 (SS)	00	84 98 104 112 119	< 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)
		0.108 (POT)	89	0 15 30 45 52	0.19, 0.16 < 0.01 (2) ≤ 0.01 (2) < 0.01 (2) < 0.01 (2)
		0.107 (PD)	89	0 14 21 28 35	< 0.01 (2) < 0.01 (2) < 0.01 (2) ≤ 0.01 (2) < 0.01 (2)
		0.228 (SS) + 0.105 (POT)	00 + 89	0 15 30 45 52	0.09, 0.2 < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)

State, trial	Okra variety	Application rate, kg)	Growth stage	DAT (days)	Residues (mg/kg)
		0.223 (SS) + 0.106 (PD)	00 + 89	0 14 21 28 35	< 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)
Oklahoma, SC-HR2005-6264	Clemson Spineless	0.220 (SS)	00	NA	< 0.01 (2)
		0.105 (POT)	13	45	< 0.01 (2)
		0.107 (PD)	53	28	< 0.01 (2)
		0.214 (SS) + 0.105 (POT)	00 + 13	45	< 0.01 (2)
		0.224 (SS) + 0.104 (PD)	00 + 59	28	< 0.01 (2)

SS=soil surface spray
POT=post over-the-top spray
PD=post directed application

Sweet corn

Eight post-emergence trials were conducted on sweet corn in France in 2003/2004, and 18 trials in the USA during 2001 and 2008, with either one pre-emergence and one post-emergence application or with two early post-emergence applications. Samples were analysed for mesotrione and MNBA using method RAM 366/1 (LC-MS/MS) or TM0643B (HPLC-FL). The data for mesotrione residue are summarised in Table 76. Residue levels for MNBA were < 0.01 mg/kg in all cases.

Table 76 Residue of mesotrione after the use of mesotrione on sweet corn

Country (Region) year	Sweet corn variety	Application rate (kg ai/ha) formulation	Growth Stage	DAT (days)	Crop Part	Residue (mg/kg)	Report; trial year
FRANCE 2003	620 Spirit	0.102 SC	BBCH 19	38 38	kernels cob	< 0.01 < 0.01	03-7049
	620 Spirit	0.153 SC	BBCH 12	38 38 61 61 62 62	kernels cob kernels cob kernels cob	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	
FRANCE 2003	620 Spirit	0.98 SC	BBCH 19	38 38	kernels cob	< 0.01 < 0.01	03-7050
	620 Spirit	0.143 SC	BBCH 12	62 62	kernels cob	< 0.01 < 0.01	
FRANCE 2004	620 Spirit	0.153 SC	BBCH 12	61 61 74 74	kernels cob kernels cob	< 0.01 < 0.01 < 0.01 < 0.01	04-7012
	620 Spirit	0.104 SC	BBCH 59	39 39	kernels cob	< 0.01 < 0.01	
FRANCE 2004	620 Spirit)	0.154 SC	BBCH 12	61 61 74 74	kernels cob kernels cob	< 0.01 < 0.01 < 0.01 < 0.01	04-7012
	620 Spirit	0.103 SC	BBCH 59	39 39	kernels cob	< 0.01 < 0.01	
USA (Wisconsin) 2001	NK 199	0.302 + 0.177 SC	pre-emergence + Vt (tassel fully emerged)	30	ears	< 0.01 (2)	487-01; NI-HR001-01
USA (Washington) 2001	Jubilee	0.303 + 0.179 SC		28	ears	< 0.01 (2)	487-01; WF-HR003-01
USA (California) 2001	Silver Queen	0.300 + 0.182 SC	BBCH 01 + BBCH 59	23 30 37	ears ears ears	< 0.01 (2) < 0.01 (2) < 0.01 (2)	487-01; W2-HR102-01

Country (Region) year	Sweet corn variety	Application rate (kg ai/ha) formulation	Growth Stage	DAT (days)	Crop Part	Residue (mg/kg)	Report; trial year
USA (N. Carolina) 2001	G90 F1	0.308 + 0.182 SC	BBCH 55	26	ears	< 0.01 (2)	487-01; SJ-HR003-01
USA (Ohio) 2001	Bodacious	0.314 + 0.190 SC		30	ears	< 0.01 (2)	487-01; NK-HR001-01
USA (New York) 2001	GH-2783	0.305 + 0.182 SC	at planting + 8–9 leaves	30	ears	< 0.01 (2)	487-01; EE-HR003-01
USA (Idaho) 2001	Sugar Buns	0.303 + 0.179 SC	post planting + pollen shed	30	ears	< 0.01 (2)	487-01; WG-HR005-01
USA (Illinois) 2001	Kandy King	0.301 + 0.186 SC	BBCH 00 + BBCH 34	31	ears	< 0.01 (2)	487-01; N4-HR003-01
USA (Pennsylvania) 2001	Argent	0.320 + 0.186 SC	BBCH 00 + early tassel	30	ears	< 0.01 (2)	487-01; EC-HR002-01
USA (Florida) 2001	Silver Queen	0.313 + 0.177 SC	Just planted + visible tassel	28	ears	< 0.01 (2)	487-01; VB-HR101-01
USA (Michigan) 2001	Excellency	0.306 + 0.180 SC	pre-emergence + Vt	23 30 36	ears ears ears	< 0.01 (2) < 0.01 (2) < 0.01 (2)	487-01; ED-HR006-01
USA (Maine) 2001	Maple Sweet	0.304 + 0.189 SC	0 + tassel initiation	30	ears	< 0.01 (2)	487-01; NF-HR002-01
USA N. Carolina) 2008	Rogers WH0809	0.107 + 0.106 SC	BBCH 36 + BBCH 37	32	ears	< 0.01 (2)	T001589-08; E10NC081871
		0.104 + 0.104 WG	BBCH 36 + BBCH 37	32	ears	< 0.01 (2)	
USA (N. Dakota 2008	Peaches & Cream	0.107 + 0.105 SC	BBCH 16 + BBCH 55	28	ears	< 0.01 (2)	T001589-08; C13ND081872
		0.107 + 0.106 WG	BBCH 16 + BBCH 55	28	ears	< 0.01 (2)	
USA (California) 2008	Sweetie 82	0.103 + 0.107 SC	BBCH 15 + BBCH 17	45	ears	≤ 0.01 (2)	T001589-08; W30CA081873
		0.105 + 0.105 WG	BBCH 15 + BBCH 17	45	ears	< 0.01 (2)	

Soya bean, dry

Twenty three supervised residue trials were conducted on soya bean in the USA during 2007 (Report T005595-06), with mesotrione applied pre-emergence direct to the soil. The DAT is driven by the normal vegetation period of the crop and is in the range of 113 to 160 days. Samples were analysed for mesotrione and MNBA using RAM 366/1. The results for mesotrione are shown in Table 77. MNBA residues were < 0.01 mg/kg in all samples.

Table 77 Summary of residue data for mesotrione (SC formulation) on soya bean seed from trials conducted in the USA in 2007

State (Location)	Soya bean variety	Application rate, kg ai/ha	Growth Stage	DAT (days)	Residues (mg/kg)	Trial
North Carolina	S56-D7	0.212	BBCH 00	158	≤ 0.01 (2)	E10NC078240
South Carolina	S76-L9	0.215	BBCH 00	160	≤ 0.01 (2)	E11SC078241
Arkansas (New Port)	S56-D7	0.213	BBCH 00	137	≤ 0.01 (2)	C23AR078242
Louisiana	S56-D7	0.214	BBCH 00	140	≤ 0.01 (2)	E17LA078243
Arkansas (Proctor)	Garst 3512RR/	0.213	BBCH 00	113	≤ 0.01 (3)	C24AR078244
		1.07	BBCH 00	113	< 0.01 (3)	
Iowa (Richland)	S29-C)	0.212	BBCH 00	127 134 141	≤ 0.01 (2) < 0.01 (2) < 0.01 (2)	C18IA078245

State (Location)	Soya bean variety	Application rate, kg ai/ha	Growth Stage	DAT (days)	Residues (mg/kg)	Trial
Iowa (Ollie)	Garst 3512 R/N	0.217	BBCH 00	152	< 0.01 (2)	C18IA078246
Illinois (Carlyle)	3512RR/N	0.213	BBCH 00	134	< 0.01 (2)	C06IL078247
		0.668	BBCH 00	134	< 0.01 (2)	
		1.111	BBCH 00	134	< 0.01 (2)	
Illinois (Wyoming)	S29-C9	0.214	BBCH 00	147	< 0.01 (2)	C06IL078248
Minnesota	CL081215	0.215	BBCH 00	126 133 140	< 0.01 (2) < 0.01 (2) < 0.01 (2)	C09MN078249
Indiana (Sheridan)	S29-C9	0.216	BBCH 00	141	< 0.01 (2)	C05IN078250
Indiana (Frankfort)	S29-C9	0.215	BBCH 00	141	< 0.01 (2)	C05IN078251
Missouri	S29-C9 RR	0.210	BBCH 00	122	< 0.01 (2)	C19MO078252
Nebraska	NK S19-R5 RR	0.218	BBCH 00	117	< 0.01 (2)	C17NE078253
Ohio	3512 RR/N	0.220	BBCH 00	126 134 139	< 0.01 (2) < 0.01 (2) < 0.01 (2)	C02OH078254
South Dakota	S19-R5	0.215	BBCH 01	119	< 0.01 (2)	C16SD078255
Kansas	04RM820605	0.212	BBCH 00	174	< 0.01 (2)	C22KS078256
Michigan	S19-R5	0.214	BBCH 00	156	< 0.01 (2)	C03MI078257
North Dakota	S10-T1	0.215	BBCH 00	140	< 0.01 (2)	C13ND078258
Wisconsin	CL081215	0.213	BBCH 00	127	< 0.01 (2)	C08WI078259

Mesotrione-tolerant soya bean, dry

Forty-nine supervised residue trials were conducted on herbicide-tolerant soya bean in the USA during 2009 and 2012 with either one pre-emergence and one post-emergence application at growth stage R1 (BBCH 60) or with one early post-emergence application at growth stage V2 (BBCH 13). Samples were analysed for mesotrione and MNBA using RAM 366/1. The results for mesotrione are shown in Table 78. MNBA residues were < 0.01 mg/kg in all samples.

Table 78 Summary of residue data for mesotrione on herbicide-tolerant soya bean (SC formulation)

State (location) year	HT Soya bean variety	Application rate (kg ai/ha)	Growth Stage at Application	DAT (days)	Portion	Residues (mg/kg)	Report; Trial
South Carolina 2009	Jack/ SYHT04R	0.226 + 0.125	BBCH 00 + 60	89	Seed (m)	< 0.01 (2)	T000908-07; E11-9652
		0.225	BBCH 14	98	Seed (m)	< 0.01 (2)	
Arkansas 2009	Jack/ SYHT04R	0.226 + 0.125	BBCH 00 + 60	50 76	Seed Seed (m)	< 0.01 (2) < 0.01 (2)	T000908-07; C24-9653
Louisiana 2009		0.226	BBCH 13	59 79 85 92 99	Seed Seed (– 7d) Seed (m) Seed (+7d) Seed +14d)	< 0.01 (2) < 0.01 < 0.01 (2) < 0.01 < 0.01	
Missouri (Fisk) 2009	Jack/ SYHT04R	0.234 + 0.125	BBCH 00 + 61	45	Seed (m)	< 0.01 (2)	T000908-07; E18-9654
		0.234	BBCH 12	66	Seed (m)	< 0.01 (2)	
Iowa (Richland) 2009	Jack/SYHT04R	0.225 + 0.125	BBCH 00 + 63	49 58	Seed Seed (m)	< 0.01 (2) 0.02 (2)	T000908-07 C23-9655
		0.226 + 0.124	BBCH 00 + 63	49 58	Seed Seed (m)	0.01, 0.02 0.02 (2)	
		0.225	BBCH 12	67 76	Seed Seed (m)	< 0.01 (2) < 0.01 (2)	
Missouri (La Plata) 2009	Jack/SYHT04R	0.226 + 0.126	BBCH 00 + 16	48 102	Seed Seed (m)	< 0.01 (2) < 0.01 (2)	T000908-07 C18-9656
		0.222	BBCH 12.5	97 151	Seed Seed (m)	< 0.01 (2) < 0.01 (2)	
		1.130 + 0.623	BBCH 00 + 16	102	Seed (m)	< 0.01 (3)	

State (location) year	HT Soya bean variety	Application rate (kg ai/ha)	Growth Stage at Application	DAT (days)	Portion	Residues (mg/kg)	Report; Trial
Iowa (Miles) 2009	Jack/SYHT04R	0.228 + 0.123	BBCH 0 + 18	45 85	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 C18-0657
		0.224	BBCH 12	66 106	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
Iowa (Bagley) 2009	Jack/SYHT04R	0.227 + 0.122	BBCH 0 + 59	47 90	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 C18-0658
		0.223 +	BBCH 12	73 116	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
Iowa (Berkley) 2009	Jack/SYHT04R	0.226 + 0.117	BBCH 00 + 63	45 76	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 C30-9659
		0.222	BBCH 12	77 108	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
		1.147 + 0.640	BBCH 00 + 63	76	Seed (m)	0.04 (3)	
Missouri (Oregon) 2009	Jack/ SYHT04R	0.233 + 0.118	BBCH 00 + 63	43 75	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 C30-9660
		0.224	BBCH 12	70 102	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
Kansas 2009	Jack/ SYHT04R	0.226 + 0.121	BBCH 0 + 60-65	47 69	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 2 C19-9661
		0.225	BBCH 13	82 93 104 110 117	Seed Seed Seed (m) Seed Seed	< 0.01 (2) < 0.01 ≤ 0.01 (2) < 0.01 < 0.01	
Michigan 2009	Jack/ SYHT04R	0.230 + 0.121	BBCH 00 + 60–65	47 70	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 C19-9662
		0.229	BBCH 13	76 99	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
Missouri (Dudley) 2009	Jack/ SYHT04R	0.224 + 0.124	BBCH 00 + 60	45 76	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 C03-9663
		0.225	BBCH 13	81 112	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
Nebraska (Stromsburg) 2009	HT Soya bean/ Jack/ SYHT04R	228 128	BBCH 00 + 61	47 55	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 C23-9664
		0.223	BBCH 12	64 72	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
Nebraska (Hampton) 2009	HT Soya bean/ Jack/ SYHT04R	0.228 + 0.123	BBCH 00 + 61	46 85	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 E13-9665
		0.227	BBCH 12	76 115	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
North Carolina (York)	Jack/ SYHT04R	0.225 + 0.125	BBCH 00 + 61	48 94	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 E13-9666
		0.231	BBCH 12	83 129	Seed Seed (m)	< 0.01 (2) < 0.01 (2)	
Nebraska (York) 2009	Jack/ SYHT04R	0.219 + 0.123	BBCH 00 + 61	49 86	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 E13-9667
		0.230	BBCH 12	76 113	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
Ohio (Richwood) 2009	Jack/ SYHT04R	0.227 + 0.125	BBCH 00 + 61	47 87	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 C01-9668
		0.226	BBCH 12	66 106	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
Ohio (Marysville) 2009	Jack/ SYHT04R	0.227 + 0.124	BBCH 00 + 61	47 87	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 C01-9669
		0.230	BBCH 12	67 107	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
Iowa (Lime Springs) 2009	Jack/ SYHT04R	0.222 + 0.126	BBCH 00 + 61	46 123	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 E19-9670
		0.231	BBCH 12	68 145	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	

State (location) year	HT Soya bean variety	Application rate (kg ai/ha)	Growth Stage at Application	DAT (days)	Portion	Residues (mg/kg)	Report; Trial
North Carolina (Seven springs) 2009	Jack/ SYHT04R	0.226 + 0.125	BBCH 00 + 62	50 79	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	T000908-07 E10-9671
		0.223	BBCH 13	67 96	Seed Seed (m)	< 0.01 (2) ≤ 0.01 (2)	
Iowa (Richland) 2012	Jack/ SYHT0H2	0.225 + 0.126	BBCH 00 + 60	94	Seed (m)	≤ 0.01 (2)	TK0112226 -1
Iowa (Bagley) 2012	Jack/ SYHT0H2	0.237 + 0.125	BBCH 00 + 60	90	Seed (m)	0.02 (2)	TK0112226 -2
Iowa (Lime Spring) 2012	Jack/ SYHT0H2	0.228 + 0.122	BBCH 00 + 60	97	Seed (m)	≤ 0.01 (2)	TK0112226 -3
Minneapolis 2012	Jack/ SYHT0H2	0.225 + 0.127	BBCH 00 + 60	106	Seed (m)	≤ 0.01 (2)	TK0112226 -4
Nebraska 2012	Jack/ SYHT0H2	0.228 + 0.126	BBCH 00 + 60	79	Seed (m)	≤ 0.01 (2)	TK0112226 -5
Iowa (Atlanta) 2012	Jack/ SYHT0H2	0.235 + 0.127	BBCH 00 + 61-62	77	Seed (m)	≤ 0.01 (2)	TK0112226 -6

(m)—Mature

Asparagus

Twenty four supervised residue trials were conducted on asparagus in the USA (Report T021572-04 2005) during 2005 using either one pre-emergence soil surface spray (PSS), post-emergence over-the-top of the weeds (POT) or a combination of the two applications. Samples were analysed for mesotrione using RAM 366/1. The results are shown in Table 79.

Table 79 Summary of residue data for mesotrione on asparagus (spears) using SC formulation in the USA during 2005

State (location)	Asparagus variety	Application (kg ai/ha)	Growth Stage at Application	DAT (days)	Residue (mg/kg)	Trial
North Caroline	Jersey Knight	0.276 (PSS)	BBCH 00	9	≤ 0.01 (2)	SJ-HR-05-6270
		0.106 (POT)	emerged	2	0.09 (2)	
		0.278 (PSS) + 0.105 (POT)	BBCH 00 + emerged	2	0.05, 0.18	
Michigan (Conklin)	Centennial	0.266 (PSS)	BBCH 00	13 14 15 16	≤ 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)	NL-HR-05-6271
		0.106 (POT)	mature spears	0 1 2 3	0.61, 0.87 0.17, 0.21 0.08, 0.06 0.05, 0.04	
		0.271 (PSS) + 0.105 (POT)	BBCH 00 + mature spears	0 1 2 3	0.59, 0.66 0.14, 0.15 0.09, 0.06 0.05, 0.07	
Michigan (Comstock)	Jersey Giant	0.270 (PSS)	BBCH 00	16	≤ 0.01 (2)	NL-HR-05-6272
		0.106 (POT)	mature spears	2	0.35, 0.67	
		0.269 (PSS) + 0.105 (POT)	BBCH 00 + mature	2	0.25, 0.21	
California (Gonzales)	UC 157	0.265 (PSS)	BBCH 00	25	≤ 0.01 (2)	WC-HR-05-6273
		0.104 (POT)	market size spears	2	0.05, 0.03	
		0.270 (PSS) + 0.105 (POT)	BBCH 00 + mature	2	0.04, 0.03	
California (Walnut Grove)	UC157	0.267 (PSS)	BBCH 08	11	≤ 0.01 (2)	WD-HR-05-6274
		0.106 (POT)	BBCH 45	3	≤ 0.01 (2)	
		0.268 (PSS) + 0.105 (POT)	BBCH 08 + BBCH 45	3	< 0.01 (2)	
California (Fire	UC 157	0.275 (PSS)	BBCH 00	12	≤ 0.01 (2)	WC-HR-05-
		0.108 (POT)	emerging spears	2	0.13, 0.14	

State (location)	Asparagus variety	Application (kg ai/ha)	Growth Stage at Application	DAT (days)	Residue (mg/kg)	Trial
Baugh)		0.280 (PSS) + 0.109 (POT)	BBCH 00 + emerging	2	0.16, 0.13	6275
Oregon	Martha Washington	0.274 (PSS)	BBCH 00	8	< 0.01 (2)	WF-HR-05-6277
		103 (POT)	BBCH 09	2	0.03, 0.05	
		0.274 (PSS) + 0.103 (POT)	BBCH 00 + BBCH 09	2	0.05, 0.08	
Washington	902-62	0.272 (PSS)	BBCH 00	10	< 0.01 (2)	WF-HR-05-6278
		0.107 (POT)	spears 2-12" tall	2	0.03 (2)	
		0.266 (PSS) + 0.106 (POT)	BBCH 00 spears 2-12" tall	2	0.04, 0.04	

PSS: Pre-emergence soil surface spray
POT: post-emergence over-the-top of the weeds

Rhubarb

Eight supervised residue trials were conducted on rhubarb in the USA (Report T014372-05) during 2006 with one application performed pre-emergence. The results are shown in Table 80.

Table 80 Summary of residue data for the use of mesotrione on rhubarb from trials conducted in USA in 2006 using SC formulation

Country (Region)	Rhubarb variety	Application rate (kg ai/ha)	Growth Stage at Application	DAT (days)	Residues (mg/kg)
Illinois		0.202	BBCH 00	28 35 42 47	< 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)
		0.350	BBCH 00	28 35 42 47	0.01, < 0.01 < 0.01 (2) < 0.01 (2) < 0.01 (2)
Michigan	McDonald	0.212	pre-emergence	42	< 0.01 (2)
		0.340	pre-emergence	42	< 0.01 (2)
Oregon	Crimson	0.210	dormant	42	< 0.01 (2)
		0.343	dormant	42	< 0.01 (2)
Washington	RubyRed	0.217	BBCH 08	42	< 0.01 (2)
		0.337	BBCH 08	42	< 0.01 (2)

Field corn (maize)

Three trials with field corn were conducted in Europe in 2009, 24 in Canada in 1996/1997 and 42 in the USA in 1995 or 2001 with either one pre-emergence and one post-emergence application or with two early post-emergence applications. The results on maize grain are shown in Table 81.

Table 81 Summary of residue data for the use of mesotrione on maize (grain)

Country (Region) year	Maize variety	Application			DAT (days)	Residues (mg/kg)	Report trial
		Formulation	Rate (kg ai/ha)	Growth Stage			
Canada (Ontario) 1996	Pioneer 3902	SC	0.300	Pre-emergence	123	< 0.01	RR 97-043B 94-CN-96-201
		SC	0.600	Pre-emergence	123	< 0.01	
		SC	0.200	5–6 Leaf	108	< 0.01	
		SC	0.400	5–6 Leaf	108	< 0.01	
		SC	0.300 0.200	Pre-emergence 5–6 leaf	108	< 0.01	
		SC	0.600 0.400	Pre-emergence 5–6 leaf	108	< 0.01	
Canada (Ontario) 1996	Ciba seeds G-4064	SC	0.300	Pre-emergence	122	< 0.01	RR 97-043B 94-CN-96-202
		SC	0.600	Pre-emergence	122	< 0.01	
		SC	0.200	4–5 Leaf stage	111	< 0.01	

Country (Region) year	Maize variety	Application			DAT (days)	Residues (mg/kg)	Report trial
		Formulation	Rate (kg ai/ha)	Growth Stage			
		SC	0.400	4–5 Leaf stage (	111	< 0.01	
		SC	0.300 0.200	Pre-emergence 4–5 leaf	111	< 0.01	
		SC	0.600 0.400	Pre-emergence 4–5 leaf	111	< 0.01	
Canada (Ontario) 1997	Funks-BT Maximizer	SC	0.300	Pre-emergence	155	< 0.01	RR 98-035B 94-CN-97-901
		SC	0.600	Pre-emergence	155	< 0.01	
		SC	0.200	24	126	< 0.01	
		SC	0.400	24	126	< 0.01	
		SC	0.300 0.200	Pre-emergence 24	126	< 0.01	
		SC	0.600 0.400	Pre-emergence 24	126	< 0.01	
Canada (Ontario) 1997	Funks-BT Maximizer	SC	0.300	Pre-emergence	145	< 0.01	RR 98-035B 94-CN-97-902
		SC	0.600	Pre-emergence	145	< 0.01	
		SC	0.200	23	126	< 0.01	
		SC	0.400	23	126	< 0.01	
		SC	0.300 0.200	Pre-emergence 23	126	< 0.01	
			0.600 0.400	Pre-emergence 23	126	< 0.01	
Germany 2009	Nescio	WG	0.138	BBCH 16–18	82 91 143	< 0.01 < 0.01 < 0.01	T000920-09-REG
Spain 2009	Castellano	WG	0.154	BBCH 15	42 71 82	< 0.01 < 0.01 < 0.01	T000921-09-REG
United Kingdom 2009	Ohio	WG	0.142	BBCH 16–17	98 112	< 0.01 < 0.01	T000920-09-REG
USA (Iowa, Sheffield), 1995	ICI 8543	SC	0.336 0.224	Pre-plant vegetative	109	< 0.01 (2)	RR 96-018B 63-IA-95-805
USA (Illinois, Brimfield), 1995	Hoblit 428	SC	0.336 0.224	pre-emergence	95	< 0.01 (2)	RR 96-018B 60-IL-95-806
USA (Indiana, Lafayette), 1995	Pioneer 3394	SC	0.336 0.224	pre-emergence 7–9 leaves	96	< 0.01 (2)	RR 96-018B 67-IN-95-807
USA (Michigan) 1995	NK 4640	SC	0.336 0.224	pre-bloom	114	< 0.01 (2)	RR 96-018B 24-MI-95-808
USA (Nebraska) 1995	Ottilie RO 2455	SC	0.336 0.224	Pre-plant V6	88	< 0.01 (2)	RR 96-018B 68-NE-95-809
USA (Iowa, Albia), 1995	ICI 8532	SC	0.336 0.224	Pre-plant vegetative	102	< 0.01 (2)	RR 96-018B 63-IA-95-810
USA (Illinois, Towanda), 1995	Ainsworth 640	SC	0.336 0.224	Pre-plant post emergence	87	< 0.01 (2)	RR 96-018B 60-IL-95-811
USA (Indiana, Rochester), 1995	Pioneer 3394	SC	0.336 0.224	Early pre-plant 5–7 leaves	96	< 0.01 (2)	RR 96-018B 67-IN-95-812
USA (Nebraska, Waverly), 1995	Producers PH785	SC	0.336 0.224	Pre-plant V5–V6	96	< 0.01 (2)	RR 96-018B 68-NE-95-814
USA (Kansas, La Cygnet), 1995	CIBA 4575	SC	0.336 0.224	early pre-plant post	68	< 0.01 (2)	RR 96-018B 37-KS-95-825
USA (Pennsylvania, Ephrata), 1995	CI 8541	SC	0.336 0.224	Pre-emergence vegetative	98	< 0.01 (2)	RR 96-018B 70-PA-95-815
		SC	0.336 0.224	pre-emergence vegetative	98	< 0.01 (2)	
USA (Minnesota, St. Peter)	Cenex 424	SC	0.336 0.224	Pre-emergence vegetative	92	< 0.01 (2)	RR 96-018B 36-MN-95-816

Country (Region) year	Maize variety	Application			DAT (days)	Residues (mg/kg)	Report trial
		Formulation	Rate (kg ai/ha)	Growth Stage			
1995		SC	0.336 0.224	Pre-emergence vegetative	92	< 0.01 (2)	
USA (Ohio, Urbana) 1995	Vigoro V1122	SC	0.336 0.224	Pre-emergence	113	< 0.01 (2)	RR 96-018B 24-OH-95-817
		SC	0.336 0.224	Pre-emergence	113	< 0.01 (2)	
USA (Wisconsin, Baraboo) 1995	Cenex LOL 357	SC	0.336 0.224	Pre-emergence	104	< 0.01 (2)	RR 96-018B 79-WI-95-818
		SC	0.336 0.224	Pre-emergence	104	< 0.01 (2)	
USA (Texas) 1995	G4673B (D&PL Co.)	SC	0.336 0.224	Pre-emergence pre-tassel	92	< 0.01 (2)	RR 96-018B 25-TX-95-819
		SC	0.336 0.224	Pre-emergence pre-tassel	92	< 0.01 (2)	
USA (North Carolina) 1995	Field corn (Pioneer 3165)	SC	0.336 0.224	Pre-plant rapidly growing	95	< 0.01 (2)	RR 96-018B 01-NC-95-820
		SC	0.336 0.224	Pre-plant rapidly growing	88 95 101 108	< 0.01 < 0.01 (2) < 0.01 < 0.01	
USA (Iowa, Boone) 1995	ICI 8543	SC	0.336 0.224	Early pre-plant vegetative	112	< 0.01 (2)	RR 96-018B 63-IA-95-821
		SC	0.336 0.224	Early pre-plant vegetative	112	< 0.01 (2)	
USA (Illinois, Champagne) 1995	Pioneer 3394	SC	0.336 0.224	Early pre-plant post emergence	107	< 0.01 (2)	RR 96-018B 04-IL-95-822
		SC	0.336 0.224	Pre-plant post-emergence	100 107 113 121	< 0.01 < 0.01 (2) < 0.01 < 0.01	
USA (Indiana, New Richmond) 1995	Pioneer 3394	SC	0.336 0.224	Early pre-plant 6–8 leaf	86	< 0.01 (2)	RR 96-018B 67-IN-95-823
		SC	0.336 0.224	Early pre-plant 6–8 leaf	86	< 0.01 (2)	
USA (Nebraska, Crete) 1995	ICI 8541	SC	0.336 0.224	Early pre-plant V6–V7	89	< 0.01 (2)	RR 96-018B 68-NE-95-824
		SC	0.336 0.224	Pre–plant V6–V7	89	< 0.01 (2)	
USA Iowa) 2001	Pioneer 34B23)	SC	0.268 0.225	BBCH 00 BBCH 18–19	99	< 0.01 (2)	1847-01 NE-HR-003-01
		SE SC	0.267 0.233	BBCH 00 BBCH 18/19	99	< 0.01 (2)	
		SC	0.274 0.234	BBCH 13 BBCH 18/19	99	< 0.01 (2)	
		SE SC	0.267 0.223	BBCH 13 BBCH 18/19	99	< 0.01 (2)	
USA (North Carolina)	ICI 8543)	SC	0.269 0.226	BBCH 00 75 cm high	98	< 0.01 (2)	1847-01

Country (Region) year	Maize variety	Application			DAT (days)	Residues (mg/kg)	Report trial
		Formulation	Rate (kg ai/ha)	Growth Stage			
2001		SE SC	0.269 0.227	BBCH 00 75 cm high	98	< 0.01 (2)	SJ-HR-013-01
		SC	0.271 0.227	BBCH 12/13 75 cm high	98	< 0.01 (2)	
		SE SC	0.270 0.227	BBCH 12/13 75 cm high	98	< 0.01 (2)	
USA (Illinois) 2001	Pioneer 34B24	SC	0.285 0.253	BBCH 00 BBCH 36	112	< 0.01 (2)	1847-01 N4-HR-005-01
		SE SC	0.278 0.236	BBCH 00 BBCH 36	112	< 0.01 (2)	
		SC	0.286 0.244	BBCH 12 BBCH 36	112	< 0.01 (2)	
		SE SC	0.268 0.237	BBCH 12 BBCH 36	112	< 0.01 (2)	
USA (Nebraska) 2001	ICI 8543	SC	0.270 0.227	BBCH 00 BBCH 19	103	< 0.01 (2)	1847-01 NB-HR-004-01
		SE SC	0.273 0.227	BBCH 00 BBCH 19	103	< 0.01 (2)	
		SC	0.266 0.226	BBCH 12/13 BBCH 19	103	< 0.01 (2)	
		SE SC	0.268 0.226	BBCH 12/13 BBCH 19	103	< 0.01 (2)	

Millet

Fifteen supervised residue trials were conducted on millet in the USA during 2004 (Report T010289-04) with one application performed pre-emergence. The results on millet grain are shown in Table 82.

Table 82 Summary of residue data for the use of mesotrione on millet (grain) using SC formulation in the USA in 2004

State	Millet variety	Application Rate (g ai/ha)	Growth Stage	PHI (days)	Residue (mg/kg)	Trial number
Illinois	Max Perl	0.109	at planting	130	< 0.01 (2)	4A-HR-04-5640
		0.214	at planting	130	≤ 0.01 (2)	
		0.108	BBCH 32	113	< 0.01 (2)	
Nebraska	Huntsman	0.103	at planting	84	< 0.01 (2)	4A-HR-04-5641
		0.210	at planting	84	≤ 0.01 (2)	
		0.103	BBCH 12	61	< 0.01 (2)	
South Dakota	Rise	0.104	at planting	95	< 0.01 (2)	4A-HR-04-5642
		0.208	at planting	95	≤ 0.01 (2)	
		0.105	BBCH 21	69	< 0.01 (2)	
Colorado (Ault) [a]	Early Bird	0.107	at planting	132	< 0.01 (2)	4A-HR-04-5643
		0.212	at planting	132	≤ 0.01 (2)	
		0.107	vegetative	92	< 0.01 (2)	
Colorado (Ault) [a]	Early Bird	0.110	at planting	104 111 120	< 0.01 (2) < 0.01 (2) < 0.01 (2)	4A-HR-04-5644
		0.218	at planting	104 111 120	≤ 0.01 (2) < 0.01 (2) < 0.01 (2)	
		0.108	vegetative	64 71 80	< 0.01 (2) < 0.01 (2) < 0.01 (2)	

[a] Trials conducted at the same site during the same period. Only one was considered

Oat

Thirty four supervised residue trials were conducted in oat in the USA (Report T004407-05) during 2005 with either one pre-emergence or one post-emergence application. The results on oat grain are shown in Table 83.

Table 83 Summary of residue data for the use of mesotrione on oat (grain) using SC formulation in 2005 in the USA

State (location)	Oat variety	Application rate (kg ai/ha)	Growth Stage	DAT (days)	Residues (mg/kg)	Trial
New York	Armor	0.214	BBCH 00	90	< 0.01 (2)	5A-HR-05-6380
		0.104	BBCH 59–61	49	≤ 0.01 (2)	
Virginia	Coker	0.216	BBCH 00	246	< 0.01 (2)	SJ-HR-05-6381
		0.108	BBCH 75	51	≤ 0.01 (2)	
North Dakota (Northwood)	Morton	0.211	bare soil	90	< 0.01 (2)	NN-HR-05-6382
		0.104	BBCH 23	50	≤ 0.01 (2)	
South Dakota (Lesterville)	Jerry	0.209	BBCH 01	84	< 0.01 (2)	NF-HR-05-6383
		0.106	BBCH 32	54	≤ 0.01 (2)	
Wisconsin	Esker	0.216	pre-emergence	91	< 0.01 (2)	NI-HR-05-6384
		0.106	late boot -early head	49	≤ 0.01 (2)	
Minnesota	Drumlin	0.209	BBCH 00	80	< 0.01 (2)	NF-HR-05-6385
		0.107	BBCH 21	52	≤ 0.01 (2)	
Nebraska (York)	Jerry	0.213	BBCH 00	87	< 0.01 (2)	NB-HR-05-6386
		0.105	BBCH 31	49	≤ 0.01 (2)	
Iowa	Jerry	0.213	BBCH 00	96	< 0.01 (2)	NE-HR-05-6387
		0.106	BBCH 80	49	≤ 0.01 (2)	
Kansas (Sabetha)	Loyal	0.210	pre-emergence	83	< 0.01 (2)	ND-HR-05-6388
		0.107	1–3 tillers	50	≤ 0.01 (2)	
Michigan	Prairie	0.213	pre-emergence	88	< 0.01 (2)	NL-HR-05-6389
		0.104	5–6 leaves	50	≤ 0.01 (2)	
Illinois	VHS	0.209	BBCH 00	81	< 0.01 (2)	4A-HR-05-6390
		0.104	BBCH 26	52	≤ 0.01 (2)	
		0.317	BBCH 26	52	< 0.01 (2)	
		0.531	BBCH 26	52	< 0.01 (2)	
Texas	La-604	0.209	BBCH 00	180	< 0.01 (2)	SA-HR-05-6391
		0.106	BBCH 43	54	≤ 0.01 (2)	
North Dakota (New Rockford)	La-604	0.211	soil surface spray	92	< 0.01 (2)	NM-HR-05-6392
		0.104	BBCH 43	49	≤ 0.01 (2)	
South Dakota (Frederick)	Morton	0.211	BBCH 01	81	< 0.01 (2)	NF-HR-05-6393
		0.106	BBCH 21–31	51	≤ 0.01 (2)	
Nebraska (Grand Island)	Reeves	0.215	BBCH 00	90	< 0.01 (2)	NB-HR-05-6394
		0.105	BBCH 31	49	≤ 0.01 (2)	
Kansas (Larned)	Jerry	0.210	pre-emergence	83	< 0.01 (2)	NM-HR-05-6395
		0.107	1–2 tillers	50	≤ 0.01 (2)	

Rice

Two residue trials were conducted in rice in Korea in 2005 and eight in Japan in 2004 and 2006 using one or two applications into the water, post-transplanting. None of the trials were under GLP. The results in brown rice (husked rice) are shown in Table 84.

Table 84 Summary of residue data for mesotrione on rice (brown rice) after application using a granular formulation

Country, year	Rice variety	Application rate (g ai/ha)	Growth Stage	DAT (days)	Residue (mg/kg)	Trial
Korea 2005		0.180	5–15 days after transplanting	140	< 0.05 (3)	A14928B
		0.360	5–15 days after transplanting	140	< 0.05 (3)	

Country, year	Rice variety	Application rate (g ai/ha)	Growth Stage	DAT (days)	Residue (mg/kg)	Trial
Japan, 2004	Matsuribare	0.100	21 days after transplanting	91	< 0.002 (2)	A137723B
Japan, 2004	Hi-no-hikari	0.100	21 days after transplanting	89	< 0.002 (2)	A137723B
Japan 2006	Koshihikari	0.100 0.100	4.5 leaf period growing period	76	< 0.002 (2)	A137723B
		0.100 0.100	4.5 leaf period growing period	61	< 0.002 (2)	
		0.100 0.100	4.5 leaf period before harvest	45	< 0.002 (2)	
Japan 2006	Hi-no-hikari	0.100 0.100	10 days after plant 75 days before harvest	75	< 0.002 (2)	A137723B
		0.100 0.100	10 days after plant 60 days before harvest	60	< 0.002 (2)	
		0.100 0.100	10 days after plant 45 days before harvest	45	< 0.002 (2)	

Sorghum

Twenty eight supervised residue trials were conducted on sorghum in the USA (T020419-04) during 2005, with one application made pre-emergence of the crop (SC formulation). The results on sorghum grain are shown in Table 85.

Table 85 Summary of residue data for mesotrione (SC formulation) in sorghum in the USA in 2005

State (location)	Sorghum variety	Application rate (kg ai/ha)	Growth Stage	DAT (days)	Residues (mg/kg)	Trial
South Caroline	NK8416	0.225	Soil surface at planting	113	≤ 0.01 (2)	SJ-HR-05-6225
		0.227	Pre-planting incorporated	113	< 0.01 (2)	
		0.224 [a]	BBCH 17	86	< 0.01 (2)	
Louisiana	Pioneer 83G66	0.231	Soil surface at planting	120	≤ 0.01 (2)	SD-HR-05-6226
		0.228	Pre-planting incorporated	120	< 0.01 (2)	
		0.222 [a]	6–8 leaf	87	< 0.01 (2)	
Kansas	Dekalb DKS5400	0.228	Soil surface at planting	134	≤ 0.01 (2)	ND-HR-05-6227
		0.224 [a]	4–6 collar	111	< 0.01 (2)	
Nebraska (York)	NC + 6B50	0.225	Soil surface at planting	127	≤ 0.01 (2)	NB-HR-05-6228
		0.224 [a]	BBCH 16	94	< 0.01 (2)	
Missouri	Pioneer 8500	0.223	Soil surface at planting	127	≤ 0.01 (2)	ND-HR-05-6229
		0.221 [a]	BBCH 16	98	< 0.01 (2)	
South Dakota	Partner 251	0.224	Soil surface at planting	128	≤ 0.01 (2)	NF-HR-05-6230
		0.226 [a]	BBCH 18	101	< 0.01 (2)	
Texas (Wharton)	DK52	0.219	Soil surface at planting	102 108 116	≤ 0.01 (2) < 0.01 (2) < 0.01 (2)	SA-HR-05-6231
		0.225 [a]	BBCH 23–32	63 69 77	< 0.01 (2) < 0.01 (2) < 0.01 (2)	
Oklahoma	SG95207	0.229	Pre-planting incorporated	128	< 0.01 (2)	SC-HR-05-6232
		0.226 [a]	4–5 leaf	90	< 0.01 (2)	
Nebraska (Grand Island)	NC + 6B50	0.222	Soil surface at planting	132	≤ 0.01 (2)	NB-HR-05-6233
		0.225	Pre-planting incorporated	132	< 0.01 (2)	
		0.228 [a]	BBCH 16	99	< 0.01 (2)	
Texas (Levelland)	F222E	0.228	Pre-planting incorporated	128	< 0.01 (2)	SC-HR-05-6234
		0.223 [a]	BBCH 16	103	< 0.01 (2)	
Colorado	DG-720B	0.228	Pre-planting incorporated	145	< 0.01 (2)	NM-HR-05-6235
		0.231 [a]	vegetative	85	< 0.01 (2)	
New Mexico	7117	0.229	Soil surface at planting	113	≤ 0.01 (2)	NB-HR-05-6236
		0.226	Pre-planting incorporated	113	≤ 0.01 (2)	
		0.226 [a]	8 leaf	78	< 0.01 (2)	

[a] Formulation with non-ionic surfactant

Sugarcane

Twenty six supervised residue trials were conducted on sugarcane in the USA during 2005 and four trials were conducted in South Africa during the growing period 1998/99. The trial data are summarised in Table 86.

Table 86 Summary of residue data for mesotrione in sugarcane (SC) formulation

Country (Region)	Sugarcane variety	Application Rate (g ai/ha)	Growth Stage	DAT (days)	Residues (mg/kg)	Report; trial
USA (Florida, South Bay)	CP-2143	0.27 (SS) + 0.11 (POT)	pre-emergence + 114 days to harvest	0 30 62 118 125	0.03, 0.02 < 0.01 (2) < 0.01 (2) ≤ 0.01 (2) < 0.01 (2)	T020420-04/VN-HR-05- 6240
		0.27 (SS) + 0.11 (PD)	pre-emergence + 100 days to harvest	0 30 61 104 111	0.02, < 0.01 < 0.01 (2) < 0.01 (2) < 0.01 (2) ≤ 0.01 (2)	
		0.10 (POT) + 0.11 (PD)	114 days + 100 days to harvest	0 30 61 104 111	0.02, 0.07 < 0.01 (2) < 0.01 (2) < 0.01 (2) ≤ 0.01 (2)	
USA (Florida, South Bay)	CP-2086	0.27 (SS) + 0.10 (POT)	pre-emergence+ 114 days to harvest	118	≤ 0.01 (2)	T020420-04/VN-HR-05- 6241
		0.27 (SS) + 0.10 (PD)	pre-emergence + 100 days to harvest	104	≤ 0.01 (2)	
		0.10 (POT) + 0.106 (PD)	114 days + 100 days to harvest	104	≤ 0.01 (2)	
		0.52 (POT) + 0.52 (PD)[j]	114 days + 100 days to harvest	104	< 0.01 (2)	
USA (Florida, South Bay)	CP-2086	0.28 (SS) + 0.10 (POT)	pre-emergence + 114 days to harvest	118	≤ 0.01 (2)	T020420-04/VN-HR-05- 6242
		0.27 (SS) + 0.11 (PD)	pre-emergence + 100 days to harvest	104	≤ 0.01 (2)	
		0.11 (POT) + 0.10 (PD)	114 days + 100 days to harvest	104	≤ 0.01 (2)	
USA (Louisiana, Bunkie)	LCP 85384	0.25 (SS) + 0.10 (POT)	BBCH 00 + pre-internode	0 30 60 114 121	3.72, 5.75 < 0.01 (2) < 0.01 (2) ≤ 0.01 (2) < 0.01 (2)	T020420-04/ SD-HR- 2005
		0.26 (SS) + 0.10 (PD)	BBCH 00 + pre-internode	0 30 60 100 107	0.70, 0.31 < 0.01 (2) < 0.01 (2) < 0.01 (2) ≤ 0.01 (2)	
		0.11 (POT) + 0.10 (PD)	pre-internode + pre-internode	0 30 60 100 107	0.07, 0.20 < 0.01 (2) < 0.01 (2) < 0.01 (2) ≤ 0.01 (2)	
USA (Louisiana, Cheney Ville)	LCP85384 Kleentek	0.29 (SS) + 0.11 (POT)	BBCH 00 + pre-internode	113	≤ 0.01 (2)	T020420-04/ SD-HR-05- 6244
		0.28(SS) + 0.10 (PD)	BBCH 00 + pre-internode	99	≤ 0.01 (2)	
		0.11 (POT) + 0.12 (PD)	pre-internode + pre-internode	99	≤ 0.01 (2)	

Country (Region)	Sugarcane variety	Application Rate (g ai/ha)	Growth Stage	DAT (days)	Residues (mg/kg)	Report; trial
		0.56 (POT) + 0.54 (PD)	pre-internode + pre-internode	99	< 0.01 (2)	
USA (Louisiana, Washington)	384	0.27(SS) + 0.11 (POT)	BBCH 00 + 75	114	< 0.01 (2)	T020420-04/ SD-HR-05- 6245
		0.27 (SS) + 0.11 (PD)	BBCH 00 + 43	100	< 0.01 (2)	
		0.11 (POT) + 0.11 (PD)	BBCH 00 + 43	100	< 0.01 (2)	
USA (Texas)	3388	0.28 (SS) + 0.11 (POT)	BBCH 08+ 37	114	< 0.01 (2)	T020420-04/ SA-HR-05- 6246
		0.28 (SS) + 0.11 (PD)	BBCH 08 + 37	100	< 0.01 (2)	
		0.11 (POT) + 0.11 (PD)	BBCH 37 + 38	100	< 0.01 (2)	
USA (Hawaii)	65-7052	0.27 (SS) + 0.11 (POT)	prior emergence + pre-crop closure	114	< 0.01 (2)	T020420-04/ WD-HR-05- 6247
		0.27(SS) + 0.10 (PD)	prior emergence + prior to layby	100	< 0.01 (2)	
		0.11 (POT) + 0.10 (PD)	pre-canopy close + prior to layby	100	< 0.01 (2)	
South Africa	N27	0.25	growth high 50–70 cm	182	< 0.01	RJ3076B/ ZA18-99-H310
South Africa	N14	0.25	growth high 60–75 cm	182 273	< 0.01 < 0.01	RJ3076B/ ZA18-99-H311
South Africa	N19	0.25	high 50–60 cm	181	< 0.01	RJ3076B/ ZA22-99-H410
		0.50	growth high 50–60 cm	181	< 0.01	

SS= soil surface spray
POT= post-emergence over-the-top
PD= post-emergence application directed to the base of the sugarcane

Linseed

Seventeen supervised residue trials were conducted in linseed in the USA during 2004 with one pre-emergence application of a suspension concentrate (SC) formulation (Report T010290-04 2004). The results are shown in Table 87.

Table 87 Summary of residue data for the use of mesotrione on linseed in the USA in 2004 using SC formulation

State (location)	Linseed variety	Application Rate (g ai/ha)	Growth Stage	PHI (days)	Crop Part	Residues (mg/kg)	Trial number
North Dakota (Northwood)	Rehab	0.11	at planting	144	seed	< 0.01 (2)	NN-HR-04-5650
		0.21	at planting	144	seed	< 0.01 (2)	
		0.11	multiple stems and no buds	103	seed meal	< 0.01 (2) < 0.01	
		0.32	multiple stems and no buds	103	seed	< 0.01 (2)	
		0.53	multiple stems and no buds	103	seed meal	< 0.01 (2) < 0.01	
Minnesota	York	0.10	pre-emergence	170	Seed	< 0.01 (2)	NF-HR-04-5651
		0.21	pre-emergence	170	Seed	< 0.01 (2)	
		0.10	25 cm high	130	seed	< 0.01 (2)	
North Dakota (New Rockford)	Rehab	0.11	at planting	136	seed	< 0.01 (2)	NN-HR-04-5652
		0.21	at planting	136	seed	< 0.01 (2)	
		0.10	ca. 25 cm high	104	seed	< 0.01 (2)	
Montana	Neche	0.10	at planting	89	seed	< 0.01 (2)	NN-HR-04-5653
		0.21	at planting	89	seed	< 0.01 (2)	
		0.11	stem elongation	46	seed	< 0.01 (2)	

State (location)	Linseed variety	Application Rate (g ai/ha)	Growth Stage	PHI (days)	Crop Part	Residues (mg/kg)	Trial number
South Dakota	Webster	0.10	BBCH 01 (at planting)	133 140 147	seed	< 0.01 (2) < 0.01 (2) < 0.01 (2)	NF-HR-04-5654
		0.21	BBCH 01 (at planting)	133 140 147	seed	< 0.01 (2) < 0.01 (2) < 0.01 (2)	
		0.10	BBCH 39	95 102 109	seed	< 0.01 (2) < 0.01 (2) < 0.01 (2)	

Animal Feed

Cereal trials from the studies reported previously have included the analysis of feed samples. The results are shown in Tables 88 to 92.

Table 88 Summary of residue data for the use of mesotrione on feed from corn (sweet and field)

Country (Region)	Corn variety	Application			DAT	Crop Part	Residue (mg/kg)	Report; trial
		Form.	kg ai/ha	Growth Stage				
Canada (Ontario) 1996	Pioneer 3902	SC	0.300	Pre-emergence	102	silage	< 0.01	RR 97-043B 94-CN-96-201
		SC	0.60	Pre-emergence	102	silage	< 0.01	
		SC	0.200	5–6 Leaf	87	silage	< 0.01	
		SC	0.400	5–6 Leaf	87	silage	< 0.01	
		SC	0.300 0.200	Pre-emergence 5–6 leaf	87	silage	< 0.01	
		SC	0.600 0.400	Pre-emergence 5–6 leaf	87	silage	< 0.01	
Canada (Ontario) 1996	Ciba seeds G-4064	SC	0.300	Pre-emergence	101	silage	< 0.01	RR 97-043B 94-CN-96-202
		SC	0.600	Pre-emergence	101	silage	< 0.01	
		SC	0.200	4–5 Leaf	90	silage	< 0.01	
		SC	0.400	4–5 Leaf	90	silage	< 0.01	
		SC	0.300 0.200	Pre-emergence 4–5 leaf	90	silage	< 0.01	
		SC	0.600 0.400	Pre-emergence 4–5 leaf	90	silage	< 0.01	
Canada (Ontario) 1997	Funks-BT Maximizer	SC	0.300	Pre-emergence	120 155	silage grain	< 0.01 < 0.01	RR 98-035B 94-CN-97-901
		SC	0.600	Pre-emergence	120	silage	< 0.01	
		SC	0.200	24	91	silage	< 0.01	
		SC	0.400	24	91	silage	< 0.01	
		SC	0.300 0.200	Pre-emergence 24	91	silage	< 0.01	
		SC	0.600 0.400	Pre-emergence 24	91	silage	< 0.01	
Canada (Ontario) 1997	Funks-BT Maximizer	SC	0.300	Pre-emergence	112	silage	< 0.01	RR 98-035B 94-CN-97-902
		SC	0.600	Pre-emergence	112	silage	< 0.01	

Country (Region)	Corn variety	Application			DAT	Crop Part	Residue (mg/kg)	Report; trial
		Form.	kg ai/ha	Growth Stage				
		SC	0.200	23	93	silage	< 0.01	
		SC	0.400	23	93	silage	< 0.01	
		SC	0.300 0.200	Pre-emergence 23	93	silage	< 0.01	
		SC	0.600 0.400	Pre-emergence 23	93	silage	< 0.01	
France (South)	620 Spirit	SC	0.102	BBCH 19	38	Cob	< 0.01	03-7049 2003
	620 Spirit		0.153	BBCH 12	38 61 62	cob cob cob	< 0.01 < 0.01 < 0.01	
France (South)	620 Spirit		0.98	BBCH 19	38	Cob	< 0.01	03-7050 2003
	620 Spirit		0.143	BBCH 12	62	cob	< 0.01	
France (South)	620 Spirit		0.153	BBCH 12	61 74	cob cob	< 0.01 < 0.01	04-7012 2004
	620 Spirit		0.104	BBCH 59	39	Cob	< 0.01	
France (South)	620 Spirit)	SC	0.154	BBCH 12	61 74	cob cob	< 0.01 < 0.01	04-7012 2004
	620 Spirit		0.103	BBCH 59	39	Cob	< 0.01	
France (South)	LG35.05	WG	0.148	BBCH 15–16	27 35 43 43 61 68 68 99 99 99 127 127	whole plant whole plant whole cob remaining plant whole plant whole cob remaining plant whole plant whole cob remaining plant whole cob remaining plant	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	T000921-09-REG 2009
Germany	Nescio	WG	0.138	BBCH 16–18	34 47 47 47 82 82 66 91 91 110 143 143	whole plant whole plant whole cobs remaining plant cobs remaining plant whole plant cobs remaining plant whole plant cobs remaining plant	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	T000920-09-REG 2009
Spain	Castellano	WG	0.154	BBCH 15	7 14 42 42 63 71 71 82 82	whole plant whole plant cobs remaining plant whole plant cobs remaining plant cobs remaining plant	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	T000921-09-REG 2009

Country (Region)	Corn variety	Application			DAT	Crop Part	Residue (mg/kg)	Report; trial
		Form.	kg ai/ha	Growth Stage				
United Kingdom	Ohio	WG	0.142	BBCH 16–17	20 35 41 41 53 53 60 87 98 98 112 112	whole plant whole plant whole cobs remaining plant whole cobs remaining plant whole plant whole plant cobs remaining plant cobs remaining plant	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	T000920-09-REG 2009
USA (Wisconsin) 2001	NK 199	SC	0.302 0.177	pre-emergence Vt (tasseling)	14 30 56	forage with ears forage without stover	< 0.01 (2) < 0.01 (2) < 0.01 (2)	487-01; NI-HR001-01
USA (Washington) 2001	Jubilee	SC	0.303 0.179		14 28 71	forage w/ ears forage w/o ears stover	0.02, 0.07 < 0.01 (2) < 0.01 (2)	487-01; WF-HR003-01
USA (California) 2001	Silver Queen	SC	0.300 0.182	BBCH 01 BBCH 59	0 7 14 23 30 37 58	forage w/ ears forage w/ ears forage w/ ears forage w/o ears forage w/o ears forage w/o ears stover	4.29, 4.96 0.82, 1.28 0.73, 0.88 0.45, 0.34 0.40, 0.38 0.23, 0.33 1.2, 0.90 (1.1)	487-01; W2-HR102-01
USA (N. Carolina) 2001	G90 F1	SC	0.308 0.182	BBCH 55	14 26 54	forage w/ ears forage w/o ears stover	< 0.01, 0.02 < 0.01 (2) < 0.01 (2)	487-01; SJ-HR003-01
USA (Ohio) 2001	Bodacious	SC	0.314 0.190		14 30 52	forage w/ ears forage w/o ears stover	< 0.01 (2) < 0.01 (2) < 0.01 (2)	487-01; NK-HR001-01
USA (New York) 2001	GH-2783	SC	0.305 0.182	at planting + 8–9 leaves	14 30 67	forage w/ ears forage w/o ears stover	< 0.01 (2) < 0.01 (2) < 0.01 (2)	487-01; EE-HR003-01
USA (Idaho) 2001	Sugar Buns		0.303 0.179	post planting + pollen shed	14 30 61	forage w/ ears forage w/o ears stover	0.02.,0.01 0.05 , < 0.01 < 0.01 (2)	487-01; WG-HR005-01
USA (Illinois) 2001	Kandy King	SC	0.301 0.186	BBCH 00 + BBCH 34	14 31 60	forage w/ ears forage w/o ears stover	< 0.01 (2) < 0.01 (2) < 0.01 (2)	487-01; N4-HR003-01
USA (Pennsylvania) 2001	Argent	SC	0.320 0.186	BBCH 00 + early tassel	14 30 70	forage w/ ears forage w/o ears stover	< 0.01 (2) < 0.01 (2) < 0.01 (2)	487-01; EC-HR002-01
USA (Florida) 2001	Silver Queen	SC	0.313 0.177	Just planted + visible tassel	14 28 62	forage w/ ears forage w/o ears stover	< 0.01 (2) < 0.01 (2) < 0.01 (2)	487-01; VB-HR101-01
USA (Michigan) 2001	Excellency	SC	0.306 0.180	pre-emergence Vt	0 7 14 23 30 36 70	forage w/ ears forage w/ ears forage w/ ears forage w/o ears forage w/o ears forage w/o ears stover	3.09. 3.96 0.02. 0.01 < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)	487-01; ED-HR006-01
USA (Maine) 2001	Maple Sweet	SC	0.304 0.189	0 + tassel initiation	14 30 55	forage w/ ears forage w/o ears stover	< 0.01 (2) < 0.01 (2) < 0.01 (2)	487-01; NF-HR002-01
USA N. Carolina)	Rogers WH0809	SC	0.107 0.106	BBCH 36 + BBCH 37	32 53	forage w/o ears stover	< 0.01 (2) < 0.01 (2)	T001589-08; E10NC081871

Country (Region) 2008	Corn variety	Application			DAT	Crop Part	Residue (mg/kg)	Report; trial
		Form.	kg ai/ha	Growth Stage				
		WG	0.104 0.104	BBCH 36 + BBCH 37	32 53	forage w/o ears stover	< 0.01 (2) < 0.01 (2)	
USA (N. Dakota 2008	Peaches & Cream	SC	0.107 0.105	BBCH 16 + BBCH 55	28 66	forage w/o ears stover	< 0.01 (2) < 0.01 (2)	T001589-08; C13ND081872
		WG	0.107 0.106	BBCH 16 + BBCH 55	28 66	forage w/o ears stover	< 0.01 (2) < 0.01 (2)	
USA (California) 2008	Sweetie 82	SC	0.103 0.107	BBCH 15 + BBCH 17	45 69	forage w/o ears stover	0.12 (0.07, 0.17) 0.06, 0.09	T001589-08; W30CA081873
		WG	0.105 0.105	BBCH 15 + BBCH 17	45 69	forage stover	(0.06) 0.07, 0.06 0.09, 0.07	
USA (Iowa, Sheffield) 1995	ICI 8543	SC	0.336 0.224	Pre-plant vegetative	82 109	forage stover	< 0.01 (3) < 0.01 (2)	RR 96-018B 63-IA-95-805
USA (Illinois, Brimfield) 1995	Hoblit 428	SC-	0.336 0.224	pre- emergence	85 95	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 60-IL-95-806
USA (Indiana, Lafayette) 1995	Pioneer 3394	SC	0.336 0.224	pre- emergence 7–9 leaves	76 96 96	forage grain stover	< 0.01 (2) < 0.01 (2) < 0.01 (2)	RR 96-018B 67-IN-95-807
USA (Michigan) 1995	NK 4640	SC	0.336 0.224	pre-bloom	85 114	forage stover	< 0.01 (2) < 0.01	RR 96-018B 24-MI-95-808
USA (Nebraska) 1995	Ottilie RO 2455	SC	0.336 0.224	Pre-plant V6	62 88	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 68-NE-95-809
USA (Iowa, Albia) 1995	ICI 8532	SC	0.336 0.224	Pre-plant vegetative	74 102	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 63-IA-95-810
USA (Illinois, Towanda) 1995	Ainsworth 640	SC	0.336 0.224	Pre-plant post emergence	76 87	forage stover	< 0.01 (3) < 0.01 (2)	RR 96-018B 60-IL-95-811
USA (Indiana, Rochester) 1995	Pioneer 3394	SC	0.336 0.224	Early pre- plant 5–7 leaves	92 96	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 67-IN-95-812
USA (Nebraska, Waverly) 1995	Producers PH785	SC	0.336 0.224	Pre-plant V5–V6	71 96	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 68-NE-95-814
USA (Kansas, La Cygne) 1995	CIBA 4575	SC	0.336 224	early pre- plant post	46 68	forage stover	< 0.01 (3) < 0.01 (2)	RR 96-018B 37-KS-95-825
USA (Pennsylvania, Ephrata) 1995	CI 8541	SC	0.336 224	pre- emergence vegetative	76 98	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 70-PA-95-815
		SC	0.336 0.224	pre- emergence vegetative	76 98	forage stover	< 0.01 (2) < 0.01 (2)	
USA (Minnesota, St. Peter) 1995	Cenex 424	SC	0.336 0.224	pre- emergence vegetative	76 92	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 36-MN-95-816
		SC	0.336 0.224	pre- emergence vegetative	76 92	forage stover	< 0.01 (2) < 0.01 (2)	
USA (Ohio, Urbana) 1995	Vigoro V1122	SC	0.336 0.224	pre- emergence	85 113	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 24-OH-95-817
		SC	0.336 0.224	pre- emergence	85 113	forage stover	< 0.01 (2) < 0.01 (2)	
USA (Wisconsin,	Cenex LOL 357	SC	0.336 0.224	pre- emergence	72 104	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 79-WI-95-818

Country (Region)	Corn variety	Application			DAT	Crop Part	Residue (mg/kg)	Report; trial
		Form.	kg ai/ha	Growth Stage				
Baraboo) 1995		SC	0.336 0.224	pre-emergence	72 104	forage stover	< 0.01 (2) < 0.01 (2)	
USA (Texas) 1995	G4673B (D&PL Co.)	SC	0.336 0.224	pre-emergence pre-tassel	56 92	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 25-TX-95-819
		SC	0.336 0.224	pre-emergence pre-tassel	56 92	forage stover	< 0.01 (2) < 0.01 (2)	
USA (north Carolina) 1995	Field corn (Pioneer 3165)	SC	0.336 0.224	pre-plant rapidly growing	68 95	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 01-NC-95-820
		SC	0.336 0.224	pre-plant rapidly growing	62 68 75 82 88 95 101 108	forage forage forage forage stover stover stover stover	< 0.01 < 0.01 (2) < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	
USA (Iowa, Boone) 1995	ICI 8543	SC	0.336 0.224	Early pre-plant vegetative	86 112	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 63-IA-95-821
		SC	0.336 0.224	Early pre-plant vegetative	86 112	forage stover	< 0.01 (2) < 0.01 (2)	
USA (Illinois, Champagne) 1995	Pioneer 3394	SC	0.336 0.224	pre-plant post emergence	74 107	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 04-IL-95-822
		SC	0.336 0.224	pre-plant post emergence	60 74 81 88 100 107 113 121	forage forage forage forage stover stover stover stover	< 0.01 < 0.01 (2) < 0.01 < 0.01 < 0.01 < 0.01 (2) < 0.01 < 0.01	
USA (Indiana, N. Richmond) 1995	Pioneer 3394	SC	0.336 20.24	pre-plant 6–8 leaf	64 86	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 67-IN-95-823
		SC	0.336 0.224	pre-plant 6–8 leaf	64 86	forage stover	< 0.01 (2) < 0.01 (2)	
USA (Nebraska, Crete) 1995	ICI 8541	SC	0.336 0.224	pre-plant V6-V7	62 89	forage stover	< 0.01 (2) < 0.01 (2)	RR 96-018B 68-NE-95-824
		SC	0.336 0.224	pre-plant V6-V7	62 89	forage stover	< 0.01 (2) < 0.01 (2)	
USA Iowa) 2001	Pioneer 34B23)	SC	0.268 0.225	BBCH 00 BBCH 18–19	46 99	forage stover	< 0.01 (2) < 0.01 (2)	1847-01 NE-HR-003-01
		SE SC	0.267 0.233	BBCH 00 BBCH 18/19	46 99	forage stover	< 0.01 (2) < 0.01 (2)	
		SC	0.274 0.234	BBCH 13 BBCH 18 19	46 99	forage stover	< 0.01 (2) < 0.01 (2)	
		SE SC	0.267 0.223	BBCH 13 BBCH 18/19	46 99	forage stover	< 0.01 (2) < 0.01 (2)	
USA (North Carolina) 2001	ICI 8543)	SC	0.269 0.226	BBCH 00 75 cm high	45 98	forage stover	< 0.01 (2) < 0.01 (2)	1847-01 SJ-HR-013-01
		SE SC	0.269 0.227	BBCH 00 75 cm high	45 98	forage stover	< 0.01 (2) < 0.01 (2)	

Country (Region)	Corn variety	Application			DAT	Crop Part	Residue (mg/kg)	Report; trial
		Form.	kg ai/ha	Growth Stage				
		SC	0.271 0.227	BBCH 12/13 75 cm high	45 98	forage stover	< 0.01 (2) < 0.01 (2)	
		SE SC	0.270 0.227	BBCH 12/13 75 cm high	45 98	forage stover	< 0.01 (2) < 0.01 (2)	
USA (Illinois) 2001	Pioneer 34B24	SC	0.285 0.253	BBCH 00 BBCH 36	45 112	forage stover	< 0.01 (2) < 0.01 (3)	1847-01 N4-HR-005-01
		SE SC	0.278 0.236	BBCH 00 BBCH 36	45 112	forage stover	< 0.01 (2) < 0.01 (2)	
		SC	0.286 0.244	BBCH 12 BBCH 36	45 112	forage stover	< 0.01 (2) < 0.01 (2)	
		SE SC	0.268 0.237	BBCH 12 BBCH 36	45 112	forage stover	< 0.01 (2) < 0.01 (2)	
USA (Nebraska) 2001	ICI 8543	SC	0.270 0.227	BBCH 00 BBCH 19	41 103	forage stover	< 0.01 (2) < 0.01 (2)	1847-01 NB-HR-004-01
		SE SC	0.273 0.227	BBCH 00 BBCH 19	41 103	forage stover	< 0.01 (2) < 0.01 (2)	
		SC	0.266 0.226	BBCH 12/13 BBCH 19	41 103	forage stover	< 0.01 (2) < 0.01 (2)	
		SE SC	0.268 0.226	BBCH 12/13 BBCH 19	41 103	forage stover	< 0.01 (2) < 0.01 (2)	

Table 89 Summary of residue data for mesotrione on millet (feed) using SC formulation in the USA in 2004 (Report T010289-04)

State	Millet variety	Application Rate (g ai/ha)	Growth Stage	DAT	Crop Part	Residue (mg/kg)	Trial number
Illinois	Max Perl	0.109	at planting	31 31	forage hay	< 0.01 (2) < 0.01 (2)	4A-HR-04-5640
		0.214	at planting	31 31	forage hay	≤ 0.01 (2) ≤ 0.01 (2)	
		0.108	BBCH 32	31 31	forage hay	< 0.01 (2) < 0.01 (2)	
Nebraska	Huntsman	0.103	at planting	51 51 84	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	4A-HR-04-5641
		0.210	at planting	51 51 84	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	
		0.103	BBCH 12	28 28 61	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	
South Dakota	Rise	0.104	at planting	34 34 95	forage hay straw	< 0.01 (2) 0.01, < 0.01 < 0.01 (2)	4A-HR-04-5642
		0.208	at planting	34 34 95	forage hay straw	0.01, < 0.01 0.01 (2) ≤ 0.01 (2)	
		0.105	BBCH 21	30 30 69	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	
Colorado (Ault)	Early Bird	0.107	at planting	70 70 132	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	4A-HR-04-5643
		0.212	at planting	70 70 132	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	

State	Millet variety	Application Rate (g ai/ha)	Growth Stage	DAT	Crop Part	Residue (mg/kg)	Trial number
		0.107	vegetative	30 30 92	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	
Colorado (Ault)	Early Bird	0.110	at planting	63 63 70 70 77 77 104 111 120	forage hay forage hay forage hay straw straw straw	< 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)	4A-HR-04-5644
		0.218	at planting	63 63 70 70 77 77 104 111 120	forage hay forage hay forage hay straw straw straw	≤ 0.01 (2) ≤ 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) ≤ 0.01 (2) < 0.01 (2) < 0.01 (2)	
		0.108	vegetative	23 23 30 30 37 37 64 71 80	forage hay forage hay forage hay straw straw straw	≤ 0.01 (2) 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) ≤ 0.01 (2) < 0.01 (2) < 0.01 (2)	

Table 90 Summary of residue data for the use of mesotrione on oats (feed) (SC formulation) in 2005 in the USA (Report T004407-05)

State (location)	Oat variety	Application rate (kg ai/ha)	Growth Stage at Application	DAT	Crop Part	Residues (mg/kg)	Trial number
New York	Armor	0.214	BBCH 00	70 70 90	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	5A-HR-05-6380
		0.104	BBCH 59–61	29 29 49	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	
Virginia	Coker	0.216	BBCH 00	225 225 246	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	SJ-HR-05-6381
		0.108	BBCH 75	30 30 51	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	
North Dakota (Northwood)	Morton	0.211	bare soil application	73 73 90	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	NN-HR-05-6382
		0.104	BBCH 23	33 33 50	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	
South Dakota (Lesterville)	Jerry	0.209	BBCH 01	60 60 84	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	NF-HR-05-6383
		0.106	BBCH 32	30 30 54	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2))	

State (location)	Oat variety	Application rate (kg ai/ha)	Growth Stage at Application	DAT	Crop Part	Residues (mg/kg)	Trial number
Wisconsin	Oat (Esker)	0.216	pre-emergence	70 70 91	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	NI-HR-05-6384
		0.106	late boot to early head	28 28 49	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2))	
Minnesota	Oat (Drumlin)	0.209	BBCH 00	58 58 80	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	NF-HR-05-6385
		0.107	BBCH 21	30 30 52	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	
Nebraska (York)	Oat (Jerry)	0.213	BBCH 00	54 54 63 63 68 68 75 75 87	forage hay forage hay forage hay forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)	NB-HR-05-6386
		0.105	BBCH 31	16 16 25 25 30 30 37 37 49	forage hay forage hay forage hay forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)	
Iowa	Oat (Jerry)	0.213	BBCH 00	75 75 96	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	NE-HR-05-6387
		0.106	BBCH 80	28 28 49	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	
Kansas (Sabetha)	Oat (Loyal)	0.210	pre-emergence	63 63 83	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	ND-HR-05-6388
		0.107	tillering (1–3 tillers)	30 30 50	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	
Michigan	Oat (Prairie)	0.213	pre-emergence	55 55 61 61 68 68 75 75 88	forage hay forage hay forage hay forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)	NL-HR-05-6389
		0.104	5–6 leaves	17 17 23 23 30 30 37 37 50	forage hay forage hay forage hay forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)	
Illinois	Oat (VHS)	0.209	BBCH 00	62 62 81	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	4A-HR-05-6390

State (location)	Oat variety	Application rate (kg ai/ha)	Growth Stage at Application	DAT	Crop Part	Residues (mg/kg)	Trial number
		0.104	BBCH 26	33 33 52	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	
		0.317	BBCH 26	33 33 52	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	
		0.531	BBCH 26	33 33 52	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	
Texas	Oat (La-604)	0.209	BBCH 00	156 156 180	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	SA-HR-05-6391
		0.106	BBCH 43	30 30 54	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	
North Dakota (New Rockford)	Oat (La-604)	0.211	soil surface spray	73 73 92	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	NM-HR-05-6392
		0.104	BBCH 43	30 30 49	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	
South Dakota (Frederick)	Oat (Morton)	0.211	BBCH 01	60 60 81	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	NF-HR-05-6393
		0.106	BBCH 21–31	30 30 51	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	
Nebraska (Grand Island)	Oat (Reeves)	0.215	BBCH 00	70 70 90	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	NB-HR-05-6394
		0.105	BBCH 31	29 29 49	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	
Kansas (Larned)	Oat (Jerry)	0.210	pre-emergence	63 63 83	forage hay straw	< 0.01 (2) < 0.01 (2) < 0.01 (2)	NM-HR-05-6395
		0.107	tillering (1–2 tillers)	30 30 50	forage hay straw	≤ 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	

Table 91 Summary of residue data for mesotrione on rice (feed) after application using a granular formulation

Country year	Rice variety	Application rate (kg ai/ha)	Growth Stage	DAT	Crop Part	Residue (mg/kg)	Trial number
Korea 2005		0.180	5–15 days after transplanting	140	Straw	< 0.1 (3)	A14928B
		0.360	5–15 days after transplanting	140	Straw	< 0.1 (3)	
Japan 2004	Matsuribare	0.100	21 days after transplanting	63 91	Forage Straw	< 0.002 (2) < 0.01 (2)	A13723B
Japan 2004	Hi-no-hikari	0.100	21 days after transplanting	77 89	Forage Straw	< 0.002 (2) < 0.01 (2)	A13723B
Japan 2006	Koshihikari	0.100 0.100	4.5 leaf period growing period	76	Straw	< 0.01 (2)	A13723B
		0.100 0.100	4.5 leaf period growing period	61	Straw	< 0.01 (2)	
		0.100 0.100	4.5 leaf period before harvest	45	Straw	< 0.01 (2)	

Country year	Rice variety	Application rate (kg ai/ha)	Growth Stage	DAT	Crop Part	Residue (mg/kg)	Trial number
Japan 2006	Hi-no-hikari	0.100 0.100	10 days after plant 75 days before harvest	75	Straw	< 0.01 (2)	A13723B
		0.100 0.100	10 days after plant 60 days before harvest	60	Straw	< 0.01 (2)	
		0.100 0.100	10 days after plant 45 days before harvest	45	Straw	< 0.01 (2)	
Japan 2007	Koshihikari	0.100 0.100	growing period 21 cm high	75	Forage	< 0.002 (2)	A13723B
		0.100 0.100	growing period growing period	60	Forage	< 0.002 (2)	
		0.100 0.100	growing period before harvest	45	Forage	< 0.002 (2)	
Japan	Hi-no-hikari	0.100	24 days after plant	53	Forage	< 0.002 (2)	A13723B
		0.100 0.100	24 days after plant 35 days before harvest	46	Forage	< 0.002 (2)	
		0.100 0.100	24 days after plant formation of young panicle	34	Forage	< 0.002 (2)	

Table 92 Summary of residue data for mesotrione in sorghum feed in USA in 2005 (SC formulation) (Report T020419-04)

State (location)	Sorghum variety	Application rate (kg ai/ha)	Growth Stage	DAT (days)	Crop Part	Residues (mg/kg)	Trial
South Caroline	NK8416	0.225	pre-emergence	57 113	forage stover	≤ 0.01 (2) ≤ 0.01 (2)	SJ-HR-05-6225
		0.227	before planting	57 113	forage stover	≤ 0.01 (2) ≤ 0.01 (2)	
		0.224	BBCH 17	30 86	forage stover	< 0.01 (2) < 0.01 (2)	
Louisiana	Pioneer 83G66	0.231	pre-emergence	65 120	forage stover	≤ 0.01 (2) ≤ 0.01 (2)	SD-HR-05-6226
		0.228	pre-plant	65 120	forage stover	≤ 0.01 (2) ≤ 0.01 (2)	
		0.222	6–8 leaf	32 87	forage stover	< 0.01 (2) < 0.01 (2)	
Kansas	Dekalb DKS5400	0.228	pre-emergence	54 134	forage stover	≤ 0.01 (2) ≤ 0.01 (2)	ND-HR-05-6227
		0.224	4–6 collar	31 111 111	forage stover AGF	< 0.01 (2) < 0.01 (2) < 0.01	
Nebraska (York)	NC + 6B50	0.225	pre-emergence	33 43 49 63 127	forage forage forage forage stover	< 0.01 (2) < 0.01 (2) < 0.01 (2) ≤ 0.01 (2) ≤ 0.01 (2)	NB-HR-05-6228
		0.224	BBCH 16	0 10 16 30 94	forage forage forage forage stover	14.4, 11.8 < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)	
Missouri	Pioneer 8500	0.223	pre-emergence	57 127	forage stover	≤ 0.01 (2) ≤ 0.01 (2)	ND-HR-05-6229
		0.221	BBCH 16	28 98	forage stover	< 0.01 (2) < 0.01 (2)	
South Dakota	Partner 251	0.224	BBCH 00	57 128	forage stover	≤ 0.01 (2) ≤ 0.01 (2)	NF-HR-05-6230
		0.226	BBCH 18	30 101	forage stover	< 0.01 (2) < 0.01 (2)	

State (location)	Sorghum variety	Application rate (kg ai/ha)	Growth Stage	DAT (days)	Crop Part	Residues (mg/kg)	Trial
Texas (Wharton)	DK52	0.219	BBCH 00	39 49 55 70 102 108 116	forage forage forage forage stover stover stover	< 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)	SA-HR-05-6231
		0.225	BBCH 23–32	0 10 16 31 63 69 77	forage forage forage forage stover stover stover	15.0, 15.1 < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2) < 0.01 (2)	
Oklahoma	SG95207	0.229	pre-planting	71 128	forage stover	< 0.01 (2) < 0.01 (2)	SC-HR-05-6232
		0.226	4–5 leaf	33 90	forage stover	< 0.01 (2) < 0.01 (2)	
Nebraska (Grand Island)	NC + 6B50	0.222	pre-emergence	63 132	forage stover	< 0.01 (2) < 0.01 (2)	NB-HR-05-6233
		0.225	BBCH 00	63 132	forage stover	< 0.01 (2) < 0.01 (2)	
		0.228	BBCH 16	30 99	forage stover	< 0.01 (2) < 0.01 (2)	
Texas (Levelland)	F222E	0.228	pre-planting	55 128	forage stover	< 0.01 (2) < 0.01 (2)	SC-HR-05-6234
		0.223	BBCH 16	30 103 103	forage stover AGF	< 0.01 (2) < 0.01 (2) < 0.01	
Colorado	DG-720B	0.228	at planting	90 145	forage stover	< 0.01 (2) < 0.01 (2)	NM-HR-05-6235
		0.231	vegetative	30 85	forage stover	< 0.01 (2) < 0.01 (2)	
New Mexico	7117	0.229	pre-emergence	64 113	forage stover	< 0.01 (2) < 0.01 (2)	NB-HR-05-6236
		0.226	pre-plant	64 113	forage stover	< 0.01 (2) < 0.01 (2)	
		0.226	8 leaf	29 78	forage stover	0.02, 0.01 < 0.01 (2)	

Processing studies

A residue trial on soya beans conducted in the USA with one pre-emergence application at a 1.1 kg ai/ha (Table 77; report T005595-06). Soya beans harvested at 113 DAT were processed into meal, hulls and refined oil simulating commercial practices, and samples analysed using method RAM 366/01. Residues of mesotrione were < 0.01 mg/kg in the soy sample, meal, hulls and refined oil, and no processing factors were derived

Two residue trials on mesotrione-tolerant HT soya beans were conducted in the USA using pre- plus post-emergence applications at 1.1 and 0.6 kg ai/ha, respectively (Table 93, Report T000908-07). Soya bean samples were harvested at 76 or 102 DAT, processed according to commercial practices, and samples analysed using method RAM 366/01. The results are show in in Table 93.

Table 93 Processing factors for mesotrione residues in mesotrione-tolerant soya beans

Mesotrione	Soya bean	Meal	Hulls	Crude oil	Refined oil	AGF	Flour	Soya milk	Tofu	Soya sauce	Miso
Residue (mg/kg) [a]	0.04	0.01	0.02	< 0.01	< 0.01	0.02	0.07	< 0.01	< 0.01	< 0.01	< 0.01

Processing factor		0.25	0.5	< 0.25	< 0.25	0.5	1.8	< 0.25	< 0.25	< 0.25	< 0.25
Residue (mg/kg) [b]	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	< 0.01
Processing factor		–	–	–	< 0.01	–	> 2	–	–	–	–

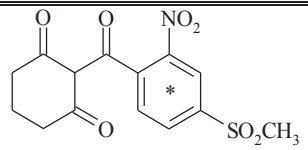
[a] Trial C30-9659, 79 DAT
[b] Trial C18-9656, 102 DAT

RESIDUES IN ANIMAL COMMODITIES

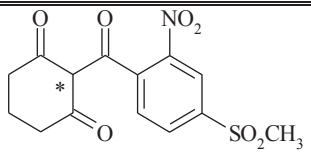
No studies were provided

APPRAISAL

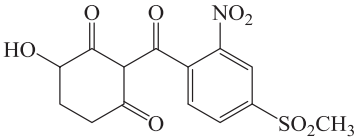
Mesotrione is a systemic pre-emergence and post-emergence herbicide for the selective contact and residual control of broadleaf weeds. The compound was scheduled for evaluation by 2014 JMPR as a new compound at the Forty-fifth Session of the CCPR (2013). Metabolism studies on animal and plants, confined rotational crops and environmental fate studies, analytical methods and residue trials on berries, okra, sweet corn, soybean, asparagus, rhubarb maize, millet, oat, rice, sorghum, sugarcane and linseed were submitted for evaluation. The structure of mesotrione and the main metabolites found in livestock, plant tissues and soil are shown below



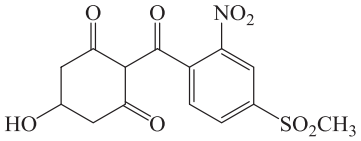
[Phenyl-U-^{14}C] Mesotrione



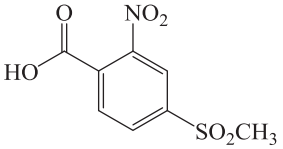
[Cyclohexane-2-^{14}C] Mesotrione



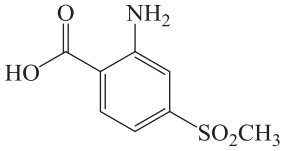
4-Hydroxy-mesotrione



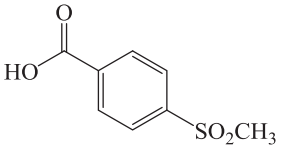
5-Hydroxy-mesotrione



MNBA [4-(methylsulphonyl)-2-nitrobenzoic acid]



AMBA [(2-amino-4-(methylsulphonyl)-benzoic acid)]



MBA [4-(methylsulphonyl) benzoic acid]

Animal metabolism

Rats

The metabolism of mesotrione was evaluated at the present Meeting by the JMPR WHO Panel. The compound is rapidly and extensively absorbed, minimally metabolized and excreted primarily in urine after a single or repeated dose. The majority of the radioactivity was excreted as the parent compound within 12 hours post-dose, accounting for 43–64% of the dose in urine. The metabolites found in the excreta includes 4 and 5-hydroxy mesotrione, MNBA and AMBA.

Livestock animals

Metabolism studies with mesotrione were conducted in lactating cows, swine and poultry. Additionally, the metabolism of AMBA, was investigated in the cow.

In two metabolism studies conducted in lactating cows, the animals were dosed with [phenyl-U-^{14}C-]-mesotrione or [cyclohexane-2-^{14}C]-mesotrione for 7 consecutive days at a nominal rate of 10 ppm in the diet, and sacrificed 16 hours after the final dose. Over 90% of the administered dose was found in excreta, mostly in faeces. TRR was higher in liver and kidney (0.07 to 0.11 mg eq./kg), reached 0.007 mg eq./kg in muscle, 0.013 mg/kg eq in fat and 0.08 mg eq./kg in milk (at least 90% TRR in skimmed milk). Mesotrione accounted for 10–18% TRR in liver and kidney (0.01–0.02 mg eq./kg). AMBA was identified in kidney of the phenyl label experiment (0.01 mg eq./kg).

One female swine was dosed orally with [phenyl-U-^{14}C]-mesotrione for 5 consecutive days at 6 ppm, and sacrificed 23 hours after the final dose. About 90% of the administered dose was recovered in the excreta, mostly in the faeces. Highest TRRs were found in liver (1.75 mg eq./kg) and kidney (0.12 mg eq./kg), with 0.01 mg eq./kg in muscle and 0.006 mg eq./kg in fat. Mesotrione was the main identified residues (90% TRR in liver, 73% TRR in kidney and 78% TRR in muscle). AMBA accounted for up to 2% TRR in tissues (up to 0.029 mg eq./kg in liver). MNBA was only detected in liver (0.005 mg eq./kg).

Two metabolism studies were conducted in poultry, in which hens were dosed for 10 consecutive days at 11 ppm either with [phenyl-U-^{14}C]-mesotrione or [cyclohexane-2-^{14}C]-mesotrione; the hens were sacrificed 16 hours after the final dose. The radioactivity in excreta accounted for over 90% of the administered dose, and contained mesotrione (up to 55% TRR) and AMBA (18% TRR). TRRs were similar in both experiments for liver (1.1–1.2 mg eq./kg) and kidney (0.06–0.07 mg eq./kg), but were higher in the cyclohexane experiment in muscle (up to 0.012 mg/kg eq), fat (up to 0.048 mg eq./kg), reaching 0.094 mg eq./kg in egg yolk, and 0.025 mg eq./kg in the white. Mesotrione was not detected in muscle in any experiment, and was the only compound identified in tissues and eggs in both experiments, corresponding to at least 70% TRR in the liver and fat. In egg yolk, mesotrione accounted for 81% TRR in the phenyl experiment, and 19.5% TRR in the cyclohexane experiment, in which about 15% TRR was shown to be incorporated into palmitic/oleic acid.

A lactating cow received [phenyl-U-^{14}C]-AMBA for 7 days at 12.2 ppm in the diet and was sacrificed 23 hours after the final dose. About 90% of the dose was recovered in the excreta, mostly in the faeces. Highest residues were found in kidney (0.053 mg eq./kg), with AMBA accounting for 79% TRR. Perineal fat contained 0.018 mg eq./kg, 62% identified as AMBA. TRR in liver were 0.005 mg eq./kg, and reached a maximum of 0.009 mg eq./kg in milk (day 6), but were not characterized. No radioactive residues were detected in muscle.

In summary, the biotransformation of mesotrione in livestock involves the oxidative cleavage of the parent molecule to yield MNBA, which is reduced in the nitro group to give AMBA. Highest residues were found in liver and kidney, and the levels in muscle were low, reaching a maximum of 0.012 mg eq./kg Mesotrione accounted for up to 18% TRR in cow liver and kidney, at least 70% TRR in tissues of swine and poultry, and up to 80% TRR in egg yolk. No single compound was detected in muscle. The metabolism of Mesotrione in rats was found to be similar to that described for livestock.

Plant metabolism

Metabolism studies were conducted in cranberries, tolerant soya bean, maize, rice and peanuts. [Phenyl-U-^{14}C]-mesotrione was applied twice to cranberry plants at 0.331 + 0.242 kg ai/ha (1×) or 0.919 + 0.642 kg ai/ha (3× rate), and samples harvested 46 days after the last treatment (DAT). TRRs in mature foliage were 16.8 mg eq./kg and 31.8 mg eq./kg for 1× and 3×, respectively. TRRs in the mature cranberry fruit were 2.6 mg eq./kg and 4.9 mg eq./kg, respectively, mostly as mesotrione (60–67% TRR) and AMBA (24–35% TRR), MNBA accounted for up to 3% TRR.

Mesotrione tolerant soya bean seeds grown in sandy loam soil were treated with either [phenyl-U-^{14}C]- or [cyclohexane-2-^{14}C]-mesotrione using three GAP application regimes: one pre-emergence at 0.225 kg ai/ha (T1), a combined pre-emergence at 0.225 kg ai/ha followed by a post-emergence at 0.125 kg ai/ha (T2), or one post-emergence at 0.225 kg ai/ha (T3). Forage was sampled at 22–28 DAT, hay at 40–42 DAT and seeds at 90–123 DAT.

Higher radioactivity was recovered from the phenyl label experiment. In forage, TRR were 0.16 to 0.5 mg eq./kg, mostly as MNBA (13 to 24% TRR; 0.04 to 0.06 mg eq./kg); mesotrione and its 4 and 5-hydroxy metabolite accounted for up to 14.6% TRR each (0.01 to 0.08 mg eq./kg). In hay, TRR ranged from 0.14 mg/kg eq (T1) to 2 mg eq./kg (T2), mostly MNBA (up to 20% TRR) and 4/5-hydroxy-mesotrione (up to 16% TRR); mesotrione accounted for up to 9% TRR. AMBA was only detected in T2 hay (0.055 mg eq./kg; 2.7% TRR). Residues in soya bean seed ranged from 0.052 to 0.104 mg eq./kg, with mesotrione and 4/5-hydroxy-mesotrione the main compounds identified (< 10% TRR). Low levels of MNBA and AMBA were found in the T1 and T2 samples (< 5% TRR, 0.005 mg eq./kg).

Results from the cyclohexane experiment showed mesotrione accounting for up to 18% TRR in forage, 8.2% TRR in hay and 5.1% TRR in seed (0.02 mg eq./kg). 4 and 5-hydroxy-mesotrione accounted for up to 19% TRR in forage and hay, and 7% TRR in seeds.

Three studies were conducted with maize, two with [phenyl-U-^{14}C]-mesotrione and/or one with [cyclohexane-2-^{14}C]–mesotrione. In all cases, the compound was applied to the soil surface after planting the seeds at a rate of 0.3 kg ai/ha (pre-emergence; T1) or post-emergence at 0.16–0.18 kg ai/ha, 28 days after planting (T2).

Results from the phenyl label experiments showed higher total residues in fodder/stover (0.8 to 1.1 mg eq./kg) and forage (0.244 to 0.356 mg eq./kg). Over 60% of the residues in fodder were not extracted with ACN/water. In T1 forage, MNBA and AMBA were the major residues (up to 19.7 and 12.2% TRR, respectively). In fodder, AMBA was the major residue (up to 28% TRR in T2). 4-hydroxy-mesotrione was mainly present in forage (up to 8% TRR, about 50% conjugated). Mesotrione was a minor component of the residues in all cases, present at a higher level in T1 forage samples (2.2% TRR, 0.008 mg eq./kg). TRR in grain was 0.01 mg/kg eq, and was not further characterized.

In the cyclohexane experiment, TRR reached 0.1 mg eq./kg in forage and 0.33 mg eq./kg in fodder. In forage, the identified residues were mesotrione (up to 3% TRR) and 4-hydroxy-mesotrione (up to 10% TRR). About 18% TRR was incorporated into lignin and cellulose. Residues in grain were low (up to 0.011 mg eq./kg) and were not be further characterized.

Rice plants were treated at the 2–3 leaf stage with [phenyl-U-^{14}C]-mesotrione added directly to the paddy water at either 0.09 kg ai/ha (1×) or 0.225 kg ai/ha (2.5×). TRRs were higher in whole tops and straw (0.03 to 0.06 mg eq./kg at 1×), with 60–71% extracted by ACN/water. Residues in grain and husk (109 DAT) reached 0.01 mg eq./kg, about 33% being extracted (acid released up to 75.1% TRR in grain). Immature whole tops from 1x rate contained mesotrione and 5-hydroxy-mesotrione at up to 0.01 mg/kg eq. each (11 to 15% TRR), and traces of MNBA and AMBA (< 5% TRR from 1×). In 1× stalk and straw, mesotrione and its metabolites represented < 10% TRR each. No characterization was performed in grain. Residues from 2.5× samples were 2–5 times higher (0.02 mg eq./kg in grain).

[Phenyl-U-^{14}C] or [cyclohexane-2-^{14}C]-mesotrione were applied to the soil surface after planting peanut seed (pre-emergence) at 0.3 (T1) or 0.8 kg ai/ha (T2). Peanut foliage was harvested 90 DAT (50% maturity), mature peanuts and peanut hay at 153 DAT. Residues from [phenyl-U-^{14}C] treatment were higher in foliage (0.028 and 0.064 mg eq./kg, in T1 and T2, respectively) and approximately 0.01 mg eq./kg in hay, hull and nutmeat. Traces of MNBA, MBA, AMBA and 4-hydroxy-misotrione were found in hay (< 6% TRR, ≤ 0.002 mg eq./kg), but only AMBA was found in nutmeat (up to 15% TRR, 0.002 mg eq./kg, in T1). TRR from [cyclohexane-2-^{14}C] treatment were ≤ 0.01 mg eq./kg in T1 samples ranged from 0.01 to 0.02 mg eq./kg in T2. 4-hydroxy-mesotrione was only identified in hulls (7% TRR). The peanut oil fraction was shown to be composed primarily of ^{14}C-labelled neutral lipids.

In summary, the metabolic pathway of mesotrione following pre- and/or post-emergence foliar applications in cranberries, maize, rice, peanut and tolerant soya bean are similar. It proceeds via cleavage of the parent molecule to yield MNBA and reduction to AMBA, which either conjugated or degraded to MBA. Mesotrione is also hydroxylated in the cyclohexane-dione ring to give 4 or 5-hydroxy-mesotrione. Incorporation of radioactive residues into natural products (lignin cellulose sugar or lipid) was seen in all crops, except cranberry fruit. Residues in cranberry fruits were mostly mesotrione and AMBA (over 20% TRR each). Maize, soya and rice feed commodities contained mostly MNBA and AMBA (> 10% TRR in most cases). Residues in grains were low and mesotrione only represented higher than 10% TRR in tolerant soya bean seed.

Environment fate

The photolysis of [phenyl-^{14}C] mesotrione and [cyclohexane-^{l4}C]-mesotrione was studied in silt loam soil treated at 0.3 kg ai/ha and incubated in local sunlight (latitude 37° 56') at 20 to 24°C. About half of the radioactivity was present as mesotrione at 12–13 DAT. MNBA and AMBA accounted for 2-8% TRR at 5 DAT, increasing up to 8% TRR at 30 DAT.

The metabolism of [phenyl-2-^{14}C] or [cyclohexane-^{l4}C]-mesotrione applied to various soils at rates ranging from 0.165 to 0.85 kg ai/ha and kept under aerobic conditions in the dark at 25±1°C for 28 to 60 days was investigated. Mesotrione degrades relatively fast, with DT_{50} values ranging from 4.5 to 32 days. DT_{50} for MNBA was < 2 days in these studies.

In two water sediment systems experiments conducted with either [phenyl-2-^{14}C] or [cyclohexane-^{l4}C]-mesotrione at 0.20 kg ai/ha and incubated in the dark for 101 days, showed DT_{50} were from 3 to 6 days, with mesotrione in the sediment never exceeding 4% AR. MNBA and AMBA were found in both water and sediment, starting at day 3.

The aerobic degradation of [phenyl-2-^{14}C]-AMBA was studied in soils incubated up to 60 days in the dark, showing DT_{50} ranging from 2 to 6 days.

Field studies

In six studies conducted with soils collected from different regions of Europe, mesotrione was applied at 0.15–0.2 kg ai/ha. MNBA and AMBA were detected at 6 DAT in 0–10 cm horizon (0.031 and 0.006 mg eq./kg, respectively). No residues of mesotrione or metabolites were detected in the soil below 10 cm. DT_{50} ranged from 2 to 8 days.

In one study conducted with four soils from England and USA treated with MNBA at 0.22 kg ai/ha, DT_{50} ranged from 0.6 to 10.6 days.

Confined rotational crops

Endive, radish and wheat were sown 120 days after a sandy loam soil being treated with [phenyl-U-^{14}C] or [cyclohexane-2-^{14}C]-mesotrione at 0.165 kg ai/ha. Endive was harvested at 78–63 days after planting (DAP), radish roots and leaves at 56 DAP, wheat forage at 22 DAP, wheat hay at 57 DAP and wheat grain and straw at 134–131 DAP. In the [phenyl-U-^{14}C] experiment, residues in soil declined to 34% of the applied radioactivity (AR) at 120 DAT, with the most abundant metabolites being MNBA (8% AR) and AMBA (2% AR); mesotrione accounted for only 0.1% AR. TRR were

0.02 to 0.04 mg eq./kg in wheat forage, hay and straw, mostly MNBA (0.011 mg eq./kg in forage). Residues were 0.006 mg eq./kg in wheat grain, 0.014 mg eq./kg in endive and 0.004 mg eq./kg in radish root and leaves. TRR in all cyclohexane-2-^{14}C samples were < 0.005 mg eq./kg in endive, and wheat straw, and were not further characterized.

[Phenyl-U-^{14}C] or [cyclohexane-2-^{14}C]-mesotrione was applied at 0.308 kg ai/ha (T1, characteristic of pre-emergence) and 0.462 kg ai/ha (T2, characteristic of pre + post-emergence) onto a sandy loam soil, and wheat, soya, endive or radish planted at 30, 120 and/or 300 DAT. Residues in soil declined to 27% AR at 300 DAT. Residues in wheat commodities from the [phenyl-U-^{14}C] experiment were higher in straw (2.58 mg eq./kg at 30 DAT, T1). In wheat grain, residues were 0.038 mg eq./kg at 30 DAT (T1) and 0.014–0.015 mg eq./kg at 120 and 300 DAT (T2). At 30 DAT (T1), the major identified metabolite was MNBA, with residues ranging from 0.17 to 0.63 mg eq./kg in wheat forage, hay and straw and 0.003 mg eq./kg in grain. AMBA was mostly present as sulphate conjugate (total of 0.67 mg eq./kg in straw), and mesotrione and its 4-OH metabolite were only detected in forage (0.01 mg eq./kg).

At 30 DAT (T1), residues were 0.145 mg eq./kg in soya bean, and 0.46–0.64 mg eq./kg in soya feed. MNBA was 0.17–0.31 mg eq./kg in forage and hay and 0.014 mg eq./kg in soya bean. AMBA levels were 0.02-0.07 mg eq./kg Residues in endive and radish ranged from 0.037 to 0.053 mg eq./kg at 120 DAT, declining to 0.005 to 0.019 mg eq./kg at 300 DAT (T2). The major residue was MNBA (0.02 mg eq./kg at 120 DAT, T2, in endive and radish tops).

Highest residues from [cyclohexane-2-^{14}C] experiment were found at 30 DAT, T1: 0.05 - 0.06 mg eq./kg in wheat feed, 0.01 mg eq./kg in wheat grain, and 0.02–0.03 mg eq./kg in soya bean samples. Residues in endive and radish were < 0.01 mg eq./kg Mesotrione and 4-hydroxy mesotrione were identified in wheat and soya bean feed (< 0.01 mg eq./kg at 30 DAT, T1).

In summary, mesotrione degrades quickly in soil under aerobic conditions. Although mesotrione is relatively stable to hydrolysis at pH 5–9 (less than 10% degradation after 30 days at 25 °C), it degrades rapidly in flooded systems with a half-life of approximately 4 days. Mesotrione metabolites, mainly MNBA, are expected in wheat and soya bean feed, endive and radish root when the crops are planted up to 120 days after the soil is treated with mesotrione at 0.3 kg ai/ha rate or higher. As currently the compound is used at rates lower than 0.3 kg ai/ha, no residues arriving from the use of mesotrione are expected in rotational crops.

Methods of analysis

Mesotrione residues in vegetable crops may be analysed by LC-MS/MS (negative mode, m/z=338 → 291) after extraction with acetonitrile/water and cleaned up by SPE. Recovery data for mesotrione in maize commodities and cranberries showed good performance (84–114% recovery, 3–21% RSD, n=3–6) at the 0.01 mg/kg (LOQ) to 10 mg/kg range. The method was used in various supervised trials, with recovery data for mesotrione and MNBA within the acceptable levels at the LOQ or higher.

A modified QuEChERS LC-MS/MS multi-residue method (no clean up with primary-secondary amine (PSA) is used) was validated for mesotrione in oranges, maize and oilseed rape, with a LOQ of 0.01 mg/kg.

In a reversed-phase HPLC-fluorescence method, mesotrione and MNBA residues are extracted with acetonitrile:water (1:1) and cleaned up on silica SPE. The extract is submitted to reversed phase HPLC, the mesotrione fraction converted to MNBA with H_2O_2 and reduced to AMBA using acidic $SnCl_2$ and the MNBA fraction reduced to AMBA. Each fraction is cleaned-up by C18 SPE, and the AMBA conversion product quantified by HPLC-fluorescence. The method was validated for corn commodities with a LOQ of 0.01 mg/kg.

In a GC-MS method, mesotrione and MNBA residues are extracted from corn commodities with acetonitrile:water (1:1), acidified, partitioned with methylene chloride, which is evaporated and the residue heated with Jones Reagent (Cr^{VI} oxide acid solution) to oxidize mesotrione to MNBA. The total MNBA is extracted with ethyl acetate, evaporated to dryness, and the residue reacted with 2-

iodopropane and potassium carbonate to form isopropyl ester of MNBA for analyse by GC-MS. The method determines both mesotrione and MNBA at a combined LOQ of 0.01 mg/kg.

The acetonitrile:water (1:1) extraction efficiency was radio-validated using incurred radioactive residues in forage. After extraction using a high speed homogeniser, an aliquot was partitioned three times into ethyl acetate, and residues of mesotrione and MNBA quantified by TLC with storage-phosphor autoradiography. Levels of mesotrione and MNBA in forage were similar to the results obtained after exhaustive extraction within the metabolism study.

Mesotrione and MNBA residues are extracted from milk and eggs with acetone and from animal tissues with an acetone:water, the extract acidified, partitioned into methylene chloride, and residues of mesotrione oxidised to MNBA using H_2O_2. MNBA is reduced with acidic $SnCl_2$ and AMBA determined by reversed phase HPLC-fluorescence detection. The LOQ was 0.01 mg/kg in all matrices. Mesotrione may also be determined in animal matrices using the modified QuEChERS, excluding PSA, at an LOQ of 0.01 mg/kg.

The analytical methods were considered fit for purpose to determine mesotrione alone or in combination with MNBA in plant and animal commodities at a LOQ of 0.01 mg/kg.

Stability under frozen conditions

Residues of mesotrione and/or MNBA in fortified samples of maize commodities, radish root, and soya bean seed at 0.1 mg/kg were stable under frozen conditions for at least 32 months (at least 80% of the residues remained, quantified as AMBA by HPLC-FL). Samples of blueberry, asparagus, sugarcane and okra fortified with mesotrione at 1.0 mg/kg were shown to be stable for at least 13 months when stored frozen (quantified by HPLC-MS/MS). The residue trials reports also include additional information on storage stability, and the samples were stored within the period that guaranteed the integrity of the residues at the time of analysis.

Definition of the residue

Metabolism studies conducted in cow, swine and poultry fed with ^{14}C mesotrione at 6 to 11 ppm showed higher residues in liver and kidney, and ranged from 0.01 to 0.08 mg eq./kg in muscle, milk and in eggs. When detected, mesotrione was the main residue found in animal commodities, accounting for up to 18% TRR in cow liver and kidney, at least 70% TRR in tissues of swine and poultry, and up to 80% TRR in egg white. When cow was fed with ^{14}C AMBA, residues reached a maximum of 0.05 mg eq./kg in kidney and fat, with over 60% as AMBA. Residues in other tissues and in milk were < 0.01 mg eq./kg

The Meeting agreed that the residue definition of mesotrione in animal commodities for enforcement and dietary exposure assessment is mesotrione.

The residues do not concentrate in fat and mesotrione has a log P_{ow} of 0.1, confirming that mesotrione is not fat soluble.

Mesotrione is a herbicide that can be applied to the soil pre and/or post emergence of the plant, with exception of cranberry, for which the use is foliar. The compound is rapidly degraded in soil. Metabolism study showed residues in cranberry fruits mostly as mesotrione (over 60% TRR) and AMBA (over 20% TRR). Metabolism studies conducted in tolerant soya bean, maize, rice and peanut showed higher residues in feed commodities, mostly as mesotrione (up to 28% TRR in rice tops), MNBA (up to 24% TRR in soya bean forage) and AMBA (up to 29% TRR in maize fodder). Total residues in edible commodities were low (≤ 0.03 mg eq./kg) and when characterized, showed mesotrione as the main residue.

The Meeting concluded that MNBA and AMBA appear to be of low toxicological concern. When the information was available, MNBA was not detected in any sample from the residue trials.

The Meeting agreed that mesotrione is an adequate marker for the uses of mesotrione in plants and is suitable for dietary intake assessment

The Meeting agreed in the following residue definition for both plant and animal commodities for enforcement and dietary risk assessment: *Mesotrione*

The residues are not fat soluble.

Residues of supervised residue trials on crops

Cranberry

GAP in USA for cranberries is 2 broadcast foliar applications at 0.28 kg ai/ha, PHI 45 days. In five trials using 2 applications, the first being at 0.388 kg ai/ha, residues were: < 0.01 mg/kg (5), indicating that no residues are expected when the product is applied at the GAP rate.

The Meeting agreed to recommend a maximum residue level of 0.01* mg/kg, and a STMR of 0 mg/kg for mesotrione in cranberries

Bush berries and cane berries

GAP in USA for bush and cane berries is 1 post-direct spray at 0.21 kg ai/ha before bloom, with no PHI specified.

In one trial conducted in blueberry in USA according to GAP (application at BBCH 59), residues were < 0.01 mg/kg (77 DAT). In five other trials where the application was done after bloom residues at 32 to 88 DAT were < 0.01 mg/kg.

In four trials conducted with raspberry at GAP, residues at 32 to 88 DAT where < 0.01 mg/kg (4) at 52 to 83 DAT.

As no residues above the LOQ were found even in the late application trials, the Meeting agreed to estimate a maximum residue level of 0.01* mg/kg and a STMR of 0 mg/kg for bush berries and cane berries

Okra

In USA, mesotrione can be applied either at pre-emergence (0.21 kg ai/ha) or post emergence (0.105 kg ai/ha). PHI in both cases is 28 days. Five post-emergence trials conducted according to GAP gave residues < 0.01 mg/kg (5).

The Meeting agreed to recommend a maximum residue level of 0.01* mg/kg, and a STMR of 0.01 mg/kg for mesotrione in okra.

Sweet corn

Mesotrione is registered in Germany for post-emergence use on sweet-corn (BBCH 12–18) at 0.15 kg ai/ha. In four trials conducted in France at this GAP rate gave residues were: < 0.01 mg/kg (4) in the kernels and in the cob at 38 to 61 DAT.

In USA, mesotrione can be used in sweet corn via three application regimes: 1) one pre-emergence application at 0.27 kg ai/ha, 2) two post emergence applications, with a maximum of 0.21 kg ai/ha; or 3) 1× pre + 1× post emergence, with a maximum of 0.27 kg ai/ha. In all cases, the PHI is 45 days. The second application should be done up to the 8 leaf stage. In one trial, conducted according to regime 2, residues in the ears were: < 0.01 mg/kg (2); other two trials conducted at the same rate residue were the same 28 to 32 DAT. In 12 trials conducted a higher rate (0.48 to 0.50 kg ai/ha; regimes 1 or 2 residues were: < 0.01 mg/kg from 23 to 36 DAT.

Although only one trial was conducted in USA according to GAP, 14 trials conducted at higher rates and/or lower PHI showed that no residues are expected in the ears of sweet corn after treatment according to GAP.

The Meeting agreed to estimate a maximum residue level of 0.01* mg/kg and a STMR of 0 mg/kg for mesotrione in sweet corn (kernels plus cob without husk).

Soya bean, dry

In USA, GAP for mesotrione in conventional soya is one pre-emergence application at 0.21 kg ai/ha, with no PHI specified. In 20 trials conducted according to GAP, residues at 117 to 174 DAT were < 0.01 mg/kg (20). Three trials conducted at higher rates (0.6–1 kg ai/ha) gave the same results.

GAPs for mesotrione tolerant soya are i) one pre-emergence or ii) early post-mergence (up to BBCH 13) application at 0.225 kg ai/ha, or iii) one pre + one post emergence application (BBCH 14–60) at 0.225 kg ai/ha and 0.125 kg ai/ha, respectively. Forty seven trials were conducted with tolerant soya using application using regimes 2 or 3, residues in the mature seeds were: < 0.01 (44) and 0.02 (3) mg/kg.

Using the data from trials conducted in tolerant crops, the Meeting agreed to estimate a maximum residue level of 0.03 mg/kg and a STMR of 0.01 mg/kg for mesotrione in soya bean, dry.

Asparagus

In the USA, mesotrione can be use in asparagus either as a pre-emergence application on the soil surface at 0.27 kg ai/ha in the spring prior to spear emergence, one application after completion of harvesting directed to the weed at 0.105 kg ai/ha, or both at a maximum of 0.27 kg ai/ha. In eight trials conducted in USA using the pre-emergence GAP, residues at 8 to 18 DAT were < 0.01 mg/kg (8). In 16 other trials the application was done after emergence of the plant.

The Meeting agreed to estimate a maximum residue level of 0.01*mg/kg and a STMR of 0.01 mg/kg for mesotrione in asparagus.

Rhubarb

In USA, mesotrione can be use in rhubarb as pre-emergence application on the soil surface prior to any spring green-up at 0.21 kg ai/ha and 21 days PHI. In four trials conducted at GAP rate, residues at 28 to 42 DAT were < 0.01 mg/kg. Four trials were conducted at higher rates and gave the same result.

As the PHI is not relevant to a pre-emergence application, the Meeting agreed to estimate maximum residue level of 0.01* mg/kg and a STMR of 0.01 mg/kg for mesotrione in rhubarb.

Maize

Mesotrione is registered in Germany for post-emergence use on maize (BBCH 12–18) at 0.15 kg ai/ha. In two trials conducted in Germany and UK at this GAP gave results at 112 to 143 DAT of < 0.01 mg/kg (2).

In the USA, mesotrione can be used in maize in three application regimes: 1) one pre-emergence at 0.27 kg ai/ha, 2) two post emergence, with a maximum of 0.21 kg ai/ha; or 3) 1× pre + 1× post emergence, with a maximum of 0.27 kg ai/ha. The second application should be done up to the 8 leaf stage. In all cases, the PHI was 45 days. Eight trials were conducted in Canada and the USA using regime 1 and 32 trials using regime 3 at rates higher than USA GAP. Grain harvested at 68 to 145 DAT gave residues < 0.01 mg/kg.

The results from North American trials conducted at higher rate show that no residues are expected in maize grain after treatment according to GAP.

The Meeting agreed to estimate a maximum residue level of 0.01*mg/kg and a STMR of 0 mg/kg for mesotrione in maize grain.

Millet

Mesotrione is registered in the USA as one pre-emergence use at 0.21 kg ai/ha, and no PHI specified. In five trials conducted according to GAP residues were: < 0.01 mg/kg (5) in millet grain (84 to 132 DAT).

With the support from the data from other cereals, the Meeting agreed to estimate a maximum residue level of 0.01*mg/kg and a STMR of 0 mg/kg for mesotrione in millet grain.

Oat

Mesotrione is registered in USA either as one pre-emergence use at 0.21 kg ai/ha or as a post-emergence application at 0.105 kg ai/ha. PHI is 50 days. In sixteen post-emergence trials conducted at GAP, residues in oat grain were < 0.01 mg/kg (16). Two trials conducted at up to 5 times the rate gave the same results.

The Meeting agreed to estimate a maximum residue level of 0.01*mg/kg and a STMR of 0 mg/kg for mesotrione in oat grain.

Rice

Mesotrione is registered in paddy rice in Republic of Korea as post-planting into the water (5–7 days after transplanting) at 1×0.09 kg ai/ha and no PHI specified. Ten trials were conducted in Republic of Korea and Japan using either a single application at higher rate, two applications at the GAP rate and/or applying latter in the season. In all cases, residues at 45 to 140 DAT were < 0.01 mg/kg. Although the trials were not according to GAP, these results indicate that no mesotrione residues are expected when the product is used according to GAP.

The Meeting agreed to estimate a maximum residue level of 0.01*mg/kg and a STMR of 0 mg/kg for mesotrione in rice grain, husked.

Sorghum

The registered use for mesotrione in sorghum in the USA is one pre-emergence application at 0.224 kg ai/ha up to 21 days before planting. In nine trials conducted according to GAP, residues at 78 to 134 DAT were < 0.01 mg/kg (9). Twelve post-emergence trials gave the same results.

The Meeting agreed to estimate a maximum residue level of 0.01*mg/kg and a STMR of 0 mg/kg for mesotrione in sorghum.

Sugar cane

The GAP for mesotrione in sugarcane in the USA is either two post-emergence applications at 0.10 kg ai/ha to the base of the sugar cane or a combination of one pre- and one post-emergence application not exceeding a total rate of 0.36 kg ai/ha. PHI is 114 days. In twenty four trials conducted according to either of the GAPs in USA gave residues of < 0.01 mg/kg (24) from 30 to 118 DAT. Two trials conducted at 3 or 5× the rate gave the same results within 114 days PHI.

In South Africa, GAP is a single early post-emergence at 0.15 kg ai/ha, and 181 days PHI. In four trials conducted at higher rate no residues were detected.

The Meeting agreed to estimate a maximum residue level of 0.01*mg/kg and a STMR of 0 mg/kg for mesotrione in sugar cane.

Linseed

Mesotrione is registered in the USA for linseed at one pre or one post-emergence application at 0.21 kg ai/ha, and no PHI specified. Five pre-emergence trials conducted according to GAP gave residues of < 0.01 mg/kg (5). Two post-emergent trials conducted at higher rates gave the same result.

The Meeting agreed to estimate a maximum residue level of 0.01* mg/kg and a STMR of 0.01 mg/kg for mesotrione in linseed.

Animal feed

Forage

Mesotrione is registered in Germany for post-emergence use on maize (BBCH 12–18) at 0.15 kg ai/ha, and no PHI specified. In three trials conducted in maize in France, Germany and the UK matching German GAP, residues in stover (remaining plant) at 41–47 DAT were 0.01 mg/kg (3).

In the USA, mesotrione can be used in maize under three application regimes: 1) one pre-emergence at 0.27 kg ai/ha; 2) two post emergence, with a maximum of 0.21 kg ai/ha; or 3) 1× pre + 1× post emergence, with a maximum of 0.27 kg ai/ha. In all cases, PHI was 45 days for forage and stover. The second application should be made up to the 8 leaf stage (or BBCH 19).

In one trial conducted in USA according to GAP, residues in maize forage were 0.12 mg/kg.

Mesotrione is registered in USA in millet as one pre-emergence use at 0.21 kg ai/ha. In five trials conducted at GAP, residues in forage were < 0.01 mg/kg (5).

The Meeting estimated a median residue and a highest residue of 0.01 mg/kg for mesotrione in millet forage

Mesotrione is registered in oats in USA either as one pre-emergence use at 0.21 kg ai/ha or as post-emergence application at 0.105 kg ai/ha. In 16 pre-emergence trials and 16 post-emergence US trials matching GAP, residues in oat forage were < 0.01 mg/kg (32).

The Meeting estimated a median residue and a highest residue of 0.01 mg/kg for mesotrione in oat forage.

The registered use for mesotrione in sorghum in USA is one pre-emergence application at 0.224 kg ai/ha up to 21 days before planting. In 13 trials conducted according to GAP, residues in sorghum forage were < 0.01 mg/kg (13).

The Meeting estimated a median residue and a highest residue of 0.01 mg/kg for mesotrione in sorghum forage.

Hay

In 16 pre-emergence trials and 16 post-emergence trials conducted in oats in USA, matching GAP, residues in oat hay were < 0.01 mg/kg (32). Post-emergence application trials gave the same results.

In five trials conducted in millet at GAP, residues in hay were < 0.01 mg/kg.

The Meeting estimated a median residue of 0.01 mg/kg and a highest residue of 0.01 mg/kg for mesotrione in oat hay and millet hay.

Straw

Mesotrione is registered in paddy rice in Korea as post-planting into the water (5–7 days after transplanting) at 1×0.09 kg ai/ha and no PHI specified. In eight trials conducted in Japan at this GAP gave residues in straw of < 0.002 mg/kg.

The Meeting agreed to estimate a maximum residue level of 0.01* mg/kg for mesotrione in rice straw and fodder, dry

The Meeting estimates a median residue and a highest residue of 0.01 mg/kg for mesotrione in rice straw

Fate of residues during processing

A processing study conducted with soya bean containing 0.04 mg/kg mesotrione showed residues of 0.01 mg/kg in the meal and 0.07 mg/kg in flour, with calculated processing factors of 0.25 and 1.8 mg/kg, respectively. Residues in soya oil, milk, tofu, sauce and miso were < 0.01 mg/kg, with an estimated processing factor of < 0.25. Based on a STMR of 0.01 mg/kg for soya bean, dry, the Meeting estimated a STMR-P of 0.018 mg/kg in soya bean flour, and of 0.002 mg/kg for soya oil, milk, tofu, sauce and miso.

Residue in animal commodities

Farm dietary burden

The Meeting estimated the dietary burden of mesotrione in farm animals on the basis of the OECD Animal Feed data published in the 2009 FAO Manual, and the median and highest residue levels estimated at the present Meeting for oat and sorghum forage, oat hay and rice straw.

The maximum and the mean dietary burden was 0.03 ppm for cattle, 0.01 and 0.001 ppm, for swine, respectively, and 0 ppm for poultry.

Animal commodity maximum residue level

No feeding study on mesotrione was provided to the Meeting. The metabolism study conducted with cattle at 10 ppm, gave residues of mesotrione up to 0.02 mg/kg in tissues and milk. Swine fed with radiolabeled mesotrione at 6 ppm gave residues of 1.5 mg/kg in liver, 0.09 mg/kg in kidney and 0.01 mg/kg in muscle. Interpolation of the residues found in the metabolism studies to what would be expected at the calculated dietary burden indicates that no residue will exceed 0.0025 mg/kg (in swine liver).

The Meeting agreed to estimate a maximum residue level of 0.01* mg/kg for mesotrione in milks, edible offal (mammalian) and meat (from mammals other than marine mammals).

The Meeting also estimated a STMR of 0 for mesotrione in milk and meat (from mammals other than marine mammals), and edible offal (mammalian).

Metabolism study conducted with poultry at 11 ppm showed mesotrione residues of 1.1 mg/kg in liver, 0.03 mg/kg in fat, < 0.01 mg/kg in meat and 0.02 mg/kg in eggs. As the dietary burden for poultry is 0, the Meeting agreed to estimate a maximum residue level of 0.01* mg/kg, and a STMR and a HR of 0 mg/kg for mesotrione poultry meat, poultry offal and eggs.

RECOMMENDATIONS

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

The residue is not fat soluble.

CCN	Commodity name	Maximum residue level (mg/kg)	STMR (P) (mg/kg)
VS 0621	Asparagus	0.01*	0.01
FB 2006	Bush berries	0.01*	0
FB 2005	Cane berries	0.01*	0
FB 0265	Cranberry	0.01*	0
MO 0105	Edible offal (mammalian)	0.01*	0
PE 0112	Eggs	0.01*	0
SO 0693	Linseed	0.01*	0.01
GC 0645	Maize	0.01*	0
MM 0095	Meat (from mammals other than marine mammals)	0.01*	0
GC 0646	Millet	0.01*	0
MI 0106	Milks	0.01*	0
GC 0647	Oat	0.01*	0
VO 0442	Okra	0.01*	0.01
PO 0111	Poultry, Edible offal of	0.01*	0
PM 0110	Poultry meat	0.01*	0
CM 0649	Rice, husked	0.01*	0
VS 0627	Rhubarb	0.01*	0.01
GC 0651	Sorghum	0.01*	0

VD 0541	Soya bean, dry	0.03	0.01
	Miso		0.002
	Soya flour		0.018
	Soya milk		0.002
	Soya oil		0.002
	Soya sauce		0.002
	Tofu		0.002
GS 0659	Sugarcane	0.01*	0
VO 0447	Sweet corn (kernels plus cob without husk)	0.01*	0

Animal Feed items

	Median residue, mg/kg	Highest residue, mg/kg
Millet forage	0.01	0.01
Oat forage	0.01	0.01
Sorghum forage	0.01	0.01
Millet hay	0.01	0.01
Oat hay	0.01	0.01
Rice straw	0.01	0.01

DIETARY RISK ASSESSMENT

Long-term intake

The IEDI of mesotrione based on the STMRs estimated by this Meeting for the 17 GEMS/Food regional diets were 0% of the maximum ADI of 0–0.3 mg/kg bw (see Annex 3 of the 2014 Report). The Meeting concluded that the long-term dietary intake of residues of mesotrione is unlikely to present a public health concern.

Short-term intake

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

REFERENCES

Code	Author(s)	Year	Title, Institute, Report reference
RR95-077B	Goodman, M	1996	Physical and Chemical Properties of Pure Material. Study no. WRC-95-122. GLP; Unpublished. 16 April, 1996
RR96-004B	Goodman, M	1996	Physical and Chemical Properties of Technical Material. Study no. WRC-96-006. WINO 15412. GLP; Unpublished. 26 April, 1996
RJ1776B	Miles, PO and Powell, S	1995	Aqueous Hydrolysis in pH 4. 5. 7 and 9 Solutions at 25 °C and 50 °C. Study no. 94JH098. GLP; Unpublished. 21 August, 1995
RR94-071B	Eya, BK	1995	[Carbonyl-^{13}C][phenyl-U-^{14}C] and [cyclohexane-2-^{14}C]—Aqueous photolysis. Study no. PMS-392. GLP; Unpublished. 19 October, 1995
RJ1778B	Young, AA and Skidmore, MW	1995	^{14}C-Phenyl labelled: Metabolism in hens following dosing at 10 mg/kg in the diet—Nature of the residues in eggs and tissues. Study no. 94JH094. GLP; Unpublished. 5 July, 1995
RJ2071B	Grout, SJ	1996	^{14}C-Cyclohexanedione labelled: Metabolism in hens following dosing at 10 mg/kg in the diet—Nature of the residues in eggs and tissues. Study no. 94JH114. GLP; Unpublished. 17 April, 1996
RJ1890B	Powell, SP and Marples J	1996	^{14}C-Phenyl labelled: Metabolism in a Cow Following Dosing at a Nominal Rate of 10 mg kg-1 in the Diet—Nature of the Residue in Milk and Tissues. Study no. 94JH148. GLP; Unpublished. 2 October, 1996
RJ1830B	Hand, LH	1995	[^{14}C-Cyclohexanedione]-:Metabolism in the Dairy Cow Following Dosing at 10 mg kg-1 in the Diet. Study no. 94JH100 GLP; Unpublished. 14 August, 1995

Code	Author(s)	Year	Title, Institute, Report reference
RJ2309B	Hand, LH	1997	AMBA: Metabolism of orally administered multiple dose in lactating cow. Study no. 96JH251. GLP; Unpublished.1 September. 1997
T020371-04	Brown, K	2006	[Phenyl-U-^{14}C] Mesotrione: Nature of the Residue in Swine. Study no. T020371-04. GLP; Unpublished. 04 October, 2006
1286-01	Ray, WJ	2005	Mesotrione: Nature of the Residue in Cranberries. Study no. T014117-04. GLP; Unpublished. 16 December, 2005
RR 96-007B	Tarr, JB and Van Neste, L	1997	[Phenyl-U-^{14}C]: Nature of the Residue in Corn. Study no. PMS 391. GLP; Unpublished. 14 January, 1997
RR 99-006B	Vispetto, A and Smith, C	1999	[Phenyl-U-^{14}C]—Nature of the Residue in Corn [Zea Mays] after pre-emergence and post-emergence application. Study no. PMS 447. GLP; Unpublished. 29 September, 1999
RR 96-026B	Wei, Y and Dohn, DR	1997	[Cyclohexane-2-^{14}C]: Nature of the Residue in Corn (Zea mays). Study no. RR 96-026B. GLP; Unpublished. 2 January, 1997
RJ3738B	Humphries, M, Evans, J and DHL	2005	Mesotrione: Metabolism in Rice. Study no. 03JH032. GLP; Unpublished. 24th November, 2005
1286-01	Brown, K	2003	[Phenyl-U-^{14}C] Mesotrione: Nature of the Residue in Peanuts. Study no. 1286-01. GLP; Unpublished. 29 August, 2003
1287-01	Brumback, D	2003	[Cyclohexane-2-^{14}C] Mesotrione: Nature of the Residue in Peanuts. Study no. 1287-01. GLP; Unpublished. 29 August, 2003
RR 96-084B	Gorder, GW, Cheung, AC, Bowler, DT and Schwab, G	1997	[Phenyl-U-^{14}C]: Confined Accumulation Studies on Rotational Crops—Low Rate. Study no. WRC-96-126. GLP; Unpublished. 17 March, 1997
RR 96-035B	Gorder, GW, Cheung, AC, Bowler, DT and Schwab, G	1996	[Phenyl-U-^{14}C]: Confined Accumulation Studies on Rotational Crops—High Rate. Study no. WRC-96-053. GLP; Unpublished. 10 December, 1996
RR 95-042B	Spillner, C, Bowler, D and Diaz, D	1997	[Cyclohexane-2-^{14}C]: Confined Accumulation Studies on Rotational Crops—Low Rate. Study no. WRC-95-067. GLP; Unpublished. 18 March, 1997
RR 96-005B	Spillner, C, Bowler, D and Diaz, D	1996	[Cyclohexane-2-^{14}C]: Confined Accumulation Studies on Rotational Crops—High Rate. Study no. WRC-95-007. GLP; Unpublished. 26 November, 1996
RR95-047B ADD	Vispetto, AR and Tovshteyn, M	1997	Addendum to: [Cyclohexane-2-^{14}C]. Aerobic Soil Metabolism Study. Zeneca Agrochemicals. Report No: RR95-047B ADD. GLP; Unpublished, 1997
RR95-082B	Subba-Rao, RV	1996	[Phenyl ^{14}C]. Aerobic Soil Metabolism Study. Zeneca Agrochemicals. Report No: RR95-082B. GLP; Unpublished, 1996
RR97-033B	Miller, MM	1997	[Phenyl-U-^{14}C]: Route and Rate of Degradation in Wisconsin Silt Loam Soil Under Aerobic Laboratory Conditions. Zeneca Agrochemicals. Report No: RR97-033B. GLP; Unpublished,1997
RR97-033B	Miller, MM	1997	[phenyl-U-^{14}C]: Route and Rate of Degradation in Wisconsin Silt Loam Soil Under Aerobic Laboratory Conditions. Zeneca Agrochemicals. Report No: RR97-033B. GLP; Unpublished,1997
RR95-048B	Vispetto, AR and Tovshteyn, M	1996	[Cyclohexane-2-^{14}C]. Anaerobic Aquatic Soil Metabolism. Zeneca Agrochemicals. Report No: RR95-048B. GLP; Unpublished, 1996
RR96-033B	Carley, SE	1996	[Phenyl-U-^{14}C] Anaerobic Aquatic Soil Metabolism. Zeneca Agrochemicals. Report No: RR96-033B. GLP; Unpublished, 1996
RR96-060B	Van Neste, L and Eya, BK	1996	[Carbonyl-13C][phenyl-U-^{14}C] and [cyclohexane-2-^{14}C]—Soil Photolysis. Zeneca Agrochemicals. Report No: RR96-060B. GLP; Unpublished, 1996
RIC6438	Eya, BK	1997	Calculation of the Soil Photolysis Half Life at 50°N. Zeneca Agrochemicals. Letter Report No: RIC6438. Non-GLP; Unpublished, 1997
RR96-099B	Miller, MM, and Wilson, WR	1997	[Phenyl-U-^{14}C]. Rate of Degradation in Three Soils Under Aerobic Laboratory Condition. Zeneca Agrochemicals. Report No: RR96-099B. GLP; Unpublished, 1997
RR93-092B	Tarr, JB	1997	[Phenyl-U-^{14}C]. Metabolism in Thirteen Soils Under Aerobic Conditions. Zeneca Agrochemicals. Report No: RR93-092B. GLP; Unpublished, 1997
RR97-053B	Tarr, JB and Tovshteyn, M	1997	Rates of Degradation in Surface Soils and Subsoils Under Aerobic Laboratory Condition. WRC-97-114. WINO 23764. Zeneca Agrochemicals. Report No: RR97-053B. GLP; Unpublished, 1997
RR 99-098B	Lay, MM and Peyton, C	2000	MNBA: Rate of Degradation in Soil Under Aerobic Laboratory Conditions. Zeneca Western Research Center. Report No. RR 99-098B. GLP; Unpublished. 2000

Code	Author(s)	Year	Title, Institute, Report reference
RR97-032B	Marth, JL	1997	[^{14}C]AMBA. a Metabolite of: Rate of Degradation in Soil Under Aerobic Laboratory Conditions. Zeneca Agrochemicals. Report No: RR97-032B. GLP; Unpublished, 1997
RR99-096B	Lay, MM	2000	[Phenyl-U-^{14}C]AMBA Rate of Degradation in Soil Under Aerobic Laboratory Conditions. Zeneca Western Research Center Report. No RR99-096B. GLP; Unpublished. 2000
RR97-026B	Graham, DG *et al.*	1997a	Field Soil Dissipation Study Carried Out in France During 1995-1996. Zeneca Agrochemicals. Report No: RR97-026B. GLP; Unpublished, 1997
RR97-025B	Graham, DG *et al.*	1997b	Field Dissipation Study Carried Out in Italy During 1995-1996. Zeneca Agrochemicals. Report No: RR97-025B. GLP; Unpublished, 1997
RR97-051B	Graham, DG *et al.*	1997b	Field Dissipation Study Carried Out in Germany During 1995-1996. Zeneca Agrochemicals. Report No: RR97-051B. GLP; Unpublished, 1997
RR97-067B	Graham, DG *et al.*	1998a	Field Dissipation Study Carried Out in Germany During 1996-1997. Zeneca Agrochemicals. Report No: RR97-067B. GLP; Unpublished, 1998
RR97-070B	Graham, DG *et al.*	1998b	Field Dissipation Study Carried Out in Italy During 1996-1997. Zeneca Agrochemicals. Report No: RR97-070B. GLP; Unpublished, 1998
RJ1776B	Miles, PD and Powell, S	1995	Aqueous Hydrolysis in pH 4. 5. 7 and 9 Solutions at 25 °C and 50 °C. Zeneca Agrochemicals. Report No: RJ1776B. GLP; Unpublished, 1995
RR94-071B	Eya, BK	1995	[Carbonyl-13C][phenyl-U- ^{14}C] and [cyclohexane-2-^{14}C]—Aqueous Photolysis. Zeneca Agrochemicals. Report No: RR94-071B. GLP; Unpublished. 1995
6439	Eya, BK	1997b	Calculation of the Water Photolysis Half Life at 50°N. Zeneca Agrochemicals. Letter Report RIC No: 6439. Not GLP; Unpublished, 1997b
RJ2724B	Cary, CA	1999	Degradation in Natural Water Sediment Systems under Laboratory Conditions (Final Report). Zeneca Agrochemicals. Report No. RJ2724B. GLP; Unpublished, 1999
2704-01	Crook, SJ	2002	Residue Analytical Method for the Determination of Residues of Mesotrione and 4-Methylsulfonyl)-2 Nitrobenzoic Acid (MNBA) in Crop Samples. Study no. 2704-0. GLP; Unpublished. 18 December, 2001
RJ3253B	Hill, S	2001	Mesotrione and MNBA; Validation of a Residue Analytical Method for the Determination of the Residues in Maize. Study no. RJ3253B. GLP; Unpublished. 12 December. 2001
RJ3253B	Salzman, FP	2005	Mesotrione: Magnitude of the Residue on Cranberry. IR-4 Project—Rutgers. The State University of New Jersey. IR-4 Project No. 08903. GLP; Unpublished, 2005
TMR0643B	Alferness, PL	1996	Liquid Chromatographic Determination with Fluorescence Detection of and 4-(Methylsulfonyl)-2-nitrobenzoic Acid in Crops after Conversion to 2-Amino-4-(methylsulfonyl)-benzoic Acid. Study no. TMR0643B. GLP; Unpublished, 1996
TMR0643B ADD	Alferness, PL	1997	Liquid Chromatographic Determination with Fluorescence Detection of and 4-(Methylsulfonyl)-2-nitrobenzoic Acid in Crops after Conversion to 2-Amino-4-(methylsulfonyl)-benzoic Acid. Study no. TMR0643B. GLP; Unpublished, 1997
RJ2149B	Bolygo, E	1996	Independent Laboratory Confirmation of an Analytical Method for Liquid Chromatographic Determination with Fluorescence Detection of and 4-(Methylsulfonyl)-2-nitrobenzoic Acid in Crops after Conversion to 2-Amino-4-(methylsulfonyl)-benzoic Acid. Study no. RJ2149B. GLP; Unpublished, 1996
TMR0689B	Meyers, TJ	1996	Determination of and its Metabolite in Corn by Gas Chromatography with Mass-Selective Detection. Study no. TMR0689B. GLP; Unpublished, 1997
TMR0882B	Alferness, PL	1999	Liquid Chromatographic Determination with Fluorescence Detection of and 4-(Methylsulfonyl)-2-nitrobenzoic Acid in Crops after Conversion to 2-Amino-4 (methylsulfonyl)-benzoic Acid. Study no. TMR0882B. GLP; Unpublished, 1999
RR 99-062-B	James, JW	1999	Independent Laboratory Validation of TMR0882B. Liquid Chromatographic Determination with Fluorescence Detection of and 4 (Methylsulfonyl)-2-nitrobenzoic Acid in Crops after Conversion to 2-Amino-4 (methylsulfonyl)-benzoic Acid. Study no. RR 99-062-B. GLP; Unpublished. 24 August, 1999
TMR0914B	Meyers, TJ	1999	Determination of in Milk. Eggs and Animal Products using Hydrogen Peroxide Oxidation Followed by Liquid Chromatography with Fluorescence Detection. Study no. TMR0914B. GLP; Unpublished, 17 August. 1999
RR00-005B	Brookey, F	2000	Independent Laboratory Validation of TMR0914B—Determination of in Milk. Eggs and Animal Products using Hydrogen Peroxide Oxidation Followed by Liquid Chromatography with Fluorescence Detection. Study no. RR00-005B GLP; Unpublished, 01 March. 2000
S12-03251	Watson, G	2013	Mesotrione—Validation of the QuEChERS Method for the Determination of Residues of Mesotrione in Crop Matrices by LC-MS/MS. Study no. S12-03251. GLP; Unpublished, 2013
S12-03250	Watson, G	2013	Mesotrione—Validation of the QuEChERS Method for the Determination of Residues of Mesotrione in Animal Matrices by LC-MS/MS. Study no. S12-03250 GLP; Unpublished, 2013

Code	Author(s)	Year	Title, Institute, Report reference
S12-04608	Bernal, J	2013	Mesotrione—Independent Laboratory Validation of the QuEChERS Method for the Determination of Residues of Mesotrione in Animal Matrices by LC-MS/MS, Eurofins Agroscience Services Chem SAS, 30310, Vergeze, France, Report no. S12-04608
RR 97-042B FIN	Wiebe, LA and Payton, CS	1997	ZA 1296: Stability of ZA 1296 and the Metabolite MNBA in Frozen Crops. GLP; Unpublished, 1997
T004813-05	Lin, K	2007	Mesotrione: Stability of Mesotrione Residues in Blueberry. Asparagus. Sugarcane and Okra under Freezer Storage Conditions. Syngenta Crop Protection. Inc. Study no. T004813-05. GLP; Unpublished, 2007
08903.05-CAR20	Salzman, FP	2005	Mesotrione: Magnitude of the Residue on Cranberry. IR-4 Project—Rutgers. The State University of New Jersey. Study no. 08903. GLP; Unpublished, 2005
T010288-04	Lin, K	2005	Mesotrione: Mesotrione—Magnitude of the Residues in or on Berry. Group 13. Syngenta Crop Protection. Inc. Study no. T010288-04. GLP; Unpublished, 2005
T021571-04	Lin, K	2006	Mesotrione: Mesotrione—Magnitude of the Residues in or on Okra. Syngenta Crop Protection. Inc. Study no. T010288-04. GLP; Unpublished. 8 December, 2006
T000920-09	Meyer, M	2011	Mesotrione: Mesotrione—Residue Study on Field Corn in Germany and the United Kingdom. Syngenta Crop Protection. Inc. Study no. T000920-09. GLP; Unpublished. 25 February., 2011
T000921-09	Meyer, M	2011	Mesotrione: Mesotrione—Residue Study on Field Corn in Spain and France (South) in 2009. Syngenta Crop Protection. Inc. Study no. T000920-09. GLP; Unpublished. 28 February, 2011
04-7012	Richards, S and Ely, SV	2005	Mesotrione: Residue Study in or on Sweet Corn in France (South). Syngenta Crop Protection. Inc. Study no. 04-7012. GLP; Unpublished. 19 January, 2004
03-7049	Richards, S	2004	Residue study with Mesotrione (ZA 1296) in or on Sweet Corn in France (South), Syngenta File No. ZA1296/1358, Syngenta Report No. 03-7049
03-7050	Richards, S	2004	Residue study with Mesotrione (ZA 1296) in or on Sweet Corn in France (South), Syngenta File No. ZA1296/1359, Syngenta Report No. 03-7050
487-01	Cobin, J	2002	Mesotrione: Magnitude of the Residues in or on Sweet Corn. Syngenta Crop Protection. Inc. Study no. 487-01. GLP; Unpublished. 27 March, 2002
T001589-08	Hampton, RE	2009	Mesotrione—Comparison of the Magnitude of the Residues in or on Sweet Corn after Application with the SC or WG Formulations. Morse Laboratories. Inc. Study no. ML08-1498-SYN. GLP; Unpublished. 16 January, 2009
T005595-06	Mäyer, TJ and Hampton, RE	2008	Mesotrione: Mesotrione—Magnitude of the Residues in or on Soya bean. Syngenta Crop Protection. Inc. Study no. T005595-06. GLP; Unpublished. 25 July. 2008
T000908-07	Oakes, T	2012	Mesotrione: Mesotrione SC (A12738A)—Magnitude of the Residues in or on Mesotrione Tolerant Soya bean. Syngenta Crop Protection. LLC. Study no. ML10-1620-SYN. GLP; Unpublished. 3 May, 2012
TK0112226	Oakes, T	2013	Mesotrione SC (A12738A)—Magnitude of the Residues in or on Mesotrione Tolerant Soya bean (Event SYHT0H2) USA 2012—Final Report Amendment 1. Study no. TK0112226. GLP; Unpublished. 16 October, 2013
T021572-04	Lin, K	2006	Mesotrione: Mesotrione—Magnitude of the Residues in or on Asparagus. Syngenta Crop Protection. Inc. Study no. T021572-04. GLP; Unpublished, 2006
T014372-05	Lin, K	2006	Mesotrione: Mesotrione—Magnitude of the Residues in or on Rhubarb. Syngenta Crop Protection. Inc. Study no. T014372-05. GLP; Unpublished, 2006
T000920-09-REG	Meyer, M	2011	Mesotrione—Residue Study on Field Corn in Germany and the United Kingdom in 2009. SGS Institut Fresenius GmbH. Study no. IF-09/01385983. GLP; Unpublished. 25 February, 2011
T000921-09-REG	Meyer, M	2011	Mesotrione—Residue Study on Field Corn in Spain and France (South) in 2009 SGS Institut Fresenius GmbH. Study no. IF-09/01392009. GLP; Unpublished. 28 February. 2011
RR 96-018B	Barnes, JP, Elvira, DJ and Wiebe, LA	1996	Residue Levels on Field Corn from Trials Carried out in The United States During 1995. Zeneca Inc. Study no. 1296-95-MR-01. WINO 12793. GLP; Unpublished, 1996
RR 97-043B	Barnes, JP, Dykstra, Nielsen, C and Wiebe, LA	1997	Residue Levels in Field Corn from Trials Carried out in Canada During 1996. Zeneca Inc. Study no. 1296-96-MR-01. WINO 19719. GLP; Unpublished, 1997
RR 97-035B	Miller, MM, Dykstra, Nielsen, C and Wiebe, LA	1998	Residue Levels in Field Corn from Trials Carried out in Canada During 1997. Zeneca Inc. Study no. 1296-97-MR-01. WINO 19720. GLP; Unpublished, 1998
1847-01	Cobin, J and Ediger, K	2002	Mesotrione—Magnitude of Residues in or on Field Corn. Syngenta Crop Protection. Inc. Study no. 1847-01. GLP; Unpublished. 28 February, 2002
T010289-04	Lin, K	2005	Mesotrione—Magnitude of the Residues in or on Millet. Syngenta Crop Protection. Inc. Study no. T010289-04. GLP; Unpublished. 15 December,2005

Code	Author(s)	Year	Title, Institute, Report reference
T004407-05	Lin, K	2006	Mesotrione—Magnitude of the Residues in or on Oats. including Processed Commodities. Syngenta Crop Protection. Inc. Study no. T004407-05. GLP; Unpublished. 13 December, 2006
A14928B_10000	Han, YH	2006	Mesotrione Residue Study on Rice in South Korea in 2005—Summary Report. Syngenta File No. A14928B_10000. non-GLP; Unpublished. 16 January, 2006
A13723B_10005	Odanaka, Y and Wakasone, Y	2005	Mesotrione Residue Study on Rice in Japan in 2005 (IET)—Summary Report. Syngenta File No. A13723B_10005. non-GLP; Unpublished. 03 October, 2005
A13723B_10004	Iwatani, M and Kato, T	2005	Mesotrione Residue Study on Rice in Japan in 2005 (SJKK)—Summary Report. Syngenta File No. A13723B_10004. non-GLP; Unpublished. 25 August, 2005
A13723B_10003	Odanaka,Y *et al.*	2007	Mesotrione Residue Study on Rice in Japan in 2007 (IET)—Summary Report. Syngenta File No. A13723B_10003. non-GLP; Unpublished. 26 March. 2007
A13723B_10002	Iwatani, M and Kato, T	2007	Mesotrione Residue Study on Rice in Japan in 2007 (SJKK)—Summary Report. Syngenta File No. A13723B_10002. non-GLP; Unpublished. 14 June. 2007
A13723B_10001	Odanaka, Y *et al.*	2008	Mesotrione Residue Study on Rice in Japan in 2008 (IET)—Summary Report. Syngenta File No. A13723B_10001. non-GLP; Unpublished. 26 February. 2008
A13723B_10000	Iwatani, M and Kato, T	2008	Mesotrione Residue Study on Rice in Japan in 2008 (Syngenta)—Summary Report. Syngenta File No. A13723B_10000. non-GLP; Unpublished, 2008
T020419-04	Lin, K	2006	Mesotrione—Magnitude of the Residues in or on Grain Sorghum. Syngenta Crop Protection. Inc. Study no. T020419-04. GLP; Unpublished. 13 December, 2006
T020420-04	Lin, K	2006	Mesotrione—Magnitude of the Residues in or on Sugarcane. Syngenta Crop Protection. Inc. Study no. T020420-04. GLP; Unpublished. 8 December, 2006
RJ3076B	With, B and Lubbe, GJJ	2000	Mesotrione—Residue Levels in Sugarcane from Trials conducted in South Africa during 1998—1999. Zeneca Agrochemicals. Study no. 1296-98-MR-02. GLP; Unpublished. 8 September, 2000
T010290-04	Lin, K	2005	Mesotrione—Magnitude of the Residues in or on Flax and Processed Commodities. Syngenta Crop Protection. Inc. Study no. T010290-04. GLP; Unpublished, 2005
943W	Dohn, D and Chu, J	2012	^{14}C-Mesotrione—Nature of the Residue in Herbicide Tolerant (HT) Soya beans. Report Number 1943W, Syngenta Crop Protection, Inc., Greensboro, NC 27419, USA. Syngenta File Number 1296/50531

METRAFENONE (278)

The first draft was prepared by Mr David Lunn, Food Safety Authority, Wellington, New Zealand

EXPLANATION

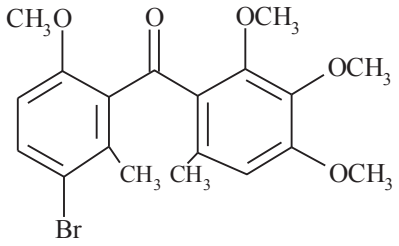
Metrafenone is a benzophenone fungicide, active mainly against powdery mildews and eyespot, inhibiting mycelium growth, leaf penetration, haustoria formation and sporulation.

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

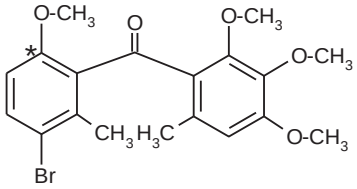
Formulations

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

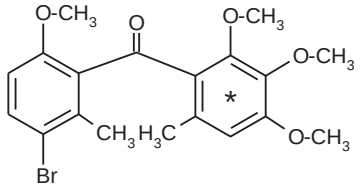
Formulation type	Active substance/s and content	Other active ingredients
SC (Soluble Concentrate)	Metrafenone 300 g/L Metrafenone 500 g/L Metrafenone 100 g/L	– – Epoxiconazole 83 g/L
SE (Suspo-emulsion)	Metrafenone 75 g/L	Fenpropimorph 200 g/L + Epoxiconazole 62.5 g/L

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:



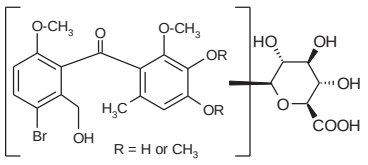
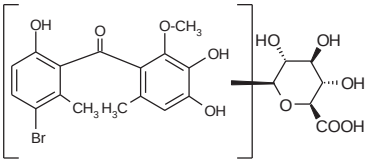
[Bromphenyl-6-^{14}C]-metrafenone
(Bromophenyl-label)
* = location of the radiolabel

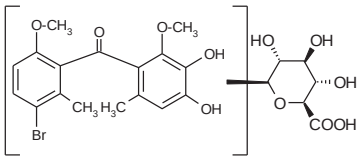
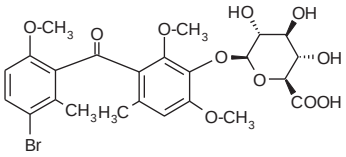
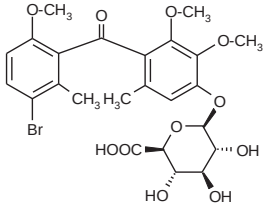
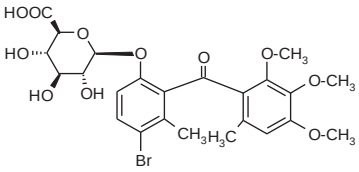
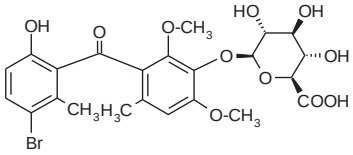
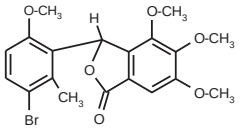
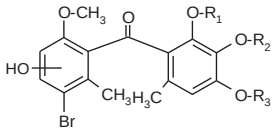
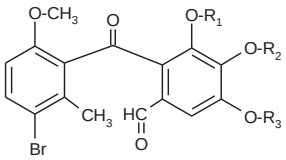
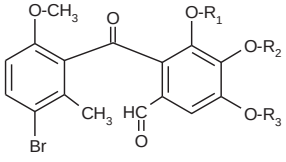


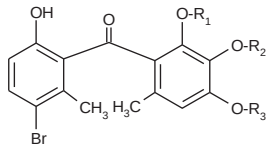
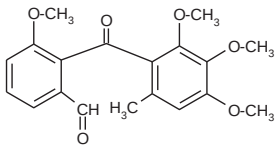
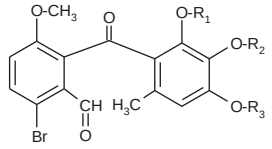
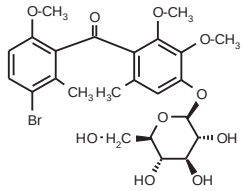
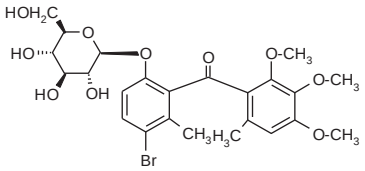
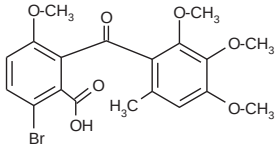
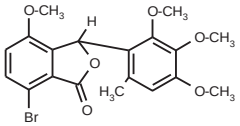
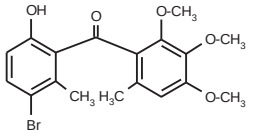
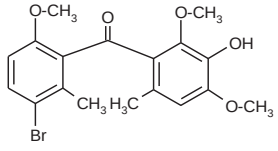
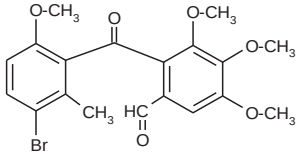
[Trimethoxyphenyl-U-^{14}C]-metrafenone
(Trimethoxyphenyl-label)
* = location of the radiolabel

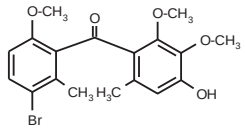
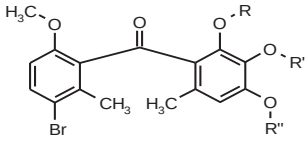
Major metabolites identified in these studies and discussed in this evaluation are listed below.

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.

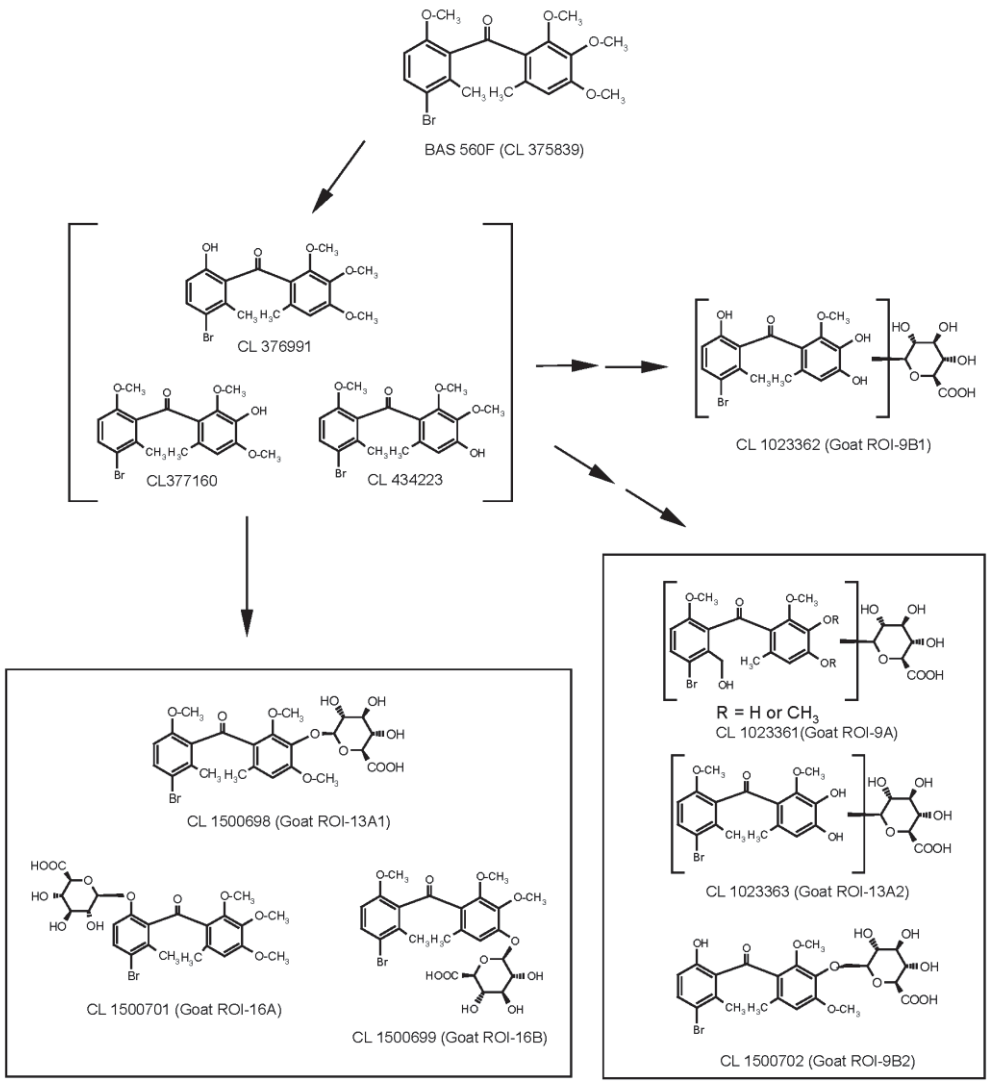


Figure 1Metabolic pathway in lactating goats

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

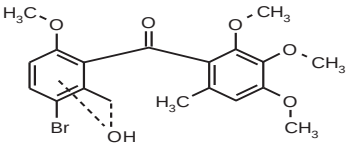
Oxidation of the methyl group on the bromomethoxytoluene ring to the carboxylic acid (via the respective isomer of M560F05) to form M560F03.

BAS 560 F

Hydroxylation

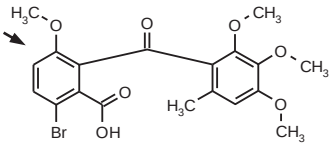
Demethylation

Methyl group oxidation

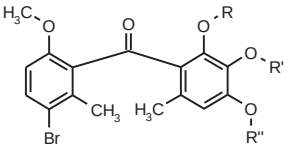


M560F05

Oxidation



M560F03



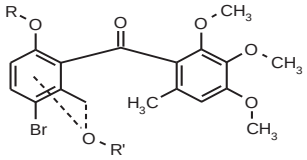
M560F06

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

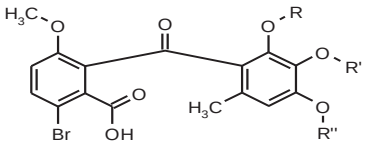
R = H, R' = GlcA

or R = GlcA, R' = H

Demethylation

Methyl group oxidation

Glucuronylation (Bile)

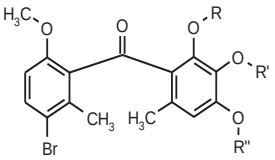


M560F01 / M560F02

R = H, R' and R" = CH_3

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

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



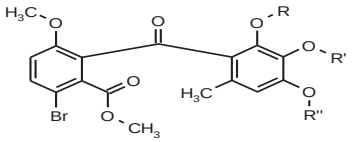
M560F08 / M560F09

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.

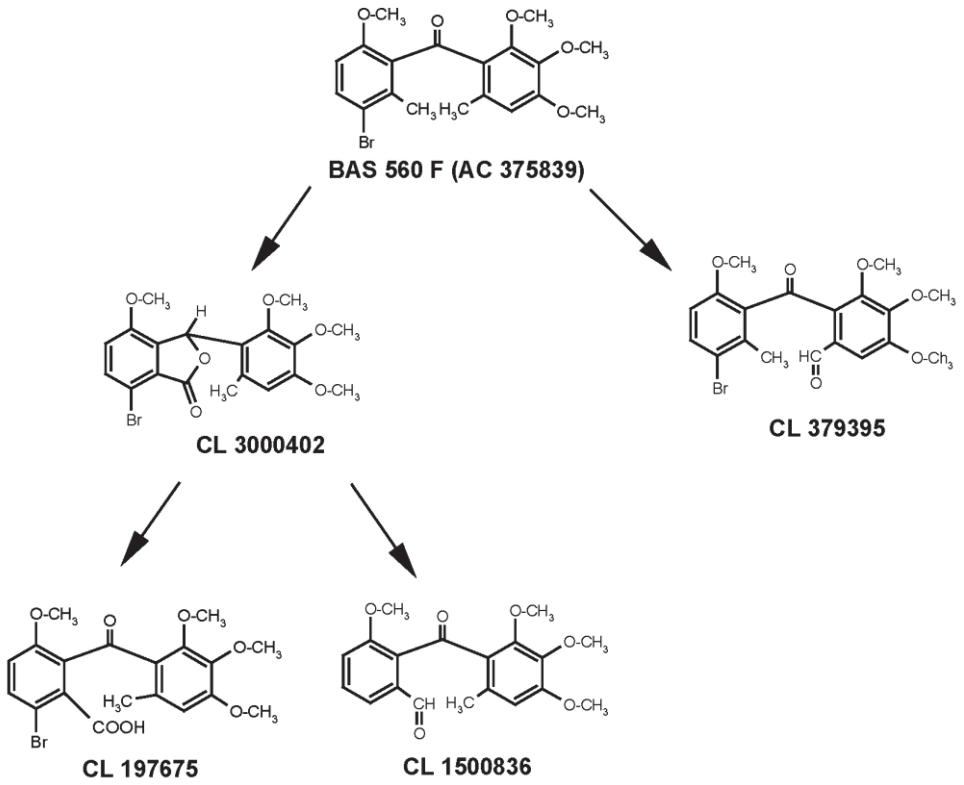


Figure 3 Metabolic pathway for metrafenone in grapevines

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.

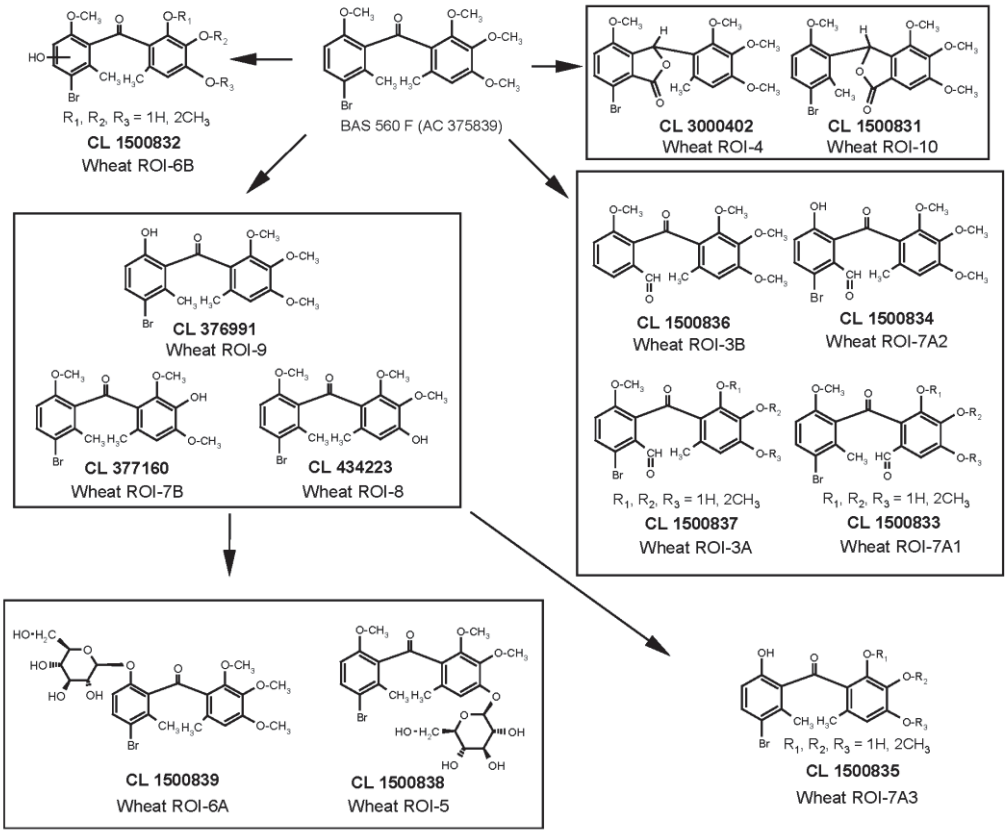


Figure 4 Metabolic pathway for metrafenone in wheat

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.

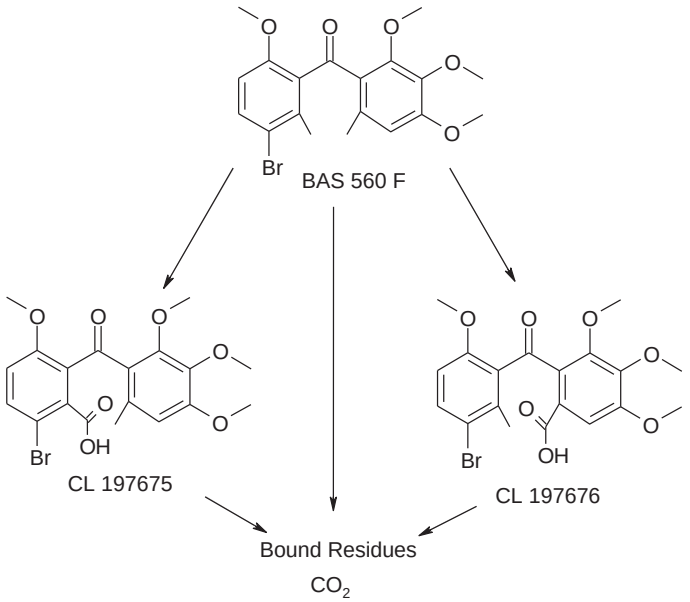


Figure 5 Proposed pathway of degradation in soil under aerobic laboratory conditions for metrafenone

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/100m^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 0.62 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 0.32 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 0.27 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 0.17 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 0.18 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 0.11 0.08	2006/70070 RCN R05016
USA, 2005 Madera, CA (Merlot)	6	0.34	0.048	710	berries	0 14 28		2.6 2.1 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 2.4 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 <u>3.0</u>	2006/70070 RCN R05019
USA, 2005 Benton, OR (Pinot Noir)	6	0.35	0.026	1320	berries	0 14 28		4.1 <u>2.3</u> 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 <u>strawberries</u> 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 <u>0.34</u> 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 <u>0.28</u> 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 <u>0.08</u> 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 <u>0.1</u> 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 <u>0.06</u> 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 0.03 < 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 0.02 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 0.01 < 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 0.04 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 0.02 < 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 0.02 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 0.02 < 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 0.01 < 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 0.02 < 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 0.01 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 0.02 < 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 0.02 < 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 0.01 < 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 0.04 < 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 0.01 < 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 <u>0.02</u> 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 <u>0.02</u> 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 <u>0.02</u> < 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 1.3 [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 0.07 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 0.12 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 0.2 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 0.11 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 0.08	2010/1199010 S09-00770-06
Spain, 2009 Valencia (Filon)	2	0.15	0.015	1000	fruit	0 1 3 7	0.17 0.17 0.21 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 0.1 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 <u>2.5</u> 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	<u>0.98</u>	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	<u>2.3</u> (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	<u>2.0</u> (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%.

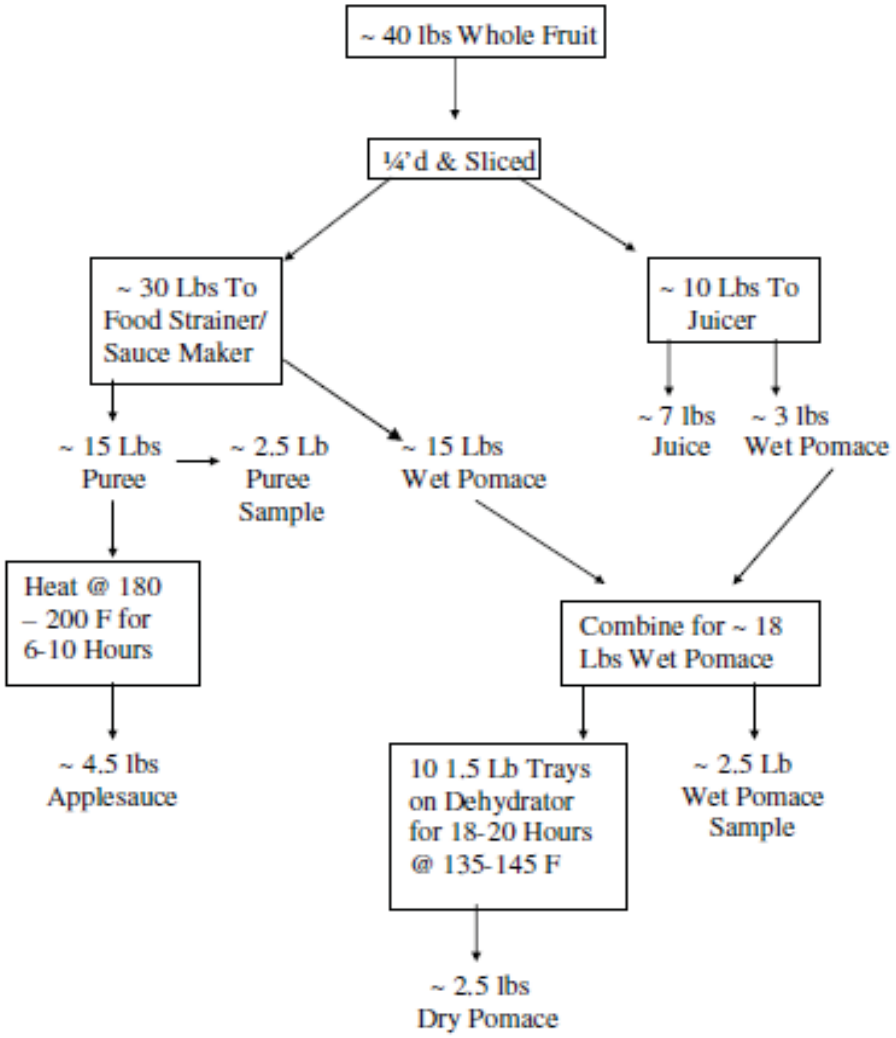


Figure 6 Processing flowchart for apple sauce, juice, and wet pomace

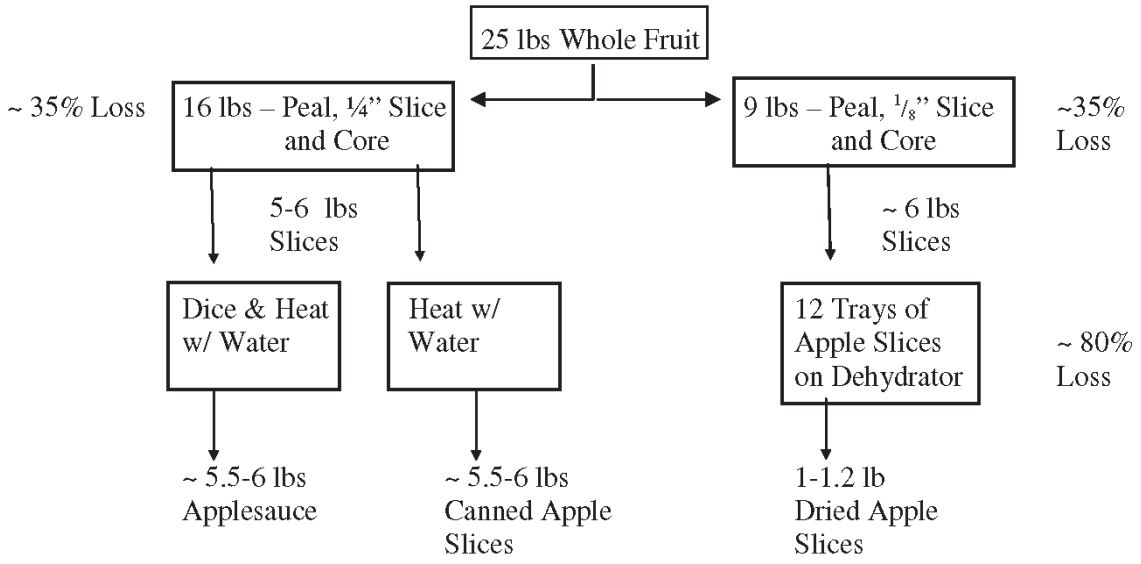


Figure 7 Processing flowchart for canned and dried apple

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

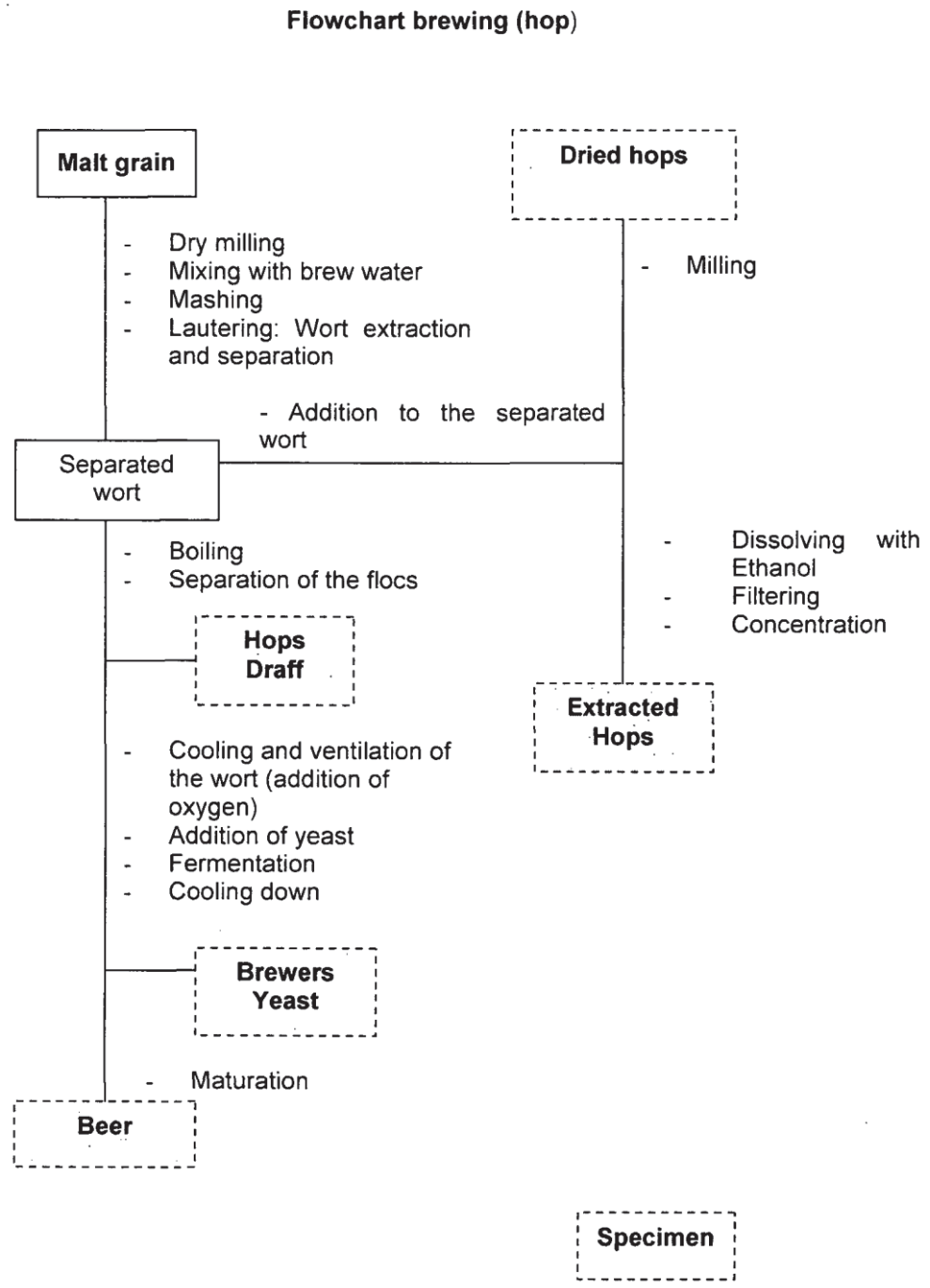


Figure 8 Processing Flowchart for Hops

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

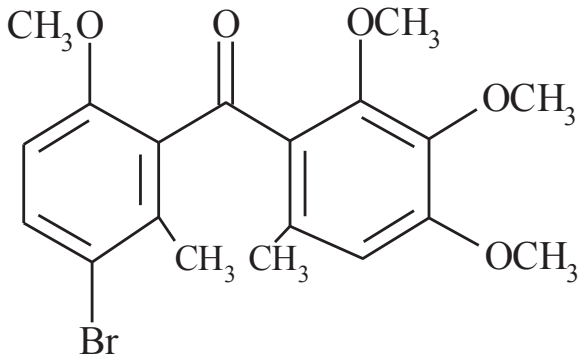
Country	MRL-compliance	Dietary intake estimation
Australia	metrafenone	metrafenone
Canada	metrafenone	metrafenone
Europe	metrafenone	metrafenone
Korea	metrafenone	metrafenone
New Zealand	metrafenone	metrafenone
USA	metrafenone	metrafenone

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.

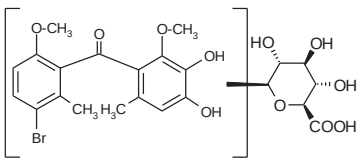
Authorisations exist for the use of metrafenone on cereals, grapes, strawberries and fruiting vegetables in over 50 countries in Europe, the Americas, Asia and the Pacific.

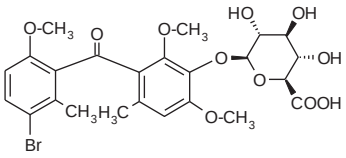
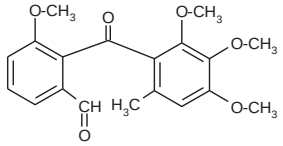
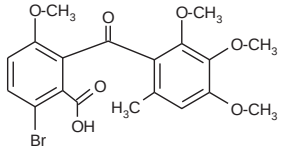
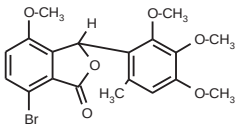
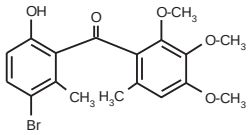
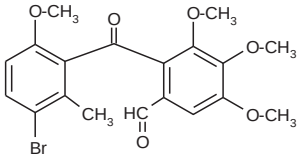
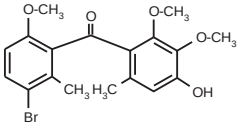
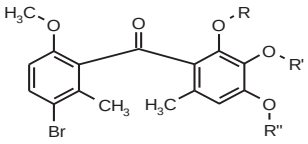


Metrafenone
(MW 409.3)

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.

REFERENCES

Code	Author	Year	Title, Institute, Report reference
7000284	An, D	1999	AC 375839: Hydrolysis. American Cyanamid Co., Ewing NJ, United States of America. 1999/7000284. GLP/GEP: Yes. Unpublished
7004412	Beigel, C	2002	BAS 560 F: Calculation of Henry Law Constant. BASF Corp. Agro Research, Princeton NJ, United States of America. 2002/7004412. GLP/GEP: No. Unpublished
1019497	Daum, A	2001	Determination of the solubility in water of Reg.No. 4082230 (metabolite of BAS 560 F) identical with CL# 377160). BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed.Rep. 2001/1019497. GLP/GEP: Yes. Unpublished
7005112	Fung, CH	2002	BAS 560 F (AC 375839): Aqueous photolysis. BASF Corp. Agro Research, Princeton NJ, United States of America. 2002/7005112. GLP/GEP: Yes. Unpublished
7000320	Heinz, W	1999	Spectral database for AC 375839 pure active ingredient. Cyanamid Forschung GmbH, Schwabenheim, Germany Fed.Rep.. 1999/7000320. GLP/GEP: Yes. Unpublished
7000293	Holman, J	1999	AC 375839: Determination of 1-octanol/water partition coefficient by HPLC method. American Cyanamid Co., Ewing NJ, United States of America. 1999/7000293. GLP/GEP: Yes. Unpublished
7004458	Huang, R	2002	BAS 560 F: Natural water photolysis. BASF Corp., Ewing NJ, United States of America. 2002/7004458. GLP/GEP: Yes. Unpublished
7000334	Mangels, G	2001	Estimation of the photochemical oxidative degradation of BAS 560 F in the atmosphere (QSAR estimates). BASF Agro Research, Princeton NJ, United States of America. 2001/7000334. GLP/GEP: No. Unpublished
7005227	Martin, CA	2002	CL 4084564 (metabolite of BAS 560 F): Calculation of dissociation constant and octanol/water partition coefficient. BASF Corp., Ewing NJ, United States of America. 2002/7005227. GLP/GEP: No. Unpublished
7005228	Martin, CA	2002	CL 375816 (metabolite of BAS 560 F): Calculation of dissociation constant and octanol/water partition coefficient. BASF Corp., Ewing NJ, United States of America. 2002/7005228. GLP/GEP: No. Unpublished
7000353	Petry, A	1998	Dissociation constant of AC 375839. American Cyanamid Co., Ewing NJ, United States of America. 1998/7000353. GLP/GEP: No. Unpublished
7000349	Sicilia, D and Ta, C	1998	AC 375839: Determination of solubility of TGAI in various organic solvents using the shake flask method. American Cyanamid Co., Ewing NJ, United States of America. 1998/7000349. GLP/GEP: Yes. Unpublished

Code	Author	Year	Title, Institute, Report reference
7000370	Werle, H	1998	Determination of the melting point of AC 375839 (CL 375839) secondary standard according to EC directive 92/69/EEC, A.1. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1998/7000370. GLP/GEP: Yes. Unpublished
7000371	Werle, ,H	1998	Determination of the boiling point of AC 375839 (CL 375839) secondary standard according to EC Directive 92/69/EEC, A.2. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1998/7000371. GLP/GEP: Yes. Unpublished
7000367	Werle, H	1998	Determination of the color of AC 375839 (CL 375839) secondary standard according to EPA guideline OPPTS 830.6302. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1998/7000367. GLP/GEP: Yes. Unpublished
7000368	Werle, H	1998	Determination of the physical state of AC 375839 (CL 375839) secondary standard according to EPA guideline OPPTS 830.6303. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1998/7000368. GLP/GEP: Yes. Unpublished
7000369	Werle, H	1998	Determination of the odor of AC 375839 (CL 375839) secondary standard according to EPA guideline OPPTS 830.6304. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1998/7000369. GLP/GEP: Yes. Unpublished
7000299	Werle, H	1999	Determination of the relative density of AC 375839 (CL 375839) secondary standard according to EC directive 92/69/EEC, A.3. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1999/7000299. GLP/GEP: Yes. Unpublished
7000296	Werle, H	1999	Determination of the relative density of AC 375839 (CL 375839) technical grade active material according to EC directive 92/69/EEC, A.3. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1999/7000296. GLP/GEP: Yes. Unpublished
7000312	Werle, H	1999	Determination of the color of AC 375839 (CL 375839) technical grade active material according to EPA guideline OPPTS 830.6302. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1999/7000312. GLP/GEP: Yes. Unpublished
7000311	Werle, H	1999	Determination of the physical state of AC 375839 (CL 375839) technical grade active material according to EPA guideline OPPTS 830.6303. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1999/7000311. GLP/GEP: Yes. Unpublished
7000313	Werle, H	1999	Determination of the odor of AC 375839 (CL 375839) technical grade active material according to EPA guideline OPPTS 830.6304. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1999/7000313. GLP/GEP: Yes. Unpublished
7000305	Werle, H	1999	Determination of the flammability (solids) of AC 375839 (CL 375839) technical grade active material according to EC Council Directive 92/69/EEC, A.10. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1999/7000305. GLP/GEP: Yes. Unpublished
7000307	Werle, H	1999	Determination of the relative self-ignition temperature of AC 375839 (CL 375839) technical grade active material according to EC Directive 92/69/EEC, A.16. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1999/7000307. GLP/GEP: Yes. Unpublished
7000309	Werle, H	1999	Determination of the surface tension of AC 375839 (CL 375839) technical grade active material according to EC Directive 92/69/EEC, A.5. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1999/7000309. GLP/GEP: Yes. Unpublished
7000310	Werle, H	1999	Determination of the oxidizing properties of AC 375839 (CL 375839) technical grade active material according to EC directive 92/69/EEC, A.17. BioChem GmbH, Karlsruhe, Germany Fed.Rep.. 1999/7000310. GLP/GEP: Yes. Unpublished
7000308	Werle, H and Angly, H	1999	Determination of the explosive properties of AC 375839 (CL 375839) technical grade active material according to EC Council Directive 92/69/EEC Part. A.14. Institute of Safety & Security, Basel, Switzerland. 1999/7000308. GLP/GEP: Yes. Unpublished
5002313	Yacoub, R	2001	BAS 560 F (AC 375839): Determination of vapor pressure. BASF Agro Research RTP, Research Triangle Park NC, United States of America. 2001/5002313. GLP/GEP: Yes. Unpublished
7000347	Yan, Z	1998	AC 375839: Determination of solubility in water using the shake flask method. American Cyanamid Co., Ewing NJ, United States of America. 1998/7000347. GLP/GEP: Yes. Unpublished
7005114	Fung, CH	2002	BAS 560 F (AC 375839)—Metabolism of ^{14}C BAS 560 F in the lactating goat. BASF Corp. Agro Research, Princeton NJ, United States of America. 2002/7005114. GLP/GEP: Yes. Unpublished

Code	Author	Year	Title, Institute, Report reference
1026047	Hoefs, R *et al.*	2008	BAS 560 F (AC 375839): Metabolism in laying hens. BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed.Rep. 2005/1026047. GLP/GEP: Yes. Unpublished
BN-123-054	Class, T and Schlueter, H	2001	AC375839 metabolism of carbon-14 labelled—AC375839 in grapevines. PTRL Europe GmbH, Ulm, Germany Fed.Rep.. BN-123-054 (See also: 2001/7000459, BN-640-001 and 2001/7000342). GLP/GEP: Yes. Unpublished
1054630	Grosshans, F and Ockert, M	2010	Metabolism of ^{14}C-BAS 560 F in cucumber. BASF SE, Limburgerhof, Germany Fed.Rep.. 2010/1054630. GLP/GEP: Yes. Unpublished
7005253	Zulalian, J	2002	BAS 560 F (AC 375839): Metabolism of carbon-14 labelled AC 375839 in wheat under field conditions. BASF Corp. Agro Research, Princeton NJ, United States of America. 2002/7005253. GLP/GEP: Yes. Unpublished
7005909	Afzal, J	2002	CL 377160 (Metabolite of BAS 560 F): Rate of degradation in three different soils under aerobic conditions. BASF Corp. Agro Research, Princeton NJ, United States of America. 2002/7005909. GLP/GEP: Yes. Unpublished
7000284	An, D	1999	AC 375839: Hydrolysis. American Cyanamid Co., Ewing NJ, United States of America. 1999/7000284. GLP/GEP: Yes. Unpublished
7000152	Steinfuehrer, T	2000	AC 375839: Metabolism in soil under aerobic conditions. Cyanamid Forschung GmbH, Schwabenheim, Germany Fed.Rep. 2000/7000152. GLP/GEP: Yes. Unpublished
7000151	Steinfuehrer, T	2000	^{14}C-AC 375839 (CL 375839): Rate of degradation in three different soils under aerobic conditions. Cyanamid Forschung GmbH, Schwabenheim, Germany Fed.Rep.. 2000/7000151. GLP/GEP: Yes. Unpublished
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
7005187	Zulalian, J	2002	BAS 560 F (AC 375839): Confined rotational crop study with carbon-14 labelled AC 375839. BASF Corp. Agro Research, Princeton NJ, United States of America. 2002/7005187. GLP/GEP: Yes. Unpublished
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
1089964	Lehmann, A	2010	Validation of BAS 560 F with BASF Method No. 535/3 (L0076/03) in hops and beer. BASF SE, Limburgerhof, Germany Fed.Rep. 2010/1089964. GLP/GEP: Yes. Unpublished
2010/1018946	Lehmann, A *et al.*	2010	Technical procedure: Method for the determination of BAS 421 F, BAS 480 F, BAS 500 F, 500M07 (BF 500-3), BAS 510 F, BAS 550 F, BAS 555 F and BAS 560 F in plant matrices. BASF SE, Limburgerhof, Germany Fed.Rep. 2010/1018946. GLP/GEP: No. Unpublished
1221605	Meyer, M	2010	Metrafenone (BAS 560 F): Validation of the multi-residue enforcement method QuEChERS for the determination of residues in plant matrices using LC/MS/MS. SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep. 2010/1221605. GLP/GEP: Yes. Unpublished
7007816	Meyer, M	2011	Metrafenone (BAS 560 F): Validation of the multi-residue enforcement method QuEChERS for the determination of residues in plant matrices using LC/MS/MS (including amendment no. 1). SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep.. 2011/7007816. GLP/GEP: Yes. Unpublished

Code	Author	Year	Title, Institute, Report reference
1285054	Meyer, M	2011	Metrafenone (BAS 560 F): Validation of the multi-residue enforcement method QuEChERS for the determination of residues in plant matrices using LC/MS/MS. SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep.. 2011/1285054. GLP/GEP: Yes. Unpublished
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
7007817	Weber, H	2011	Independent laboratory validation of multi-method QuEChERS for the determination of Metrafenone (BAS 560 F) in foodstuffs of plant origin (including amendment no. 1 and amendment no. 2). Eurofins Dr. Specht GLP GmbH, Hamburg, Germany Fed.Rep.. 2011/7007817. GLP/GEP: Yes. Unpublished
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
7000486	Pelz, S and Steinhauer, S	2001	BAS 560 F (AC 375839): Validation of DFG method S 19 for the determination of residues of BAS 560 F in milk, meat, and eggs. Dr. Specht & Partner Chemische Laboratorien GmbH, Hamburg, Germany Fed.Rep. 2001/7000486. GLP/GEP: Yes. Unpublished
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

Code	Author	Year	Title, Institute, Report reference
7001795	Homa, K	2013	Metrafenone: Magnitude of the residue on hops. IR-4 Project Headquarters, Princeton NJ, United States of America. 2013/7001795. GLP/GEP: Yes. Unpublished
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
1279083	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. 2011/1279083. GLP/GEP: Yes. Unpublished
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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1010542	Raunft, E *et al.*	2004	Study on the residue behaviour of Fenpropimorph and BAS 560 F in cereals after application of BAS 421 12 F, BAS 560 00 F and BAS 564 AF F under field conditions in France, Germany, Denmark, United Kingdom, Italy and Spain, 2003. BASF AG Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed.Rep. 2004/1010542. GLP/GEP: Yes. Unpublished
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